Chemistry Question Bank

Career Endeavor - Chem Academy - Saraswati Dham

CSIR-UGC NET-JRF Chemistry

IIT-JAM Chemistry

🏆 Chemistry - A Free Initiative for Study Material 🏆

🥭 **1. Chemistry People**
https://kutumb.app/chemistry-group?ref=ODB82

🥭 **2. CSIR NET-JRF CHEMISTRY**
https://kutumb.app/c-s-i-r-j-r-f-c?ref=TRYN4

🥭 **3. CSIR NET-GATE JAM Chemistry**
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🥭 **4. Gate Chemistry**
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S.P Sharma

ORGANIC CHEMISTRY

VOLUME - 2

IIT-JAM

INDEX

CHAPTER 3

REACTION INTERMEDIATE

EXERCISE - I

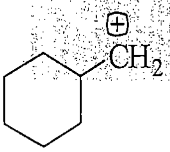
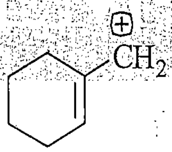
Single Correct Type

CARBOCATION

1. Some pairs of ions are given below. In which pair, first ion is more stable than second?

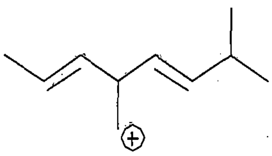
(a) $CH_3-\overset{\oplus}{C}H-CH_3$ and $CH_3-\overset{\oplus}{C}H-OCH_3$

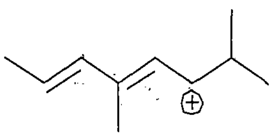
(b) $CH_3-CH_2-\overset{\oplus}{C}H-CH_3$ and $CH_2=CH-CH_2-\overset{\oplus}{C}H_2$

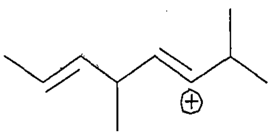
(c)  and 

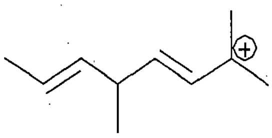
(d) $\begin{array}{c} CH_3-CH-CH_3 \\ | \\ CH_2-C_{\oplus}-CH_3 \end{array}$ and $\begin{array}{c} CH_3-N-CH_3 \\ | \\ CH_3-C^{\oplus}-CH_3 \end{array}$

2. Which carbocation is the most stable?

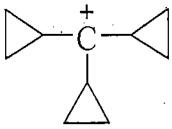
(a) 

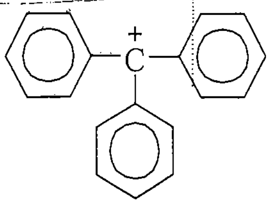
(b) 

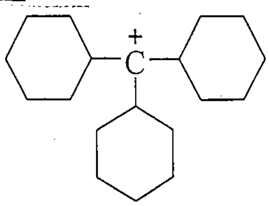
(c) 

(d) 

3. Which one among the following carbocations has the longest half-life?

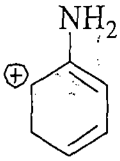
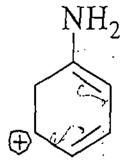
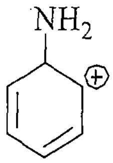
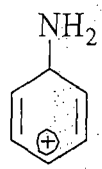
(a) 

(b) 

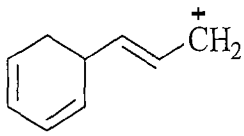
(c) 

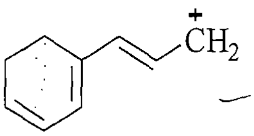
(d) $\begin{array}{c} + \\ H_3C-C-CH_3 \\ | \\ CH_3 \end{array}$

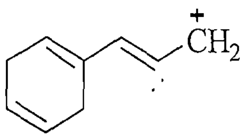
4. Which one of the most stable cation in the following?

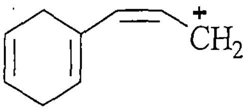
(a)  (b)  (c)  (d) 

5. Identify the most stable structure in the following

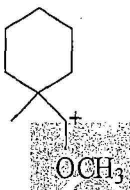
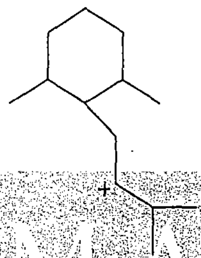
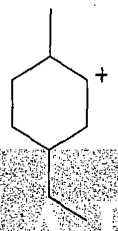
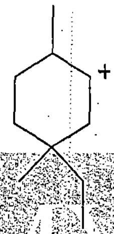
(a) 

(b)  → extended conjugation

(c) 

(d) 

6. Which of the following will rearrange?

(1)  (2)  (3)  (4) 

(a) 1 (b) 1 and 3 (c) All (d) 2, 3, 4

7. The correct order of stability of the following carbocations is

(a) $CH_3CH_2\overset{+}{C}H_2 > CH_2=CH-\overset{+}{C}H_2 > CH_2=CH\overset{+}{C}HCH_3 > CH_2=CH\overset{+}{C}(CH_3)_2$

(b) $CH_2=CH\overset{+}{C}H_2 > CH_3CH_2\overset{+}{C}H_2 > CH_2=CH\overset{+}{C}(CH_3)_2 > CH_2=CH\overset{+}{C}HCH_3$

(c) $CH_2=CH\overset{+}{C}(CH_3)_2 > CH_2=CH\overset{+}{C}HCH_3 > CH_2=CH\overset{+}{C}H_2 > CH_3CH_2\overset{+}{C}H_2$

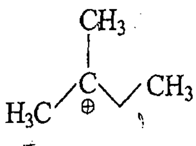
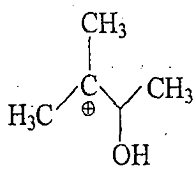
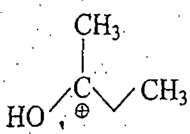
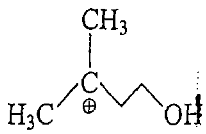
(d) $CH_2=CH-\overset{+}{C}HCH_3 > CH_2=CH\overset{+}{C}(CH_3)_2 > CH_3CH_2 > CH_3CH_2-\overset{+}{C}H_2 > CH_2=CH\overset{+}{C}H_2$

8. The order of decreasing stability of the following cations is:

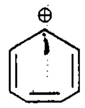
(I) $CH_3\overset{+}{C}HCH_3$ (II) $CH_3\overset{+}{C}HOCH_3$ (III) $CH_3\overset{+}{C}HCOCH_3$

(a) III > II > I (b) I > II > III (c) II > I > III (d) I > III > II

9. Which of the following cations is most stable?

(a)  (b)  (c)  (d) 

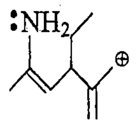
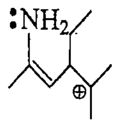
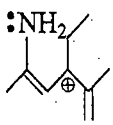
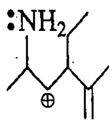
10. Arrange the following cations in decreasing order of stability



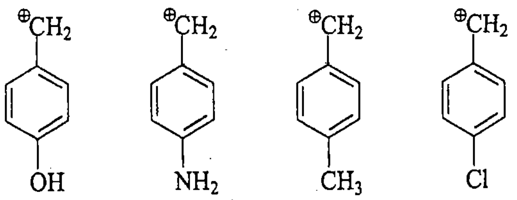
(P) $CH_2=CH-\overset{\oplus}{C}H_2$ (Q) $Ph-\overset{\oplus}{C}H_2$ (R) $CH_3-\overset{\oplus}{C}H_2$ (S)

(a) P > R > Q > S (b) R > P > S > Q (c) Q > R > P > S (d) P > Q > S > R

11. Among the following which is most stabilised cation?

(a)  (b)  (c)  (d) 

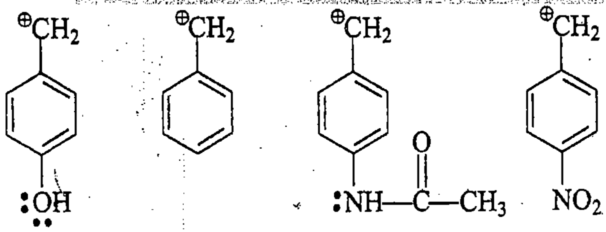
12. The decreasing order of stability of following cation is



(P) (Q) (R) (S)

(a) P > Q > R > S (b) Q > S > R > P (c) Q > P > S > R (d) Q > P > R > S

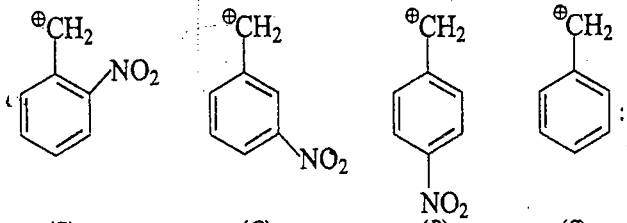
13. The decreasing order of stability of following cation is



(P) (Q) (R) (S)

(a) P > R > Q > S (b) Q > R > S > P (c) R > S > Q > P (d) P > R > S > Q

14. The decreasing order of stability of following cation is



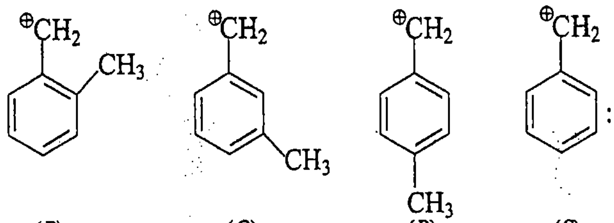
S > Q > R > P

Para, destabilise less, Ortho destabilise more, (. 2 Resonance effect

(P) (Q) (R) (S)

Good √(a) Q > R > P > S (b) S > Q > R > P (c) S . R > P > Q (d) R > P > Q > S

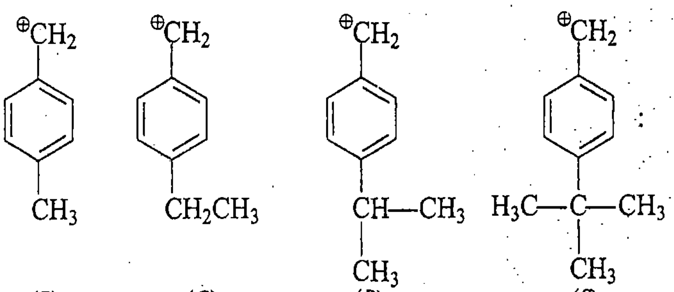
15. The decreasing order of stability of following cation is



(P) (Q) (R) (S)

(a) P > Q > R > S (b) P > S > Q > R (c) P > R > Q > S (d) S > R > Q > P

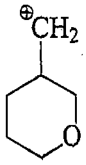
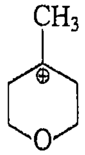
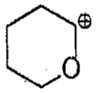
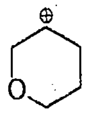
16. The decreasing order of stability of following cation is



(P) (Q) (R) (S)

(a) S > R > Q > P (b) P > Q > R > S (c) Q > R > S > P (d) R > S > P > Q

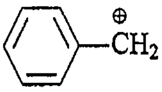
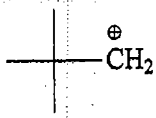
17. Identify the most stable structure among the following:

(a)  (b)  (c)  (d) 

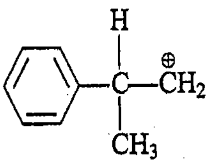
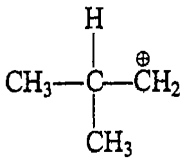
Paragraph for Q. 18 - Q.20

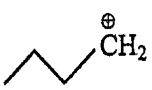
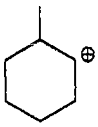
Under common reaction conditions, a carbocation rearranges to another carbocation of equal or greater stability. For example, secondary carbocation will rearrange to a tertiary carbocation. It will not rearrange to a less stable primary carbocation. This generalization is not absolute, and because there is not a high energy barrier to the rearrangement of carbocations, rearrangement to a less stable cation can occur if it offers the chance to form a more stable product.

18. In which of the following cations rearrangement takes place?

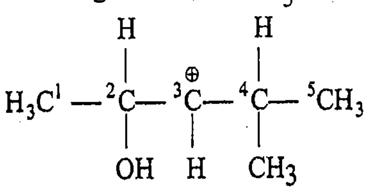
(a)  (b)  (c)  (d) 

19. In which of the following cations rearrangement takes place most rapidly?

(a)  (b) 

(c)  (d) 

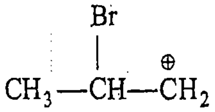
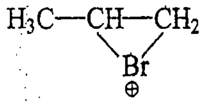
20. In the following cation, H/CH_3 that is most likely to migrate to the positively charged carbon is



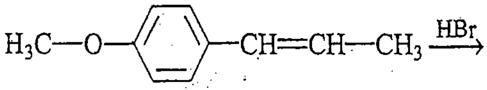
(a) CH_3 at C–4 (b) H at C – 4 (c) CH_3 at C – 2 (d) H at C – 2

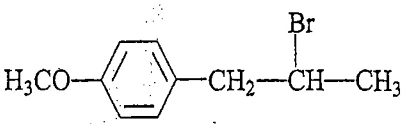
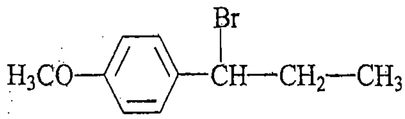
21. Which of the following is the major product when 1-butanol is heated with concentrated H_2SO_4?
(a) 1-butene (b) cis-2-butene (c) Trans-2-butene (d) All of these

22. Propene reacts with Br_2 to give 1, 2-dibromopropane. The anti-addition takes place due to the formation of intermediate:

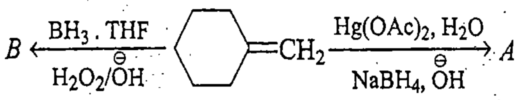
(a) 
(b) 

(c) $H_3C-\overset{\oplus}{C}H-CH_2-Br$
(d) None of these

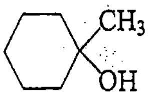
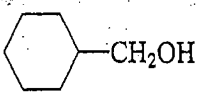
23.  Major product :

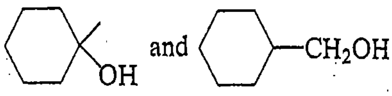
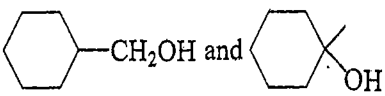
(a) 
(b) 

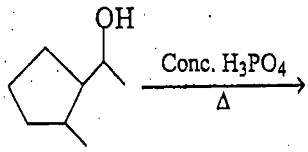
(c) Both a and b in same amount
(d) None of the above

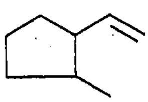
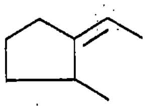
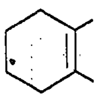
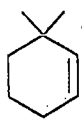
24. 

A and B are respectively

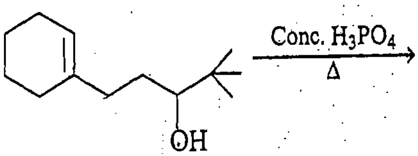
(a)  both
(b)  both

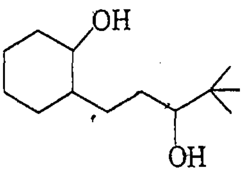
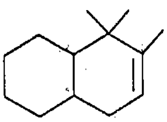
(c) 
(d) 

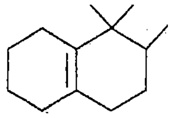
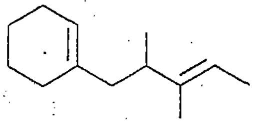
25.  Major product :

(a) 
(b) 
(c) 
(d) 

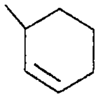
26. Which of the following will be the correct product of reaction?

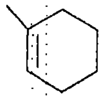


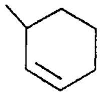
(a) 
(b) 

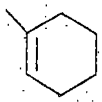
(c)    (d) 

27. Choose the reaction sequence that would best accomplish the preparation of 2-methylcyclohexanol:

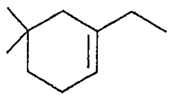
(a)  $\xrightarrow{H_2O,\ H_2SO_4}$

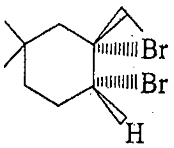
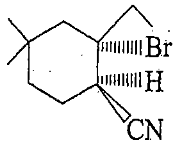
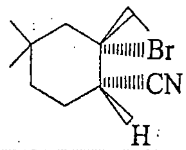
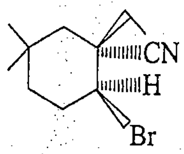
(b)  $\xrightarrow[NaBH_4,\ ^{\ominus}OH]{Hg(OAc)_2,\ H_2O}$

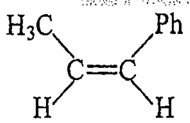
(c)  $\xrightarrow[H_2O_2,\ NaOH]{BH_3\ .\ THF}$

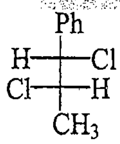
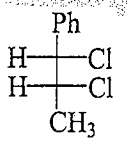
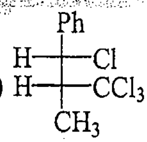
(d)  $\xrightarrow[H_2O,\ NaOH]{BH_3\ .\ THF}$

28. Give the major product of the following reaction

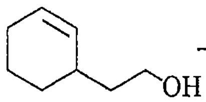
 $\xrightarrow{BrCN}$ Major product :

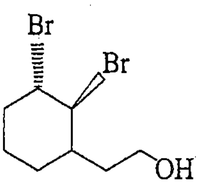
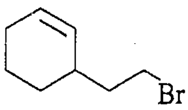
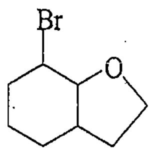
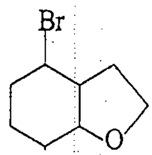
(a) 
(b) 
(c) 
(d) 

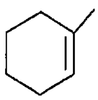
29.  $\xrightarrow{Cl_2,\ CCl_4}$

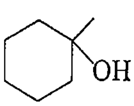
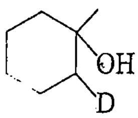
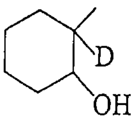
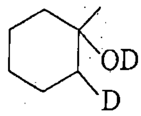
(a) 
(b) 
(c) Ph—C≡C—CH_3
(d) 

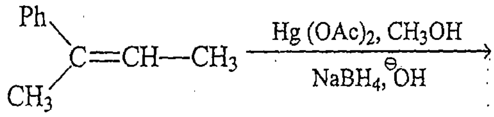
30. Give the major product of following reaction

 $\xrightarrow{Br_2/CCl_4}$ Major product :

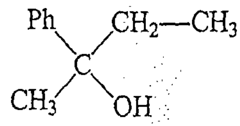
(a) 
(b) 
(c) 
(d) 

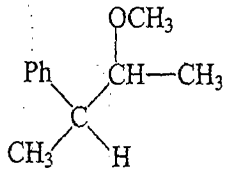
31.  $\xrightarrow[NaBD_4,\ ^{\ominus}OH]{Hg(OAc)_2,\ H_2O}$ Major product :

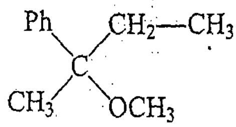
(a) 
(b) 
(c) 
(d) 

32. 

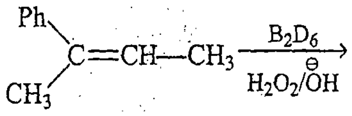
Major product :

(a) 

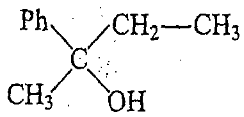
(b) 

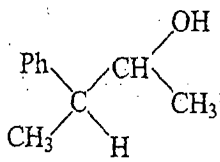
(c) 

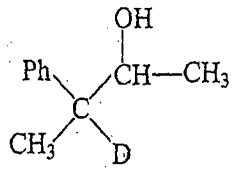
(d) None of these

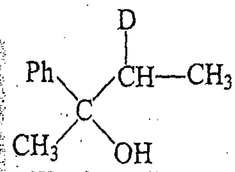
33. 

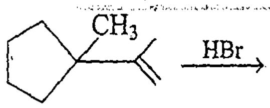
Major product :

(a) 

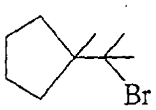
(b) 

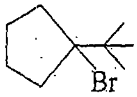
(c) 

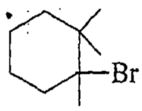
(d) 

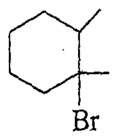
34. 

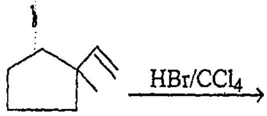
Major product :

(a) 

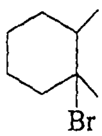
(b) 

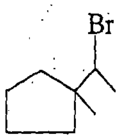
(c) 

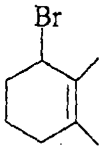
(d) 

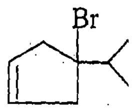
35. 

Major product :

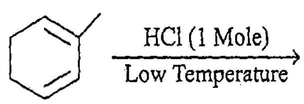
(a) 

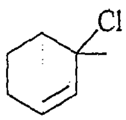
(b) 

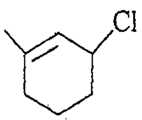
(c) 

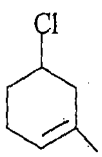
(d) 

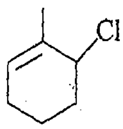
36. Which of the following is major product



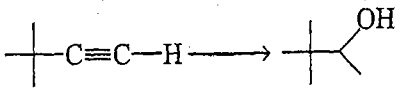
(a) 

(b) 

(c) 

(d) 

37. Select the reagent for following transformation:



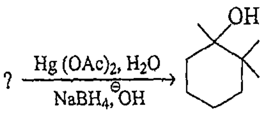
(a) H_2-Pd, HCHO, H_2SO_4

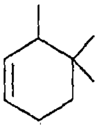
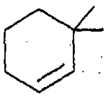
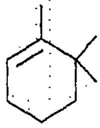
(b) H_2, $Pd-BaSO_4$; $Hg(OAc)_2$, H_2O, $NaBH_4$, $\overset{\ominus}{O}H$

(c) BH_3, H_2O_2, $\overset{\ominus}{O}H$, $Pd-C$

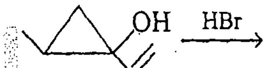
(d) Hg^{+2}, H_2SO_4, H_2, $Pd-BaSO_4$

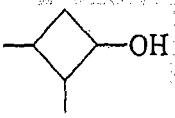
38. Select the starting material for following reaction:

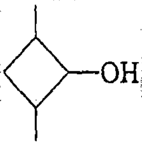


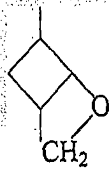
(a)  (b)  (c)  (d) Both a and b

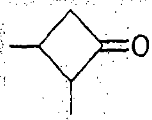
39. The product of following reaction can be:

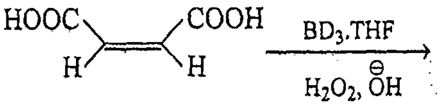


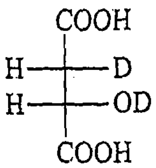
(a) 

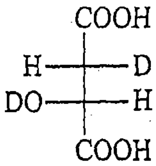
(b) 

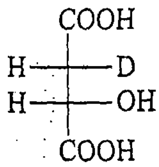
(c) 

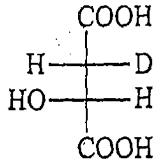
(d) 

40. 

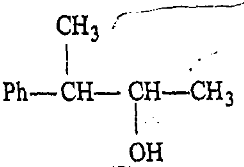
(a) 

(b) 

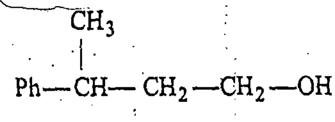
(c) 

(d) 

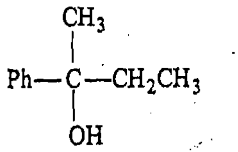
41. The relative rate of acid catalysed dehydration of following alcohols would be



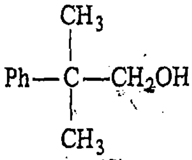
(P)



(Q)



(R)

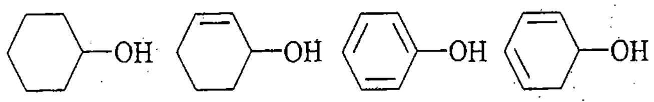


(S)

Perhaps more reactive carbocation & less prone to reagents

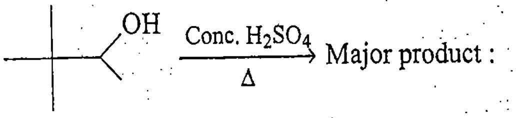
(a) R > P > S > Q (b) R > S > P > Q (c) P > R > S > Q (d) R > S > Q > P

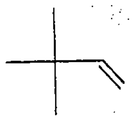
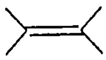
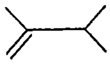
42. Dehydration of following alcohols will be in order



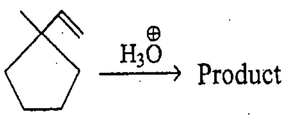
1 2 3 4

(a) 1 < 2 < 3 < 4 (b) 4 > 3 > 1 > 2 (c) 4 > 2 > 1 > 3 (d) 1 > 3 > 4 > 2

43. 

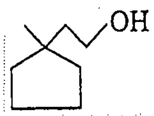
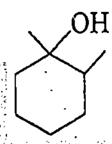
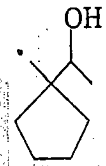
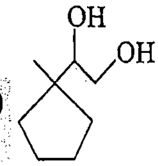
(a)  (b)  (c)  (d) None of these

44. In the following reaction



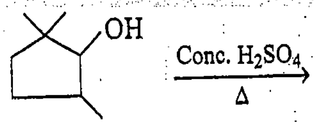
solvent is large act as nucleophile,

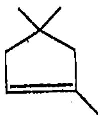
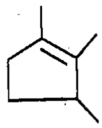
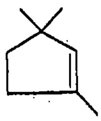
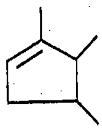
The major product is

(a)  (b)  (c)  (d) 

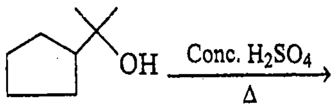
Imp

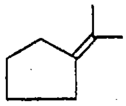
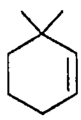
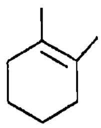
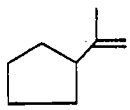
45. Find out major product of following reaction



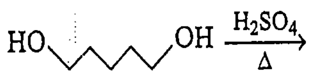
(a)  (b)  (c)  (d) 

46. Find out major product of following reaction

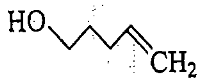


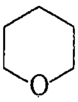
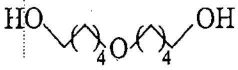
(a)  (b)  (c)  (d) 

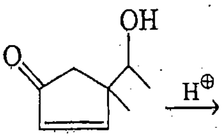
Imp

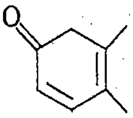
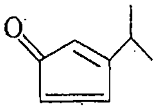
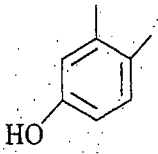
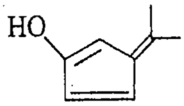
47. In the reaction 

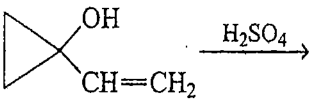
The major product formed is

(a)  (b) 

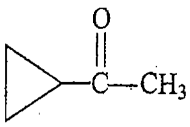
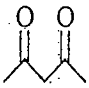
(c)  (d) 

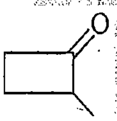
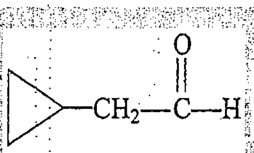
48.  Major product :

(a)  (b)  (c)  (d) 

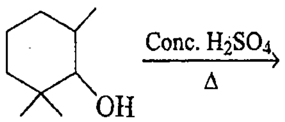
49.  'P';

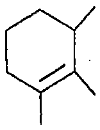
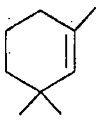
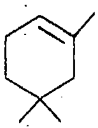
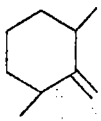
Identify 'P' in the reaction:

(a)  (b) 

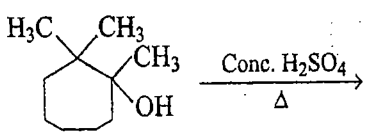
(c)  (d) 

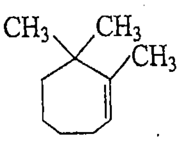
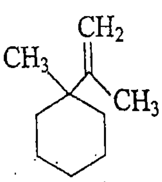
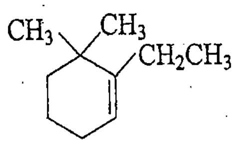
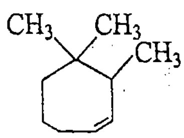
50. Identify the major product of the following reaction:



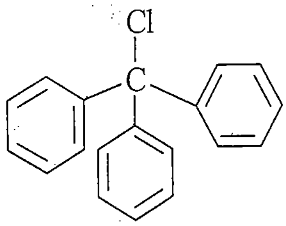
(a)  (b)  (c)  (d) 

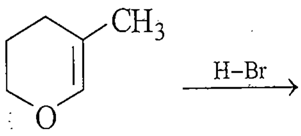
51. What would be the major product of following reaction

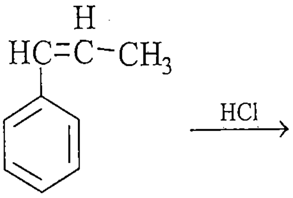


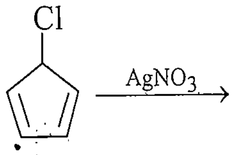
(a)  (b)  (c)  (d) 

52. Reaction which will give fastest carbocation

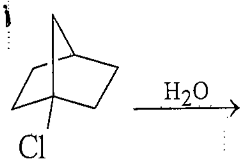
(a) 

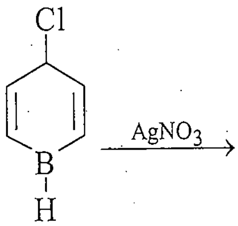
(b) 

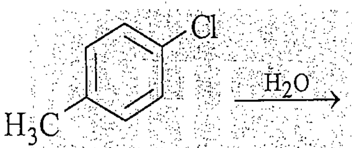
(c) 

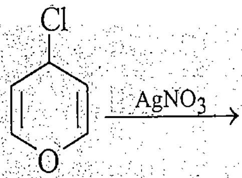
(d) 

53. Reaction which will give carbocation as intermediate

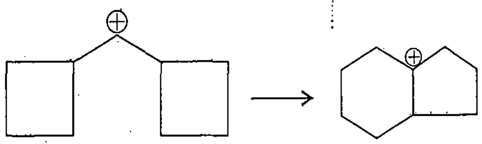
(a) 

(b) 

(c) 

(d) 

54. How many 1,2-Shifts are involved during the course of following reaction:



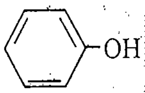
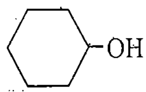
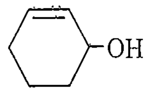
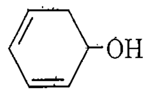
(a) 1 (b) 2 (c) 3 (d) 4

55. Which will dehydrate at fastest rate by H_3PO_4:-

(a) 2-methyl butane-2-ol (b) 3-methyl butane-2-ol

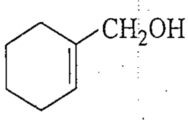
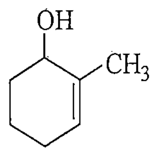
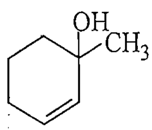
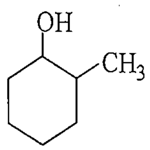
(c) Butane-1-ol (d) 2-methyl butane-1-ol

56. Among the given compounds, the correct dehydration order is:

(I)  (II)  (III)  (IV) 

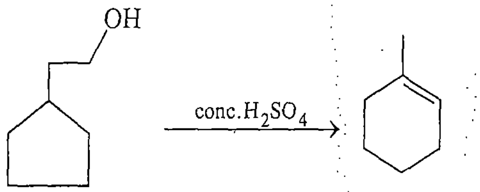
(a) I < II < III < IV (b) II < III < IV < I (c) I < III < IV < II (d) I < II < III = IV

57. Rate of dehydration when given compounds are treated with conc. H_2SO_4.

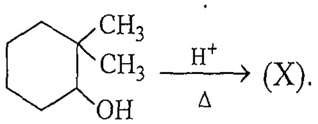
(P)  (Q)  (R)  (S) 

(a) P > Q > R > S (b) Q > P > R > S (c) R > Q > P > S (d) R > Q > S > P

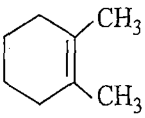
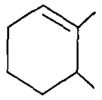
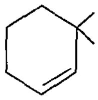
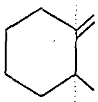
58. How many 1,2-Shifts are involved during the course of following reaction:

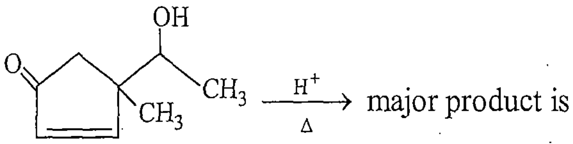


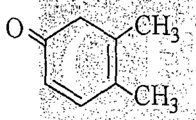
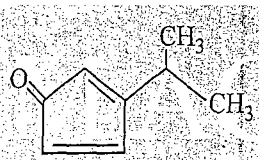
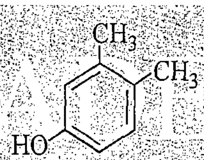
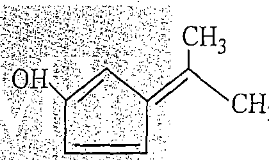
(a) 1 (b) 2 (c) 3 (d) 4

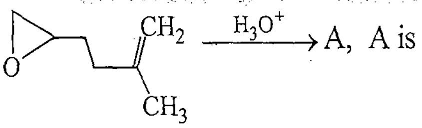
59. 

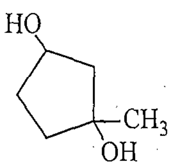
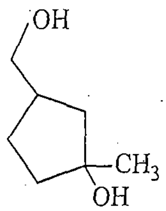
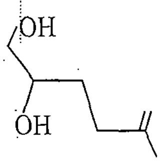
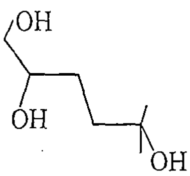
Product (X) is

(a)  (b)  (c)  (d) 

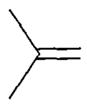
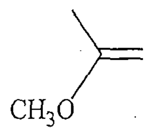
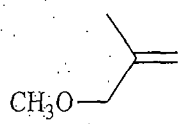
60. 

(a)  (b)  (c)  (d) 

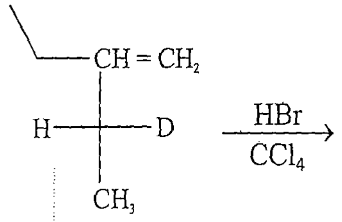
61. 

(a)  (b)  (c)  (d) 

62. What is the order of reactivity with HBr.

(a)  (b)  (c) 

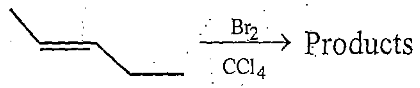
(a) a > b > c (b) b > a > c (c) c > b > a (d) b > c > a

63. 

What is stereochemistry of product?

(a) Racemic mixture (b) Optically inactive (c) Diastereomers (d) Meso product

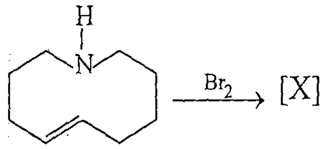
64. Select the incorrect statement about the product mixture in the following reaction :



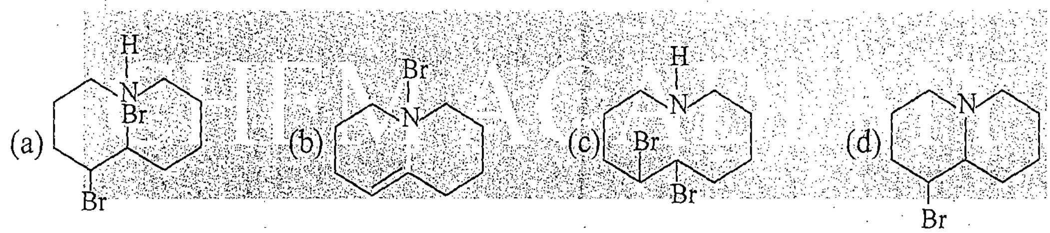
(a) it is optically active (b) it is racemic mixture

(c) it is a resolvable mixture (d) it is a mixture of erythro compounds

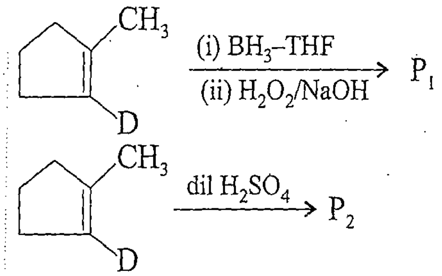
65. In the given reaction:

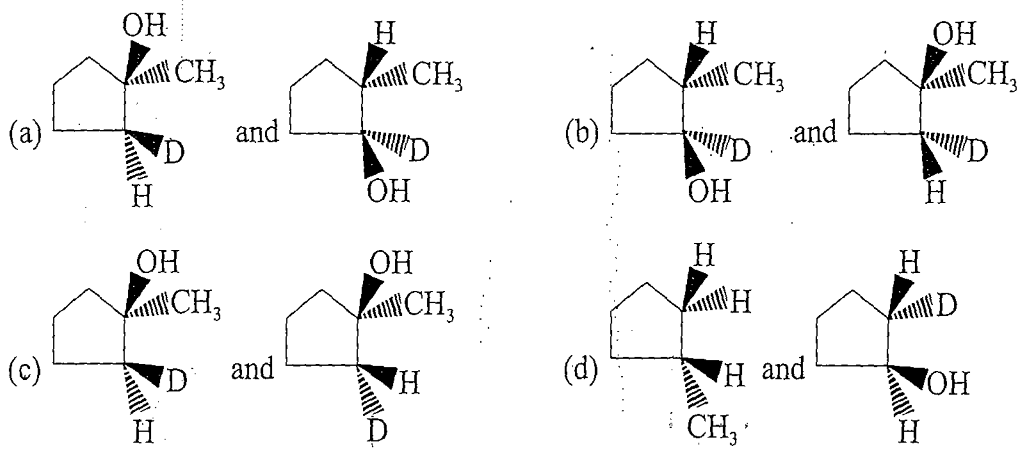


[X] is:

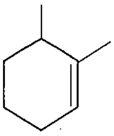
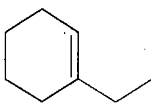
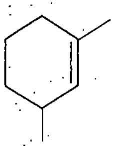
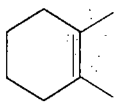


66. Get the product P_1 and P_2 in the following reaction :

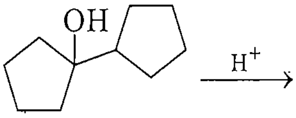


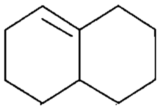
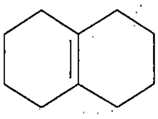
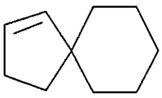
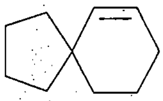


67. Which compound will yield 2-methyl-6-oxoheptanal upon treatment with ozone followed by Zn/ H_2O.

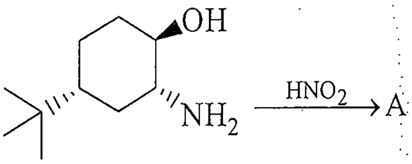
(a)  (b)  (c)  (d) 

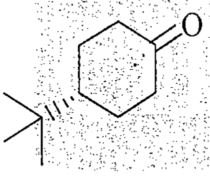
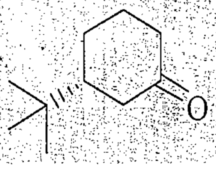
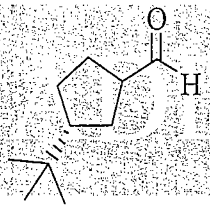
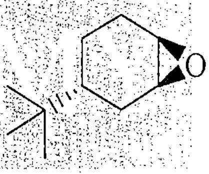
68. Major product formed in the following reaction



(a)  (b)  (c)  (d) 

69. Major product formed in the following reaction



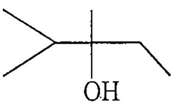
(a)  (b)  (c)  (d) 

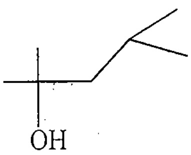
Check

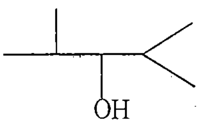
70.
$$\mathrm{CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-NH_2 \xrightarrow{HNO_2} (X)\ (major)}$$

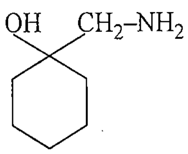
Major product of above reaction is

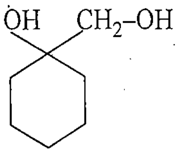
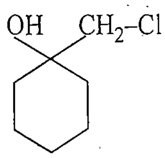
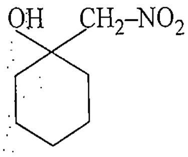
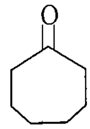
(a) $\mathrm{(CH_3)_2CH-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-OH}$

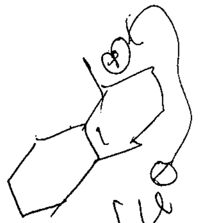
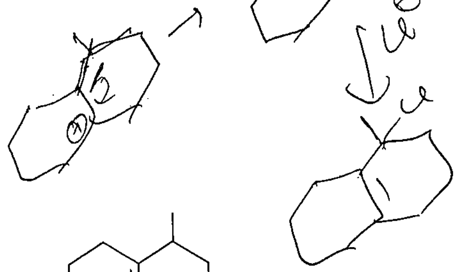
(b) 

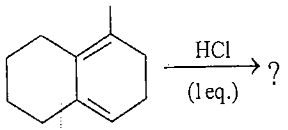
(c) 

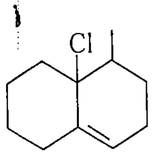
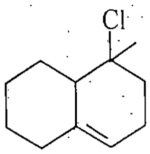
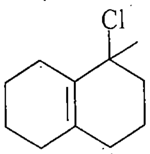
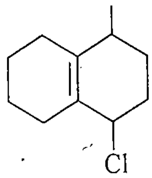
(d) 

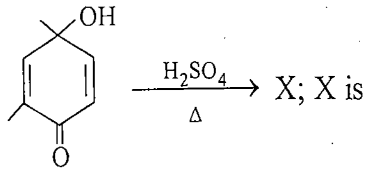
71.  $\xrightarrow[HCl,\Delta]{NaNO_2}$ A ; A is

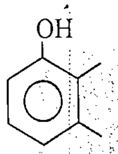
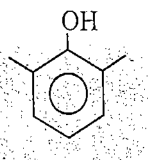
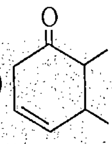
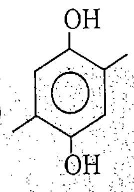
(a)  (b)  (c)  (d) 

72. 
Imp.
Major product of this reaction at 40°C is:

(a)  (b)  (c)  (d) 

73. 

(a)  (b)  (c)  (d) 

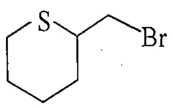
74. $CH_2{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}SH \xrightarrow[CCl_4]{Br_2} ?$

Major product of this reaction is:

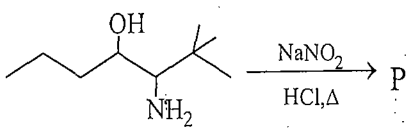
(a) $Br_2-CH_2-\underset{\displaystyle |\atop \displaystyle Br}{CH}-CH_2-CH_2-CH_2-CH_2-SH$

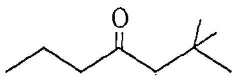
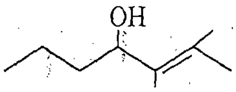
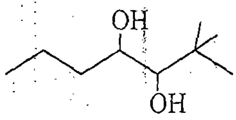
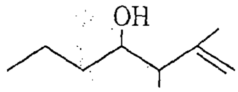
(b) $Br_2-CH_2-\underset{\displaystyle |\atop \displaystyle CCl_3}{CH}-CH_2-CH_2-CH_2-CH_2-SH$

(c) $Br_2-CH_2-\underset{\displaystyle |\atop \displaystyle Cl}{CH}-CH_2-CH_2-CH_2-CH_2-SH$

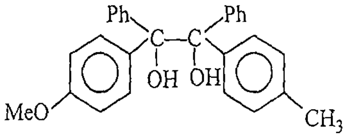
(d) 

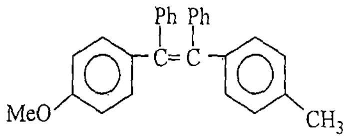
75. Predict the major product P in following reaction:

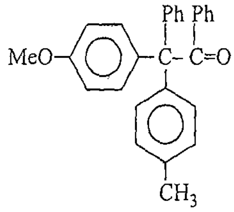


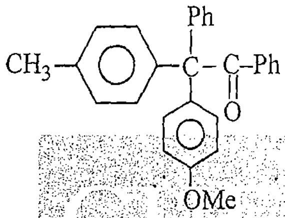
(a)  (b)  (c)  (d) 

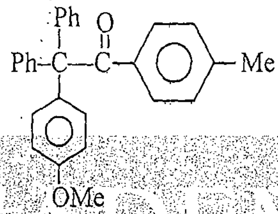
Pinacole Rearrangement

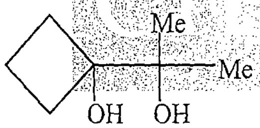
76.  $\xrightarrow[\Delta]{\text{Conc. } H_2SO_4}$ A, A is:

(a) 

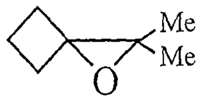
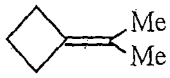
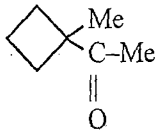
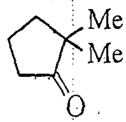
(b) 

(c) 

(d) 

77.  $\xrightarrow[\Delta]{\text{Conc. } H_2SO_4}$ A.

Product A is:

(a)  (b)  (c)  (d) 

78. $Ph-\underset{\displaystyle Me}{\underset{|}{C}}(OH)-C(I)Me_2 \xrightarrow[\Delta]{AgNO_3} ?$

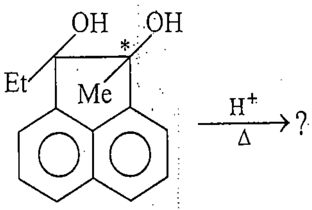
Major product is

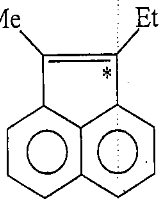
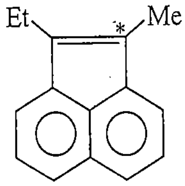
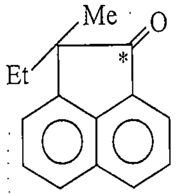
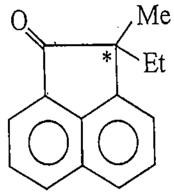
(a) $Ph\underset{\displaystyle Me}{\underset{|}{C}}(OH)-C(NO_3)Me_2$

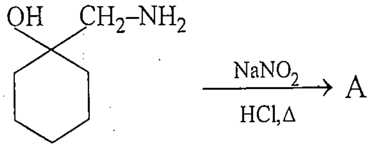
(b) $Ph\overset{\displaystyle OAg}{\overset{|}{\underset{\displaystyle Me}{\underset{|}{C}}}}-C(NO_3)Me_2$

(c) $PhCO-CMe_3$

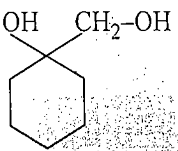
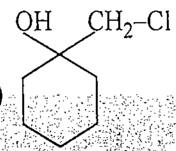
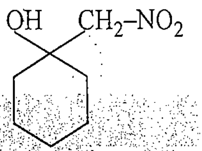
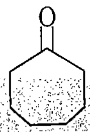
(d) $PhC(Me_2)COMe$

79.  Product is:

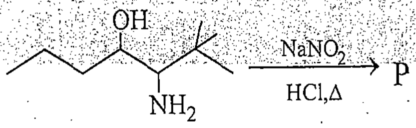
(a)  (b)  (c)  (d) 

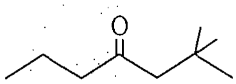
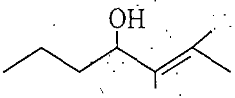
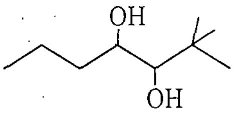
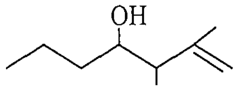
80. 

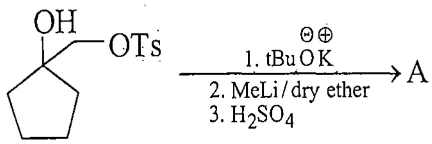
A is

(a)  (b)  (c)  (d) 

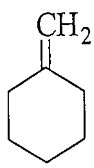
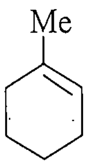
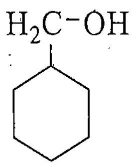
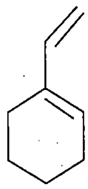
81. Predict the major product P in following reaction:

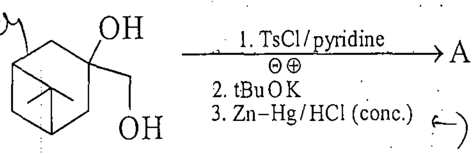


(a)  (b)  (c)  (d) 

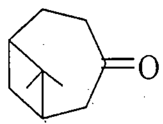
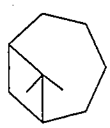
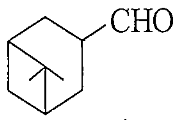
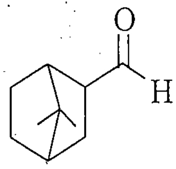
82. 

What is the major product A?

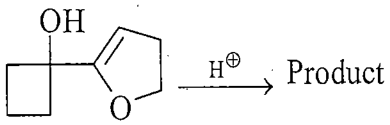
(a)  (b)  (c)  (d) 

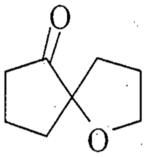
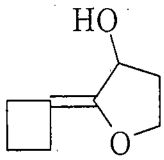
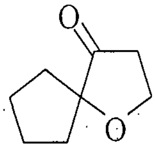
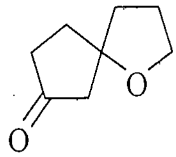
83.  → Clemensen Reduction..

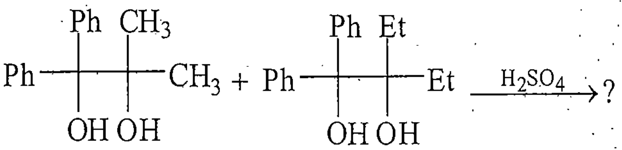
What is the major product A?

(a)  (b)  (c)  (d) 

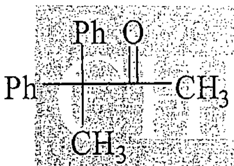
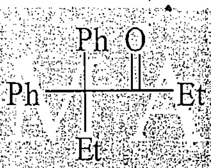
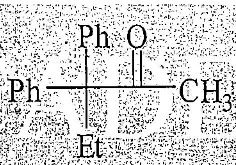
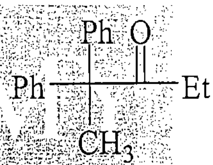
84. Identify the major product



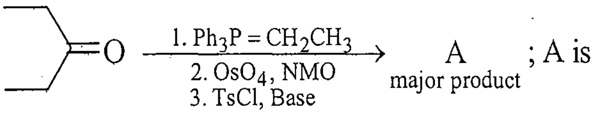
(a)  (b)  (c)  (d) 

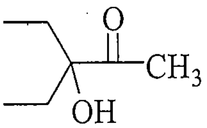
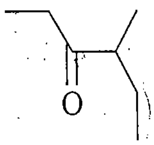
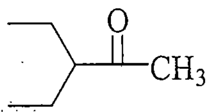
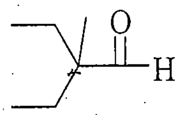
85. 

(A) (B)

(p)  (q)  (r)  (s) 

(a) p, q, r, s (b) p, q (c) p, q, r (d) p, q, s

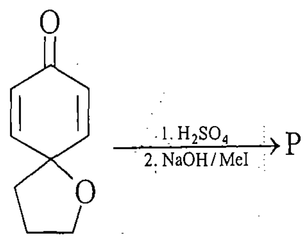
86.  ; A is

(a)  (b)  (c)  (d) 

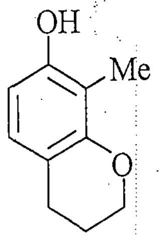
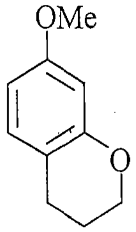
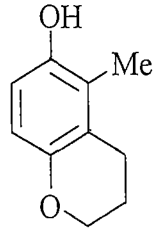
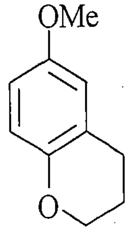
87. $R_2C(OH)CH_2NH_2 \xrightarrow{HONO} A$; A is

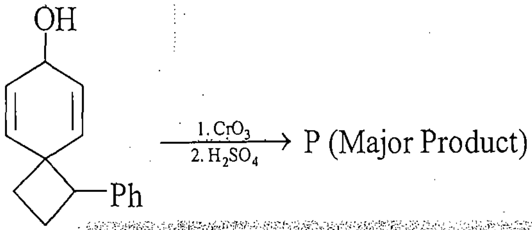
(a) $R_2C(OH)-CH_2-NO_2$ (b) $R-\overset{O}{\overset{||}{C}}-CH_2-R$ (c) $R-\overset{O}{\overset{||}{C}}-CH_2-OH$ (d) $R-\overset{O}{\overset{||}{C}}-CH(NO_2)-NO_2$

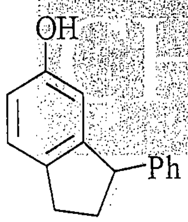
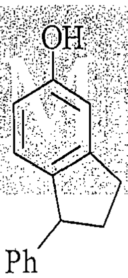
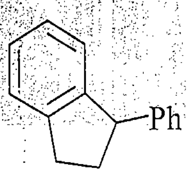
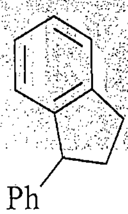
Dienone-Phenol Rearrangement

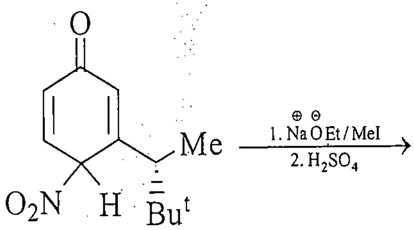
88. 

What is the major product P?

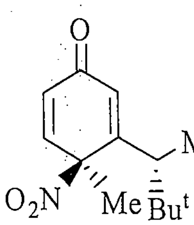
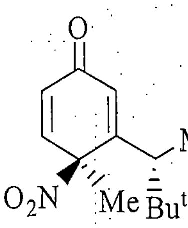
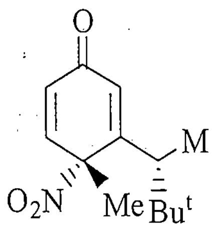
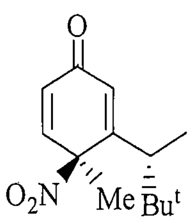
(a)  (b)  (c)  (d) 

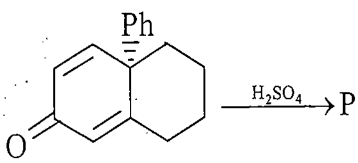
89. 

(a)  (b)  (c)  (d) 

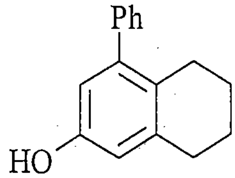
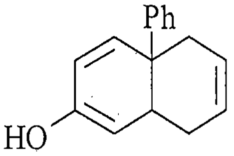
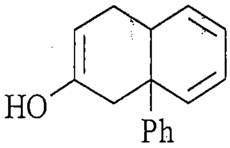
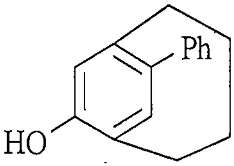
90. 

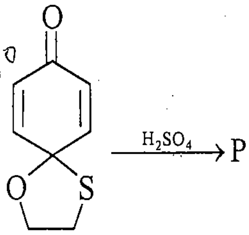
How many products form in the above reaction Including minor product and major product after Ist reaction?

(a) 2,  (b) 4,  (c) 2,  (d) 4, 

91. 

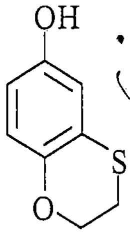
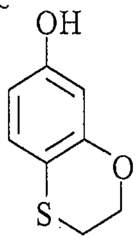
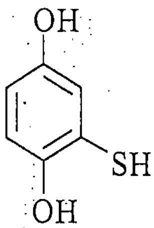
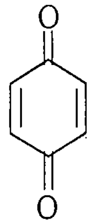
What is the major product P?

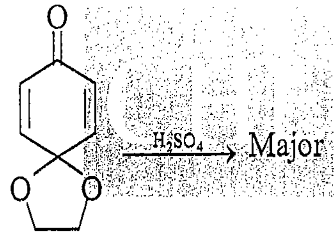
(a)  (b)  (c)  (d) 

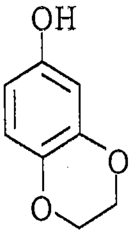
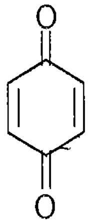
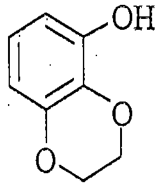
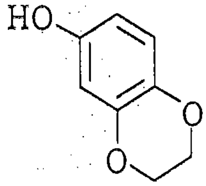
92. 

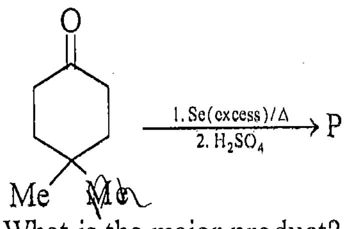
What is the major product in above reaction?

(more nucleophilic sulfur)

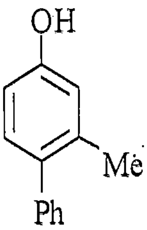
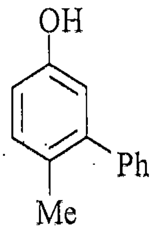
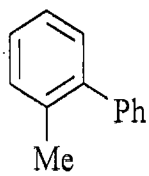
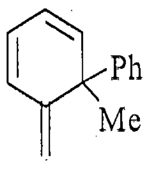
(a)  (b)  (c)  (d) 

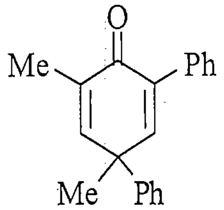
93. 

(a)  (b)  (c)  (d) 

94. 

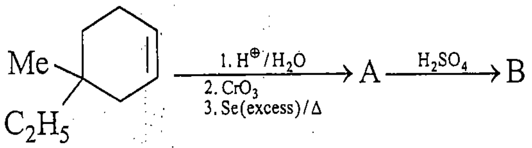
What is the major product?

(a)  (b)  (c)  (d) 

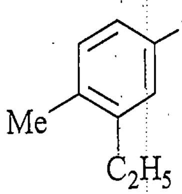
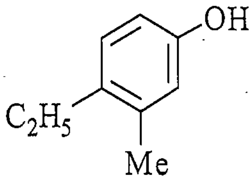
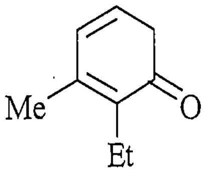
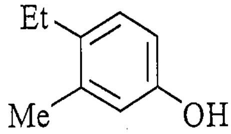
95.  $\xrightarrow{H_2SO_4}$ (Products)

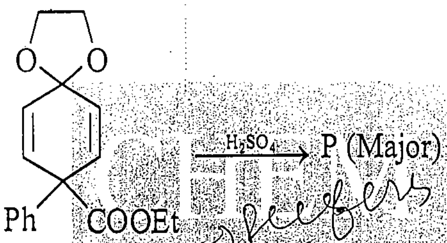
How many product may form in the above reaction?

(a) 2 (b) 4 (c) 3 (d) 5

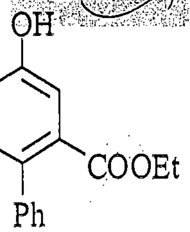
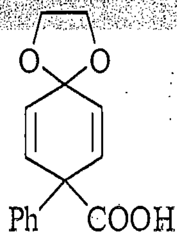
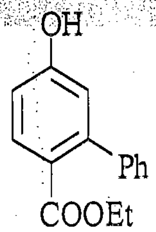
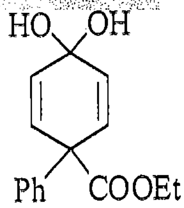


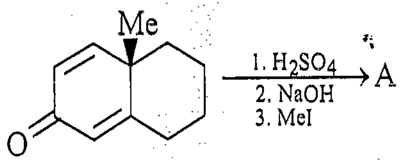
What is the major product B?

(a)  (b)  (c)  (d) 

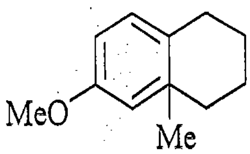
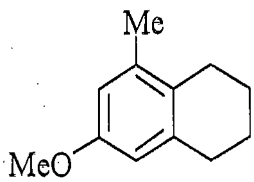
97. 

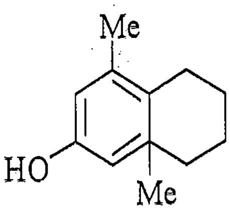
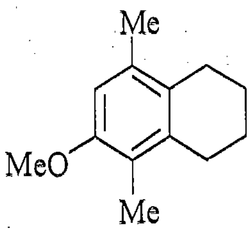
prefers to migrate

(a)  (b)  (c)  (d) 

98. 

What is the major product A?

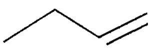
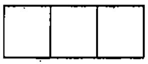
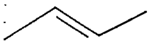
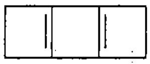
(a)  (b) 

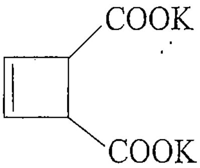
(c)  (d) 

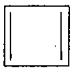
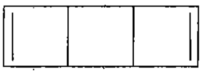
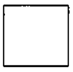
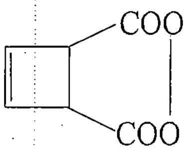
Carbon Free Radical

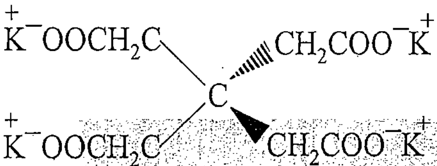
99. $\begin{array}{l} CH_3-CH-CO_2^-K^+ \\ \quad\quad | \\ CH_3-CH-CO_2^-K^+ \end{array} \xrightarrow{\text{electrolysis}}$ (A) (Major)

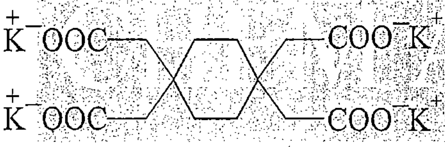
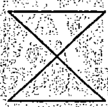
Major product (A) of above reaction

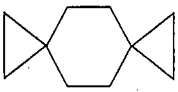
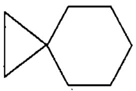
(a)  (b)  (c)  (d) 

100.  $\xrightarrow{\text{Electrolysis}}$ Major product of reaction :

(a)  (b)  (c)  (d) 

101.  on electrolysis gives:

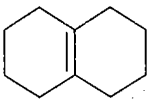
(a)  (b) 

(c)  (d) 

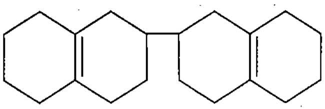
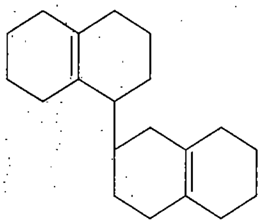
102. Find out the correct order of rate of reaction towards allylic substitution.

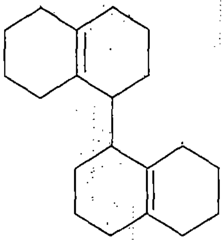
(I) $CH_3-CH=CH_2$ (II) $CH_3-CH_2-CH=CH_2$ (III) $CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-CH=CH_2$

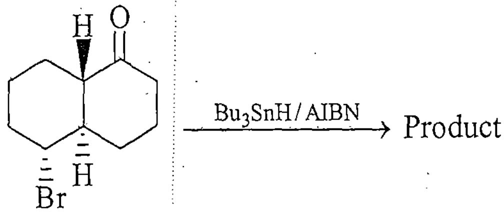
(a) I > II > III (b) II > I > III (c) III > II > I (d) III > I > II

103.  $\xrightarrow[\text{CCl}_4\text{.peroxide}]{\text{NBS}} \xrightarrow{\text{Na / Ether}}$ (X)

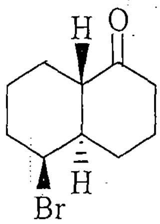
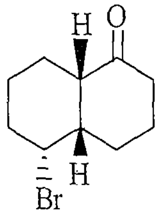
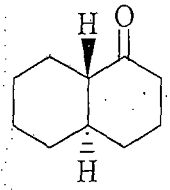
X is :

(a)  (b) 

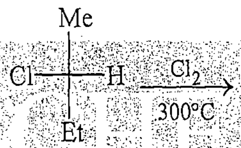
(c)  (d) None of these

104. 

through (free radical mechanism) remove Br (Halogen) " replaced "

(a)  (b)  (c)  (d) All

105. Pick the correct statement for monochlorination of R-secbutyl chloride.



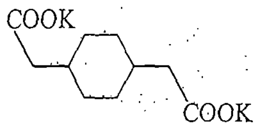
(a) There are four possible production ; three are optically active one is optically inactive

(b) There are five possible production ; three are optically inactive & two are optically active

(c) There are five possible production ; two are optically inactive & three are optically active

(d) There are four possible production ; two are optically active & two are optically inactive

106. **Statement-1** : The major product formed by the electrolysis of aqueous solution of

 is optically inactive.

Statement-2 : The product has C_3 axis of symmetry.

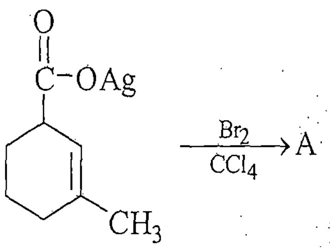
(a) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(b) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

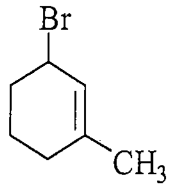
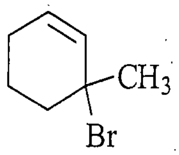
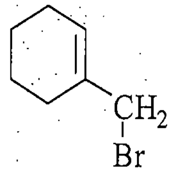
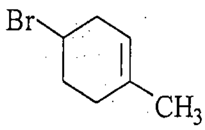
(c) Statement-1 is true, statement-2 is false.

(d) Statement-1 is false, statement-2 is true.

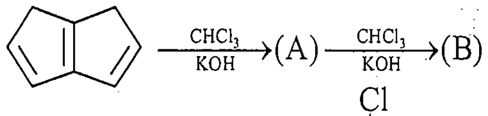
107. Major product formed in the following reaction is

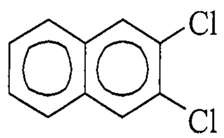
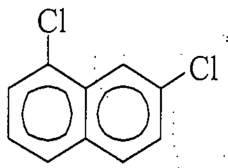
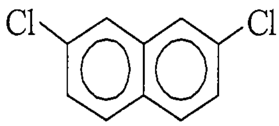
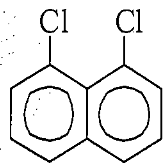


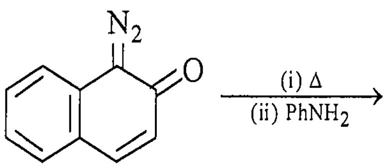
(free radical mechanism

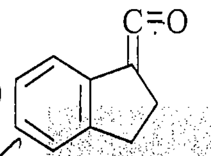
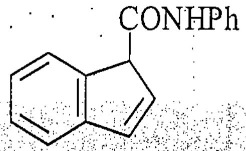
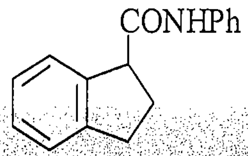
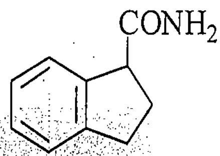
(a)  (b)  (c)  (d) 

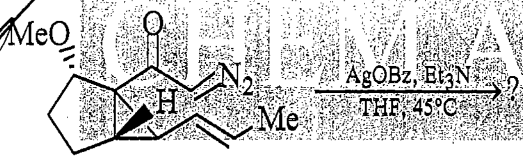
Carbene

108.  ; Product (B) is:

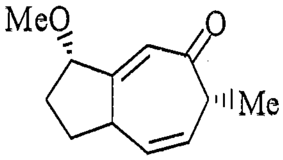
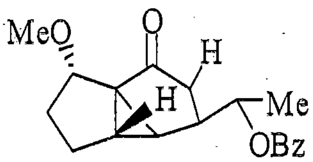
(a)  (b)  (c)  (d) 

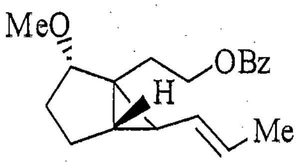
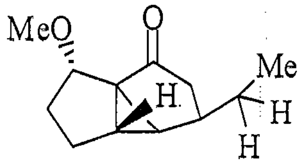
109.  Product; Product is

(a)  (b)  (c)  (d) 

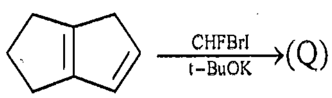
110. 

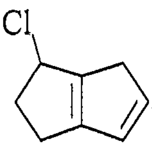
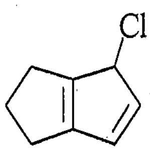
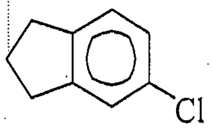
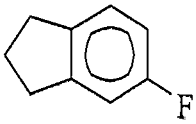
Impo. ketene formation followed by [3,3]-Sigmatropic Rearrangement

(a)  (b) 

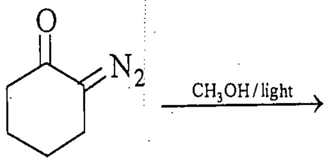
(c)  (d) 

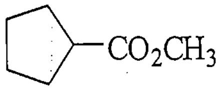
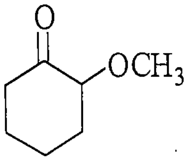
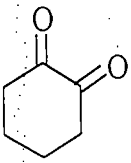
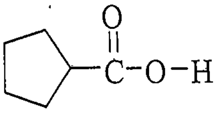
111. What is the product (Q) of the following reaction?

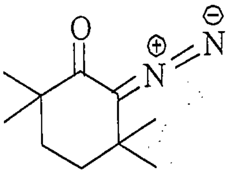


(a)  (b)  (c)  (d) 

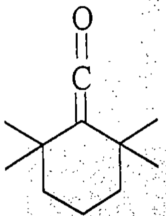
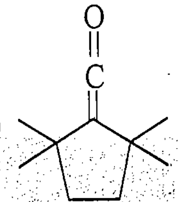
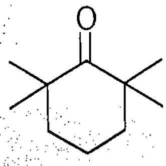
112. A rather interesting example of the Wolff rearrangement with 2-diazocyclohexanone in methanol is given below. Identify the major product:

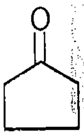


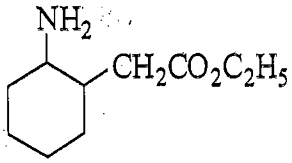
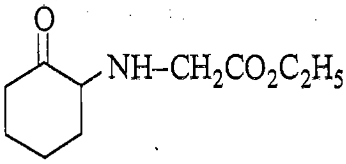
(a)  (b)  (c)  (d) 

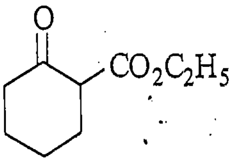
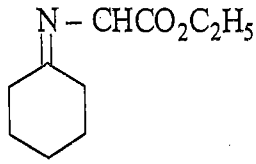
113.  $\xrightarrow{h\nu}$ Major product

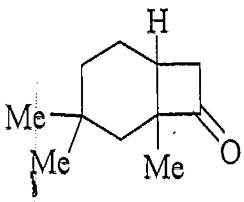
Major product is

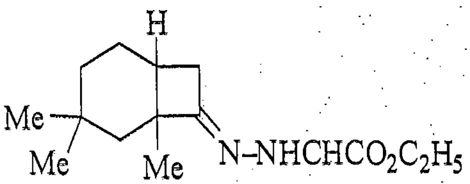
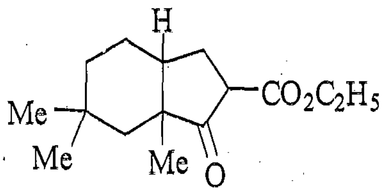
(a)  (b)  (c)  (d) 

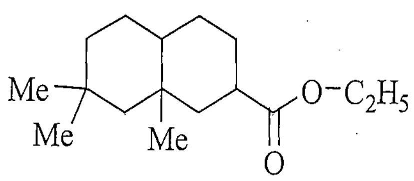
114.  $+ N_2CHCO_2C_2H_5 \xrightarrow{SbCl_5} \underset{\text{Major product}}{A}$; A is

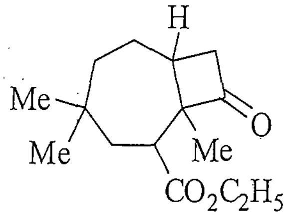
(a)  (b) 

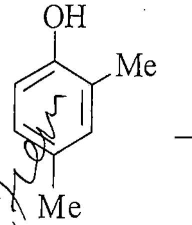
(c)  (d) 

115.  $\xrightarrow[Br_3,\ 25°C]{N_2CHCO_2C_2H_5}$ A ; A can be

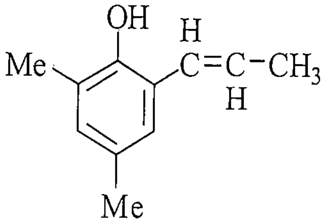
(a)  (b) 

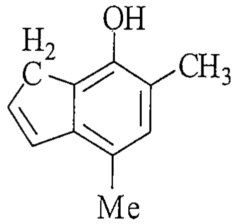
(c) 

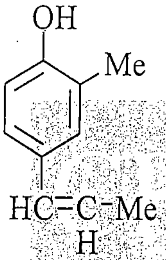
(d) 

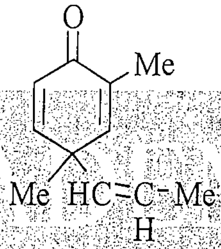
116.  $\xrightarrow{CHCl_3 + NaOH}$ A $\xrightarrow{Ph_3P=CH_2CH_3}$ B ; B is

Reimer Tiemann

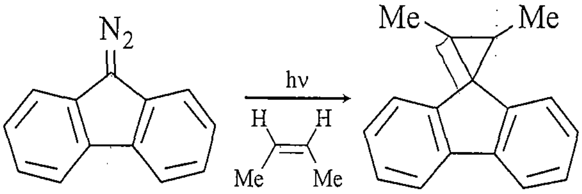
(a) 

(b) 

(c) 

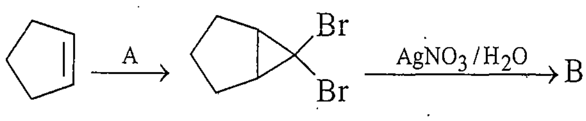
(d) 

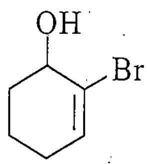
117. The intermediate involved in the reaction given below is

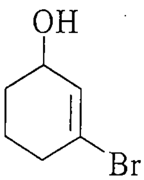


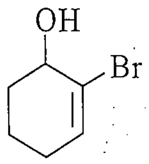
(a) free radical (b) carbocation (c) carbanion (d) carbene

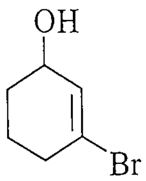
118. The reagent A required and the major product B formed in the following reaction sequence are



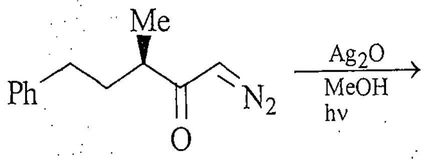
(a) A = CH_2Br_2 and KO^tBu, B = 

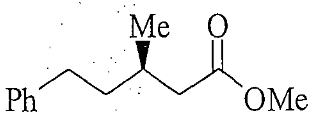
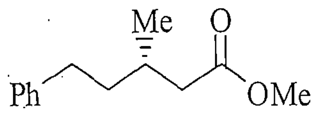
(b) A = CH_2Br_2 and KO^tBu, B = 

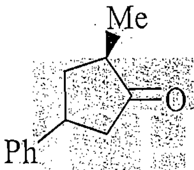
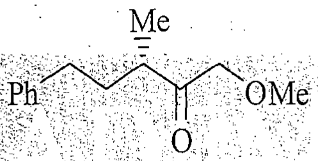
(c) A = $CHBr_3$ and KO^tBu, B = 

(d) A = $CHBr_3$ and KO^tBu B = 

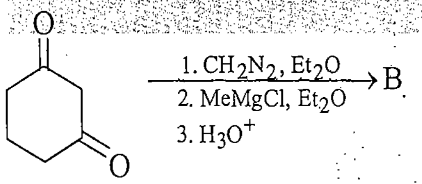
119. The major product formed in the following reaction is

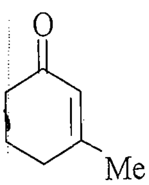
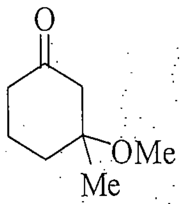
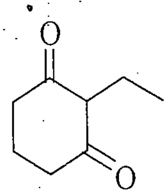
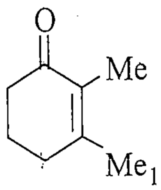


(a) 
(b) 

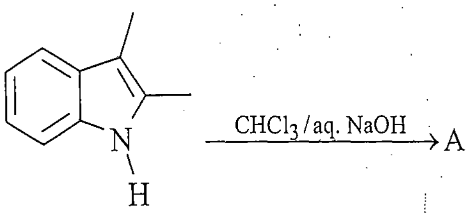
(c) 
(d) 

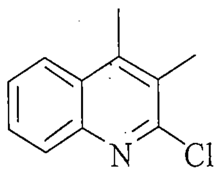
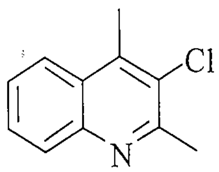
120. The major product B formed in the following reaction sequence is

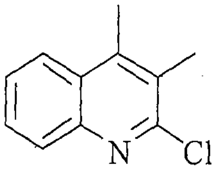


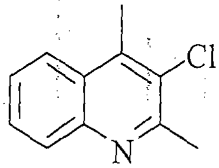
(a) 
(b) 
(c) 
(d) 

121. In the following reaction, the intermediate and the major product A are

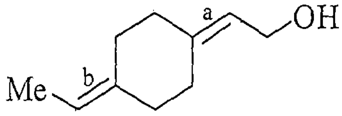


(a) :CHCl and 
(b) :CHCl and 

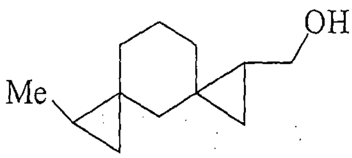
(c) :CCl_2 and 

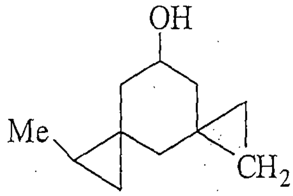
(d) :CCl_2 and 

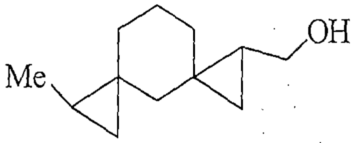
Simon Smith Reaction

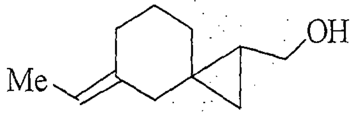
122.  $\xrightarrow{CH_2I_2/Zn-Cu}$ A

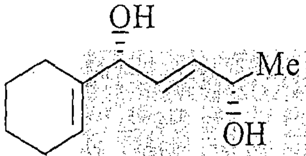
The reactivity of double bond for Simmons-Smith Reaction and major Product A?

(a) a > b, A = 

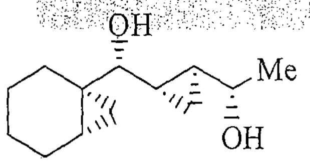
(b) a > b, A = 

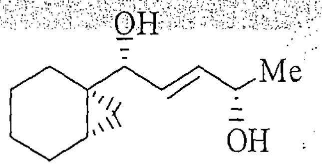
(c) b > a, A = 

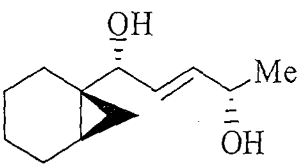
(d) b > a, A = 

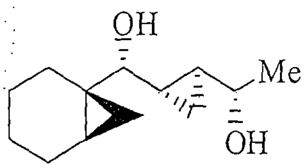
123.  $\xrightarrow{CH_2I_2/Zn-Cu}$ A

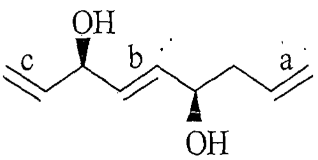
What is the major product A

(a) 

(b) 

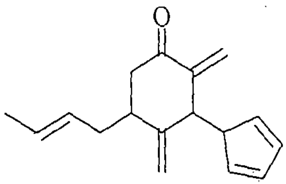
(c) 

(d) 

124. 

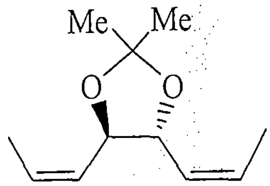
The order of reactivity for Simmons-Smith Reaction?

(a) b > c > a (b) b > a > c (c) b > a = c (d) c > b > a

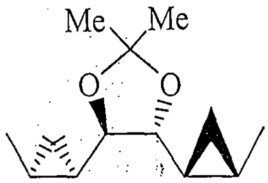
125. 

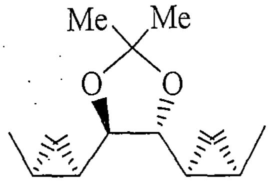
The number of double bond which involve in Simmon-Smith Reaction?

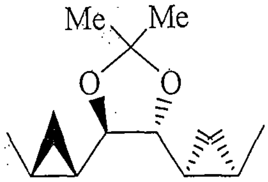
(a) 4 double bond (b) 3 double bond (c) 2 double bond (d) One double bond

126.  $\xrightarrow{CH_2I_2/Zn-Cu}$ A

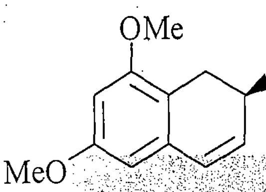
What is the major product A

(a) 

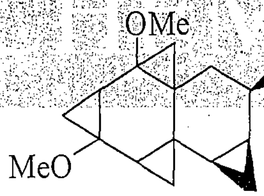
(b) 

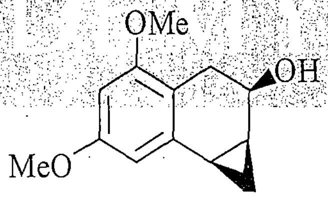
(c) 

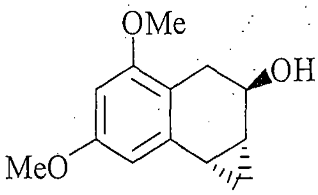
(d) None of these

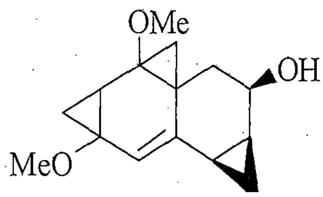
127.  $\xrightarrow{CH_2I_2/Zn-Cu}$ A

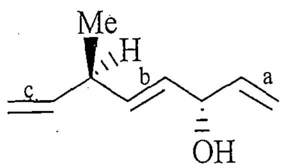
The number of double bonds involve in cyclopropanation reaction and major product?

(a) 4, A = 

(b) 1, A = 

(c) 1, A = 

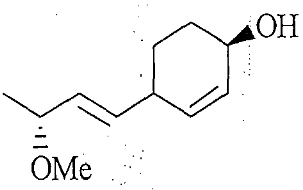
(d) 3, A = 

128. 

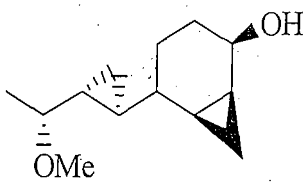
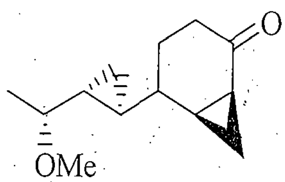
The order of Simmon-smith Reaction for double bonds?

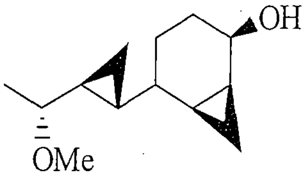
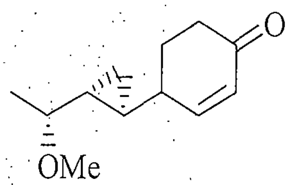
(a) a > b > c (b) b > a > c (c) a > c > b

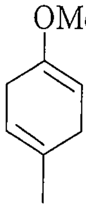
(d) a > b >>> c (c will not give the reaction)

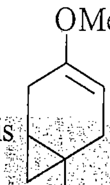
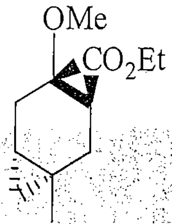
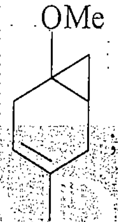
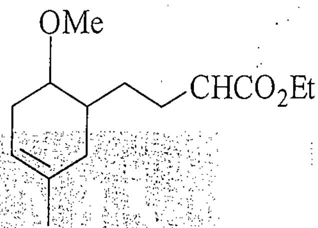
129.  $\xrightarrow[2.\ CH_2I_2/Zn-Cu]{1.\ PCC}$ A

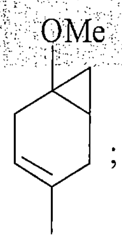
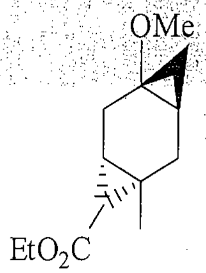
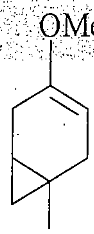
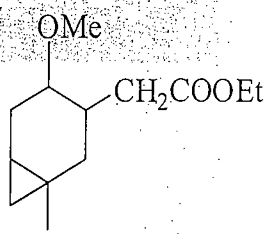
What is the major product A?

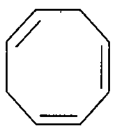
(a)  (b) 

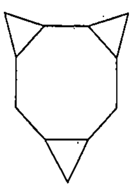
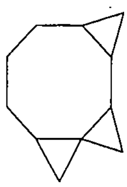
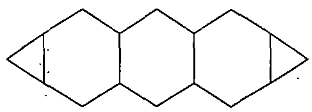
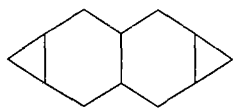
(c)  (d) 

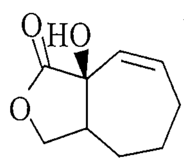
130.  $\xrightarrow[Zn/Ag]{CH_2I_2}$ A $\xrightarrow[Cu(I)]{N_2CHCO_2Et}$ B

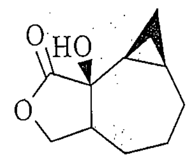
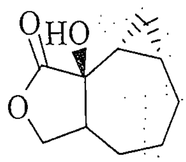
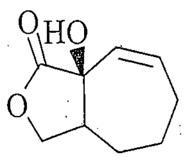
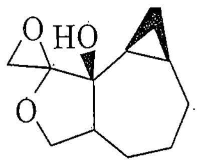
(a) A is  ; B is 
(b) A is  ; B is 

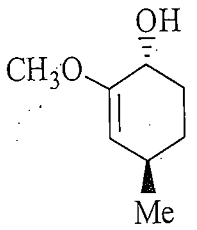
(c) A is  ; B is 
(d) A is  ; B is 

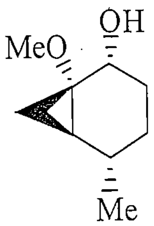
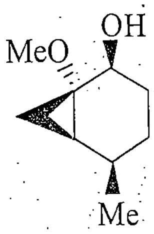
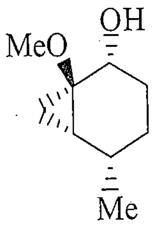
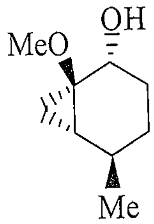
131.  $\xrightarrow[Zn/Cu]{(3\ mole)CH_2I_2}$ (A) ; Compound (A) is

(a)  (b)  (c)  (d) 

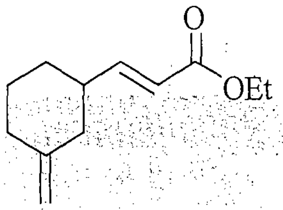
132.  $\xrightarrow{CH_2ZnI_2}$ $\underset{\text{Major product}}{D}$; D is

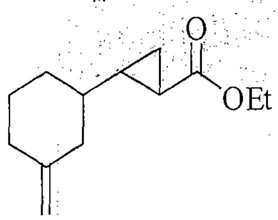
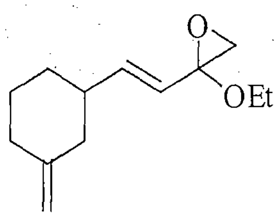
(a)  (b)  (c)  (d) 

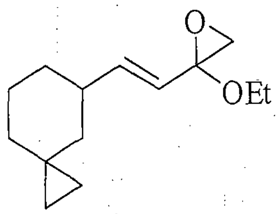
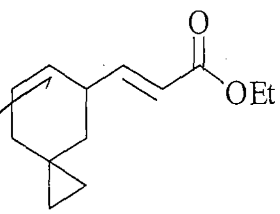
133.  $\xrightarrow[CH_2I_2]{Zn(Cu)}$ $\underset{\text{Major product}}{P}$; P is

(a)  (b)  (c)  (d) 

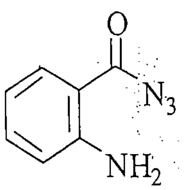
134. Major product formed in the given reaction is

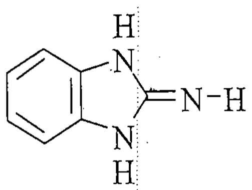
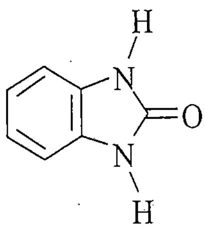
 $\xrightarrow[Zn-Cu]{CH_2I_2}$

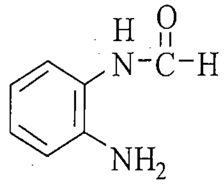
(a)  (b) 

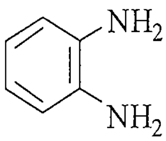
(c)  (d) 

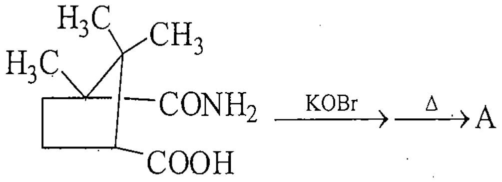
Nitrene

135.  $\xrightarrow[\text{Toluene}]{\Delta}$?

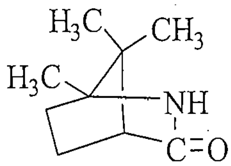
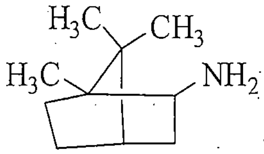
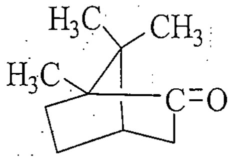
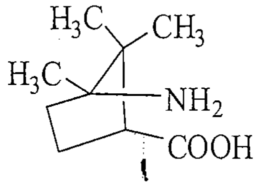
(a)  (b) 

(c) 

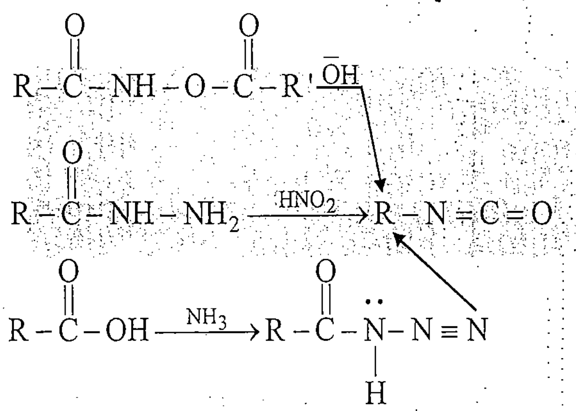
(d) 

136. 

The compound A is

(a)  (b)  (c)  (d) 

137. The following group of reaction very closely related to Hofmann involve the formation of an isocyanate, name them

I. II. III. 

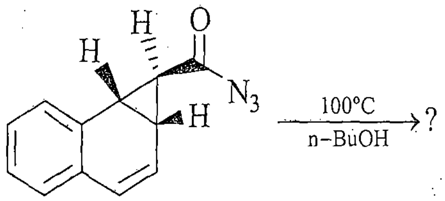
(a) (I) Schmidt (II) Curtius (III) Lossen
(b) (I) Lossen (II) Curtius (III) Schmidt
(c) (I) Curtius (II) Lossen (III) Schmidt
(d) (I) Schmidt (II) Lossen (III) Curtius

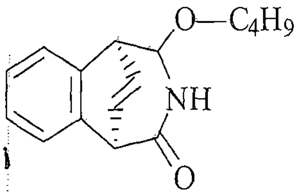
138. Match the Column I with Column II

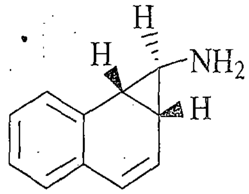
Column I		Column II
A. Hofmann rearrangement	1.	Esters
B. Benzil-benzylic acid rearrangement	2.	α-diazoketone
C. Wolff rearrangement	3.	Isocyanate
D. Bayer Villiger rearrangement	4.	α-diketone

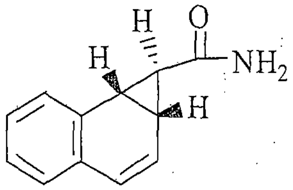
Codes

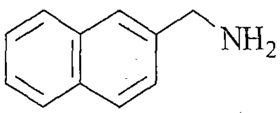
	A	B	C	D		A	B	C	D
(a)	3	4	1	2	(b)	3	4	2	1
(c)	4	3	2	1	(d)	3	1	4	2

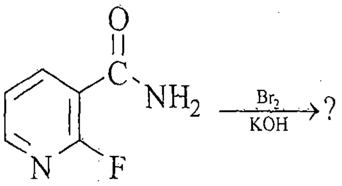
139. 

(a) 

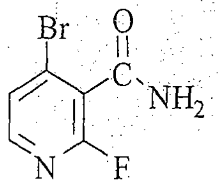
(b) 

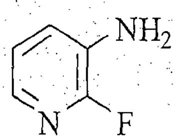
(c) 

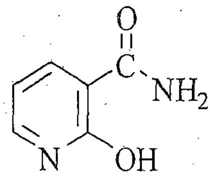
(d) 

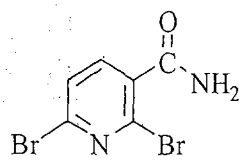
140. 

Product is

(a) 

(b) 

(c) 

(d) 

141. $R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[CH_3OH,\ CH_3\overset{\ominus}{O}Na^{\oplus}]{NBS}$ Major product

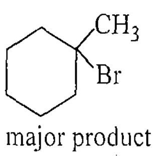
Product is

(a) $RNHCO_2CH_3$ (b) $R-NHCO_2CH_2-Br$ (c) $\underset{\underset{Br}{|}}{RN}CO_2CH_3$ (d) $R-\overset{\overset{O}{\|}}{C}-\underset{\underset{Br}{|}}{N}-CH_2OH$

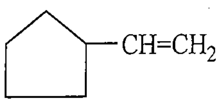
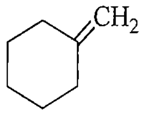
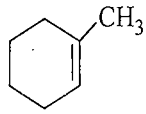
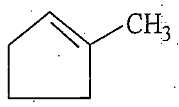
EXERCISE - II

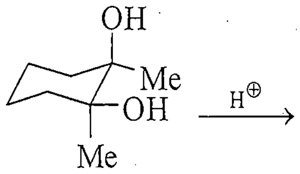
Multiple Select Questions

1. In the given reaction

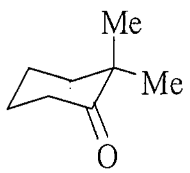
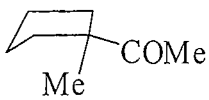
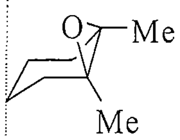
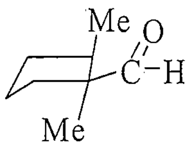
$C_7H_{12}\ (a) \xrightarrow{HBr}$  (a) can be

as major product

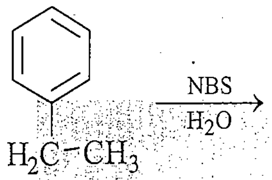
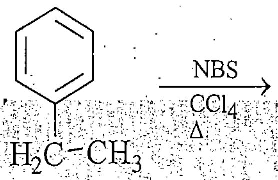
(a)  (b)  (c)  (d) 

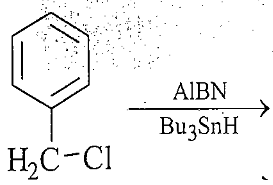
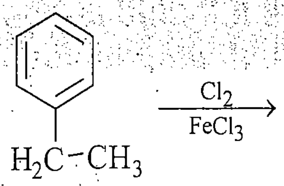
2. 

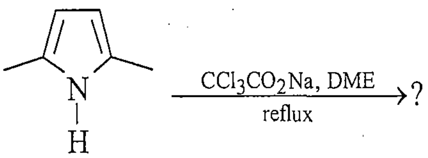
Product(s) formed is(are)

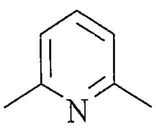
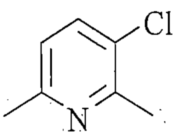
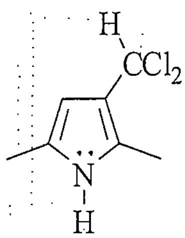
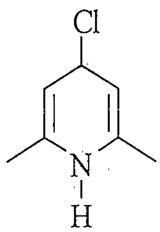
(a)  (b)  (c)  (d) 

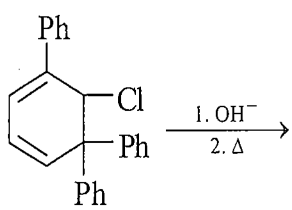
3. Which of the following is/are involves carbon free radical as an intermediate

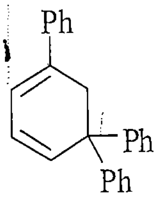
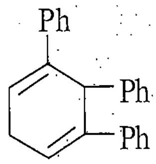
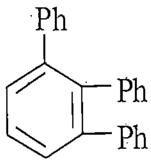
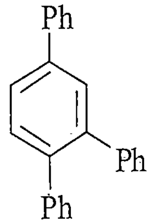
(a)  (b) 

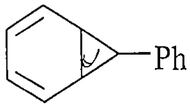
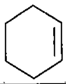
(c)  (d) 

Check.
4. 

(a)  (b)  (c)  (d) 

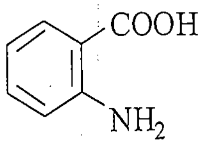
5.  Product is/are

(a)  (b)  (c)  (d) 

6.  $\xrightarrow{hv}$ A + Intermediate $\xrightarrow{\quad}$ B 

Correct statement(s) is/are

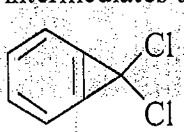
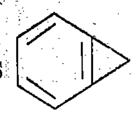
(a) A is an aromatic compound
(b) B is an aromatic compound
(c) Intermediate formed is carbene
(d) A and B has same number of carbon atoms

7.  $\xrightarrow[\text{2. } OH^-]{\text{1. } NaNO_2+HCl}$ A(Intermediate)

$CHCl_3 + KOH \longrightarrow$ B(Intermediate)

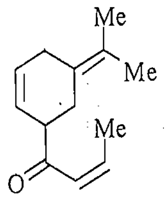
$A + B \longrightarrow C \xrightarrow[\Delta]{Zn+HCl} D$

The false statement(s) is/are

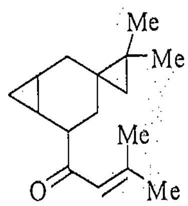
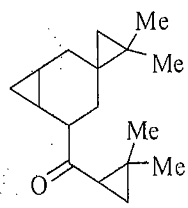
(a) both intermediates are deficient.
(b) both intermediates are back bonded stablised
(c) C is 
(d) D is 

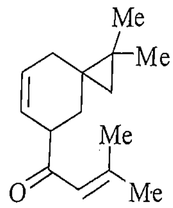
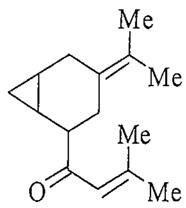
8. Select the correct statements from the following given statements.

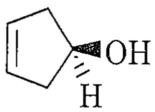
(a) Baeyer-Viliger oxidation involves 1,2-migrations to an electron deficient oxygen.
(b) In Lossen rearrangement isocyanate intermediate is formed.
(c) In Curtius rearrangement conversion of acyl azide to an isocyanate takes place.
(d) In Curtius rearrangement isocyanate cannot be isolable.

9.  $\xrightarrow[\Delta]{CH_2I_2/Zn-Cu}$ P

The possible product formed in the above reaction and number of sp^2 hybrid carbon in the major product?

(a)  and number of sp^2 carbon = 3 (b)  and number of sp^2 carbon = 1

(c)  and number of sp^2 carbon = 3 (d)  and number of sp^2 carbon = 3

10.  + $CH_2I_2 \xrightarrow{Zn(Cu)}$ Major product

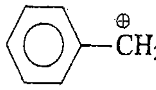
Choose the correct statement(s) regarding the major product

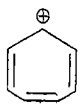
(a) Degree of unsaturation of product is 2

(b) Product can show geometrical isomerism

(c) Compound formed has plane of symmetry

(d) Compound formed is optically active

11. Among following cations which are more stabilized than  ?

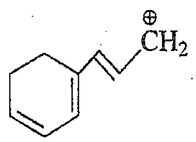
(a) 

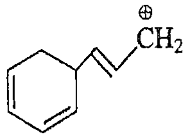
(b) $CH_3-\ddot{N}(H)-\overset{\oplus}{C}H_2$

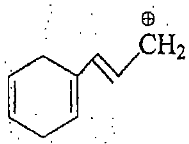
(c) $CH_3-\overset{\oplus}{C}(CH_3)-CH_3$

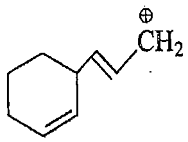
(d) $CH_2=CH-\overset{\oplus}{C}H_2$

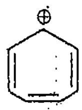
12. Identify the cations which are less stable than:



(a) 

(b) 

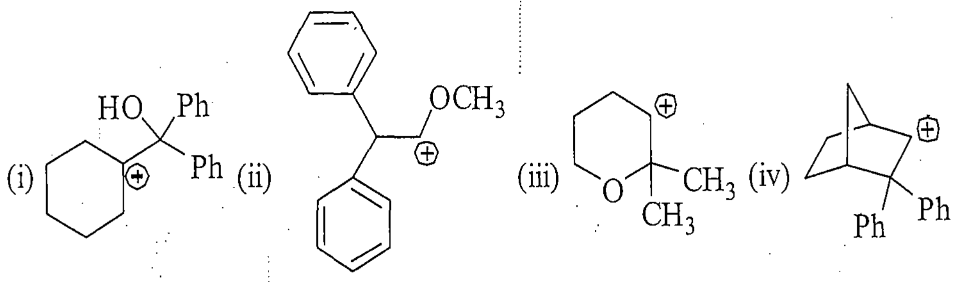
(c) 

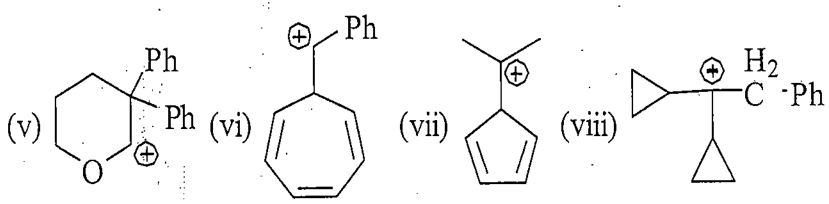
(d) 

EXERCISE - III

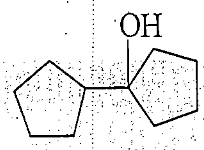
Numerical Answer Type

1. Number of carbocation which will undergoes rearrangement





2. Number of five membered ring formed during dehydration of the given alcohol is

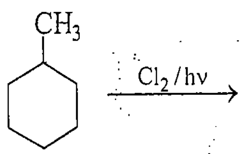


3. On monochlorination of given compound, total number of chiral compound is

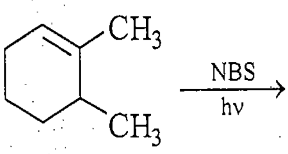
(a) $CH_3-CH_2-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-CH_2-CH_3 \xrightarrow{Cl_2/h\nu}$

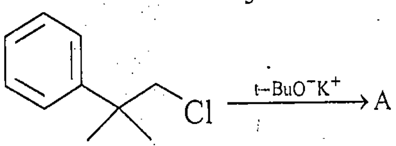
(b) $CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-CH_3 \xrightarrow{Cl_2/h\nu}$

4. Number of possible product on monochlorination of given compound is



5. Number of possible product formed (excluding stereoisomers)



6. 

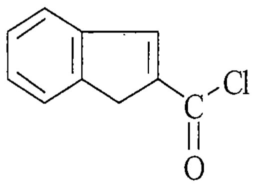
No. of sp^2 hybridized carbon in the product is

7. How many processes given below are the characterstics of carbene.

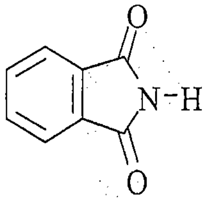
(1) Insertion in O-H bond (2) Insertion in C-H bond
(3) Insertion in pie bond (4) Wolf Rearrangement
(5) Curtius Rearrangement (6) Smith Rearrangement
(7) Lossen Rearrangement (8) Dimerisation

8. $$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow[\substack{2.\ CH_2N_2\ (1\ eq.)\\ 3.\ AgOH,\ \Delta\\ 4.\ H_2O\\ 5.\ H^+}]{1.\ SOCl_2} \text{Product} \quad (R = C_{(n-2)}H_{2n-3})$$

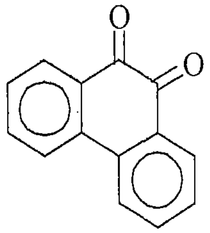
if number of hydrogens in the product is 24. The value of n is

9.  $\xrightarrow[(2)\ \Delta,\ PhCH_2OH]{(1)\ CH_2N_2\ (2\ eq)}$ Major product

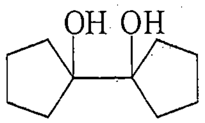
Degree of unsaturation of the product is

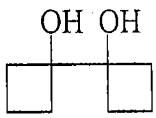
10.  $\xrightarrow[2.\ H_2O]{1.\ Br_2/KOH} A \xrightarrow[\substack{2.\ CH_2N_2\ (1\ eq.)\\ 3.\ AgOH,\ \Delta\\ 4.\ H_2O}]{1.\ SOCl_2} B$

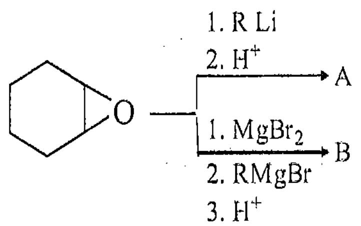
Total number of carbon in the product A and B is

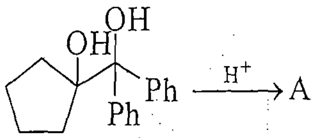
11.  $\xrightarrow[\substack{2.\ NH_3\\ 3.\ NaOH,\ Br_2\\ 4.\ H_2O}]{1.\ KOH}$ Product $(C_nH_mO_pN_q)$

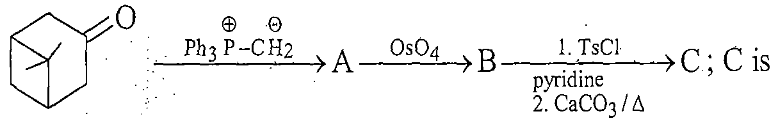
What is the value of n + m + p + q?

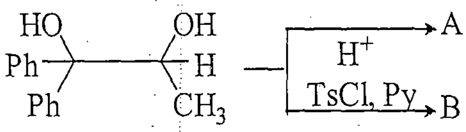
12.  $\xrightarrow{H^+}$ A

13.  $\xrightarrow{H^+} A \xrightarrow{LiAlH_4} B \xrightarrow{H^+/\Delta} C$; C is

14. 

15. 

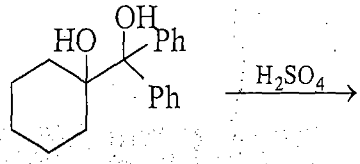
16. 

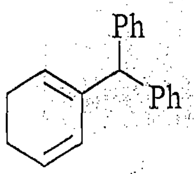
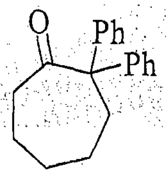
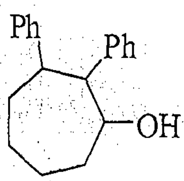
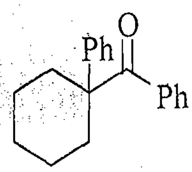
17. 

EXERCISE - IV

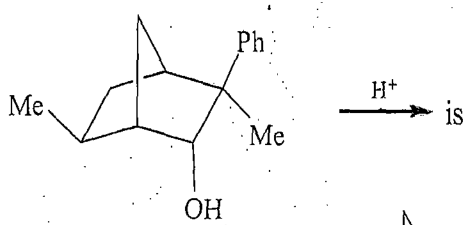
Previous Year Questions

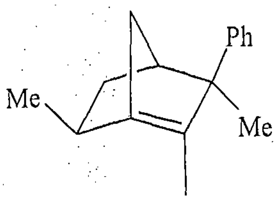
1. The major product formed in the following reaction is

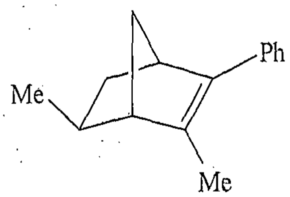


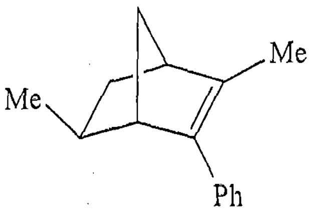
(a)  (b)  (c)  (d) 

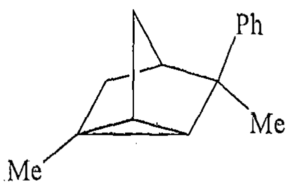
2. The major product obtained in the following reaction



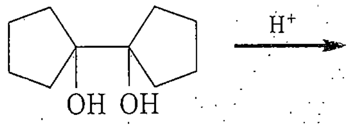
(a) 

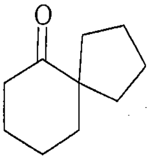
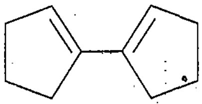
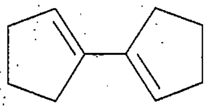
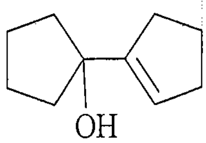
(b) 

(c) 

(d) 

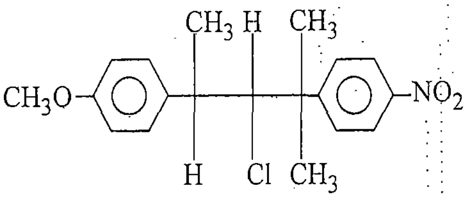
3. The major product of the reaction

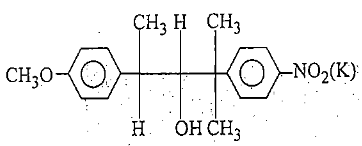
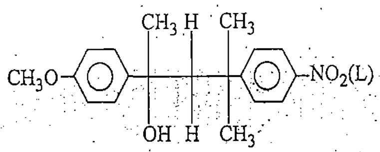
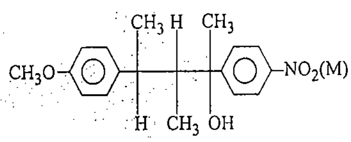
 is

(a)  (b)  (c)  (d) 

4. Which is the best reagent to convert cyclohexanol into cyclohexene.

(a) conc. HCl (b) conc. HBr (c) conc. H_3PO_4 (d) $HCl + ZnCl_2$

5. Compound (X)  is reacted with aqueous acetone it gives following products:

(a) K, L (b) K, M (c) L only (d) M only

6. Choose the correct order of reactivity for dehydration of the given alcohols using concentrated sulfuric acid

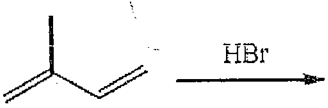
(a) 2-methylpropan-2-ol > 2-butanol > 1-butanol

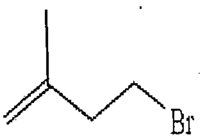
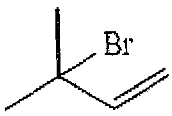
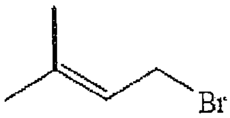
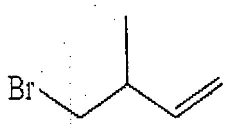
(b) 2-methylpropan-2-ol > 1-butanol > 2-butanol

(c) 2-butanol > 2-methylpropan-2-ol > 1-butanol

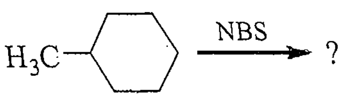
(d) 1-butanol > 2-butanol > 2-methylpropan-2-ol

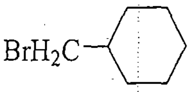
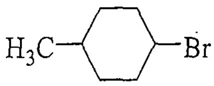
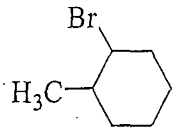
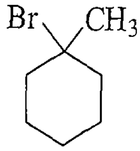
7. The major product of the reaction

 is

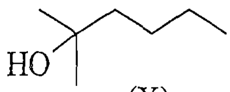
(a)  (b)  (c)  (d) 

8. The major product (X) of the monobromination reaction is

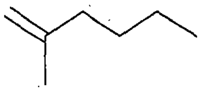
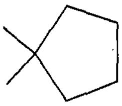
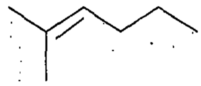
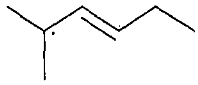


(a)  (b)  (c)  (d) 

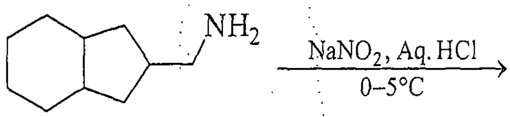
9. The major product obtained upon treatment of compound X with H_2SO_4 at 80°C is

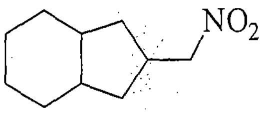
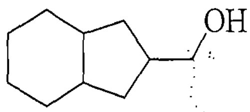
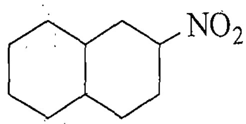
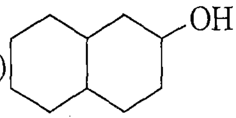


(X)

(a)  (b)  (c)  (d) 

10. The major product formed in the reaction given below is



(a)  (b)  (c)  (d) 

ANSWER KEY

EXERCISE - I

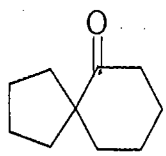
1. b	2. b	3. a	4. b	5. b	6. d	7. c
8. c	9. c	10. a	11. c	12. d	13. a	14. b
15. c	16. b	17. c	18. d	19. a	20. d	21. d
22. b	23. b	24. c	25. c	26. c	27. d	28. d
29. a	30. c	31. b	32. c	33. c	34. c	35. a
36. a	37. b	38. c	39. d	40. c	41. a	42. c
43. b	44. b	45. a	46. c	47. c	48. c	49. c
50. a	51. b	52. b	53. d	54. d	55. a	56. a
57. c	58. c	59. a	60. c	61. b	62. b	63. c
64. a	65. d	66. b	67. c	68. b	69. c	70. c
71. d	72. c	73. d	74. d	75. a	76. c	77. d
78. d	79. d	80. d	81. a	82. b	83. b	84. a
85. b	86. b	87. b	88. b	89. a	90. c	91. a
92. a	93. b	94. b	95. b	96. a	97. a	98. b
99. c	100. b	101. b	102. c	103. c	104. c	105. c
106. b	107. a	108. c	109. b	110. a	111. d	112. a
113. b	114. c	115. b	116. a	117. d	118. c	119. a
120. a	121. d	122. a	123. a	124. a	125. a	126. c
127. b	128. a	129. d	130. c	131. a	132. a	133. d
134. a	135. b	136. a	137. b	138. b	139. a	140. b
141. a						

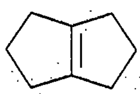
EXERCISE - II

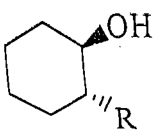
1. a,b,c	2. a,b	3. b,c	4. b	5. c	6. a,c	7. a,b
8. a,b,c	9. a,c,d	10. a,b,c	11. a,b,c	12. a,b,c		

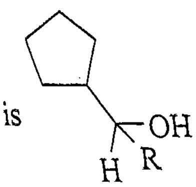
EXERCISE - III

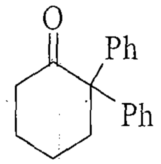
1. 4	2. 0	3. (a) 8 (b) 6	4. 12	5. 6	6. 8	7. 5
8. 12	9. 11	10. 15	11. 22			

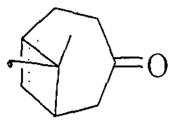
12. 

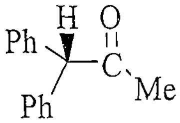
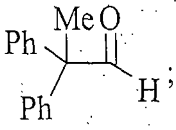
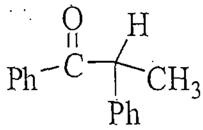
13. 

14. A is 

; B is 

15. 

16. C is 

17. A is  and  ; B is 

EXERCISE - IV

1. b	2. c	3. a	4. c	5. a	6. a	7. c
8. d	9. c	10. d				

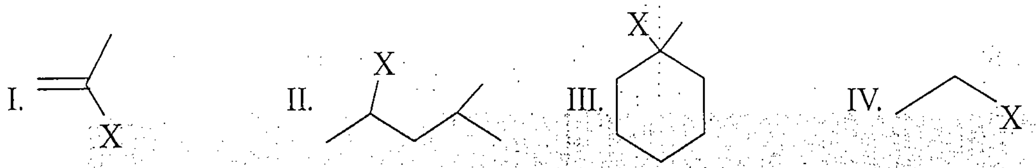
CHAPTER 4

REACTION MECHANISM

EXERCISE - I

Single Answer Correct Type

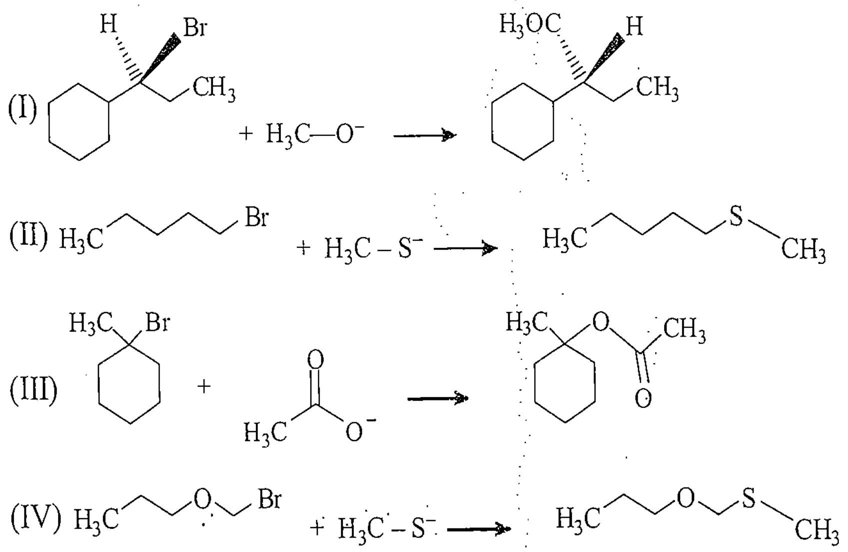
1. Which of the following shows the correct decreasing order of solvolysis with aqueous ethanol?



The correct choice is :

(a) III > II > I > IV (b) III > II > IV > I (c) II > III > IV > I (d) III > I > IV > II

2. Which of the following reaction will go faster if the concentration of the nucleophile is raised ?



(a) I and III (b) II and IV (c) I and II (d) I, II and IV

3. S_N1 reaction underoges through a carbocation intermediate as follows : -

$$R\text{–}X\,(aq.) \underset{}{\overset{\text{Slow}}{\rightleftharpoons}} R^{+}(aq.) + X^{-}(aq.) \xrightarrow[\text{fast}]{H_2O} ROH(aq.) + H^{+}(aq.)$$

[R = t-Bu, iso-Pr, Et, Me] (X = Cl, Br, I)

The correct statements are

I. The decreasing order of rate of S_N1 reaction is t-BuX > iso-PrX > EtX > MeX

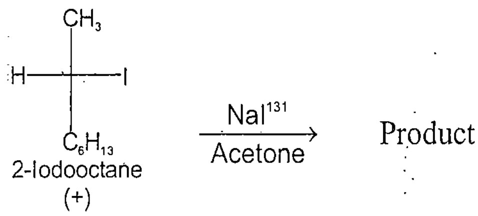
II. The decreasing order of ionisation energy is MeX > EtX > iso-PrX > t-BuX

III. The decreasing order of energy of activation is t-BuX > iso-PrX >EtX > MeX

(a) I & II are correct (b) I & III are correct

(c) II and III are correct (d) I, II & III are correct

4. Which statement is incorrect about the following reaction



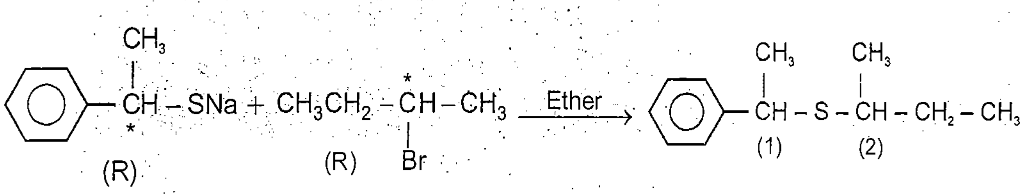
(a) The rate of these reaction depends on both [R–I] and $[^{131}I^{\ominus}]$

(b) Loss of optical activity was twice as fast as gain of radioactivity.

(c) Each molecule undergoing substitution, suffers Inversion of configuration

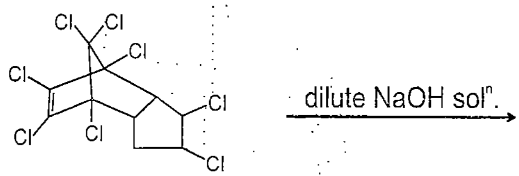
(d) Final solution has radioactive iodine only

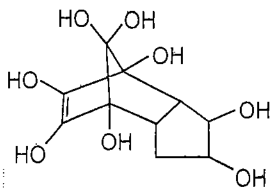
5. Which configuation will be adopted by the poduct at cabon atoms marked (1) and (2) respectively in the given reaction.

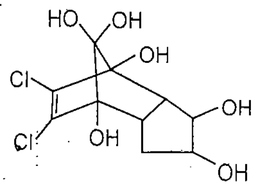


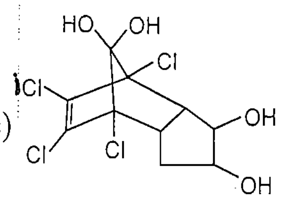
(a) R, R (b) R, S (c) S, S (d) S, R

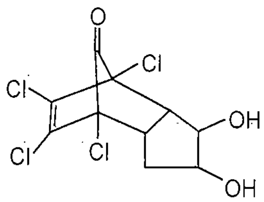
6. The insecticide chlordane is warmed with dilute NaOH solution for some time. The expected product would be :



(a) 

(b) 

(c) 

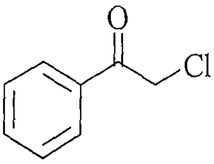
(d) 

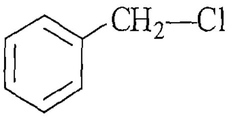
7. Aryl halides are less reactive towards nucleophilic substitution reactions as compared to alkyl halides due to

(a) The formation of less stable carbanion (b) Longer carbon halogen bond

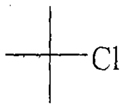
(c) The inductive effect (d) sp^2–hybridized carbon attached to the halogen

8. Which one is an excellent substrate for S_N2 reaction ?

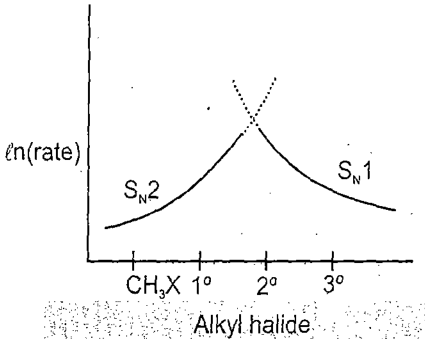
(a) 

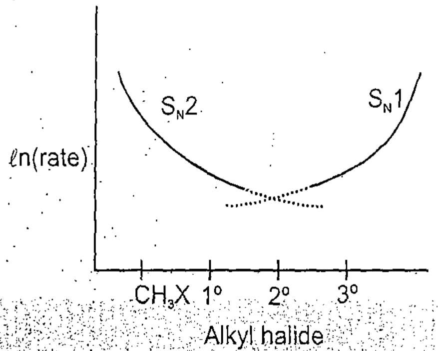
(b) 

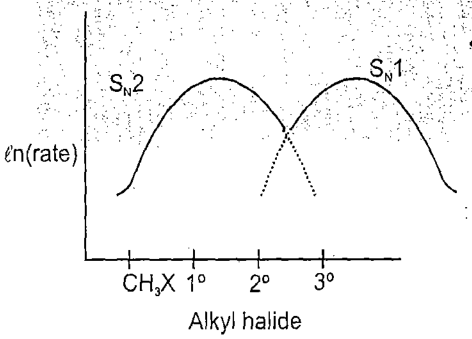
(c) $CH_3—CH_2—Cl$

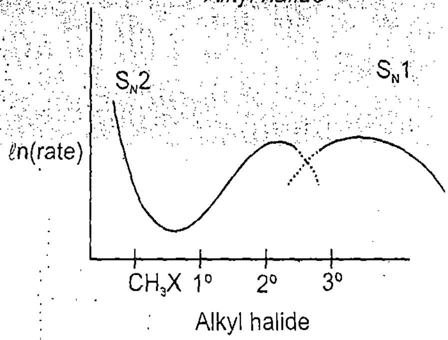
(d) 

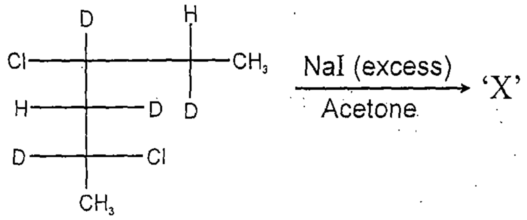
9. Which of the following curves correctly represents S_N1 vs S_N2 :

(a) 

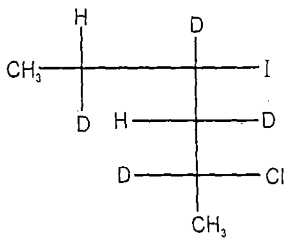
(b) 

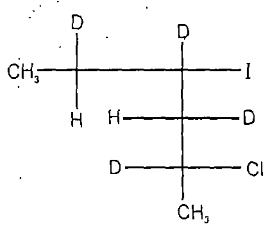
(c) 

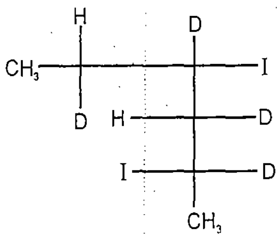
(d) 

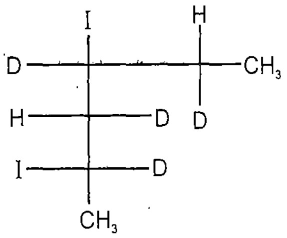
10. 

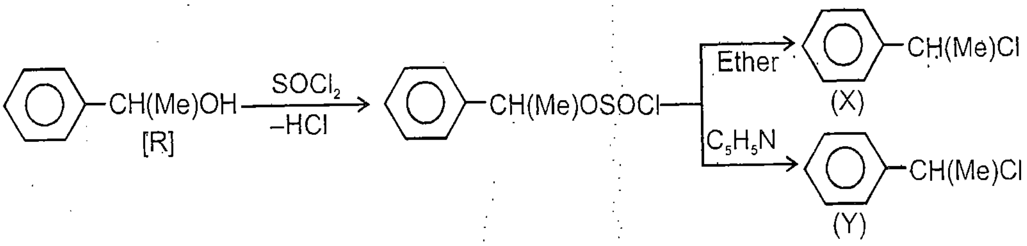
Identify the 'X'.

(a) 

(b) 

(c) 

(d) 

11. 

Which configuration will be adopted by X and Y respectively :

(a) R, R (b) R, S (c) S, S (d) S, R

Imp.

12. The correct order of S_N2 / E2 ratio for the % yield of product of the following halide is

(P) $CH_3-CH_2-C(Ph)(I)-CH_3$

(Q) $CH_3-CH(Ph)-CH(I)-CH_3$

(R) CH_3-CH_2-I

(S) $CH_3-CH-CH(I)-CH_3$

(a) R > S > Q > P (b) R > Q > S > P (c) P > R > S > Q (d) Q > P > R > S

Good

13. For the following reaction

$$CH_3-\underset{Cl}{\overset{CH_3}{C}}-CH_3 \xrightarrow[30\%\ H_2O]{70\%\ Ethanol} CH_3-\underset{OCH_2CH_3}{\overset{CH_3}{C}}-CH_3 + CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3 + CH_3-\overset{CH_3}{C}=CH_2$$

Which of the following statement is incorrect ?

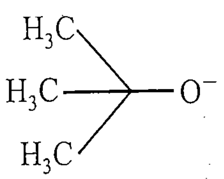
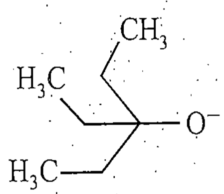
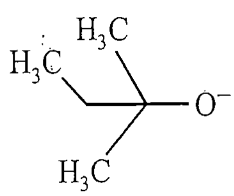
(a) the rate of reaction depends only on the concentration of the *t*-butyl chloride

(b) the rate constant will remain same

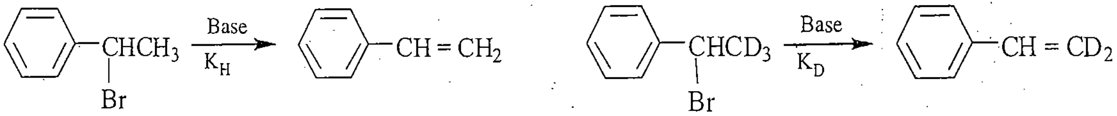
(c) the rate of reaction drops as *t*-butyl chloride is used up in the reaction

(d) the rate of reaction will become 1/4th as the concentration of *t*-butyl chloride become half

14. Which of the following bases would give the high percentage of alk-1-ene from 2-bromo-2,3-dimethylbutane?

(a)  (b)  (c) $H_3C-CH_2-O^-$ (d) 

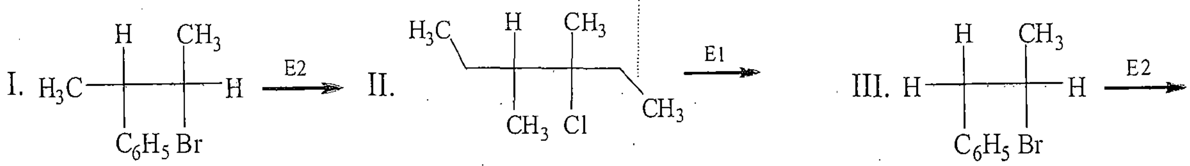
Imp.

15. 

Assuming both the reactions as E1, the expected ratio between K_H/K_D lies between

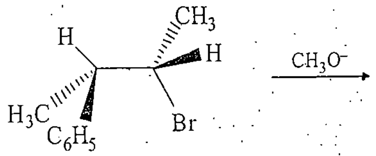
(a) nearly 1 (b) nearly 3 (c) nearly 5 (d) anything in between 2 to 8

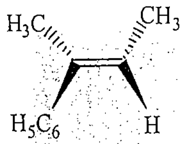
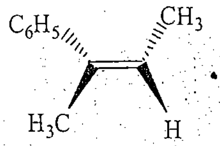
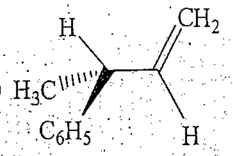
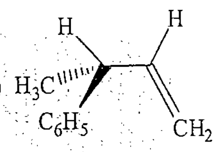
16. Which of the following reactions cannot give both 'E' and 'Z' products ?



(a) I (b) III (c) I and II (d) II and III

17. Identify the product.



(a)  (b)  (c)  (d) 

Check.

18. Consider the following reaction

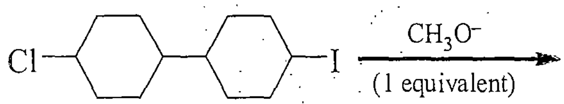
$$\underset{\underset{X}{|}}{H_3C-CH}-CH_2-CH_2-CH_2-CH_3 \xrightarrow{CH_3O^-} \underset{\text{Product-1}}{H_3C-CH=CH-CH_2-CH_2-CH_3} + \underset{\text{Product-2}}{H_2C=CH-CH_2-CH_2-CH_2-CH_3}$$

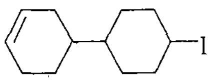
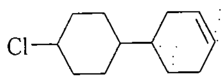
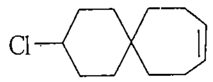
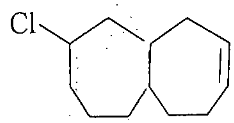
The ratio between product-1 and product-2 is ________.

(a) 1 : 4 when X is I (b) 1 : 4 when X is Br

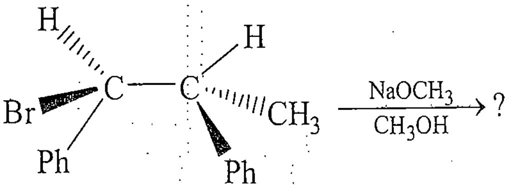
(c) 1 : 3 when X is Cl (d) 1 : 3 when X is F

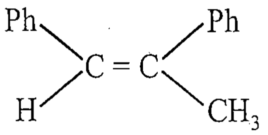
19. Predict the product for the following elimination reaction

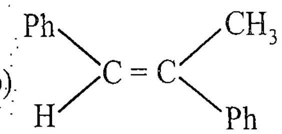


(a)  (b)  (c)  (d) 

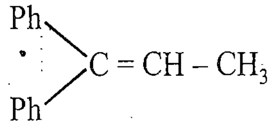
20. The following substrate can give rise to which of the following product ?

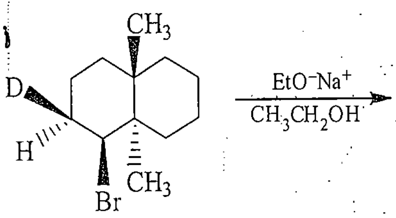
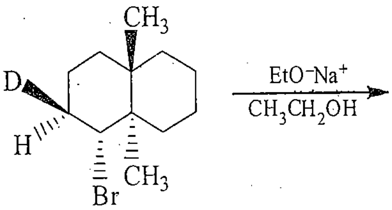


(a) 

(b) 

(c) $Ph-CH_2-\underset{\displaystyle Ph}{\underset{|}{C}}=CH_2$

(d) 

21. (I)  (II) 

In which of the above reaction(s), deuterium will be lost in the product ?

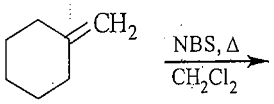
(a) Reaction I (b) Reaction II (c) Both (d) None

22. Give are three reactions

(I) $(CH_3)_3CCl \xrightarrow{H_2S,\ CH_3OH}$ (II) $(CH_3)_3CCl \xrightarrow[CH_3OH]{CH_3COO^-K^+}$ (III) $(CH_3)_3CCl \xrightarrow[CH_3OH]{CH_3O^-K^+}$

Out of the above three reactions which would show the primary isotope effect ?

(a) I only (b) I and II (c) II and III (d) III only

23. I. 

II. $CH_3-CH=CH-CH_2-CH_3 \xrightarrow[CH_2Cl_2]{NBS,\ \Delta}$

Pick the correct sentence about the products of the above reactions.

(a) I and II both would give two structural isomer each

(b) II would give three structural isomers

(c) I would give only one product (d) II would give only one product

24. $CD_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CD_3 \xrightarrow[alcohol]{KOH} \underset{I}{CD_2=CH-CD_3} + \underset{II}{CD_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CD_3}$

$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3 \xrightarrow[alcohol]{KOH} \underset{III}{CH_2=CH-CH_3} + \underset{IV}{CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3}$

Pick the incorrect sentence.

(a) Rate of formation of II and IV would be identical

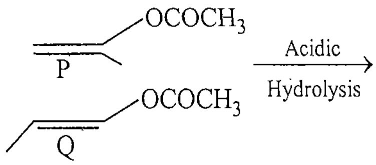
(b) Rate of formation of I would be slower than that of III

(c) Formation of I would show primary isotope effect

(d) Formation of III involves E1 reaction

25. $CH_3CHO + H_2NOH \longrightarrow CH_3 - CH = N - OH$. The above reaction occurs at:

(a) pH = 1 (b) pH = 4.5 (c) Any value of pH (d) pH = 12

26.  Products formed by P & Q can be differentiated by:

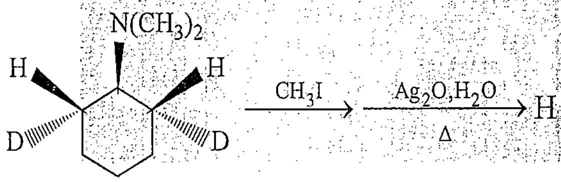
(a) 2, 4 DNP (b) Lucas reagent ($ZnCl_2$) conc. HCl

(c) $NaHSO_3$ (d) Fehlings solution

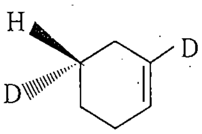
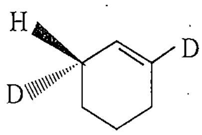
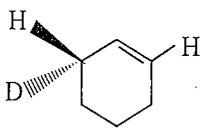
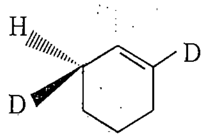
27. The smallest compound, which on photochlorination produces diastereomers is

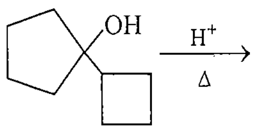
(a) 3-methyl, 3-chloro hexane (b) 2-chloro butane

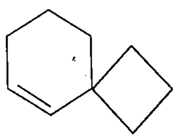
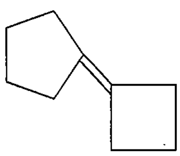
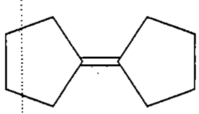
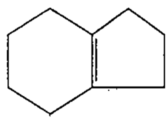
(c) 1-bromo propane (d) 1-bromo-3-methyl butane

28. 

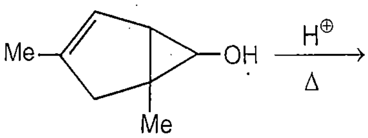
The structure of 'H' is

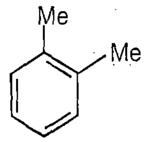
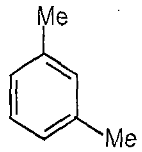
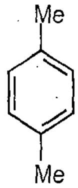
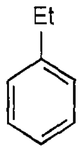
(a)  (b)  (c)  (d) 

29. 

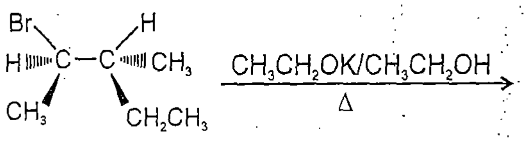
(a)  (b)  (c)  (d) 

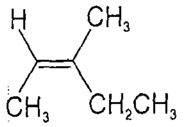
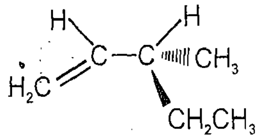
30. Write the product of the following reaction

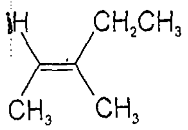
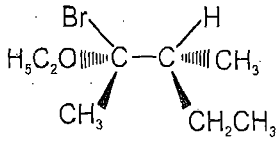


(a)  (b)  (c)  (d) 

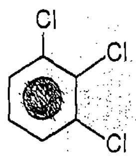
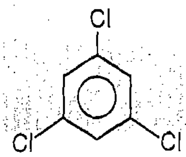
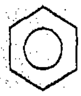
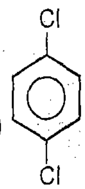
31. Select the formula representing the major product of the following reaction



(a) 
(b) 

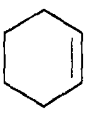
(c) 
(d) 

32. When the all-cis isomer of $C_6H_6Cl_6$ (1, 2, 3, 4, 5, 6-Hexachlorocyclohexane) is heated with alc. KOH, the most probable product is :

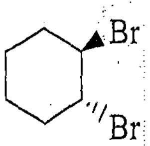
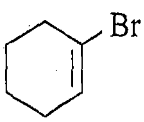
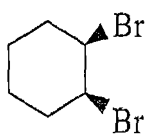
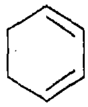
(a)  (b)  (c)  (d) 

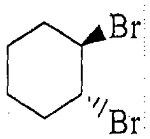
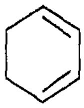
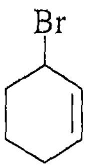
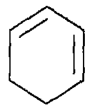
33. When (1R, 2R)-1, 2-Dibromo-1, 2-diphenyl ethane is treated with alcoholic solution of KOH, the most probable product would be :

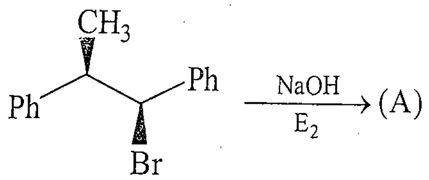
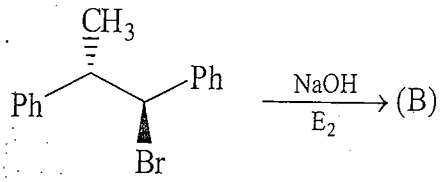
(a) trans-1, 2-diphenyl ethene
(b) A mixture of cis, trans alkenyl bromide
(c) cis-alkenyl bromide
(d) trans-alkenyl bromide (with respect to phenyl)

34.  $\xrightarrow[CCl_4]{Br_2}$ (A) $\xrightarrow{t\text{-BuOK}}$ (B)

A and B respectively are

(a)  , 
(b)  , 

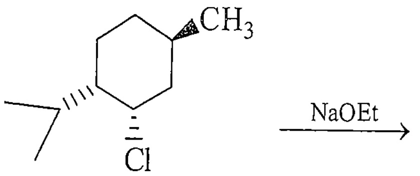
(c)  , 
(d)  , 

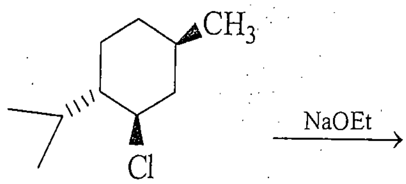
35.  

The correct statement regarding the above reaction is

(a) Both give same alkene
(b) A is 'E' alkene
(c) B is 'E' alkene
(d) A is 'Z' alkene

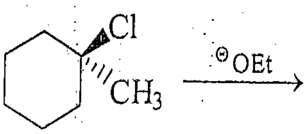
36. For the given reaction which statement is correct

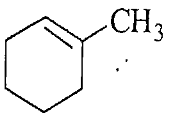
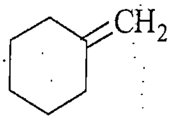
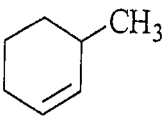

(A)


(B)

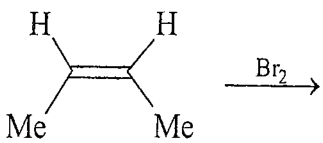
(a) Compound A and B give single product
(b) Compound A give one product and compound B give two product
(c) Compound B react 250 time slower than A
(d) Compound A react 250 time slower than B

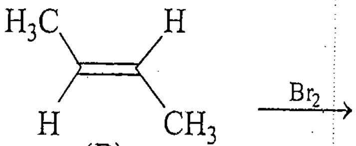
37. Which one will be the major product of the given reaction



(a)  (b)  (c)  (d) Both (a) and (c)

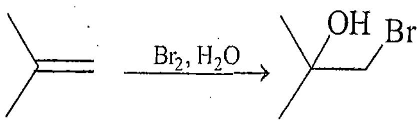
38. Which is the correct statement for the following reaction

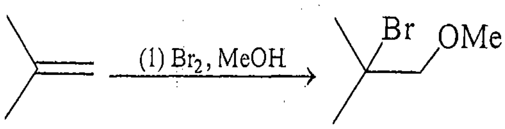

(A)

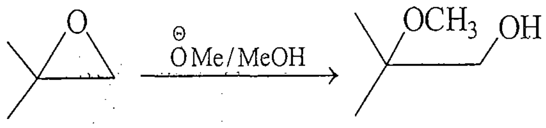
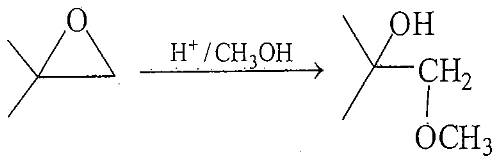

(B)

(a) Product is formed via syn addition
(b) Compound A give meso product
(c) Compound B give racemic product
(d) Compound A give opticaly inactive mixture

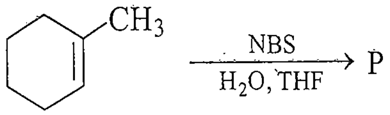
39. Which reaction is correct

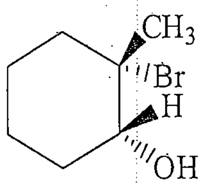
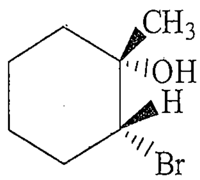
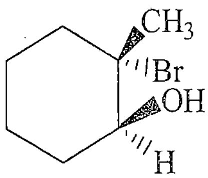
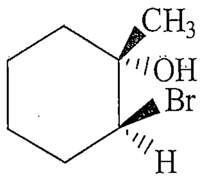
(a) 

(b) 

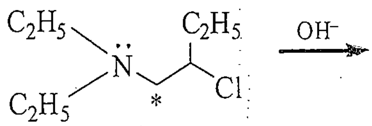
(c)  (d) 

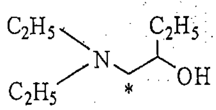
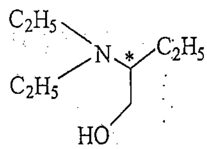
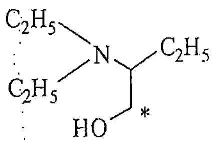
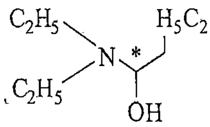
40. Major Product of the given reaction is



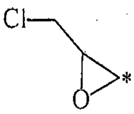
(a)  (b)  (c)  (d) 

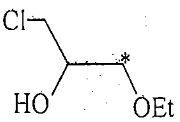
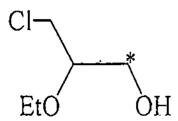
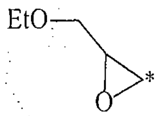
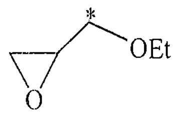
41. Trace the major product in the following reaction,



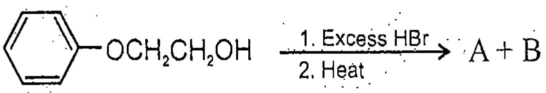
(a)  (b)  (c)  (d) 

Check

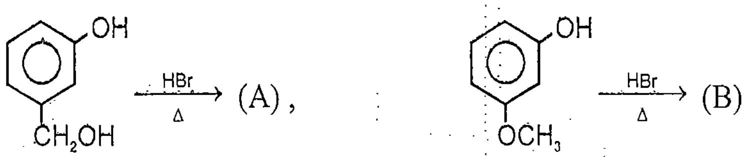
42.  $\xrightarrow{OEt^-}$ The major product is

(a)  (b)  (c)  (d) 

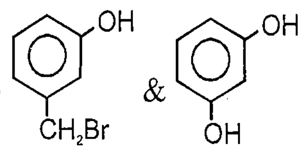
43. What are the products of the following reaction ?

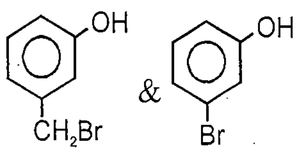


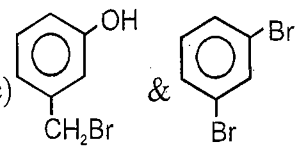
(a) p Br – C_6H_4 – OCH_2CH_2 – Br
(b) Ph – Br + Br–CH_2CH_2–OH
(c) Ph – Br + Br – CH_2CH_2 – Br
(d) Ph – OH + CH_2Br–CH_2Br

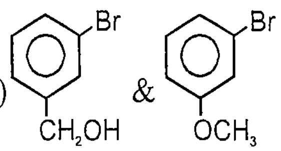
44. 

The product (A) and (B) are respectively :

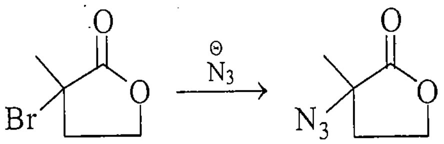
(a) 

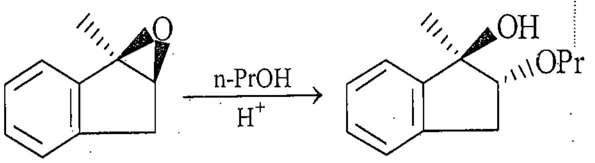
(b) 

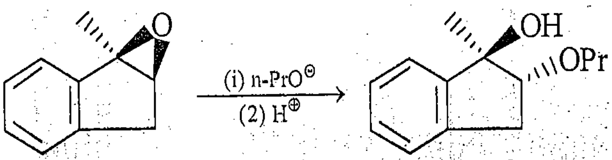
(c) 

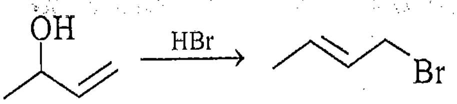
(d) 

45. Among the following reactions, which one is incorrect

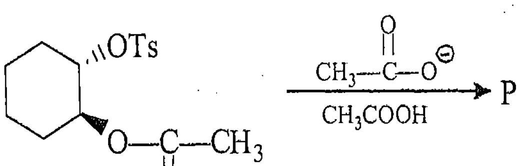
(a) 

(b) 

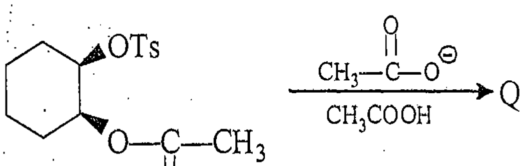
(c) 

(d) 

46. Correct statement for the given reactions.



(A)



(B)

(a) B react very fast than A
(b) Both give same product
(c) A give trans and B give cis product
(d) A give cis and B give trans product

47. When Nitrobenzene is treated with Br_2 in presence of $FeBr_3$, the major product formed is m-bromonitro benzene. Statements which are related to obtain m-isomer are:

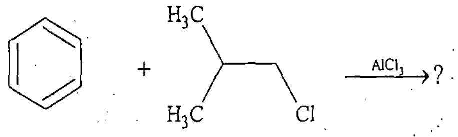
(a) The electron density on meta carbon is more than that on ortho and para positions.

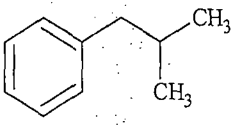
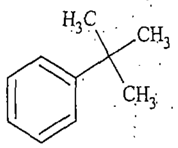
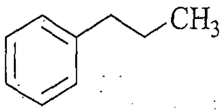
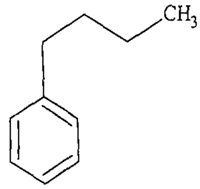
(b) The intermediate carbonium ion formed after initial attack of Br^+ at the meta position is least destabilized.

(c) Loss of aromaticity when Br^+ attacks at the ortho and para positions not at meta position

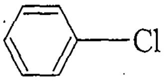
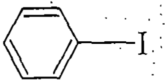
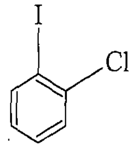
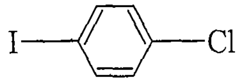
(d) Easier loss of H^+ to regain aromaticity from the meta position than from ortho and para positions.

48. Which of the following is the major organic product of the following reaction?

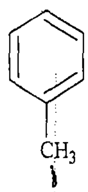


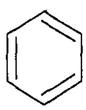
(a)  (b)  (c)  (d) 

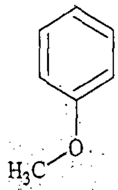
49. Benzene on reaction with ICl in presence of anhydrous $AlCl_3$ gives?

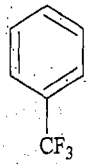
(a)  (b)  (c)  (d) 

50. Among the following compounds, the decreasing order of reactivity towards electrophilic substitution is


I


II

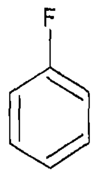

III

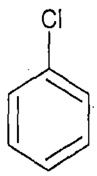

IV

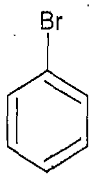
Later

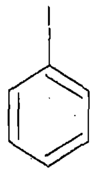
(a) III > I > II > IV (b) IV > I > II > III (c) II > I > IV > III (d) I > III > II > IV

51. Arrange the following in order of increasing rate of nucleophilic substitution

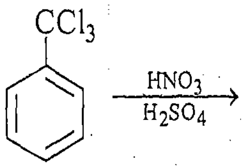

(I)

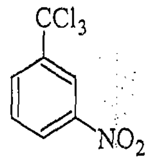
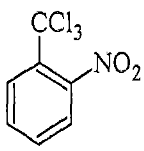
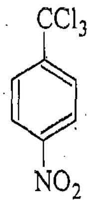

(II)


(III)


(IV)

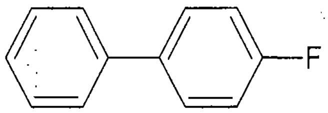
(a) I > II > III > IV (b) II > III > IV > I (c) IV > III > II > I (d) IV > III > I > II

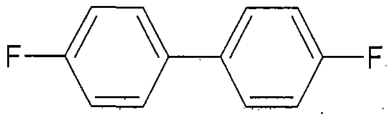
52.  Major Product is

(a)  (b)  (c)  (d) No reaction

53. $Ph-NH_2 \xrightarrow[0^\circ C]{HNO_2} A \xrightarrow[BF_3]{HF} B \xrightarrow{\Delta} C$, C is

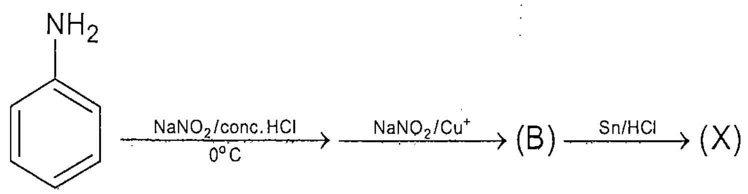
(a) $Ph-N^+ \equiv N\ddot{B}F_4$

(b) 

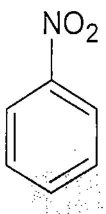
(c) 

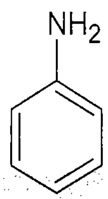
(d) Ph – F

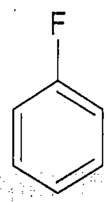
54. In the reaction sequence

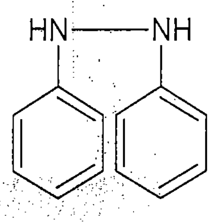


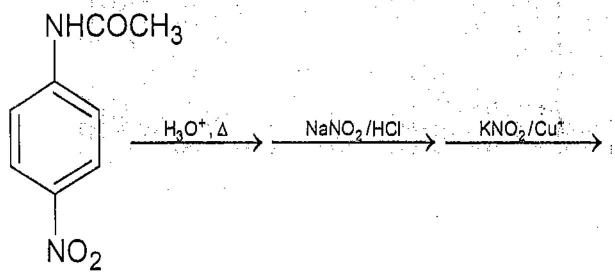
(X) will be

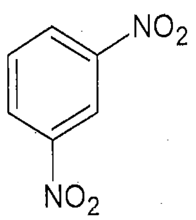
(a) 

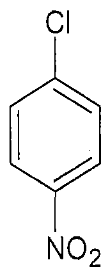
(b) 

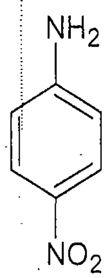
(c) 

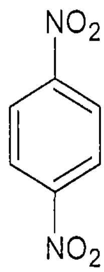
(d) 

55. 

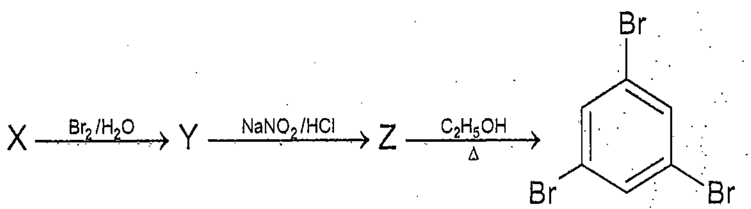
(a) 

(b) 

(c) 

(d) 

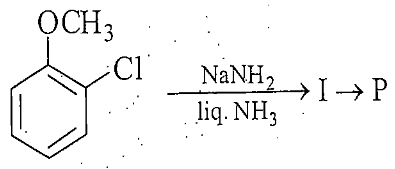
56. In the given reaction sequence

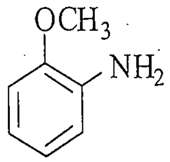


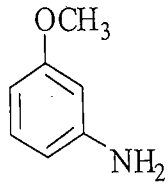
(X) will be:

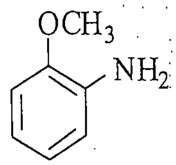
(a) Benzoic acid (b) Salicylic acid (c) Phenol (d) Aniline

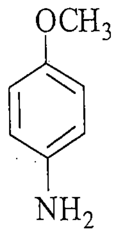
57. Intermediate and major product form during the given reaction are



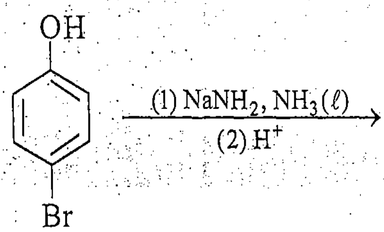
(a) I → Benzyne, P — 

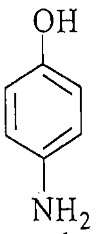
(b) I → Benzyne, P — 

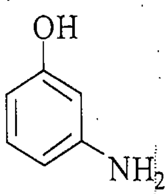
(c) I → Carbene, P — 

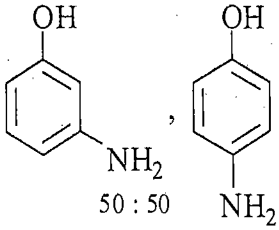
(d) I → Carbene, P — 

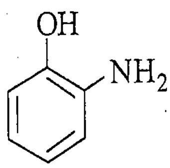
58. Major product form during the given reaction is



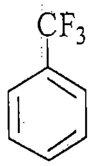
(a) 

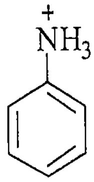
(b) 

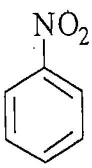
(c) 

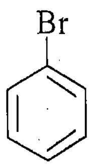
(d) 

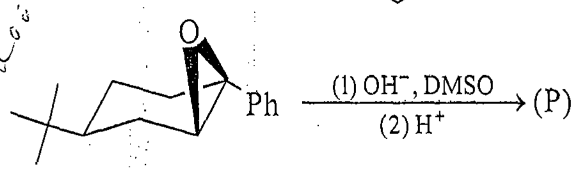
59. Among the following, which one is not a meta directing group in an electrophilic attack.

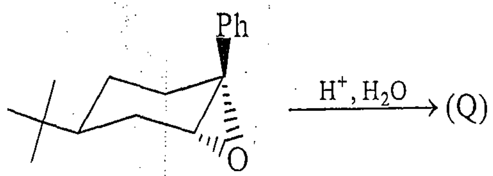
(a) 

(b) 

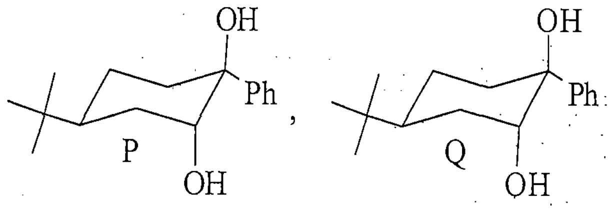
(c) 

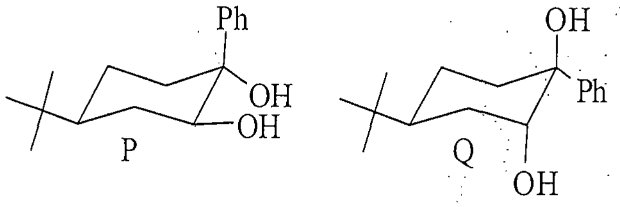
(d) 

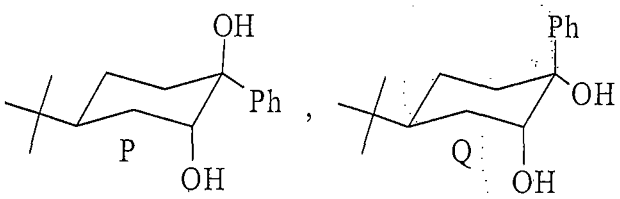
60. 

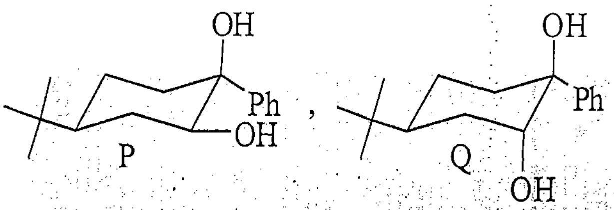


For the given reaction product P and Q are

(a) 

(b) 

(c) 

(d) 

EXERCISE II

One of More Than One Correct Type

1. Which of these statements are correct about nucleophiles :

   (a) Nucleophiles have an unshared electron pair and can make use of this to react with an electron deficient species.

   (b) The nucleophilicity of an element (as electron donor) generally increases on going down a group in the periodic table.

   (c) A nucleophile is electron-deficient species

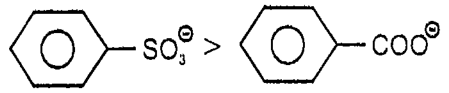
   (d) All good nucleophiles are good bases when we deal across the period.

2. The correct nucleophilicity order is/are :

   (a) $(CH_3)_3CO^\ominus > CH_3^\ominus$ (b) $CH_3S^\ominus > CH_3SH$

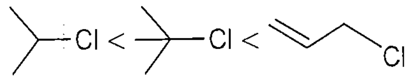
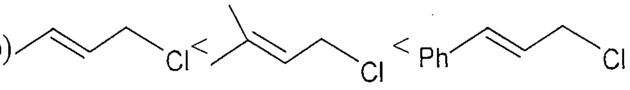
   (c) $CH_3CH_2CH_2O^\ominus > (CH_3)_3CO^\ominus$ (d) $(CH_3CH_2)_3N > (CH_3CH_2)_3P$

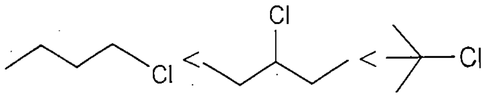
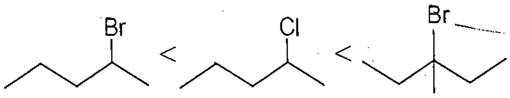
3. The correct order of leaving group ability is/are :

   (a)  (b) $CF_3SO_3^\ominus > CCl_3SO_3^\ominus$

   (c) $\overset{\ominus}{C}N > I^\ominus$ (d) $\overset{\ominus}{N}H_2 > \overset{\ominus}{O}H$

4. Which of the following order is/are correct for the solvolysis in 50% aqueous ethanol at 44.6°C.

(a)  (b) 

(c)  (d) 

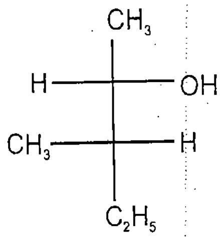
5. Which of the following is / are true for S_N1 reactions ?

(a) They occur through a single step concerted reaction.

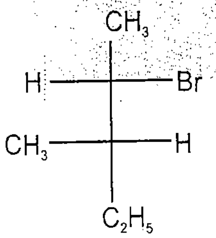
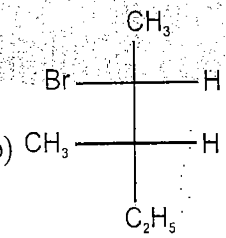
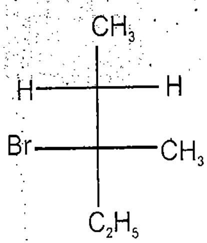
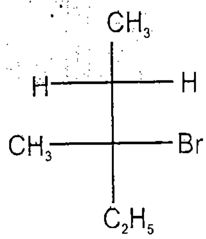
(b) They are favoured by polar solvents.

(c) 3° alkyl halides generally react through this mechanism.

(d) Concentration of nucleophile does not affect the rate of such reactions.

6.  $\xrightarrow{HBr}$ Product,

Which of the following structures represent the correct major product.

(a)  (b)  (c)  (d) 

7. Identify correct steps representing S_N1 mechanism for the cleavage of ether with HI

$$R-O-R' + HI \longrightarrow R-\overset{\oplus}{\underset{|\atop H}{O}}-R' + I^{\ominus}$$

(a) $I^{\ominus} + R-\overset{H \atop |}{\underset{\oplus}{O}}-R' \xrightarrow[\text{(RDS)}]{\text{slow}} RI + HOR'$ (R is 1°) (as not involved in SN1 mechanism)

(b) $R-\overset{H \atop |}{\underset{\oplus}{O}}-R' \xrightarrow[\text{(RDS)}]{\text{slow}} R^{\oplus}$ (R is 3°) + R'OH

(c) $R^{\oplus} + I^{\ominus} \xrightarrow{\text{fast}} RI$

(d) $R^{\oplus} + I^{\ominus} \xrightarrow[\text{(RDS)}]{\text{slow}} R-I$

8. The relative rates of nucleophilic substitution for the given substrates are as follows

Compoud	Approx. Relative rate
CH_3CH_2Br	1.0
$CH_3CH_2CH_2Br$	0.28
$(CH_3)_2CHCH_2Br$	0.030
$(CH_3)_3\,CCH_2Br$	0.00000042

The correct statement (s) is/are :

(a) Each of the above reactions is likely to be S_N2

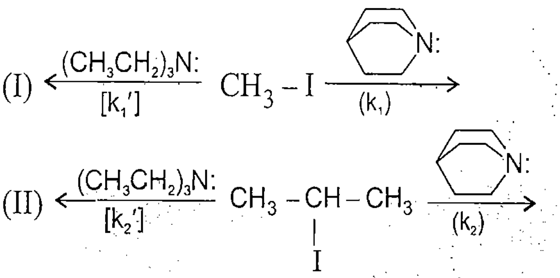
(b) Each of the above reactions is likely to be S_N1

(c) First two reactions follow S_N2 and next two reactions follow S_N1 pathway

(d) The important factor behind this order of reactivity is "steric effect"

Good Que,

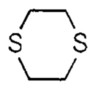
9. Observe the following reaction I and II $k_1\ k_1'$, $k_2\ k_2'$ are rate constants. Select the correct option(s).

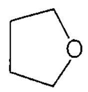


(a) $k_1 > k_1'$ (b) $k_1 > k_2$ (c) $k_2' > k_2$ (d) $k_2' > k_1'$

10. Which of the following reaction is correct ?

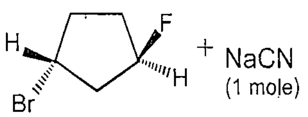
(a) 1, 4-Dichlorohexane + NaI (1eq.) $\xrightarrow{\text{Acetone}}$ $CH_3-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_2-\underset{\underset{I}{|}}{CH_2}$ + NaCl

(b) 1, 2-Dibromoethane + $NaS-CH_2-CH_2-SNa \longrightarrow$  + 2NaBr

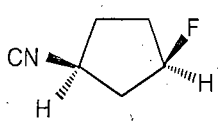
(c) 4-Chloro-1-butanol + NaH $\xrightarrow{Et_2O}$ C_4H_8ClONa $\xrightarrow{\Delta}$ 

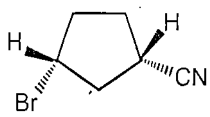
(d) Propyne + $NaNH_2$ $\xrightarrow{-NH_3}$ C_3H_3Na $\xrightarrow{CH_3I}$ C_4H_6

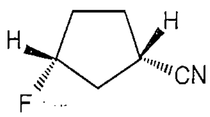
Very nice.

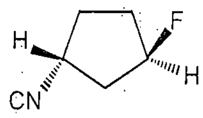
11.  + NaCN (1 mole) $\longrightarrow$ A (Major)

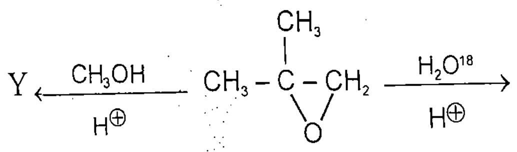
major product of this reaction is.

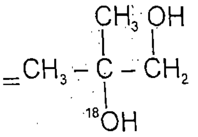
(a) 

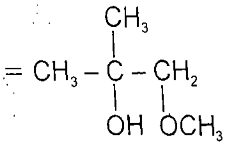
(b) 

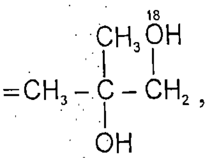
(c) 

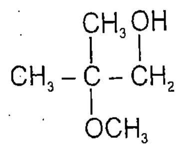
(d) 

12.  X, Identify X & Y :

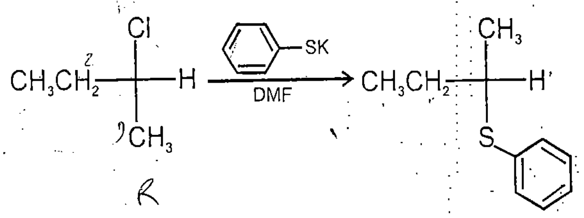
(a) X = 

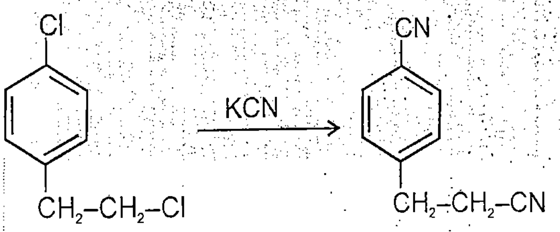
(b) Y = 

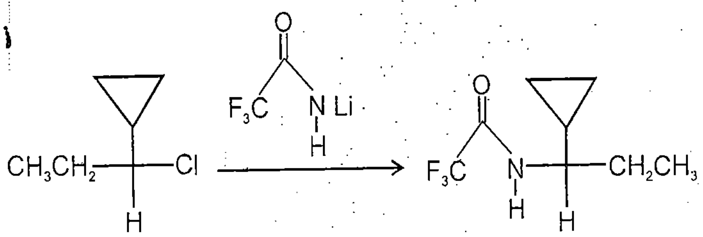
(c) X = 

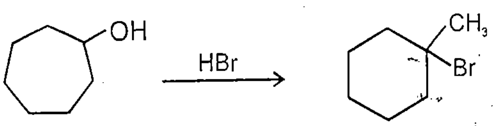
(d) Y = 

13. Which of the following reaction is / are possible :

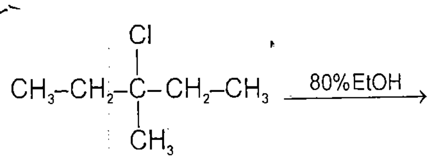
(a) 

(b) 

(c) 

(d) 

Check Once

14. 

What is / are true about above reaction ?

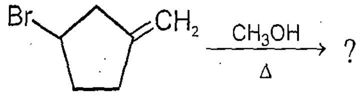
(a) Major product is given by S_N1 reaction.

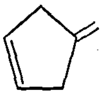
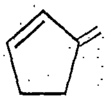
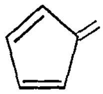
(b) Through E1 mechanism 3 alkenes are formed.

(c) 3-Methylpentan -3-ol is also formed as one of the product.

(d) Fractional distilation of elimination product will give two fractions.

15. Which of the following is/are possible product formed by E1 mechanism for given reaction ?



(a)  (b)  (c)  (d) 

16. Which of the following statements is/are correct for alkyl halide ?

(a) In most unimolecular reactions of alkyl halide S_N1 reaction is favoured over E1 reaction.

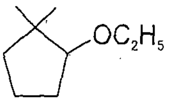
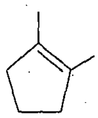
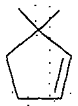
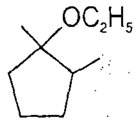
(b) E1 mechanism is favoured as compaired to S_N1 mechanism by branching at β carbon

(c) In unimolecular reaction, increasing the temperature favours E1 mechanism

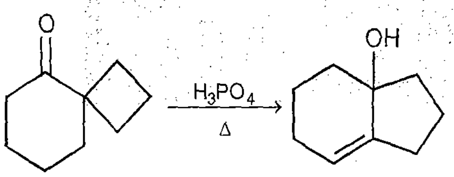
(d) E1 reactions are favoured by the use of weak bases and by the use of polar solvents.

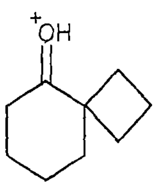
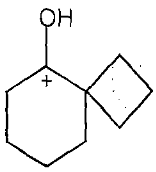
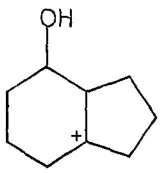
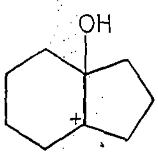
17. Predict the products expected in given reaction

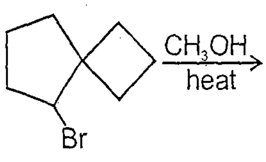
2-Bromo-1, 1-dimethylcycopentane $\xrightarrow[\Delta]{C_2H_5OH}$

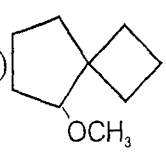
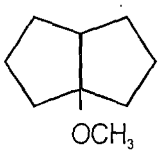
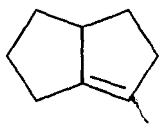
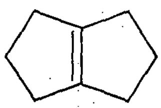
(a)  (b)  (c)  (d) 

18. What are the possible intermediates of the following reaction which form during this reaction path way ?



(a)  (b)  (c)  (d) 

19.  product, which of the following products are possible.

(a)  (b)  (c)  (d) 

20. Which of the following order is/are correct for the rate of E2 reaction.

(a) 5-Bromocycloheptene > 4-Bromocycloheptene

(b) 2-Bromo-1-phenylbutane > 3-Bromo-1-phenylbutane

(c) 3-Bromocyclohexene > Bromocyclohexane

(d) 3-Bromo-2-methylpentane > 2-Bromo-4-methylpentane

Reaction mechanism

21. Which of the following statement (s) is/are correct

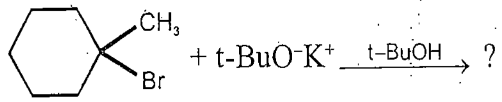
(a) E2 is a concerted reaction in which bonds break and new bonds form at the same time in a single step.

(b) Order of reactivity of alkyl halides towards E2 dehydrohalogenation is found to be 3° > 2° > 1°

(c) In E2 reaction both β hydrogen and leaving group should be antiperiplanar.

(d) In E2 elimination different stereoisomer (diastereomer) converts into different stereo product.

22. Which of the following statement (s) is/are incorrect regarding following reaction ?



(a) Major product is endocyclic alkene formed according to Saytzeff.

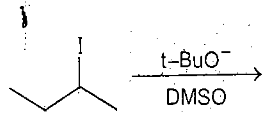
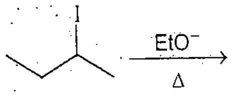
(b) Major product is exocyclic alkene formed according to Saytzeff.

(c) Major product is exocyclic alkene formed according to Hoffmann.

(d) Major product is endocyclic alkene formed according to Hoffmann.

3° > 2° > 1°

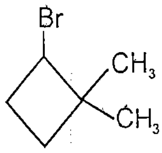
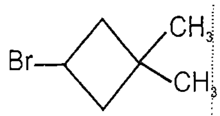
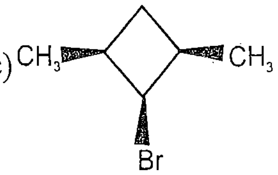
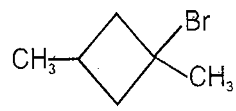
23. Which of the following statement (s) is/are true about the following eliminations ?

(I)  (II) 

(a) Hoffmann product is major product in I. (b) Saytzeff product is major product in I

(c) Hoffmann product is major product in II. (d) Saytzeff product is major product in II

24. Which of the following compound (s) will yield exclusive (only one) product on dehydrohalogenation by a strong base.

(a)  (b)  (c)  (d) 

25. Which is/are correct about alkyl bromide having molecular formula $C_5H_{11}Br$

(a) One isomeric alkyl bromide undergoes E1 elimination at the fastest rate

(b) Only one is incapable of reacting by the E2 mechanism

(c) Only one isomer gives a single alkene on E2 elimination

(d) 2-Bromopentane gives the most complex mixture of alkenes on E2 elimination

26. In which reaction product formation takes place by hoffmann rule ?

(a) $CH_3-CH_2-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow[\Delta]{t\text{-}Bu\overset{\ominus}{O}\overset{\oplus}{K}}$ (b) $CH_3-CH_2-\underset{\underset{F}{|}}{CH}-CH_3 \xrightarrow[\Delta]{CH_3CH_2\overset{\ominus}{O}\overset{\oplus}{K}}$

(c) $CH_3-CH_2-\underset{\substack{|\\CH_3}}{CH}-\overset{\oplus}{N}(CH_3)_3 \xrightarrow[\Delta]{\overset{\ominus}{O}H}$ (d) $CH_3-CH_2-\underset{\substack{|\\ \oplus S(CH_3)_2}}{CH}-CH_3 \xrightarrow[\Delta]{\overset{\ominus}{O}H}$

27. Which of the following compounds can give E1 cB reaction ?

(a) CF_3-CHCl_2 (b) $C_6H_5-CH_2-CH_2F$

(c) $CH_3-\underset{\substack{|\\NO_2}}{CH}-CH\langle^{C_6H_5}_{OAc}$ (d) $CH_3-CH_2-CH_2Br$

28. $$B:\curvearrowright H-\overset{}{X_2C^2}-C^1F_3 \underset{\text{Fast}}{\rightleftharpoons} X_2\overset{\ominus}{C}-CF_3 \xrightarrow{\text{Slow}} X_2C=CF_2$$ (X = halogen Cl, Br , I)

Correct statement (s) is (are)

(a) X being electronegative, makes the H (on C-2) more acidic.

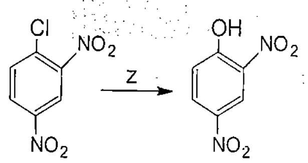
(b) Due to electron withdrawal nature of X, it stabilises the carbanion

(c) (X) destabilises the carbanion due to the presence of lone pairs.

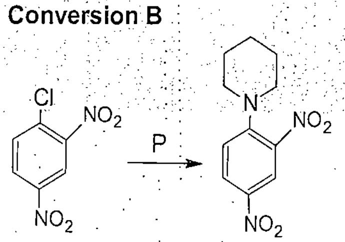
(d) The reaction proceeds by an E1 cB pathway.

29. Observe the following conversions

Conversion A



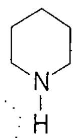
Conversion B



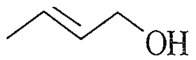
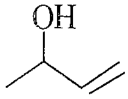
(a) For conversions A, in the steps in Z is (i) aq OH^-/Δ (ii) H^+/H_2O

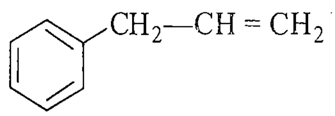
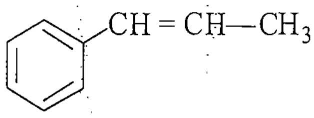
(b) For conversion B, in the steps in P is (i) $NH_3 + CuO/\Delta$ (ii) $Cl-CH_2CH_2CH_2-CH_2-CH_2-Cl$

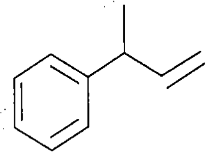
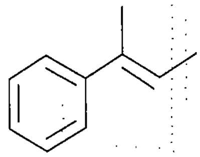
(c) For conversion A, in the steps in Z is (i) aq NaOH at – 1000°C (ii) H^+/H_2O

(d) For conversion B, in the steps in P is (i) 

30. Which pair of alcohols give same product with HBr

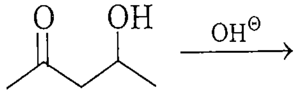
(a)  & 

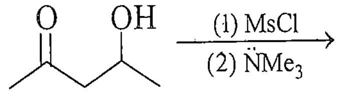
(b)  & 

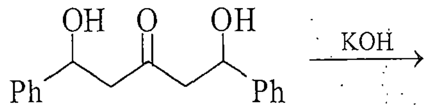
(c)  & 

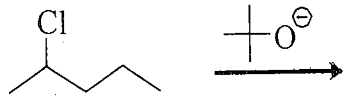
(d) $CH_3—CH—CH = CH_2$ & $CH_3—CH = CH—CH_3$

31. Among the following, the examples of E_{1CB} reaction is/are

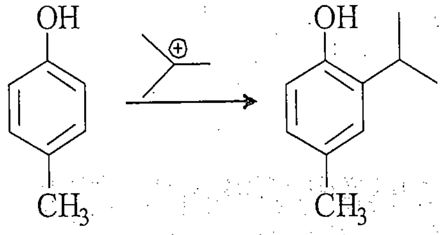
(a) 

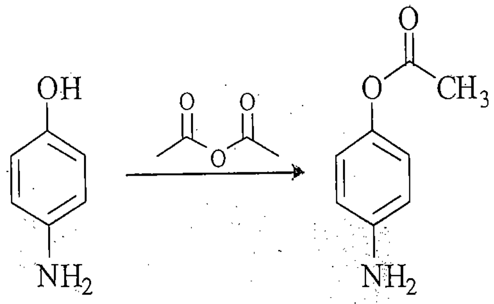
(b) 

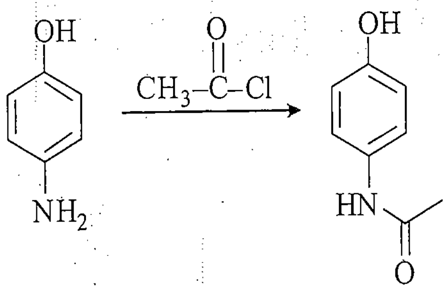
(c) 

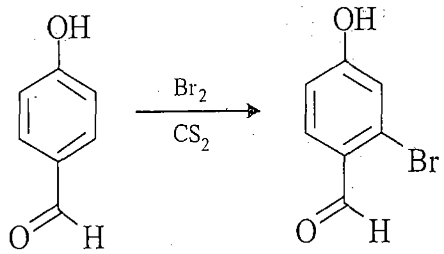
(d) 

32. Choose the correct reaction/s amongst the following

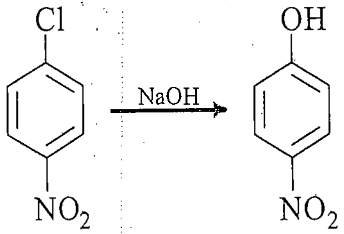
(a) 

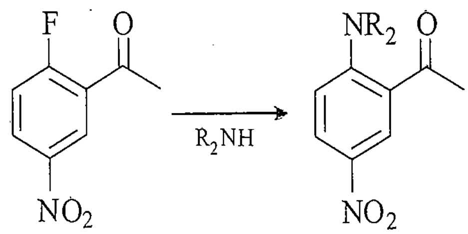
(b) 

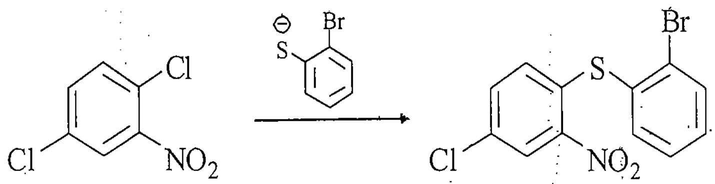
(c) 

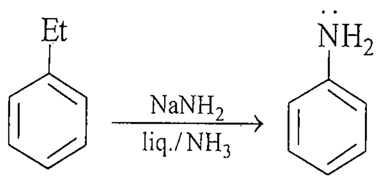
(d) 

33. Which of the following reaction/s will follow addition-elimination mechanism

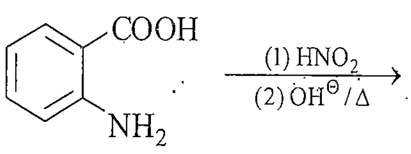
(a) 

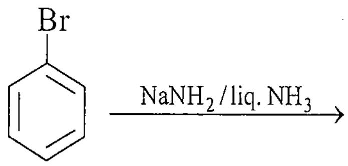
(b) 

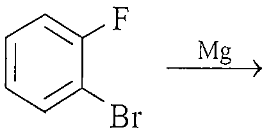
(c) 

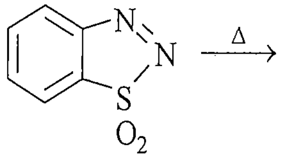
(d) 

34. Among the following reaction(s), which will give benzyne as intermediate

(a) 

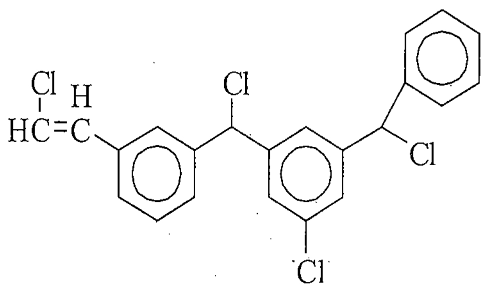
(b) 

(c) 

(d) 

EXERCISE - III

Numerical Answer Type

1. Number of possible isomers for $C_2H_2Cl_2$
2. Total number of isomers formed when 2-methyl butane is subjected to monochlorination
3. When 3- bromo-2,2-dimethyl butane is treated with alcoholic potassium hydroxide the number of possible alkene isomers formed is
4. The number of substitution products formed when metabromo anisole is treated with KNH_2/NH_3
5. During the preparation of chloroform from ethanal by treating with Cl_2 / base, the number of base molecules consumed is.
6. 

is on treating with excess $AgNO_3$. The number of moles of AgCl formed is

7. The number of πe^- present in Benzyne is
8. When m-dichorobenzene is treated with one mole of $Cl_2/FeCl_3$, the number of mono-chlorinated possible product are
9. When 3,3-dimethyl -2-butanol is treated with HBr the number of 3^0 carbons present in the major product formed is

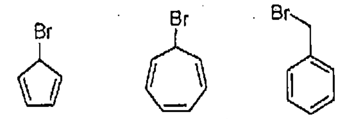
10. Cyclic hydrocarbon molecule 'A' has all the carbon and hydrogen in a single plane. All the carbon-carbon bonds are of same length less than 1.54 Å (C – C), but more than 1.34 Å (C–C). The C = C bond angle will be

EXERCISE IV

Previous Year Questions

IIT-JAM Previous Year Questions

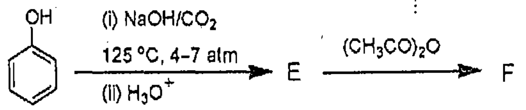
1. The correct order of rate of solvolysis for the following compound is

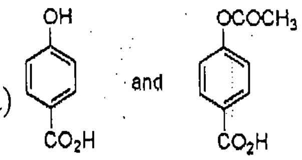


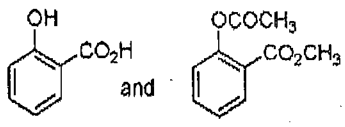
I II III

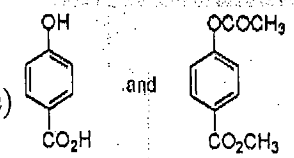
(a) III > II > I (b) II > I > III (c) III > I > II (d) II > III > I

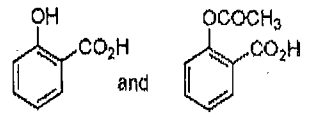
2. In the following reactions, the major products E and F, respectively are



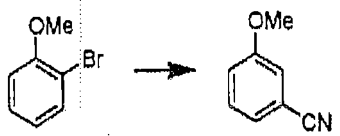
(a) 

(b) 

(c) 

(d) 

3. The correct set of reagents for the following conversion is



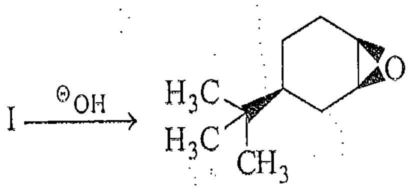
(a) (i) $NaNH_2$/liq. NH_3; (ii) $NaNO_2$/dil. HCl; (iii) CuCN, heat

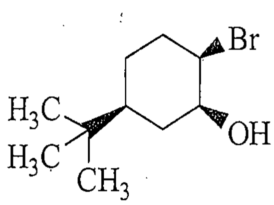
(b) (i) HNO_3/H_2SO_4; (ii) Zn/HCl; (iii) $NaNO_2$/dil. HCl; (iv) CuCN, heat

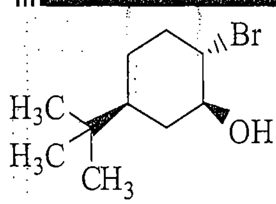
(c) (i) Mg/ether, H_2O^+; (ii) $(EtO)_2CO$; (iii) NH_4OH; (iv) PCl_5

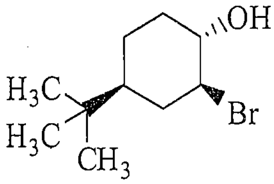
(d) (i) Mg/ether, H_2O^+; (ii) HNO_3/H_2SO_4; (iii) $NaNO_2$/dil. HCl; (iv) CuCN, heat

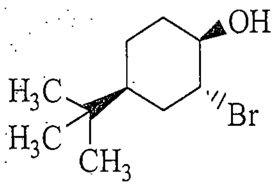
4. Identify the starting material I in the given reaction :



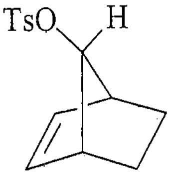
(a) 

(b) 

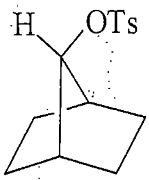
(c) 

(d) 

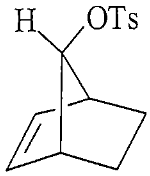
5. The rates of acetolysis for the following norbornyl derivatives are in the order



P



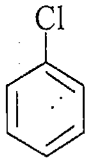
Q



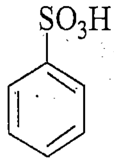
R

(a) R > Q > P (b) Q > R > P (c) P > R > Q (d) R > P > Q

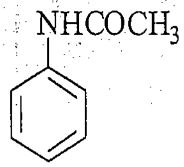
6. The decreasing order of electrophilic nitration of the following compounds will follow the trend



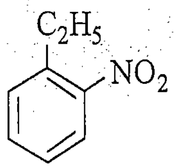
P



Q



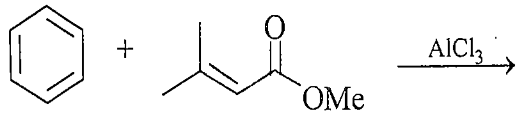
R



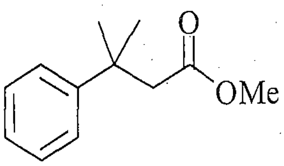
S

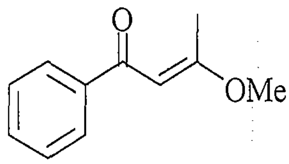
(a) S > R > P > Q (b) R > S > P > Q (c) R > P > S > Q (d) P > S > R > Q

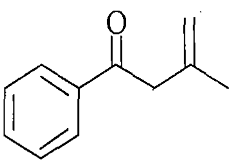
7. The major product of the reaction

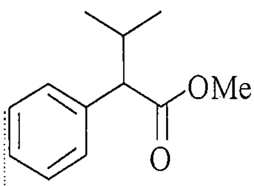


is

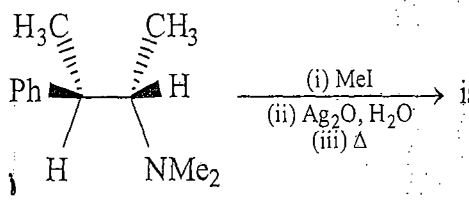
(a) 

(b) 

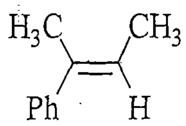
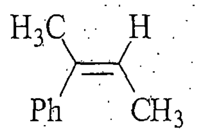
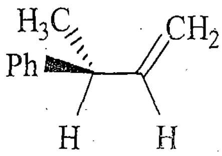
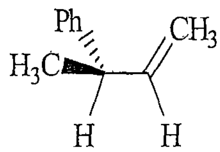
(c) 

(d) 

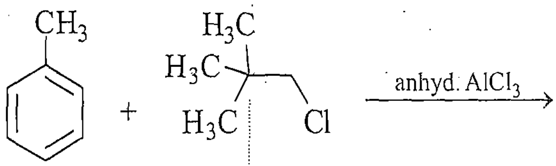
8. The major product obtained in the following reaction



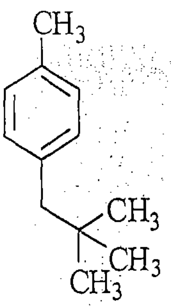
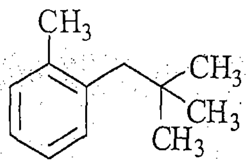
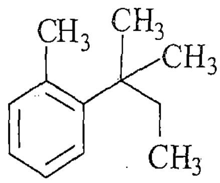
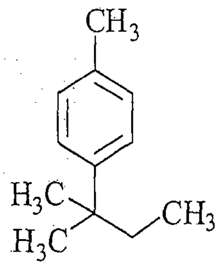
is

(a)  (b)  (c)  (d) 

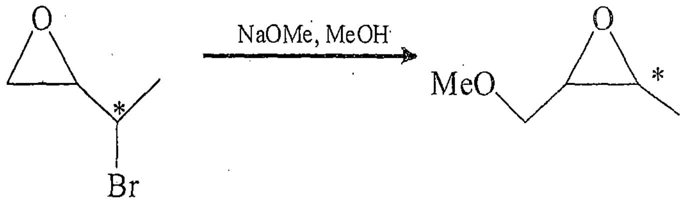
9. The major product of the following reaction



is

(a)  (b)  (c)  (d) 

10. Which of the following statement(s) is/are true about the reaction given below ?



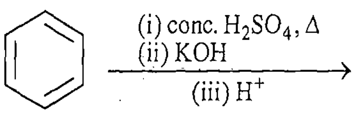
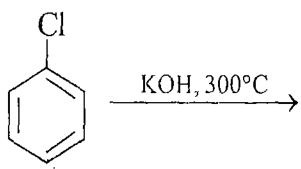
(a) It involves a carbocation intermediate

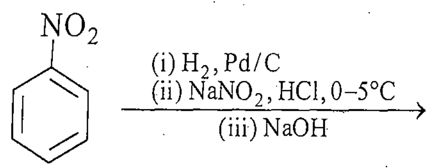
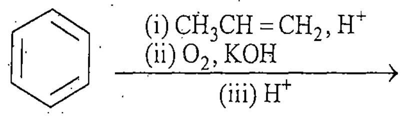
(b) Rearrangement is due to S_N1 reaction mechanism

(c) It proceeds via a concerted S_N2 pathway

(d) It involves neighbouring group participation

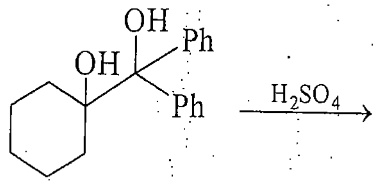
11. The reaction(s) which give(s) phenol is/are

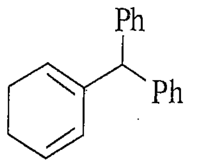
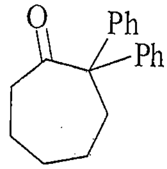
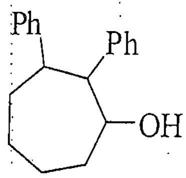
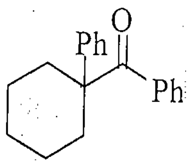
(a)  (b) 

(c)    (d) 

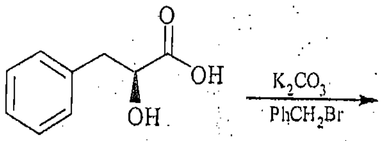
12. The number of possible monoalkylated products formed in the Friedel-Crafts reaction of anisole with 2-chloro-3-methylbutane in the presence of anhydrous $AlCl_3$ at 50°C is _______

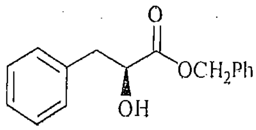
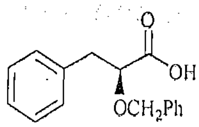
13. The major product formed in the following reaction is

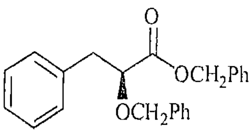
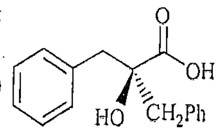


(a)    (b)    (c)    (d) 

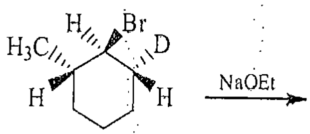
14. The major product obtained in the following reaction :

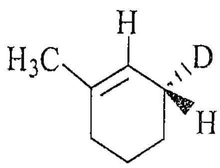
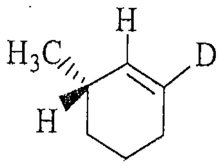
 is

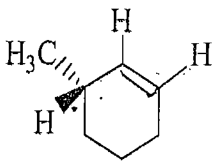
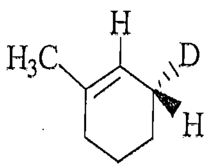
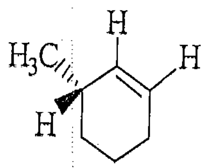
(a)    (b) 

(c)    (d) 

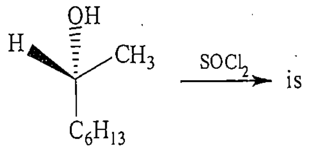
15. The reaction of the bromo compound shown below with sodium ethoxide gives predominantly

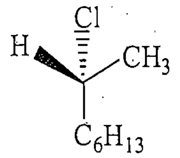
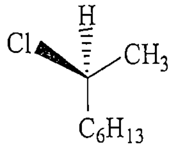
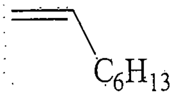
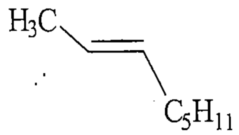


(a)    (b) 

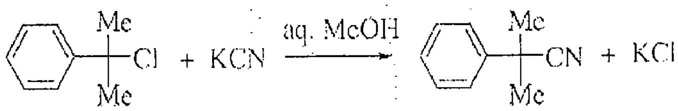
(c)    (d)  and 

16. The major product obtained in the following reaction



(a)  (b)  (c)  (d) 

17. For the reaction shown below if the concentration of KCN is increased four times, the rate of the reaction will be :



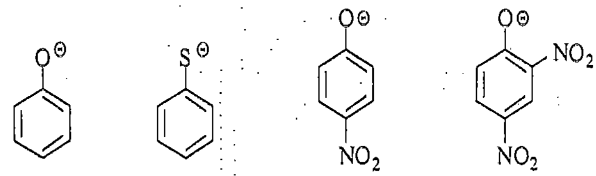
(a) double (b) increased four times
(c) unaffected (d) halved

18. Benzyl chloride is reacted with different nucleophiles shown below. Arrange them in the decreasing order of reactivity.

Nucleophiles : $HO^{\ominus}$, $CH_3COO^{\ominus}$, $PhO^{\ominus}$, $CH_3O^{\ominus}$

(a) $CH_3O^{\ominus} > HO^{\ominus} > PhO^{\ominus} > CH_3COO^{\ominus}$ (b) $HO^{\ominus} > CH_3O^{\ominus} > PhO^{\ominus} > CH_3COO^{\ominus}$
(c) $HO^{\ominus} > PhO^{\ominus} > CH_3O^{\ominus} > CH_3COO^{\ominus}$ (d) $CH_3COO^{\ominus} > CH_3O^{\ominus} > HO^{\ominus} > PhO^{\ominus}$

19. The order of nucleophilicity of the following anions in a S_N2 reaction is



P Q R S

(a) Q > R > S > P (b) Q > P > R > S (c) Q > R > P > S (d) P > S > R > Q

IIT-JEE Previous Year Questions

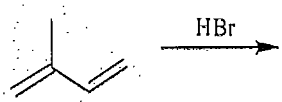
20. The product of the reaction

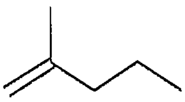
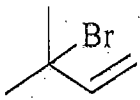
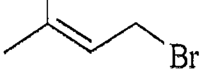
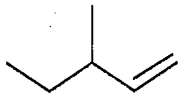
$$C_6H_6 + CO + HCl \xrightarrow[\text{heat}]{AlCl_3 / Cu_2Cl_2}$$

gives positive test with Fehling's solution. The product is :

(a) C_6H_5OH (b) $C_6H_4(Cl)CHO$ (c) $C_6H_4(OH)CHO$ (d) C_6H_5CHO

21. The major product of the reaction :



(a)  (b)  (c)  (d) 

22. The compound that will react with readily with NaOH to form methanol is :

(a) $(CH_3)_4N^+I^-$ (b) CH_3OCH_3 (c) $(CH_3)_3S^+I^-$ (d) $(CH_3)_3CCl$

23. Identify the set of reagent/reaction conditions X and Y in the following set of transformations:

$$CH_3-CH_2-CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$$

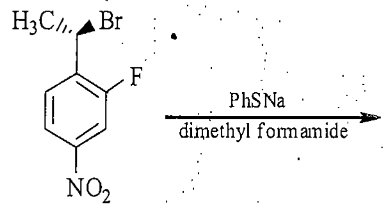
(a) X = dilute aqueous NaOH, 20°C, Y = HBr/acetic acid, 20°C

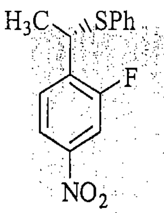
(b) X = concentrated alcoholic NaOH, 80°C Y = HBr/acetic acid, 20°C

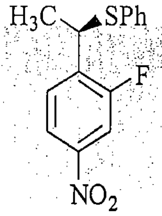
(c) X = dilute aqueous NaOH, 20°C, Y = $Br_2/CHCl_3$, 0°C

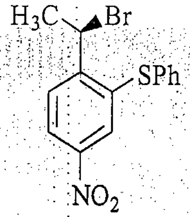
(d) X = concentrated aqueous NaOH, 80°C, Y = $Br_2/CHCl_3$, 0°C

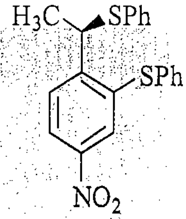
24. The major product of the following reaction is



(a) 

(b) 

(c) 

(d) 

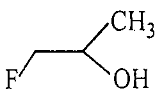
25. An organic compound C_3H_6O does not give a precipitate with 2,4-dinitrophenyl hydrazine reagent and does not react with sodium metal. It could be:

(a) $CH_3–CH_2–CHO$ (b) $CH_3–CO–CH_3$ (c) $CH_2=CH–CH_2OH$ (d) $CH_2= CH–OCH_3$

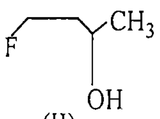
26. The reaction products of $C_6H_5OCH_3 + HI \xrightarrow{\Delta}$ are:

(a) $C_6H_5OH + CH_3I$ (b) $C_6H_5I + CH_3OH$ (c) $C_6H_5CH_3 + HOI$ (d) $C_6H_6 + CH_3OI$

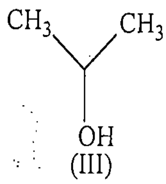
27. The order of reactivity of the following alcohols:



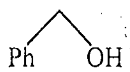
(I)



(II)



(III)

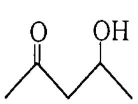


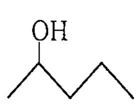
(IV)

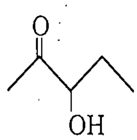
towards conc. HCl is:

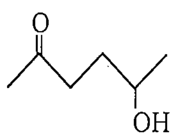
(a) I > II > III > IV (b) I > III > II > IV (c) IV > III > II > I (d) IV > II > III > I

28. Which one of the following will most readily be dehydrated in acidic condition:

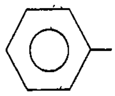
(a) 

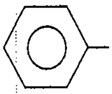
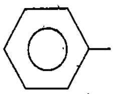
(b) 

(c) 

(d) 

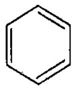
29. 1-propanol & 2-propanol can be best distinguished by :
   (a) Oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution
   (b) Oxidation with acedic dichromate followed by reaction with Fehling solution
   (c) Oxidation by heating with copper followed by reaction with Fehling solution
   (d) Oxidation with concentrated H_2SO_4 followed by reaction with Fehling

30.  $-OH + C_2H_5I \xrightarrow[C_2H_5OH\,(anhydrous)]{C_2H_5O^-Na^+\,(excess)}$

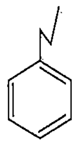
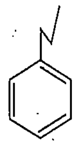
   (a)  $-OC_2H_5$ (b)  $-I$ (c) $C_6H_5OC_6H_5$ (d) $C_2H_5OC_2H_5$

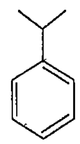
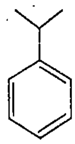
31. Reaction of enationmerically pure acid with 1 chiral carbon and racemic alcohol with 1 chiral carbon gives an ester which is:
   (a) Meso (b) Optically active mixture
   (c) Racemic mixture (d) Enationmerically pure

32. Phenyl magnesium bromide reacting with t-Butyl alcohol gives
   (a) Ph – OH (b) Ph – H (c) $Ph-O-C(CH_3)_3$ (d) $Ph-C(CH_3)_3$

33.  $+ Cl-CH_2CH_2-CH_3 \xrightarrow{AlCl_3} P \xrightarrow[(ii)\,H_3O^+]{(i)\,O_2/\Delta} Q + \text{Phenol}$

   The major products P and Q are

   (a)  and CH_3CH_2CHO (b)  and CH_3COCH_3

   (c)  and CH_3COCH_3 (d)  and CH_3CH_2CHO

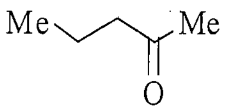
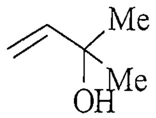
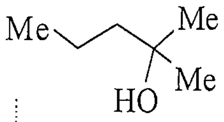
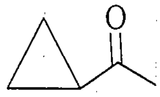
34. R-(–)-2-Bromooctane on treatment with aqueous KOH mainly gives 2-octanol that is :
   (a) optically active with 'R' configuration (b) optically active with 'S' configuration
   (c) a racemic mixture (d) a meso compound

35. In electrophilic aromatic substitution reactions, nitro group is meta-directing because the nitro group
   (a) increases electron density at meta-position
   (b) increases electrons density at ortho and para-positions
   (c) decreases electron density at meta-position
   (d) decreases electron density at ortho and para-positions

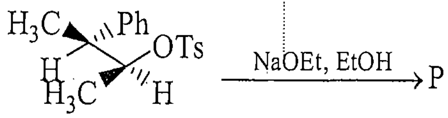
36. 2-phenyl ethanol may be prepared by the reaction of phenyl magnesium bromide with

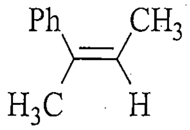
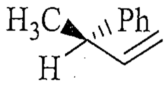
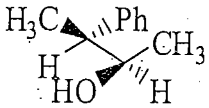
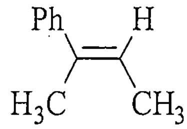
(a) HCHO (b) CH_3CHO (c) CH_3COCH_3 (d) 

37. Methyl vinyl ketone upon reaction with $LiCuMe_2$ gives a major product whose structure is

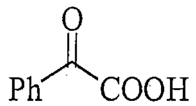
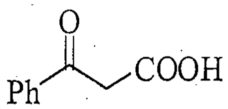
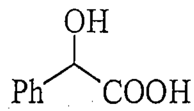
(a)  (b)  (c)  (d) 

38. The major product P formed in the given

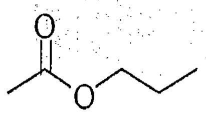
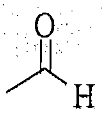
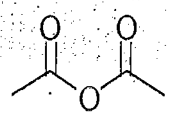
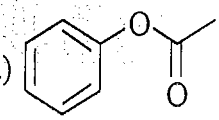


(a)  (b)  (c)  (d) 

39. Among the following the acid which undergoes fastest decarboxylation is

(a)  (b)  (c) PhCOOH (d) 

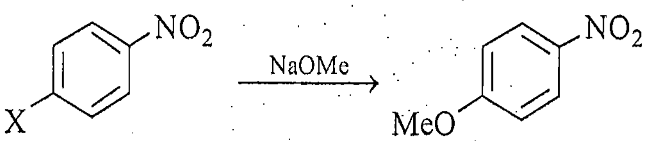
40. The compound which on reacting with aniline will not form an acetanilide is

(a)  (b)  (c)  (d) 

41. Aniline can be distinguished from methyl amine by its reaction with
(a) p-toluene sulphonyl chloride/KOH
(b) (i) $NaNO_2$/HCl, 0.5°C (ii) alkaline β naphthol
(c) Sn/HCl (d) Acetyl chloride

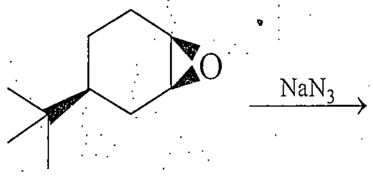
GATE Previous Year Questions

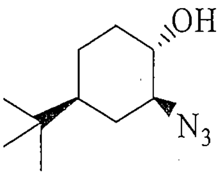
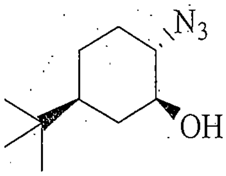
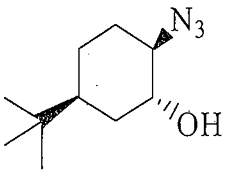
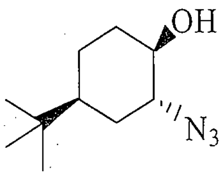
42. The corect order of reactivity of p-halonitrobenzenes in the following reaction is



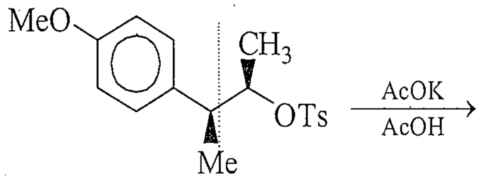
(a) p-fluoronitrobenzene > p-chloronitrobenzene > p-bromonitrobenzene > p-iodonitrobenzene
(b) p-fluoronitrobenzene > p-bromonitrobenzene > p-iodonitrobenzene > p-chloronitrobenzene
(c) p-iodonitrobenzene > p-bromonitrobenzene > p-chloronitrobenzene > p-fluoronitrobenzene
(d) p-bromonitrobenzene > p-fluoronitrobenzene > p-iodonitrobenzene > p-chloronitrobenzene

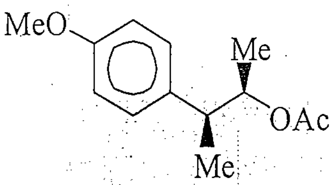
43. The major product formed in the following reaction is

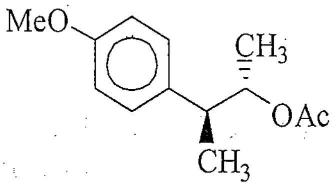


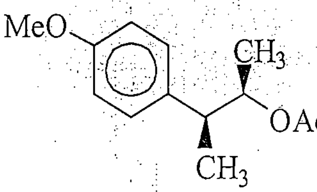
(a)  (b)  (c)  (d) 

44. Solvolysis of the optically active compound X gives, mainly

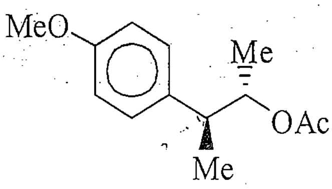


(a) 

(b) 

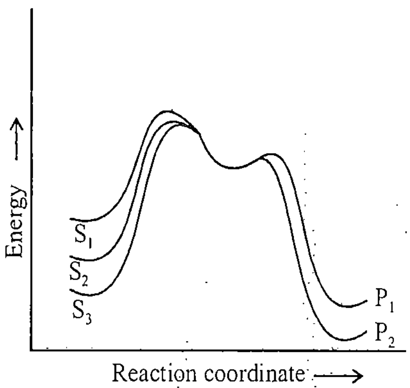
(c) 

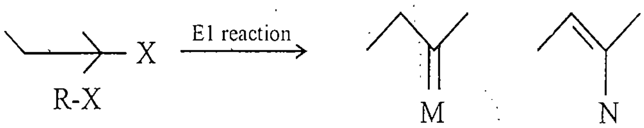
Racemic optically inactive

(d) 

Racemic optically active

Consider the E1 reaction of tert-amyl halides from the energy profile given below :





{Substrate (S)} Products (P)

45. (A) In the above reaction, X = Cl, Br or I. Based on the graph, identify the alkyl halides (R–X) as S_1 S_2 and S_3.

(a) S_1 = R—Cl, S_2 = R—Br and S_3 = R—I
(b) S_1 = R—I, S_2 = R—Br and S_3 = R—Cl
(c) S_1 = R—Cl, S_2 = R—I and S_3 = R—Br
(d) S_1 = R—I, S_2 = R—Cl and S_3 = R—Br

(B) Identify product P_1 and its yield relative to P_2

(a) P_1 is M and is the major product
(b) P_1 is N and is the minor product
(c) P_1 is N and is the major product
(d) P_1 is M and is the minor product

ANSWER KEY

EXERCISE I

1. b	2. c	3. a	4. d	5. b	6. d	7. d
8. a	9. b	10. d	11. b	12. a	13. d	14. b
15. a	16. a	17. a	18. d	19. b	20. b	21. b
22. d	23. b	24. d	25. b	26. d	27. b	28. c
29. d	30. b	31. c	32. b	33. d	34. c	35. b
36. c	37. b	38. d	39. a	40. d	41. c	42. d
43. d	44. a	45. b	46. b	47. b	48. b	49. b
50. a	51. a	52. a	53. d	54. b	55. d	56. d
57. b	58. b	59. d	60. a			

EXERCISE II

1. a,b,d	2. b,c	3. a,b	4. b,c	5. b,c,d	6. c,d	7. b,c
8. a,d	9. a,b	10. a,b,c,d	11. a,c	12. a,d	13. a,c,d	14. a,b,c
15. b,c	16. a,b,c,d	17. a,b,c,d	18. a,b,d	19. a,b,c,d	20. b,c,d	21. a,b,c,d
22. a,b,d	23. a,d	24. a,b, c	25. a,b,d	26. a,b,c,d	27. a,b,c	28. a,b,d
29. a,d	30. a,b,c,d	31. a,b,c	32. a,c	33. a,b,c	34. a,b,c	

EXERCISE III

1. 3	2. 6	3. 1	4. 3	5. 4	6. 2	7. 6
8. 3	9. 2	10. 120				

EXERCISE IV

1. d	2. d	3. a	4. d	5. d	6. c	7. a
8. c	9. d	10. c,d	11. a,b,c,d	12. 4	13. b	14. a
15. c	16. a	17. c	18. b	19. b	20. d	21. c
22. a	23. b	24. a	25. d	26. a	27. c	28. a
29. c	30. d	31. b	32. b	33. c	34. c	35. d
36. d	37. a	38. d	39. b	40. b	41. b	42. a
43. d	44. c	45. (A) a, (B) d				

CHAPTER

5

Name Reaction

Aldol Condensation: It is the condensation reaction between two moles of carbonyl compounds among which at least one must have α-hydrogen atom in dilute basic or acidic media to get α, β-unsaturated aldehyde / ketone via the formation of aldol / ketol.

$$R-CH_2-CHO + RCH_2CHO \xrightarrow[\text{or dil. HCl}]{\text{dil. NaOH}} \left[R-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{R}{|}}{C}H-CHO \right]$$

Aldol

$$\xrightarrow[\Delta]{-H_2O} R-CH_2-CH=\overset{\overset{R}{|}}{C}-CHO$$

α, β-unsaturated aldehyde

Example: $2CH_3CH=O \xrightarrow{\text{Base}} CH_3-\underset{\underset{OH}{|}}{\overset{\beta}{C}}H-\overset{\alpha}{C}H_2-CH=O \xrightarrow[-H_2O]{\Delta} \underset{\alpha-\beta \text{ unsaturated aldehyde}}{CH_3-CH=CH-CHO}$

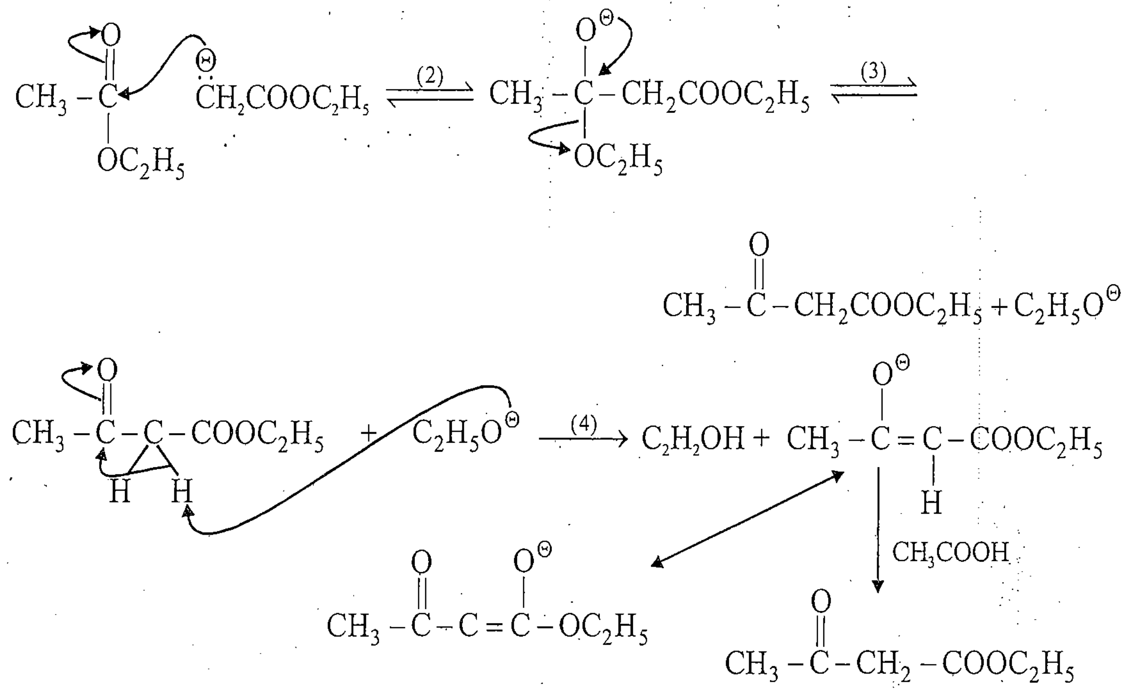
Claisen condensation: Esters having α-hydrogen on treatment with a strong base e.g. $C_2H_5\overset{-}{O}N\overset{+}{a}$ undergo self condensation to produce β-ketoesters.

$$2CH_3COOC_2H_5 \xrightarrow[\text{2. } C_2H_5OH]{\text{1. } C_2H_5ONa} CH_3COCH_2COOC_2H_5$$

The reaction is called claisen condensation.

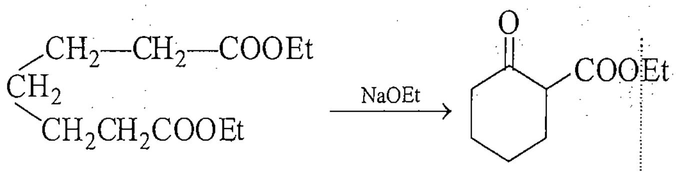
Mechanism:

$$C_2H_5O^{\ominus} + H-CH_2\cdot COOC_2H_5 \underset{}{\overset{(1)}{\rightleftharpoons}} C_2H_5OH + {}^{\ominus}CH_2COOC_2H_5$$

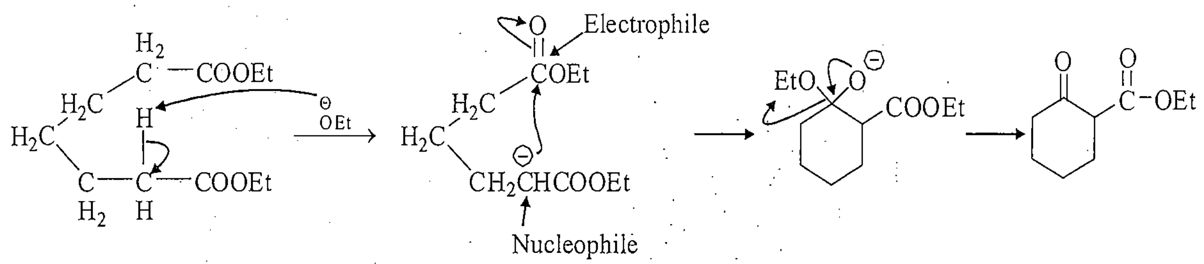


Dieckmann Cylisation (Intramolecular claisen condensation)

Intramolecular claisen reaction where both esters group (COOEt) are part of the same molecule acting as nucleophile and electrophile to give cyclic stable 5,6 or sometime 7 membered rings is known as Dieckmann cyclisation.

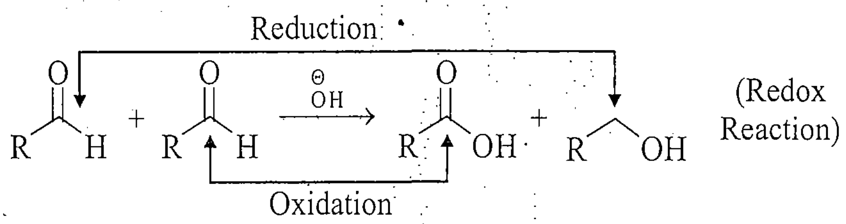


Mechanism:

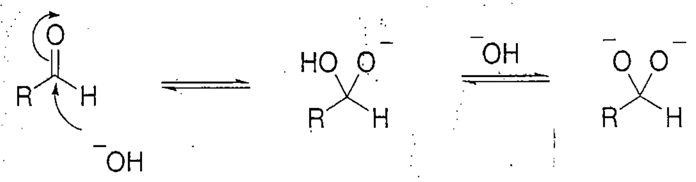


CANNIZZARO REACTION

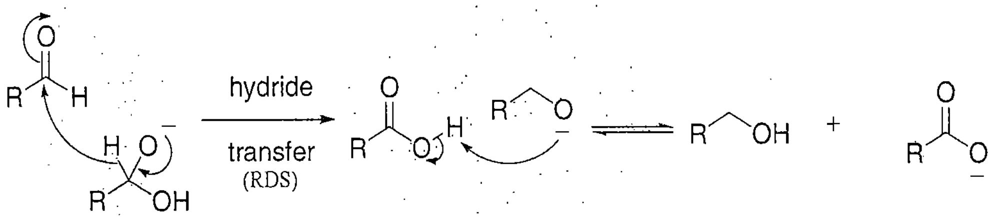
The redox reaction between aromatic aldehydes, formaldehyde or other aliphatic aldehydes without α-hydrogen in strongly basic media. is called cannizzaro reaction.



Mechanism:

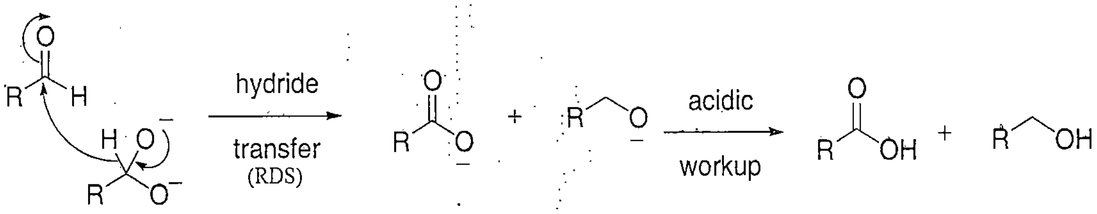


Pathway I



Rate = $K[RCHO]^2[OH^{\ominus}]$

Pathway II



Rate = $K[RCHO]^2[OH^{\ominus}]^2$

Note: (i) Ester is not formed under strongly alkaline medium.

(ii) Hydride transfer for dianion is faster than anion.

EXERCISE - I

Single Answer Correct Type

Aldol & Cannizaro Reactions

1. In the given reaction

$$X + Y \xrightarrow[5°C]{NaOH} CH_3-\underset{}{\overset{OH}{\overset{|}{C}H}}-\underset{\underset{CH_3}{|}}{CH}-CHO$$

(X) and (Y) will respectively be:

(a) CH_3-CH_2-CHO and CH_3-CH_2-CHO (b) CH_3-CHO and CH_3-CH_2-CHO

(c) CH_3-CHO and CH_3-CHO (d) CH_3-CHO and $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CHO$

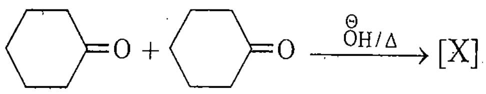
2. Number of products (excluding stereoisomers) in the given reaction :

$$C_6H_5CHO + CH_3-CHO \xrightarrow{\overset{\ominus}{O}H} \text{Product}$$

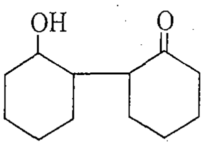
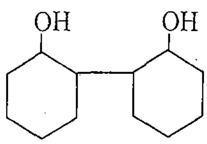
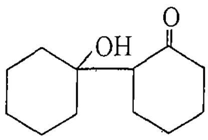
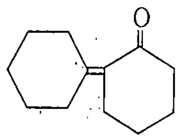
will be :

(a) One (b) Three (c) Two (d) Four

3. In the reaction :



[X] will be :

(a)  (b)  (c)  (d) 

4. Cross cannizzaro reaction is example of :

(a) Redox reaction (b) Disproportionation (c) Both (a) and (b) (d) Only oxidation

5. In the given reaction

$$CH_3-CH_2-\overset{\overset{O}{||}}{C}-CH_2COOC_2H_5 \xrightarrow{[X]} (A) \xrightarrow[(ii)H_2O/H^{\oplus}]{(i)LiAlH_4} CH_3-CH_2-\overset{\overset{O}{||}}{C}-CH_2-CH_2OH + C_2H_5OH$$

[X] will be:

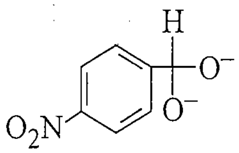
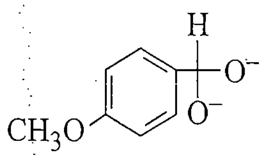
(a) HCHO (b) $\underset{CH_2OH}{\overset{CH_2-OH}{|}} + H^{\oplus}$ (c) $\underset{CH_2-OH}{\overset{CH_2-OH}{|}} + \overset{\ominus}{O}H$ (d) HCN

6. The Cannizzaro's reaction is not given by
(a) trimethyl acetaldehyde (b) acetaldehyde
(c) benzaldehyde (d) formaldehyde

7. Base catalysed aldol condensation occurs with
(a) benzoic acid (b) benzaldehyde
(c) 2-methyl propionaldehyde (d) 2,2-dimethyl propionaldehyde

8. Which of the following is an example of aldol condensation?
(a) $2CH_3CHO \xrightarrow{\text{dil.NaOH}} CH_3CH(OH)CH_2CHO$
(b) $2HCHO \xrightarrow{\text{dil.NaOH}} CH_3OH + HCOONa$
(c) $C_6H_5CHO + HCHO \xrightarrow{\text{dil.NaOH}} C_6H_5CH_2OH + HCOONa$
(d) None of these

9. In the Cannizzaro reaction given below, $2Ph\text{–}CHO \xrightarrow{OH^-} Ph\text{–}CH_2OH + PhCO_2^-$ the slowest step is:
(a) the attack of OH^- at the carbonyl group
(b) the transfer of hydride to the carbonyl group
(c) the abstraction of proton from the carboxylic acid
(d) the deprotonation of $Ph\text{–}CH_2OH$

10. In a Cannizzaro reaction the intermediate which is the best hydride donor is:
(a) $C_6H_5-\overset{H}{\underset{OH}{C}}-O^-$
(b) $C_6H_5-\overset{H}{\underset{O^-}{C}}-O^-$
(c) 
(d) 

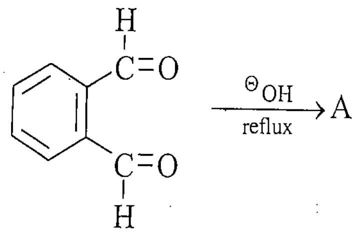
11. Which of the following will not undergo aldol condensation:
(a) Acetaldehyde (b) Propanaldehyde (c) Benzaldehyde (d) Trideutero acetaldehyde

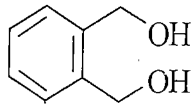
12. A new carbon-carbon bond formation is possible in
(a) Cannizzaro reaction (b) Friedel-Crafts alkylation
(c) Clemmensen reduction (d) None of these

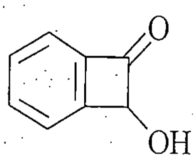
13. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives:
(a) benzyl alcohol and sodium formate (b) sodium benzoate and methyl alcohol
(c) sodium benzoate and sodium formate (d) benzyl alcohol and methyl alcohol

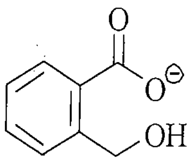
14. Which one of the following compounds will not give aldol:
(a) Acetaldehyde (b) Formaldehyde (c) Acetone (d) Crotonaldehyde

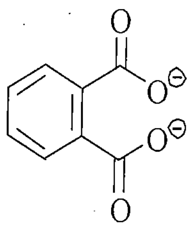
$CH_3-CH=CH-CHO$

15. 

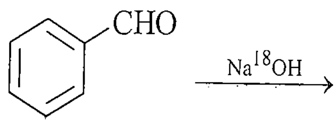
(a) A = 

(b) A = 

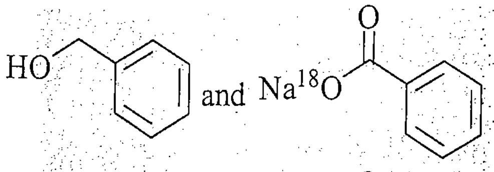
(c) A = 

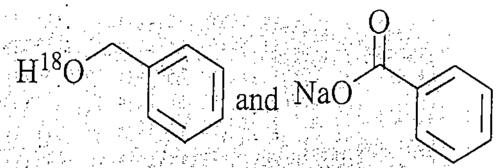
(c) A = 

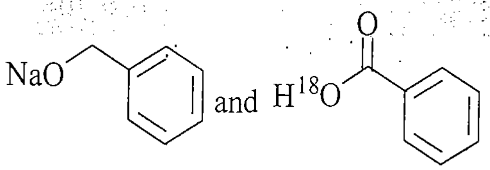
16. The product of the following reaction

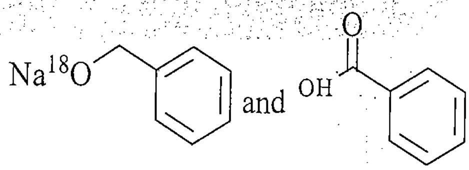
2 

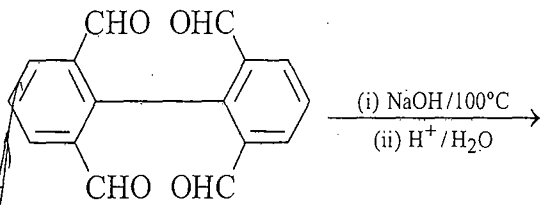
are

(a) 

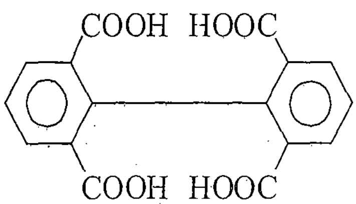
(b) 

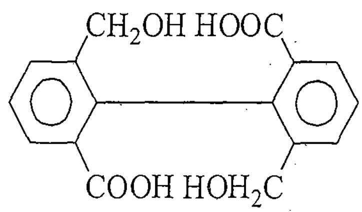
(c) 

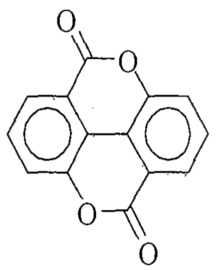
(d) 

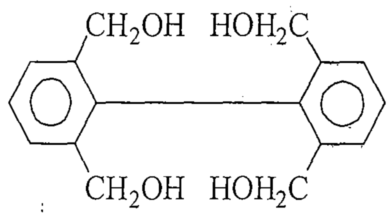
17. 

Major product is

(a) 

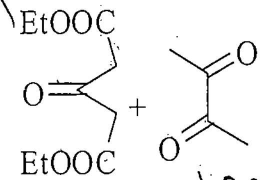
(b) 

(c) 

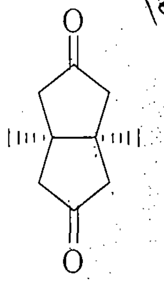
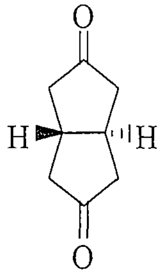
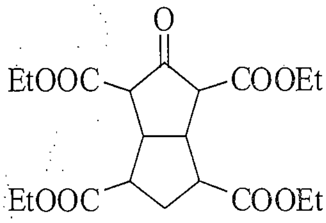
(d) 

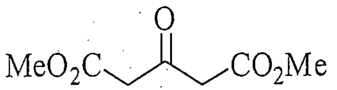
Clasien Condensation

" Knovenagel ... followed by michael addition type Rxn"

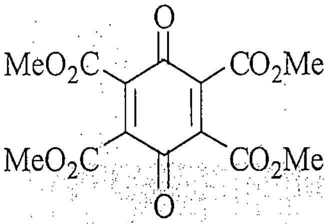
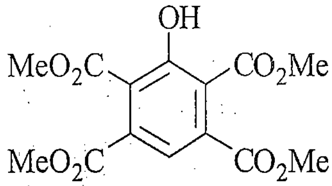
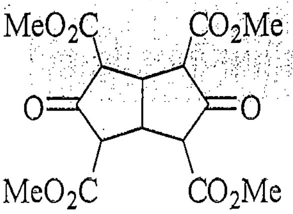
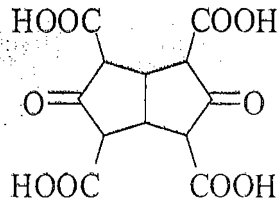
18.  $\xrightarrow[\text{EtOH}]{\text{EtO}^{\ominus}}$ A $\xrightarrow[\text{H}_2\text{O}]{\text{H}^{\oplus}}$ B ; B is

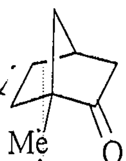
Use 2 eq. 1 eq.

(a) 
(b) 
(c) 
(d) 

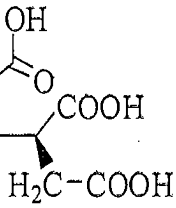
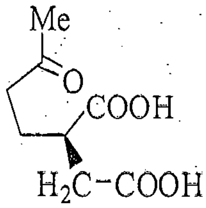
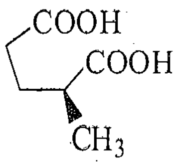
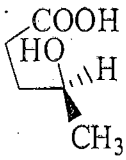
19.  + OHC – CHO $\xrightarrow{\text{MeO}^-}$?

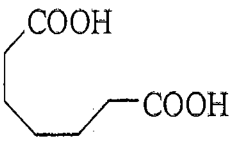
2 equivalent 1 equivalent

(a) 
(b) 
(c) 
(d) 

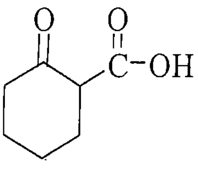
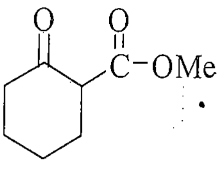
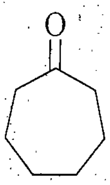
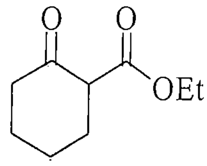
20.  $\xrightarrow[\substack{\text{2. NaOH/H}_2\text{O} \\ \text{3. H}_2\text{SO}_4/\Delta}]{\text{1. mCPBA}}$ A $\xrightarrow[\substack{\text{2. EtOH (2eq)/H}^{\oplus} \\ \text{3. Br}_2\text{/KOH (excess)}}]{\text{1. O}_3\text{/H}_2\text{O}_2}$ B

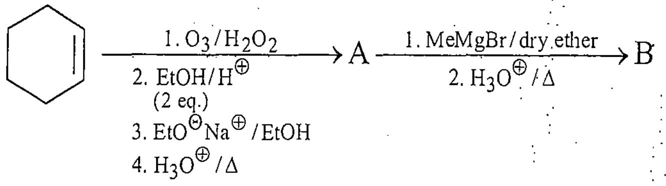
What is the structure of major product B?

(a) 
(b) 
(c) 
(d) 

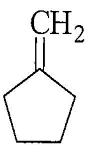
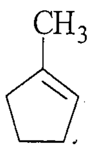
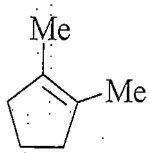
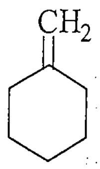
21.  $\xrightarrow[\substack{\text{2. Na}^{\oplus}\,\overset{\ominus}{\text{O}}\text{Et/EtOH} \\ \text{3. H}_3\text{O}^{\oplus}/\Delta}]{\text{1. EtOH (2eq.)/H}^{\oplus}}$ A $\xrightarrow{\text{1. CH}_2\text{N}_2}$ B

What is the major product A and B?

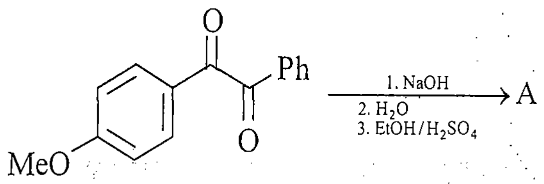
(a)  (b)  (c)  (d) 

22. 

What is the major product B?

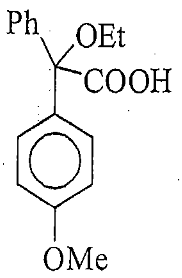
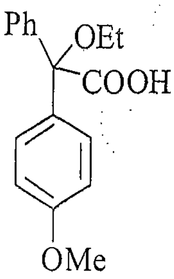
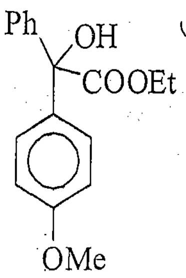
(a)  (b)  (c)  (d) 

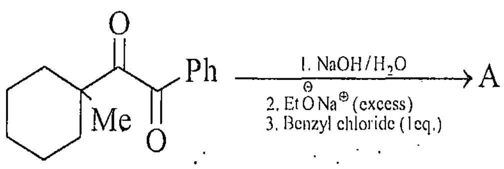
Benzil-Benzilic Acid Rearrangement

23. 

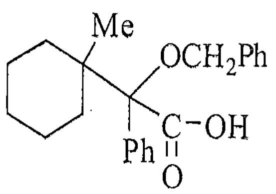
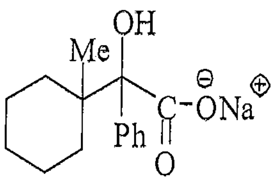
What is the major product A?

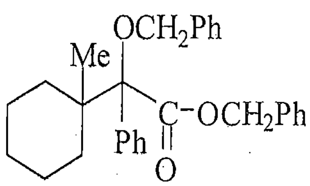
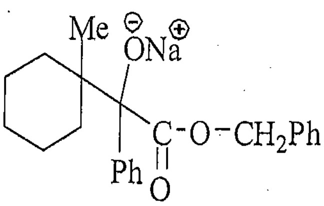
$\bar{O}H$ attacks carbonyl which on have ~~stronger~~ substi-tuent with larger migratory aptitude

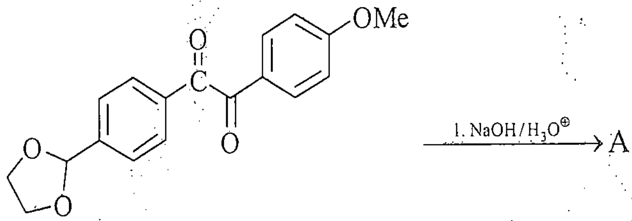
(a)  (b)  (c)  (d) None of these

24. 

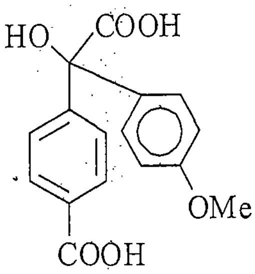
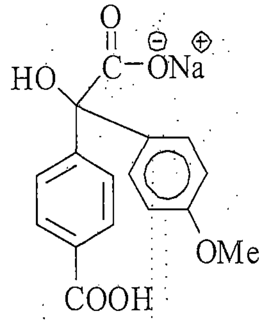
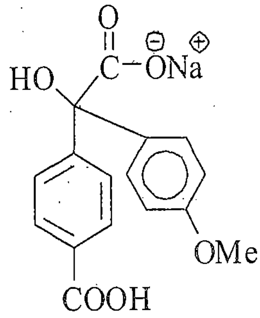
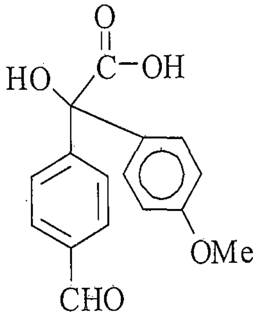
What is the major product A?

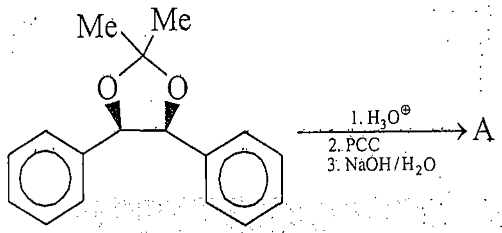
(a)  (b) 

(c)  (d) 

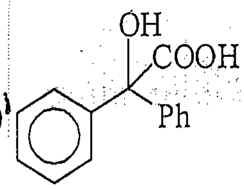
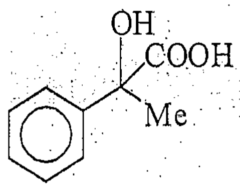
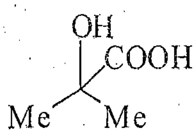
25. 

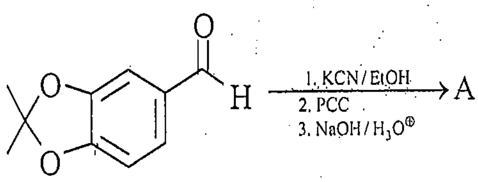
What is the major product?

(a) 
(b) 
(c) 
(d) 

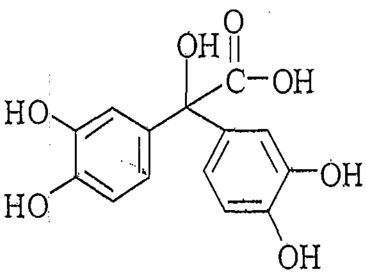
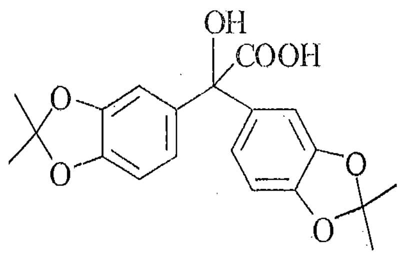
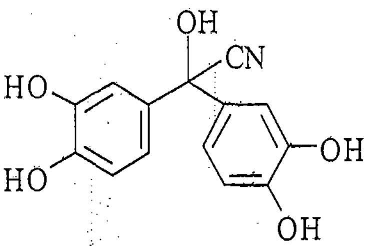
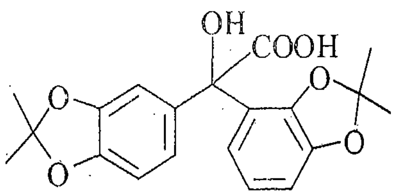
26. 

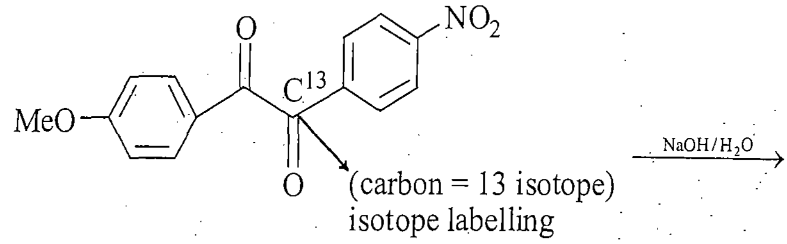
What is the major product

(a) 
(b) 
(c) 
(d) None of these

27. 

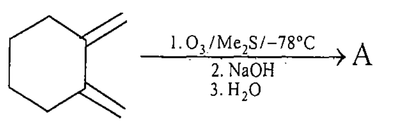
What is the major product A?

(a) 
(b) 
(c) 
(d) 

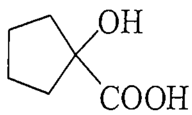
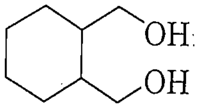
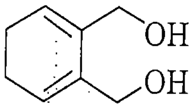
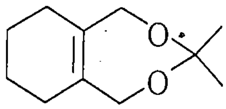
28. 

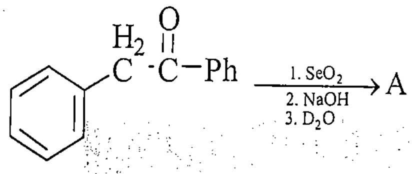
In the above reaction how many products are possible?

(a) 2 (b) 3 (c) 1 (d) None of these

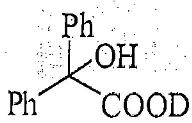
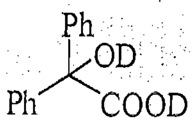
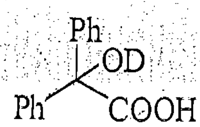
29. 

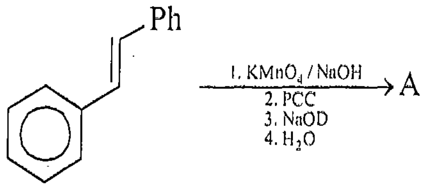
What is the major product?

(a)  (b)  (c)  (d) 

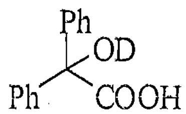
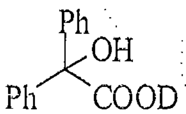
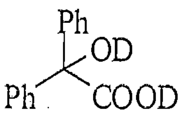
30. 

What is the major product?

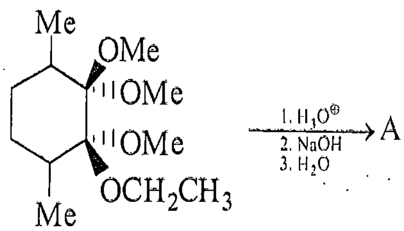
(a)  (b)  (c)  (d) None of these

31. 

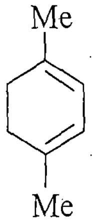
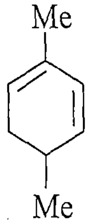
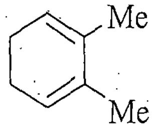
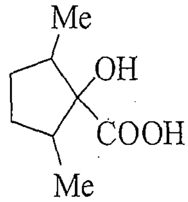
What is the major product?

(a)  (b)  (c)  (d) None of these

Check

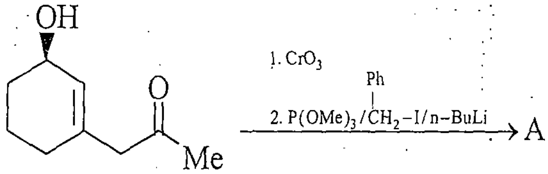
32. 

What is the major product?

(a)  (b)  (c)  (d) 

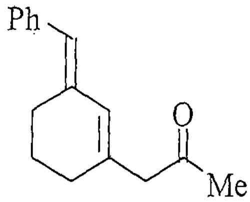
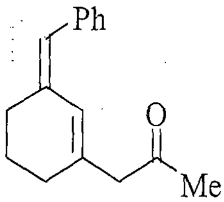
Wittig Reaction

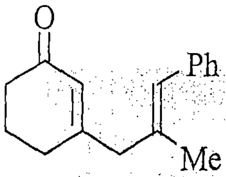
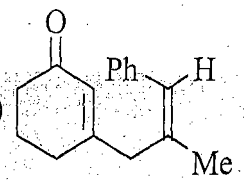
Wittig Rxn is applicable only for carbonyl compounds & it will not react with esters & amides.

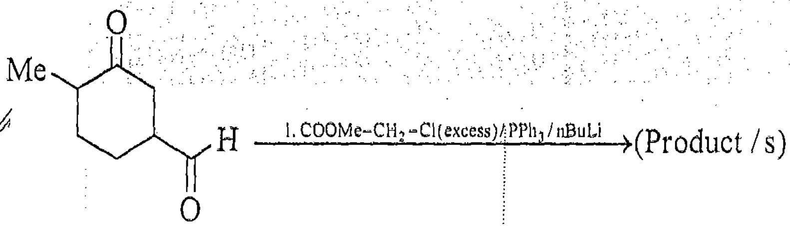
33. 

What is the major product and Its formation of selectivity?

Ph → gets E.W.G

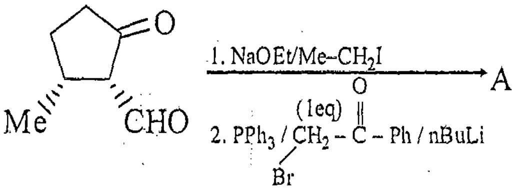
(a)  and Chemoselectivity (b)  and Chemoselectivity

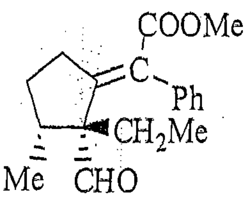
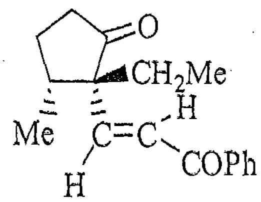
(c)  and regioselectivity (d)  and Regioselectivity

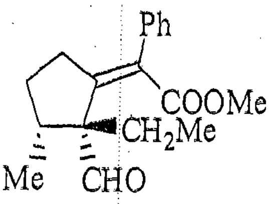
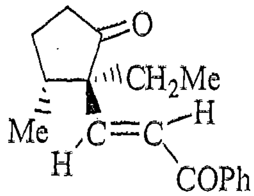
34. 

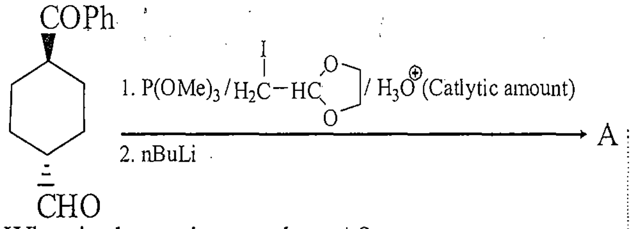
The possibility of products formation in all above reaction?

(a) 2 (b) 4 (c) 3 (d) 6

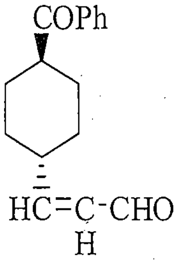
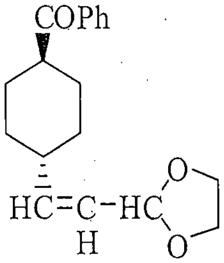
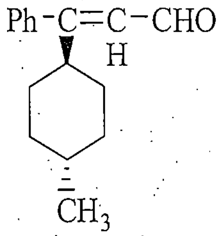
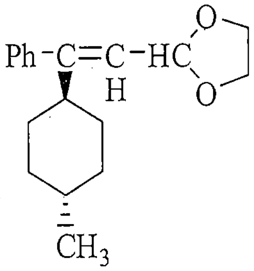
35. 

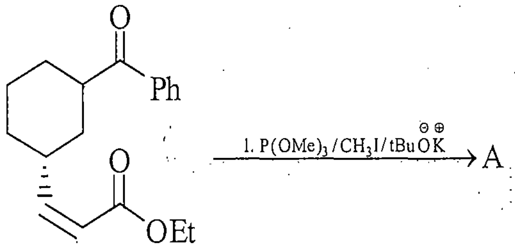
(a)  (b) 

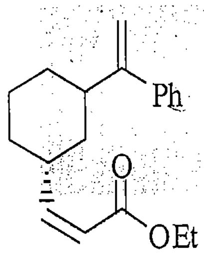
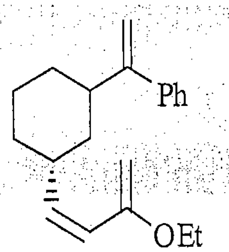
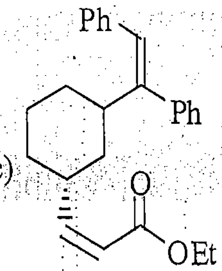
(c)  (d) 

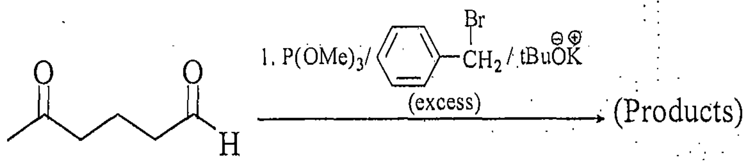
36. 

What is the major product A?

(a)  (b)  (c)  (d) 

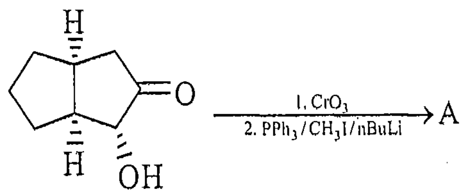
37. 

(a)  (b)  (c)  (d) None of these

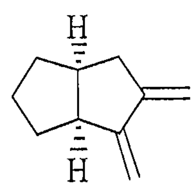
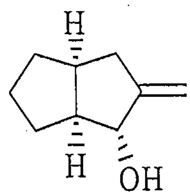
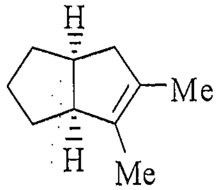
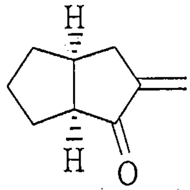
38. 

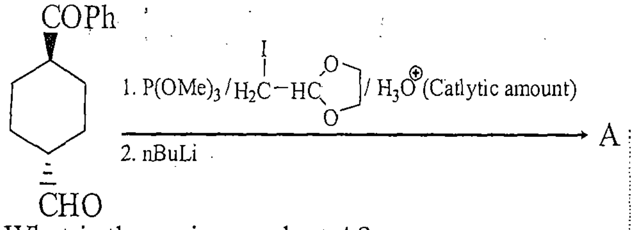
The number of possible products in the above reaction?

(a) 4 (b) 3 (c) 1 (d) 2

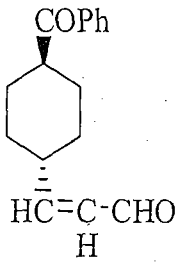
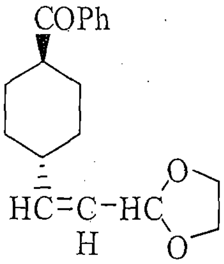
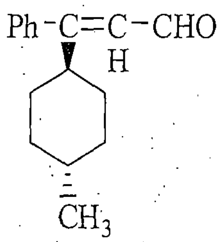
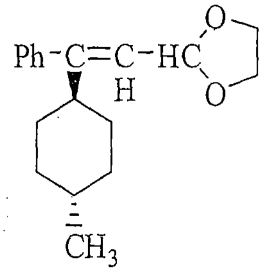
39. 

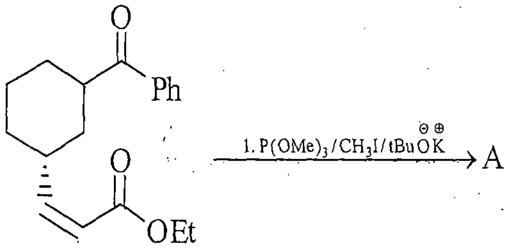
What is the major product?

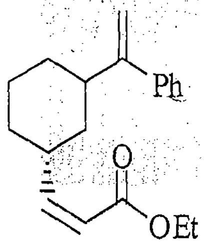
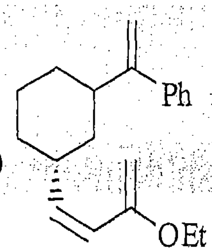
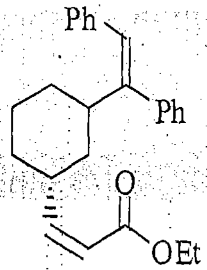
(a)  (b)  (c)  (d) 

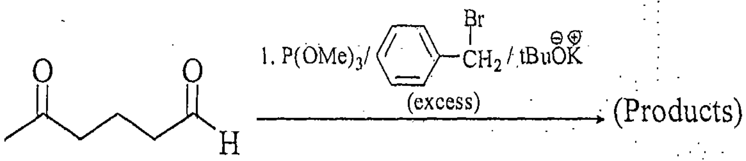
36. 

What is the major product A?

(a)  (b)  (c)  (d) 

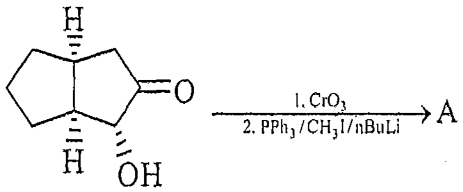
37. 

(a)  (b)  (c)  (d) None of these

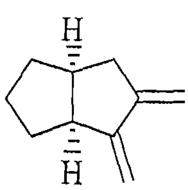
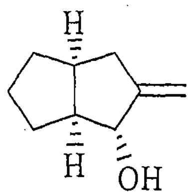
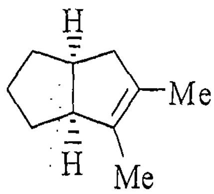
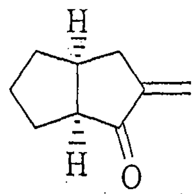
38. 

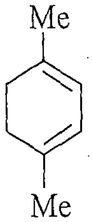
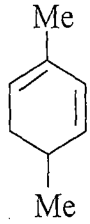
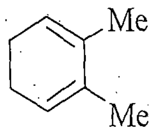
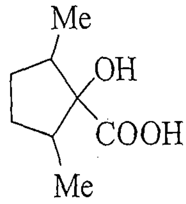
The number of possible products in the above reaction?

(a) 4 (b) 3 (c) 1 (d) 2

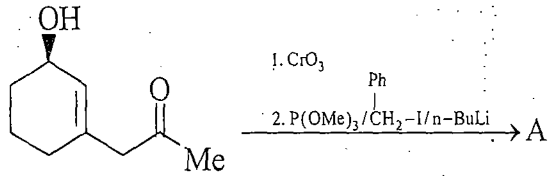
39. 

What is the major product?

(a)  (b)  (c)  (d) 

(a)  (b)  (c)  (d) 

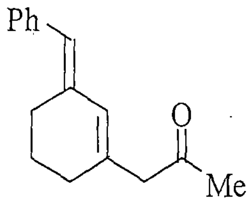
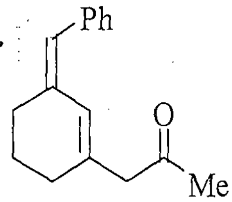
Wittig Reaction

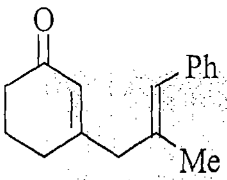
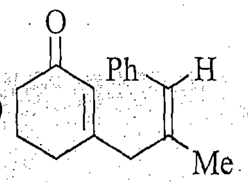
33. 

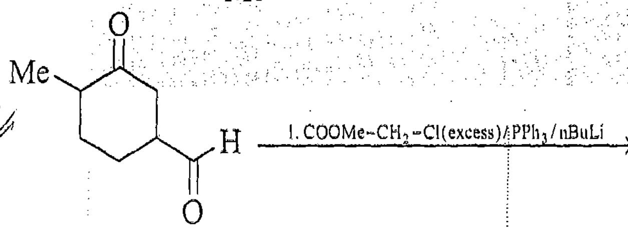
wittig Rxn is applicable only for carbonyl compounds it will not react with esters & amides.

What is the major product and Its formation of selectivity?

Ph → gets E.W.G

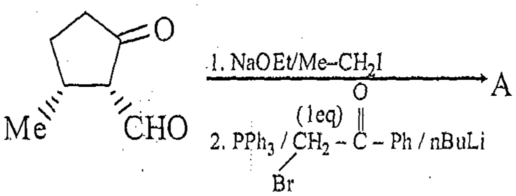
(a)  and Chemoselectivity (b)  and Chemoselectivity

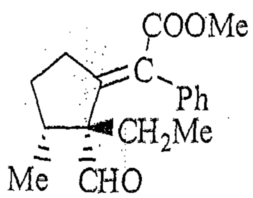
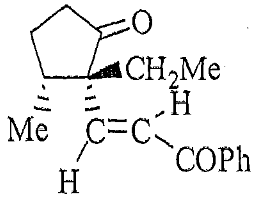
(c)  and regioselectivity (d)  and Regioselectivity

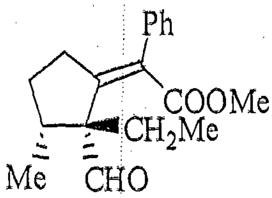
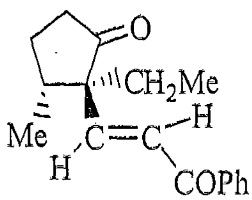
34.  (Product / s)

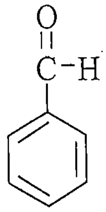
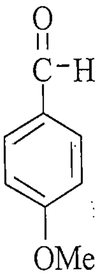
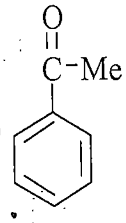
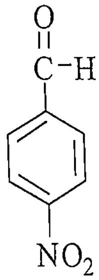
The possibility of products formation in all above reaction?

(a) 2 (b) 4 (c) 3 (d) 6

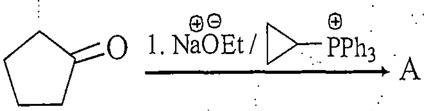
35. 

(a)  (b) 

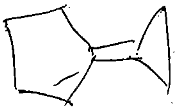
(c)  (d) 

40. (A)  (B)  (C)  (D) 

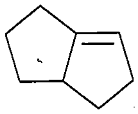
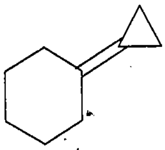
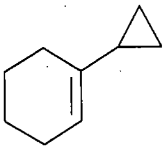
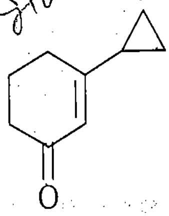
The order of reactivity of following compounds for wittig reaction?
(a) A > B > C > D (b) A > C > B > D (c) D > A > B > C (d) D > A > C > B

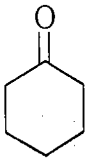
41.  A

What is the major product A

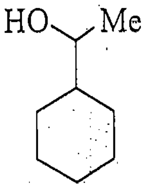
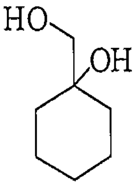


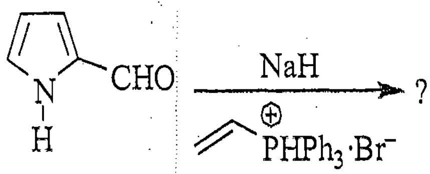
(exocyclic) rearranges to give product, in presence of Base

(a)  (b)  (c)  (d) 

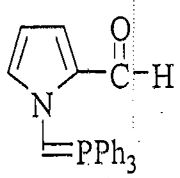
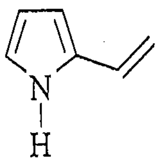
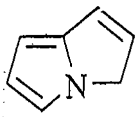
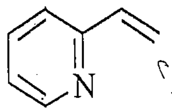
42.  $\xrightarrow[\text{2. } BH_3.SMe_2/H_2O_2/NaOH]{\text{1. } PPh_3/CH_3CH_2I/nBuLi}$ A

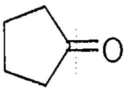
What is the major product A?

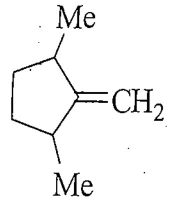
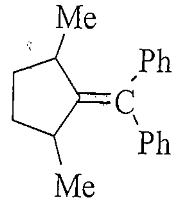
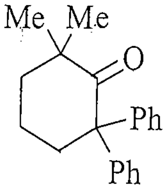
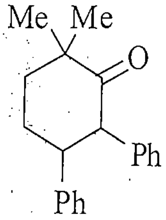
(a)  (b)  (c) (a) and (b) both (d) None of these

43. 

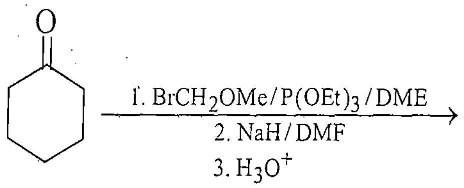
Special wittig Reagent

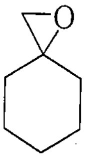
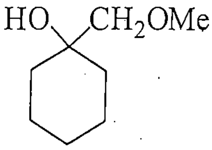
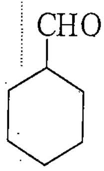
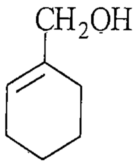
(a)  (b)  (c)  (d) 

44.  $\xrightarrow{\text{1. } Ph_2C{=}PPh_3}$ B ; B is
Major product
2. OsO_4, NMO
3. $H^{\oplus}$
4. LDA(2eq.) & MeI (2eq.)

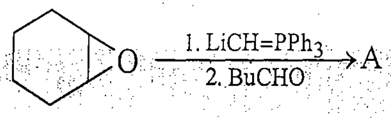
(a)  (b)  (c)  (d) 

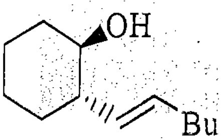
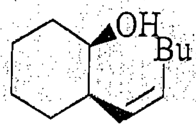
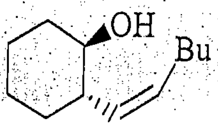
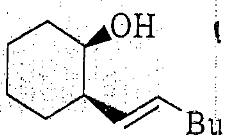
45. The product for the following sequence of reactions is



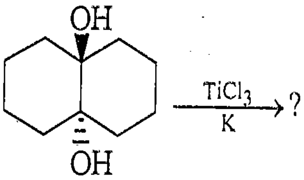
(a)  (b)  (c)  (d) 

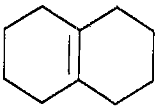
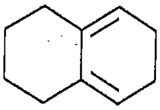
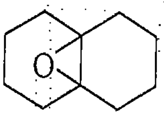
46. The major product A in the following reaction sequence are

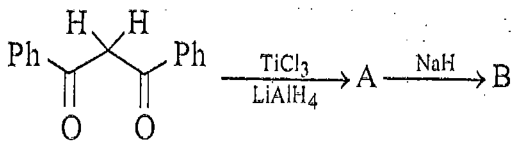


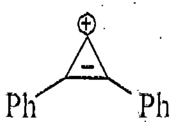
(a)  (b)  (c)  (d) 

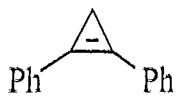
Mecmurry Coupling Reaction

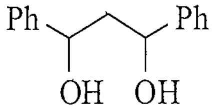
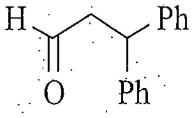
47. 

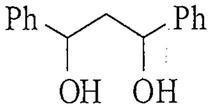
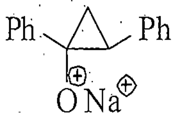
(a)  (b)  (c)  (d) No reaction

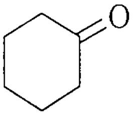
48. 

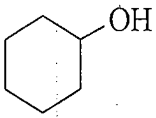
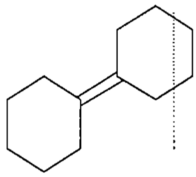
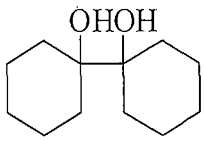
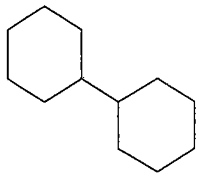
(a) A is  & B is 

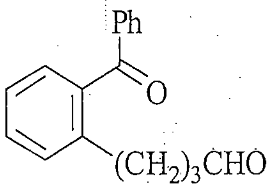
(b) A is  & B is highly unstable antiaromatic compound & difficult to form.

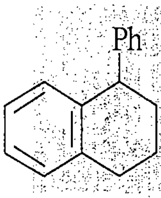
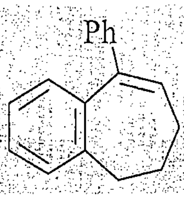
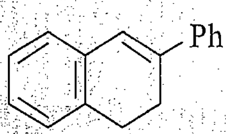
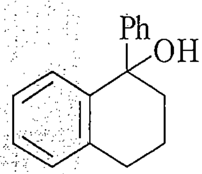
(c) A is  & B is 

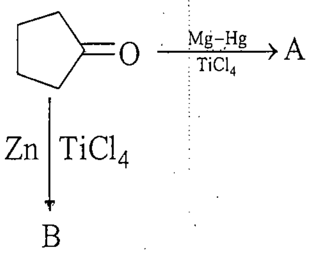
(d) A is  & B is 

49.  $\xrightarrow[K]{TiCl_3}$ A ; A is

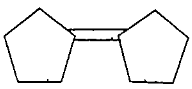
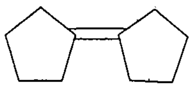
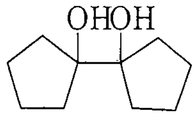
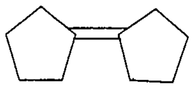
(a)  (b)  (c)  (d) 

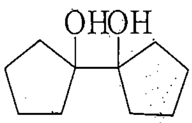
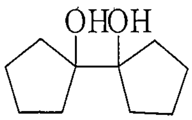
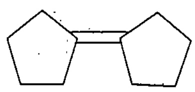
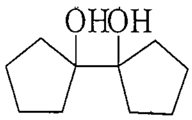
50.  $\xrightarrow[Zn-Cu]{TiCl_3}$?

(a)  (b)  (c)  (d) 

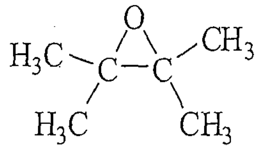
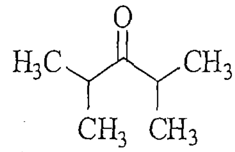
51. 

A & B respectively are

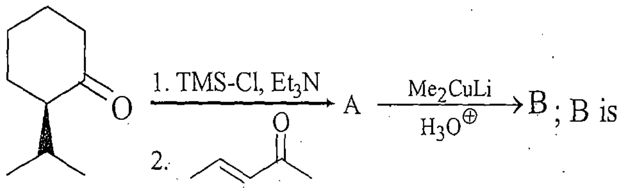
(a)  &  (b)  & 

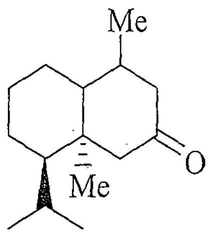
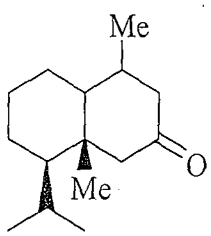
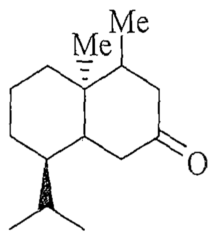
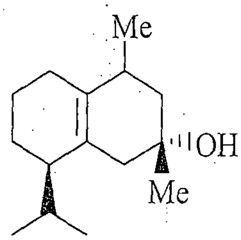
(c)  &  (d)  & 

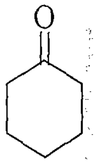
52. $(CH_3)_2C=O \xrightarrow{Mg-Hg} A \xrightarrow{H^{\oplus}} B$; B is

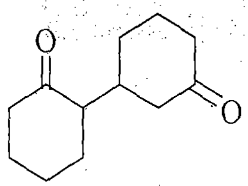
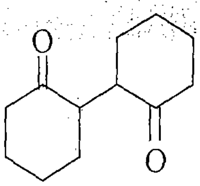
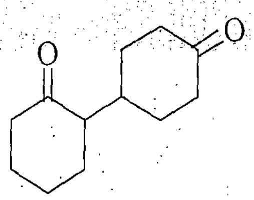
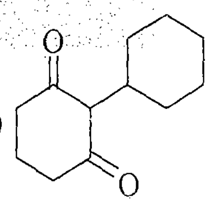
(a) $CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{C}(CH_3)_2$ (b) $CH_3-\underset{\underset{OH}{|}}{C}=\underset{\underset{OCH_3}{|}}{C}-CH_3$ (c)  (d) 

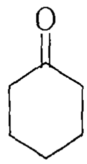
Michael Addition Reaction

53. 

(a)  (b)  (c)  (d) 

54.  $\xrightarrow[2.\ H_3O^{\oplus}]{1.\ Na\overset{\ominus}{O}Et/\text{Cyclo hexenone}}$ Major product

(a)  (b)  (c)  (d) 

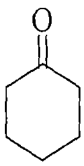
55.  $\xrightarrow[2.\ H_3O^{\oplus}]{1.\ \overset{\oplus}{Na}\overset{\ominus}{O}Et\ (\text{excess})/\text{Cyclohexadienone}}$

(excess)

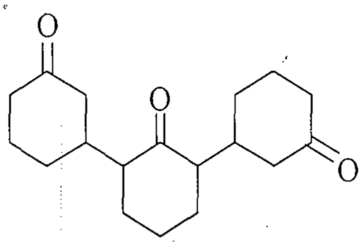
How many double bonds can give this type of reaction?

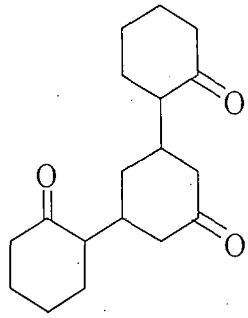
(a) 2 (b) 3 (c) 1 (d) None of these

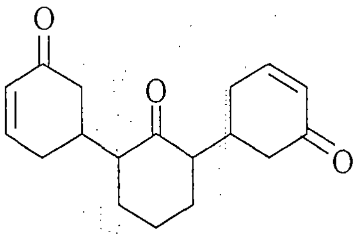
56. What is the major product in given reaction

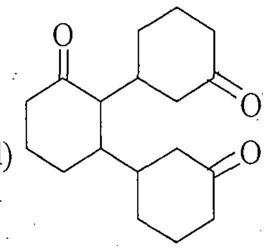
 $\xrightarrow[2.\ H_3O^{\oplus}]{1.\ \overset{\oplus}{Na}\overset{\ominus}{O}Et\ (\text{excess})/\text{Cyclohexadienone}}$

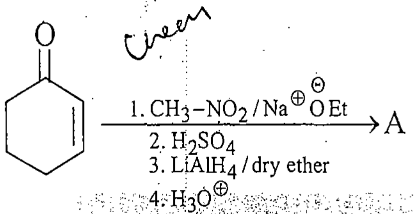
(excess)

(a) 

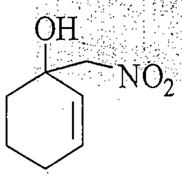
(b) 

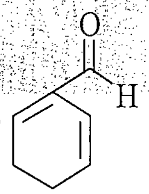
(c) 

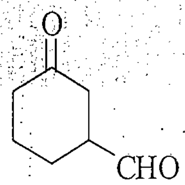
(d) 

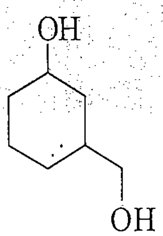
57. 

What is the major product A?

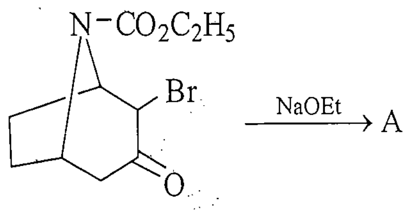
(a) 

(b) 

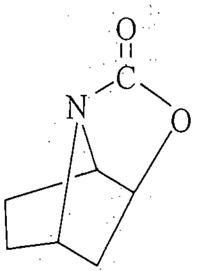
(c) 

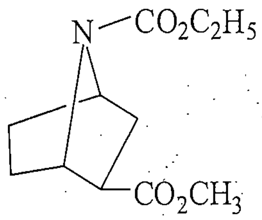
(d) 

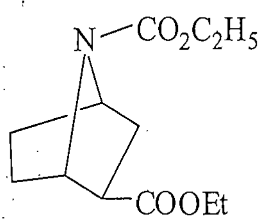
Favorskii Rearrangement

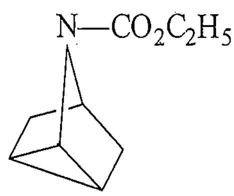
58. 

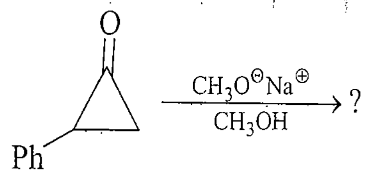
A is

(a) 

(b) 

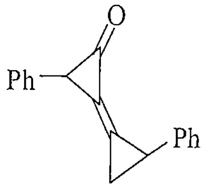
(c) 

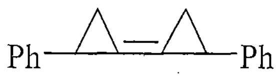
(d) 

59. 

(a) $Ph-CH_2CH_2\overset{O}{\overset{\|}{C}}-OMe$

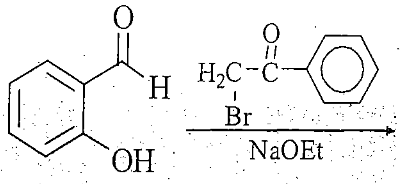
(b) $Ph-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OMe$

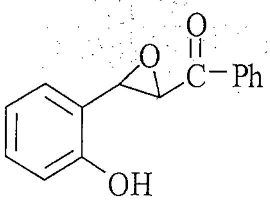
(c) 

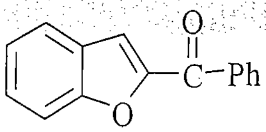
(d) 

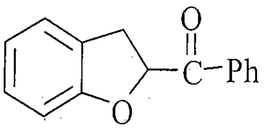
Darzon Reaction

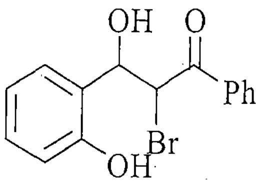
60. Major product formed in the given reaction



(a) 

(b) 

(c) 

(d) 

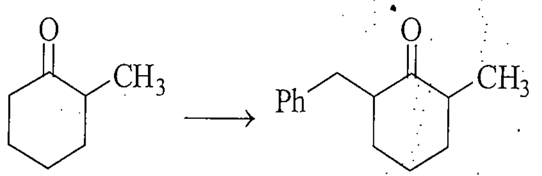
EXERCISE - II

One or More Than One Correct

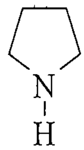
1. A new carbon-carbon bond formation is possible in

(a) wittig reaction
(b) Mecmurry reaction
(c) Michael addition
(d) Reimer-Tiemann reaction

2. Correct combination of reagent carried out following conversion



(a) (i) LDA, –78°C (ii) $Ph-CH_2-I$

(b) (i)  , H^+, (ii) $Ph-CH_2-Br$, then H^+/H_2O

(c) (i) NaH (ii) $Ph-CH_2-Br$

(d) (i) CH_3-Li (ii) $Ph-CH_2-Br$

3. Compound which will give haloform reaction is/are

(i) $Ph-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(ii) $Ph-CH_2-\overset{O}{\overset{\|}{C}}-CH_3-CH_3$

(iii) $CH_3-\overset{O}{\overset{\|}{C}}-Cl$

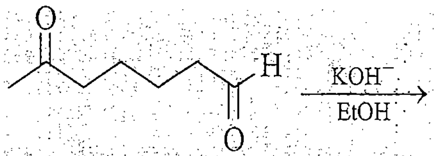
(iv) $CH_3-\overset{O}{\overset{\|}{C}}-H$

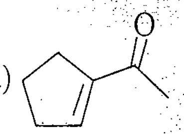
(v) $CH_3-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3$ (can't oxidise) tertiary alc

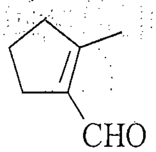
(vi) $CH_3-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-\underset{CH_3}{\underset{|}{C}}-CH_3$

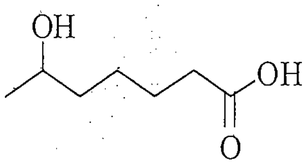
(a) (i) & (iv) (b) (vi) (c) (iii) & (ii) (d) (v)

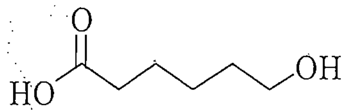
4. Possible product formed in the reaction is



(a) 

(b) 

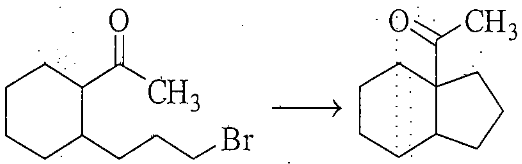
(c) 

(d) 

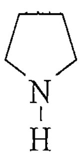
EXERCISE - III

Numerical and Subjective Answer Type

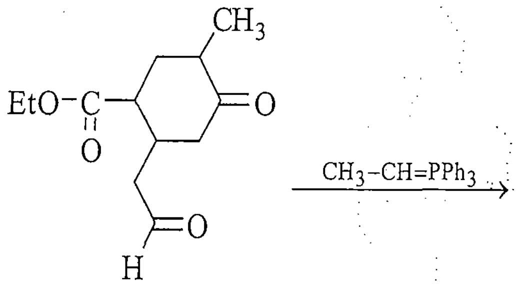
1. Number of reagent which are suitable for the given conversion is



(i) LDA – 78°C (ii) NaH (iii) CH_3Li

(iv)  , H^+ (v) CH_3-MgBr

2. Number of possible product formed in the following reaction is

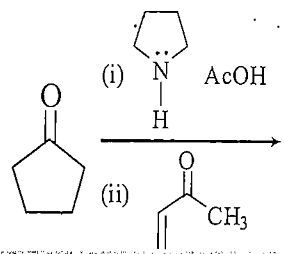


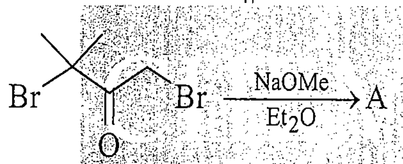
Check

3. Possible product formed in the given reaction is

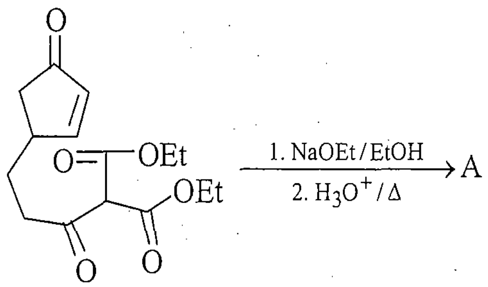
$$Ph-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{(ii) NaOEt}]{\text{1. } Br_2/AcOH}$$

4. Number of π bond formed in the given reaction is



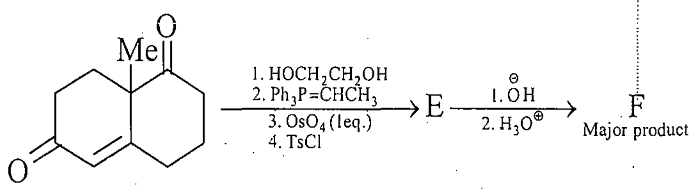
5. 

Calculate total number of sp^3 carbon in the product A.

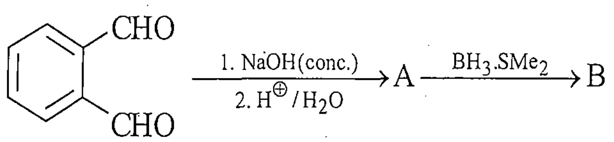
6. 

Check whether decarboxylates on heating

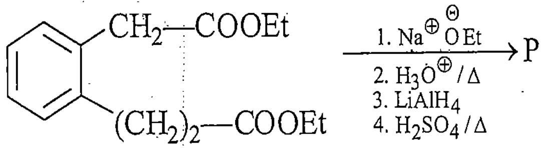
Number of carbon atom present in the product A.

7. 

Find the structure of F

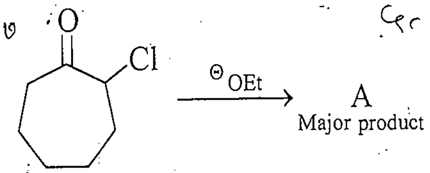
8. 

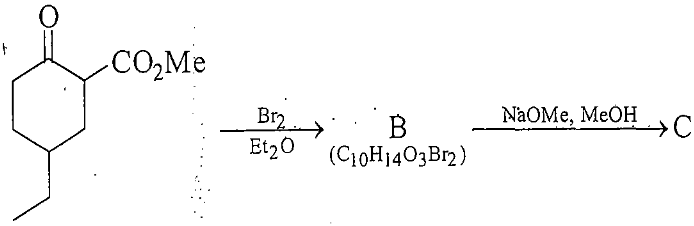
What is degree of unsaturation of A?

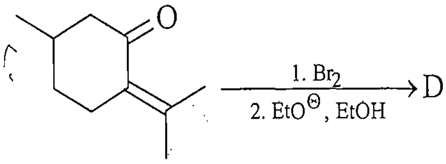
9. 

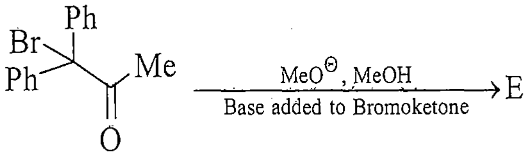
The degree of unsaturation and number of sp^2-hybridized atom in the product x and y. Calculate (x + y)

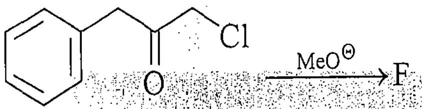
10. Favorskii Rearrangement

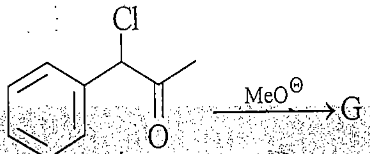


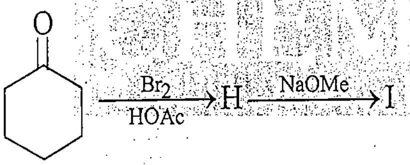


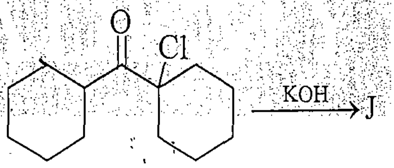


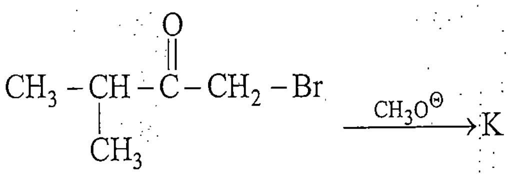


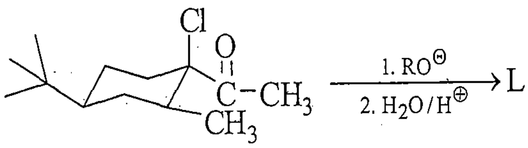


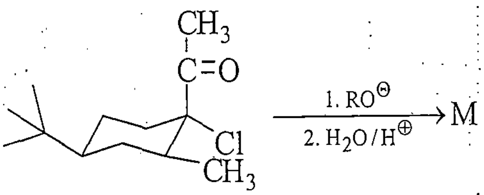


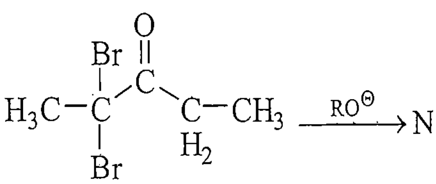


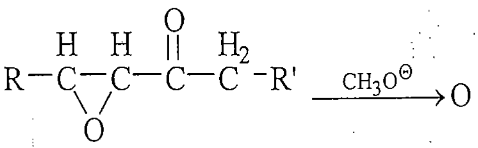


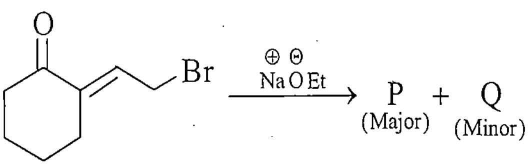


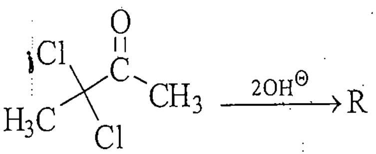


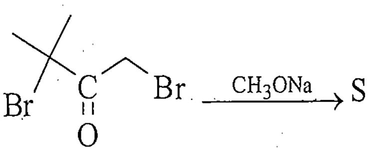


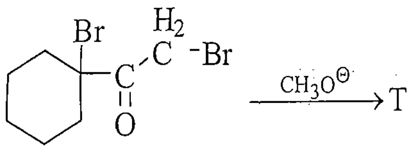


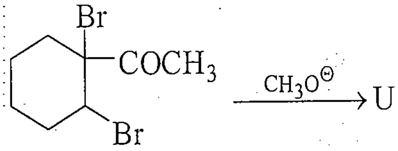


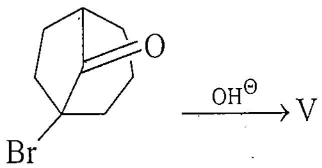


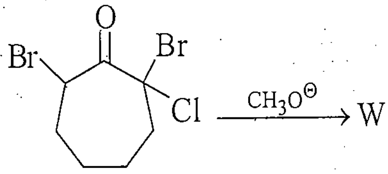












11. Claisen Condensation

$$\text{MeCOOEt} \xrightarrow[\text{(ii) Acidification}]{\text{(i) EtOK}} \text{A}$$

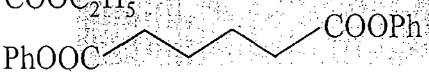
$$\text{EtCOOMe} \xrightarrow[\text{(ii) Acidification}]{\text{(i) MeOK}} \text{B}$$

$$\text{MeCOOMe} + \text{EtCOOMe} \xrightarrow[\text{(ii) Acidification}]{\text{(i) MeOK}} \text{C}$$

$$C_6H_5COOC_2H_5 + CH_3COOC_2H_5 \xrightarrow[\text{(ii) Acidification}]{\text{(i) } C_2H_5ONa} \text{D} + \text{D'}$$

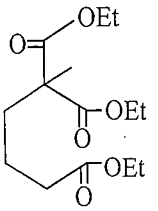
Ethyl benzoate

$$\begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} + C_6H_5CH_2COOC_2H_5 \xrightarrow[\text{(ii) Acidification}]{\text{(i) } C_2H_5ONa} \text{E}$$

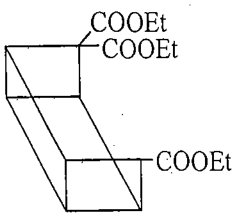


$$\xrightarrow[\text{(ii) Acidification}]{\text{(i) PhONa}} \text{F}$$

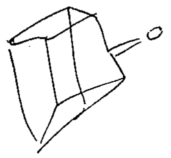
$$C_2H_5-N\begin{cases} CH_2CH_2COOEt \\ CH_2CH_2COOEt \end{cases} \xrightarrow[\text{(ii) Acidification}]{\text{(i) } C_2H_5ONa} \text{G} \xrightarrow[\Delta]{H_3O^{\oplus}} \text{H (Piperidone derivative)}$$



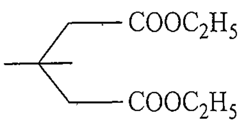
$$\xrightarrow[\text{(ii) Acidification}]{\text{(i) NaOEt in EtOH}} \text{I}$$



$$\xrightarrow{\text{NaOEt}} \text{J} \xrightarrow[\Delta]{H_3O^{\oplus}} \text{K}$$



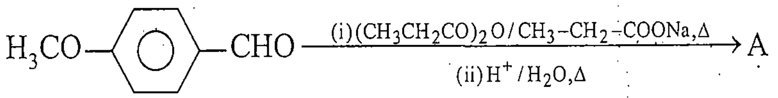
$$\begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} +$$

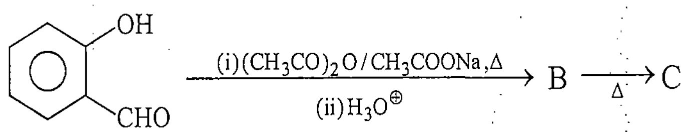


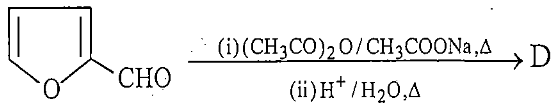
$$\xrightarrow[\text{(ii) Acidification}]{\text{(i) } C_2H_5ONa} \text{L} \xrightarrow[\Delta]{H_3O^{\oplus}} \text{M}$$

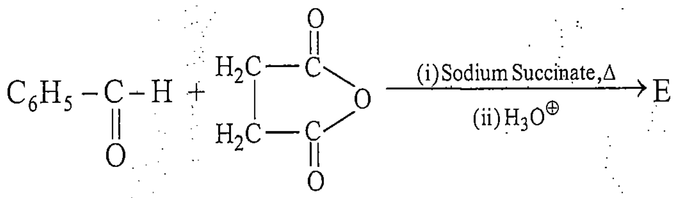
Diethyl-β, β-Dimethyl Glutarate

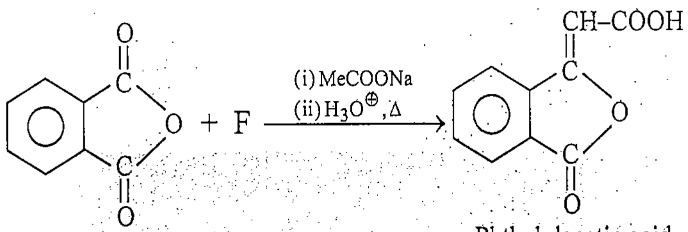
12. Perkin Condensation











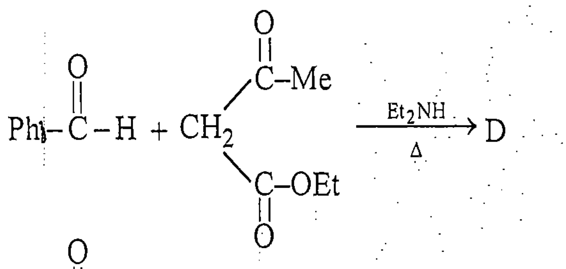
Phthalylacetic acid

13. Knoevenagel Reaction

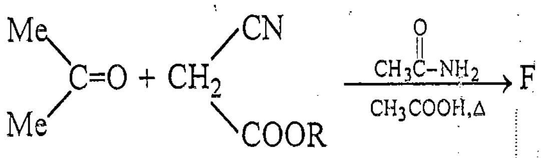
$$CH_3CHO + H_2C(COOR)_2 \xrightarrow[(ii)\,H_3O^{\oplus},\Delta]{(i)\,Pip} A$$

$$C_6H_5CHO + H_2C(COOR)_2 \xrightarrow[(ii)\,H_3O^{\oplus},\Delta]{(i)\,Pip} B$$

$$\underset{\text{Glyoxalic acid}}{HOOC-CHO} + H_2C(COOR)_2 \xrightarrow[(ii)\,H_3O^{\oplus},\Delta]{(i)\,Pip} C$$



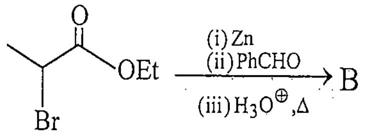
$$Ph-\overset{O}{\overset{\|}{C}}-H + CH_3-NO_2 \xrightarrow[\Delta]{n\,C_5H_{11}NH_2} E$$

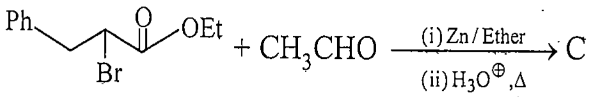


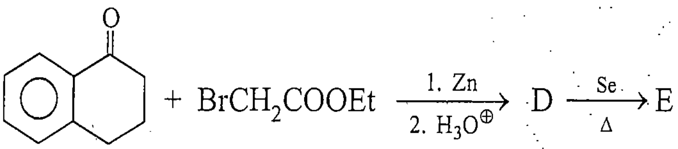
$$CH_2(CN)(NO_2) + Ph-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\Delta]{NaOEt} G$$

14. Reformatsky reaction

$$C_6H_5COCH_3 + BrCH_2COOEt \xrightarrow[2.\ H_3O^{\oplus},\Delta]{1.\ Zn} A$$

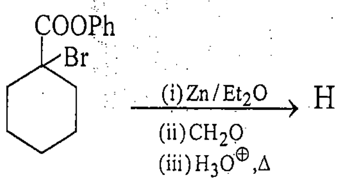


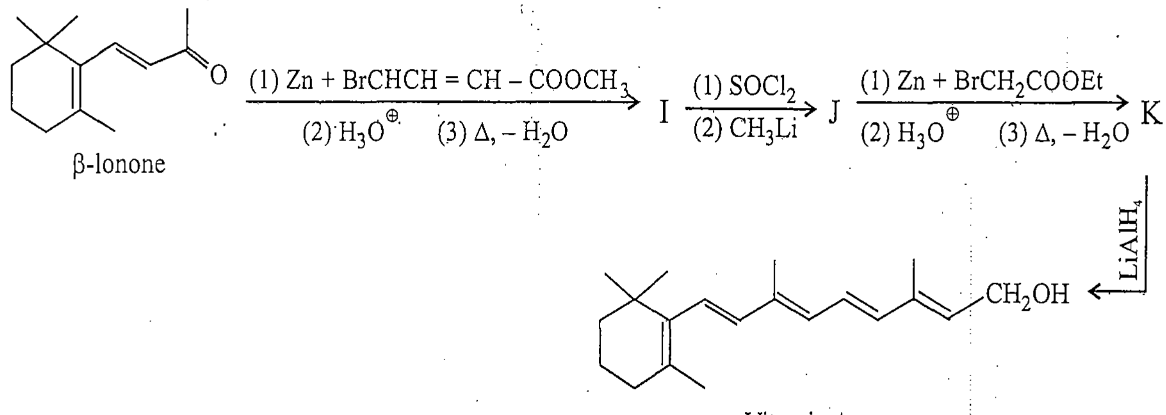




α-Tetralone

$$EtO-\underset{O}{\underset{\|}{C}}-\overset{Br}{\overset{|}{C}H}-CH_2CH_2CH_2-CH_2-CHO \xrightarrow[(ii) H_3O^{\oplus}]{(i) Zn/Et_2O} F \xrightarrow[\Delta]{Se} G$$

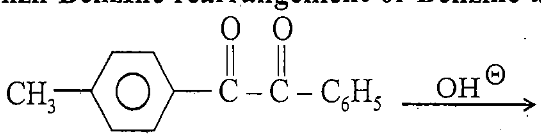


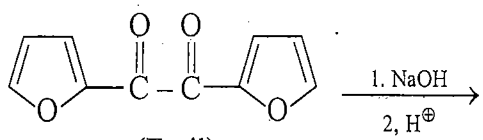


β-Ionone

Vitamin A_1

15. Benzil-BenzIlic rearrangement or Benzilic acid rearrangement

(i) 

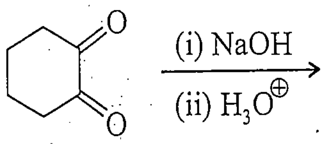
(ii) 

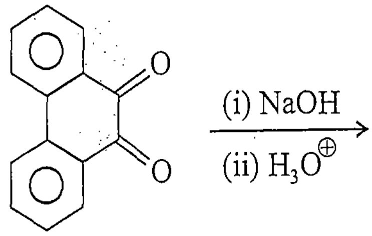
(Furil)

(iii) $Ph-CH_2-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-C_6H_5 \xrightarrow[\text{(ii) HOH / }H^{\oplus}]{\text{(i) }OH^{\ominus}}$

(iv) $C_6H_5-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{CH}-C_6H_5 \xrightarrow[\text{reagent}]{\text{Fenton}} A \xrightarrow[\text{(ii) HOH / }H^{\oplus}]{\text{(i) }OH^{\ominus}} B.$

Fenton Reagent
is a mixture
of Fe^{+2} & H_2O_2
(oxidising
agent

(v) 

(vi) 

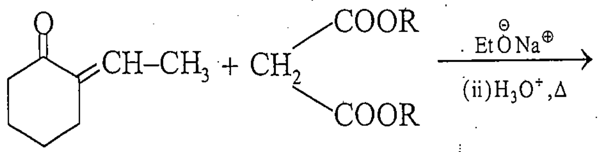
16. **Michael Addition**

(i) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 + CH_2=CH-\overset{\overset{O}{\|}}{C}H \xrightarrow[-H_2O]{OH^{\ominus}} ?$

(ii) $CH_3CH=CH-\overset{\overset{O}{\|}}{C}-CH_3 + CH_2(COOEt)_2 \xrightarrow{CH_3CH_2O^{\ominus}} ?$

(iii) $CH_3CH=CH-\overset{\overset{O}{\|}}{C}-NR_2 + CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_3 \xrightarrow{CH_3O^{\ominus}} ?$

(iv) $CH_3CH_2CH=CH-\overset{\overset{O}{\|}}{C}-OCH_3 + CH_3-\overset{\overset{O}{\|}}{C}-CH_2-C\equiv N \xrightarrow{CH_3O^{\ominus}} ?$

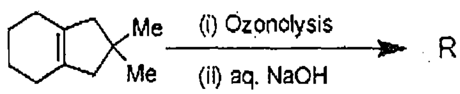
(iv) 

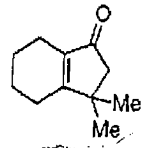
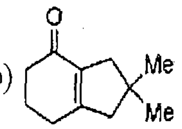
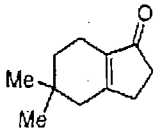
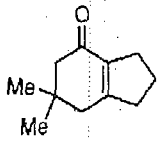
EXERCISE - IV

Previous Years Questions

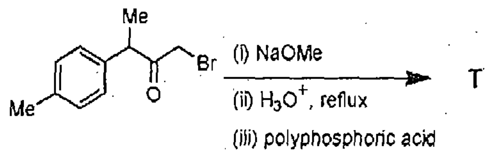
IIT-JAM Previous Year Questions

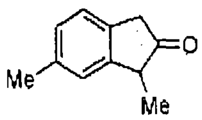
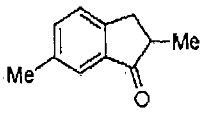
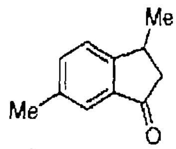
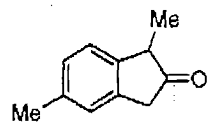
1. The product R in the following reaction is



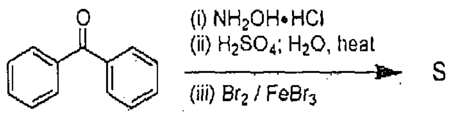
(a)  (b)  (c)  (d) 

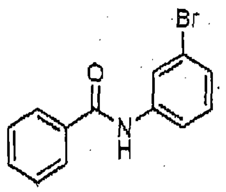
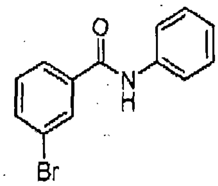
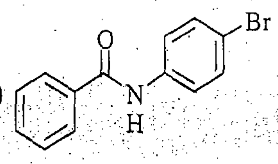
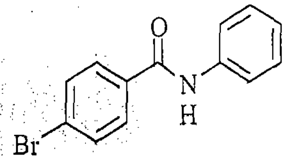
2. In the following reaction, the major product T is



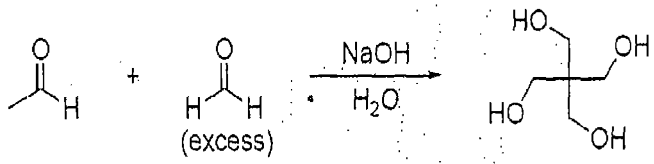
(a)  (b)  (c)  (d) 

3. The major product S of the following reaction is



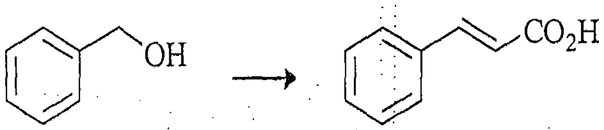
(a)  (b)  (c)  (d) 

4. The mechanism of the following transformation involves



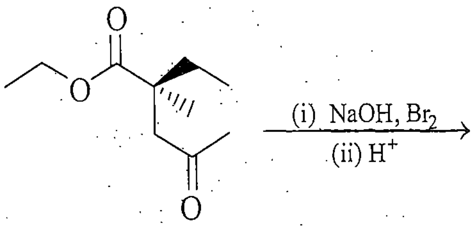
(a) Aldol reaction and Cannizzaro reaction
(b) Aldol reaction and Claisen-Schmidt reaction
(c) Knoevenagel condensation and Cannizzaro reaction
(d) Stobbe condensation and Cannizzaro reaction

5. The appropriate reagents required for carrying out the following transformation are



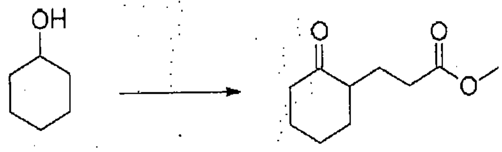
(a) (i) PCC, CH_2Cl_2; (ii) $Ph_3P{=}CHCO_2Et$; (iii) aq. NaOH, heat, then acidify
(b) (i) CrO_3, H_2SO_4, aq. acetone (ii) Ac_2O, NaOAc
(c) (i) MnO_2; (ii) $CH_2(CO_2H)_2$, piperidine, pyridine
(d) (i) PCC, CH_2Cl_2; (ii) $BrCH_2CO_2C(CH_3)_3$, Zn (iii) H_3O^+, heat

6. The set of products formed in the following reaction is



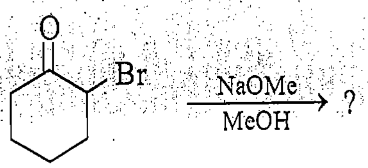
(a) $CHBr_3$ and a racemic acid
(b) $CHBr_3$ and a chiral acid
(c) $CHBr_3$ and a racemic ester
(d) CH_2Br_2 and a chiral ester

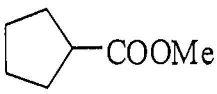
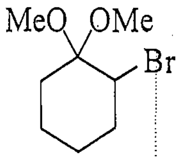
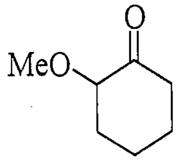
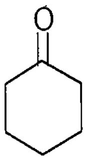
7. The correct set of reagents required for the following transformation is



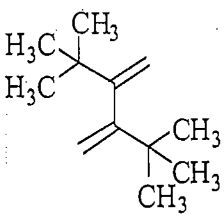
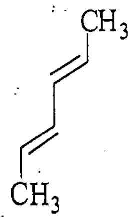
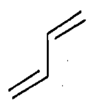
(a) (i) CrO_3; (ii) acrylonitrile; (iii) H_3O^+
(b) (i) O_2; (ii) methyl acrylate
(c) (i) CrO_3; (ii) NaOMe/MeOH, methyl acrylate; (iii) H_3O^+
(d) (i) H_2O; (ii) methyl acrylate

8. The major product formed in the following reaction is



(a)  (b)  (c)  (d) 

9. The reactivity of compound I-IV with maleic anhydride (V) follows the order :


I

II

III

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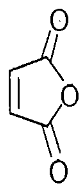
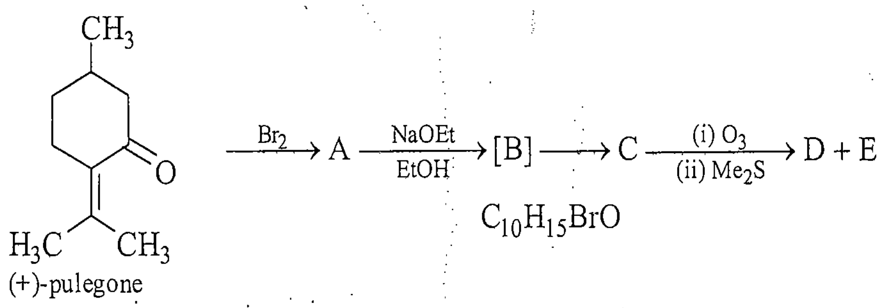
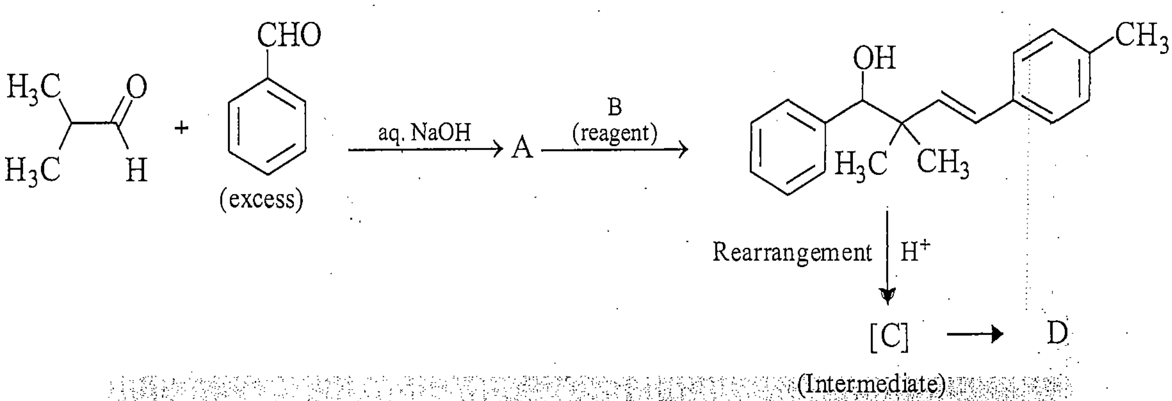

V

(a) I < II < III < IV (b) II < IV < III < I (c) II < I < III < IV (d) II < I < IV < III

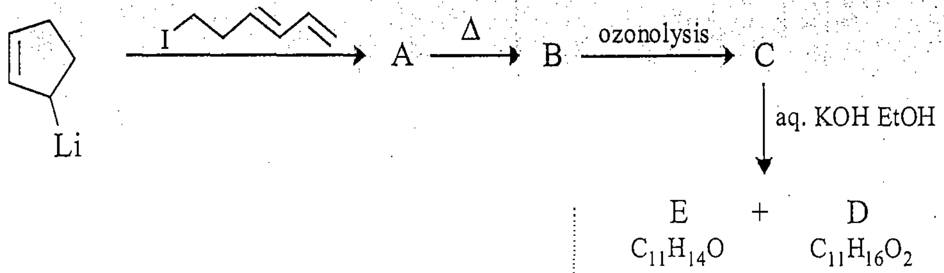
10. Draw the structures A-E for the given transformation



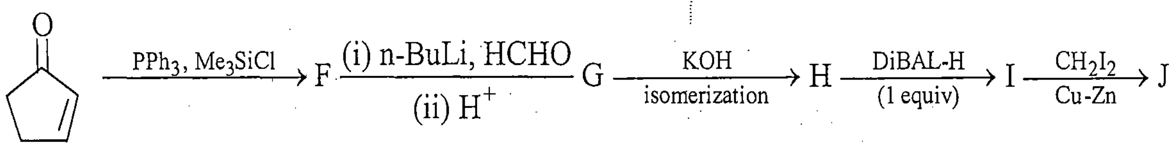
11. In the reaction seuence given below, draw the structures of A, C, D and reagent B



12. Write the structures of A to E in the following reaction sequence :

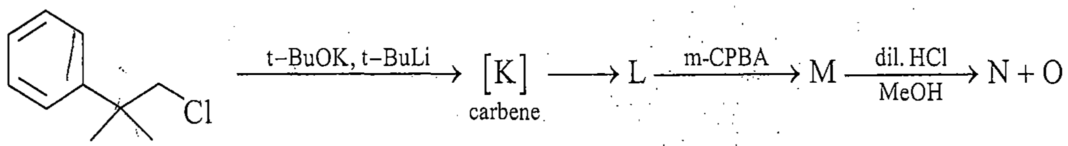


13. Write the structures of F to J in the following reaction scheme :

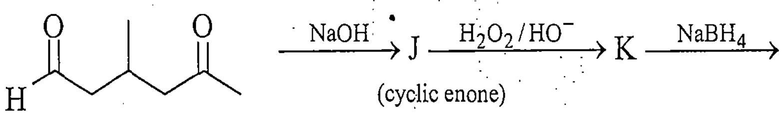


[DiBAL-H diisobutylaluminium hydride]

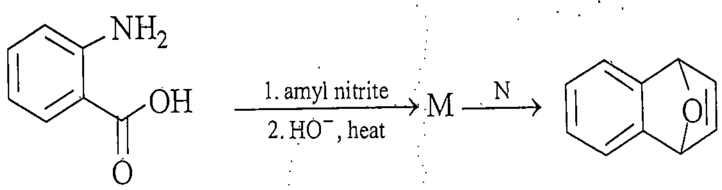
14. Complete the following reaction sequence and write structures of K to O.



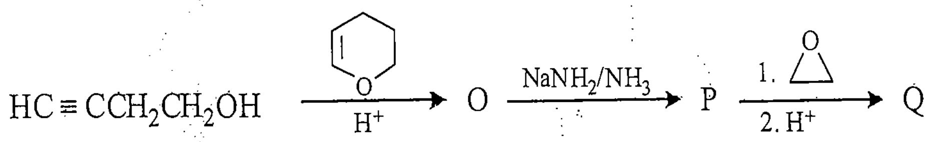
15. (A) Complete the following reaction sequence with appropriate structures of J, K and L.



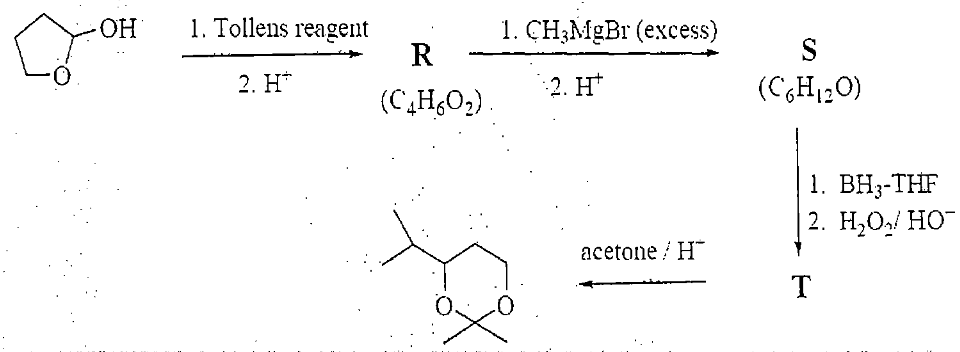
(B) Identify the structure of Ma nd N in the following synthetic transformation



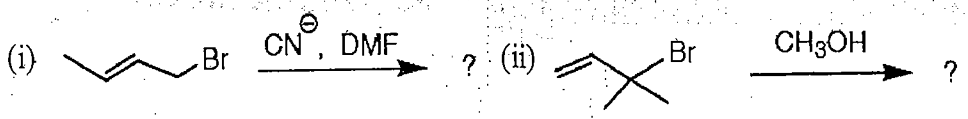
16. In the following reaction scheme, write the structures of O, P and Q.



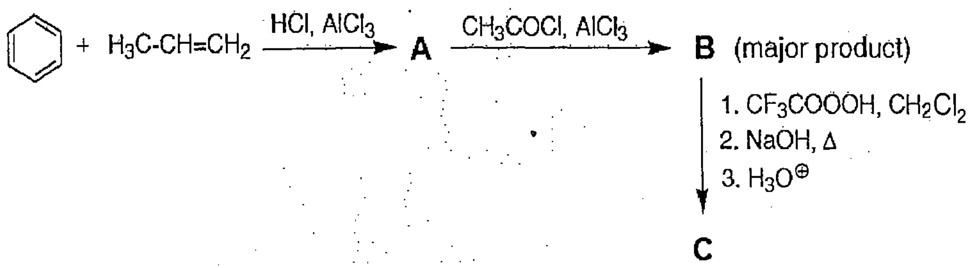
17. Write the appropriate structures for R, S and T in the following scheme.



18. Write the possible substitution products in the following reactions.
Indicate the type/s of mechanism/s ($S_N1/S_N2/S_N2'$) that is/are operative in each reaction.



19. Write the structures of A to C in the following reaction sequence.



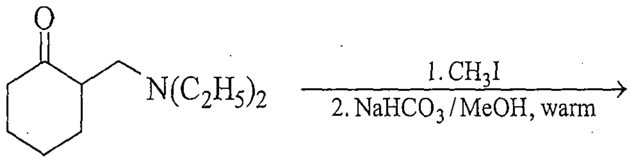
GATE Previous Year Questions

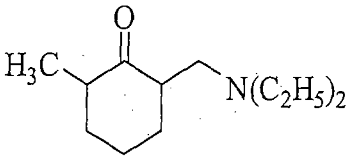
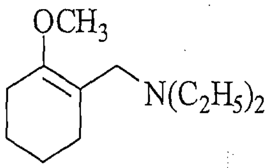
20. The major product obtained in the following reaction, is

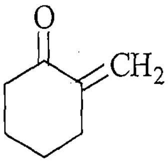
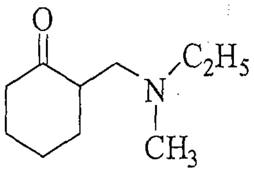
$$H-C\equiv CH_2OH \xrightarrow[\substack{2.\ C_2H_5Br\ (1\ equiv.) \\ 3.\ H_3O^{\oplus}}]{1.\ LiNH_2\ (2\ equiv.)/liq.\ NH_3}$$

(a) $CH_3CH_2-C\equiv C-CH_2OH$
(b) $H-C\equiv C-CH_2OCH_2CH_3$
(c) $CH_3CH_2-C\equiv C-CH_2NH$
(d) $H-C\equiv C-CH_2NH-CH_2CH_3$

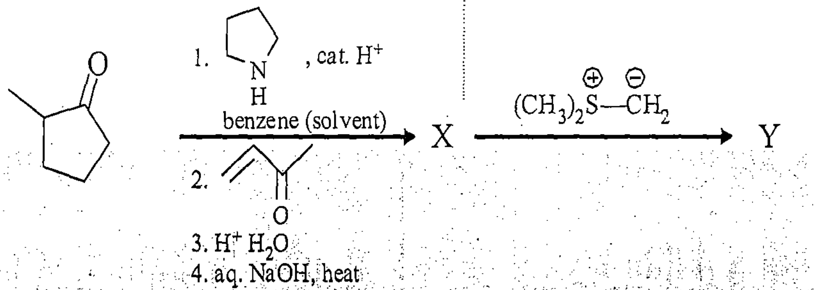
21. The major product formed in the following reaction, is

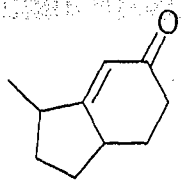
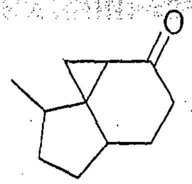
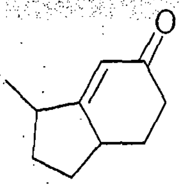
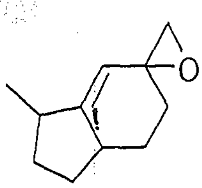


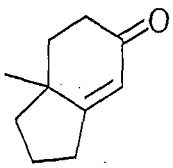
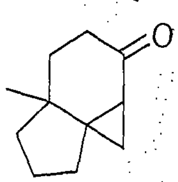
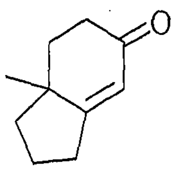
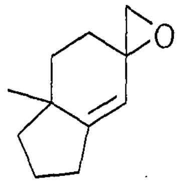
(a)  (b) 

(c)  (d) 

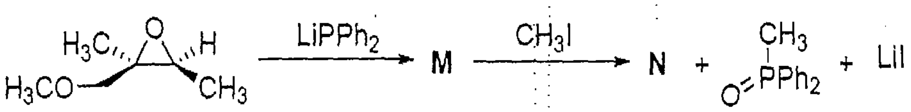
22. The major products **X** and **Y** formed in the following synthetic scheme, are

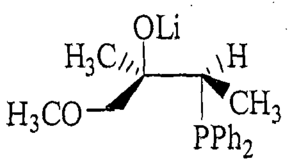
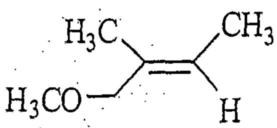


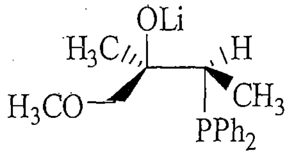
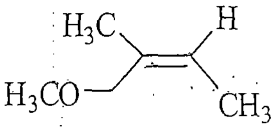
(a) X =  Y =  (b) X =  Y = 

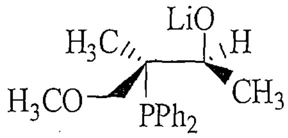
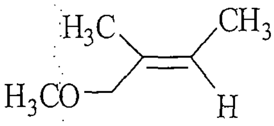
(c) X =  Y =  (d) X =  Y = 

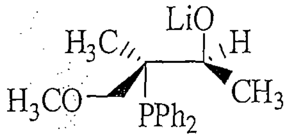
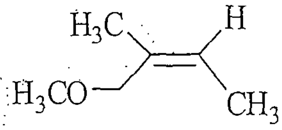
23. The major products **M** and **N** in the following reaction sequence are



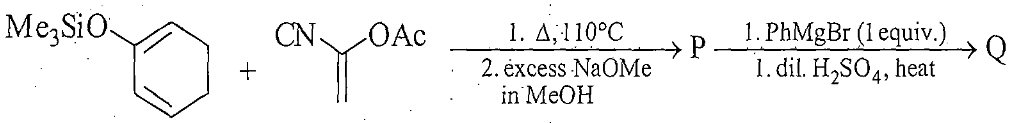
(a) M =  N = 

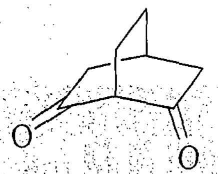
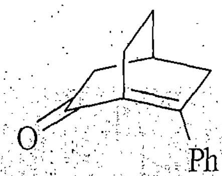
(b) M =  N = 

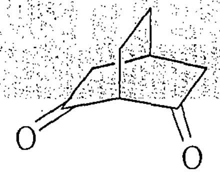
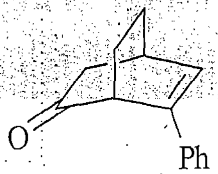
(c) M =  N = 

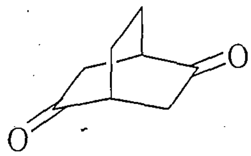
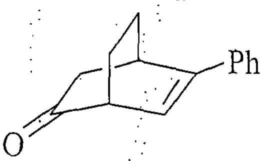
(d) M =  N = 

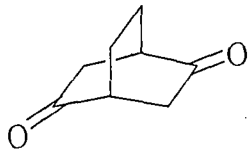
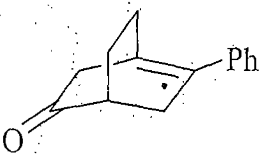
24. The major products **P** and **Q** in the following reaction sequence, are



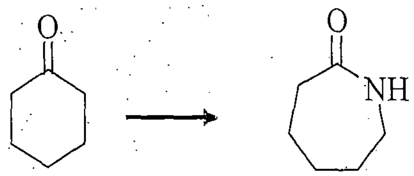
(a) P =  Q = 

(b) P =  Q = 

(c) P =  Q = 

(d) P =  Q = 

25. The following synthetic transformation can be achieved using



Reagents :

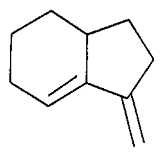
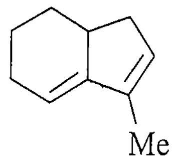
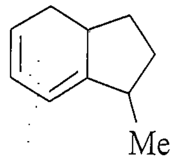
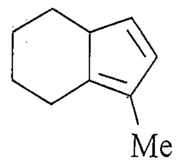
(p) (i) NH_3OH/H^+, (ii) H_2SO_4

(q) HN_3/H^+

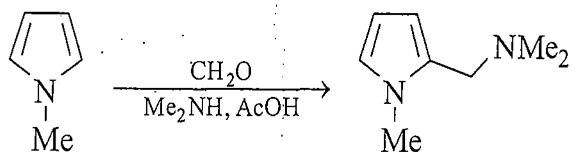
(r) (i) NH_2OH/H^+, (ii) NaOH

(a) (p) only (b) (p) and (q) (c) (q) and (r) (d) (r) only

26. Amongst the following, the compound that DOES NOT act as a diene in Diels-Alder reaction is

(a)  (b)  (c)  (d) 

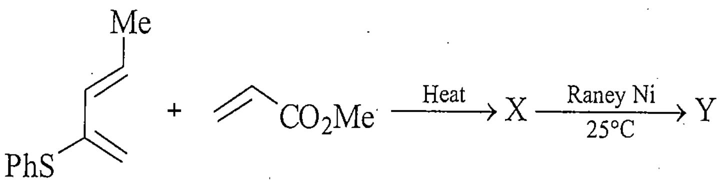
27. The folowing conversion is an example of

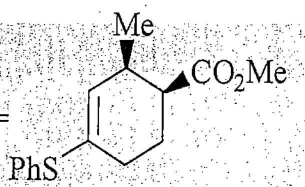
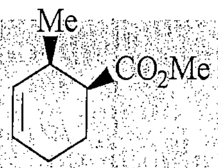


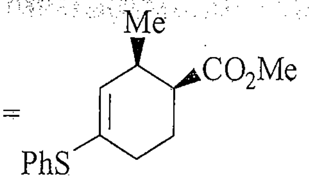
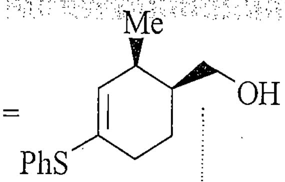
(a) Arndt-Eistert homologation (b) Mannich reaction

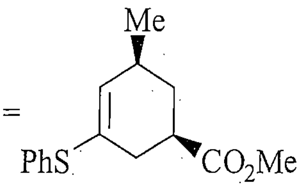
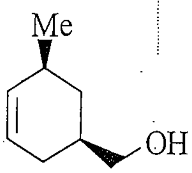
(c) Michael addition (d) Chicibabin animation reaction

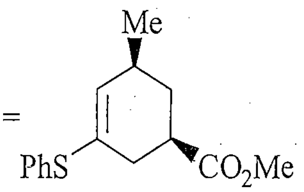
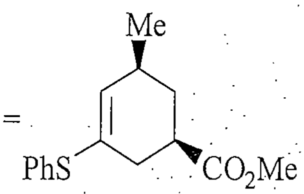
28. The major product X and Y formed in the following reaction sequence are



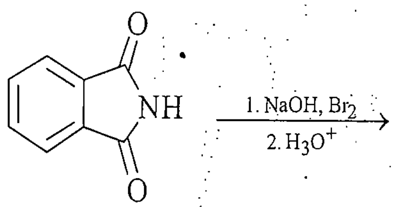
(a) X =  Y = 

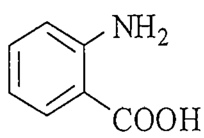
(b) X =  Y = 

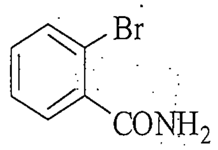
(c) X =  Y = 

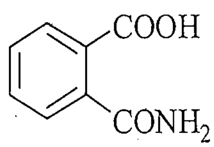
(d) X =  Y = 

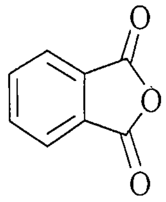
29. The major product formed in the reaction given below is



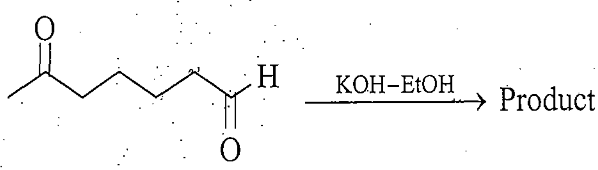
(a) 

(b) 

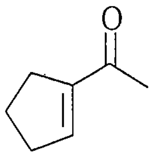
(c) 

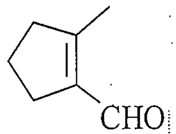
(d) 

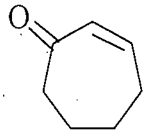
30. In the following

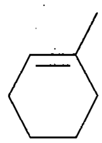


the product formed is

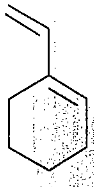
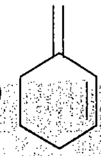
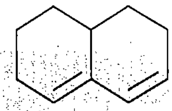
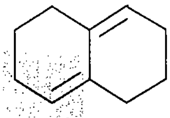
(a) 

(b) 

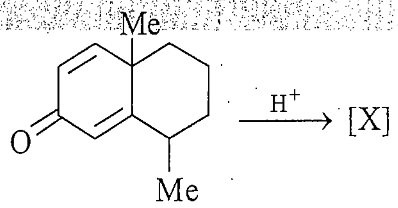
(c) 

(d) 

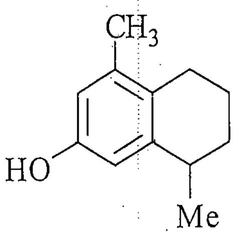
31. The diene which undergoes Diels-Alder reaction with maleic anhydride is

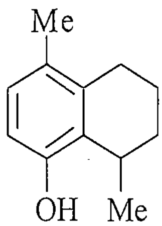
(a) 
(b) 
(c) 
(d) 

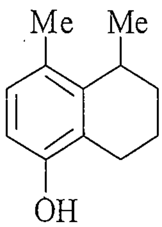
32. In the following reaction

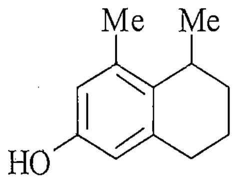


the major product [X] is

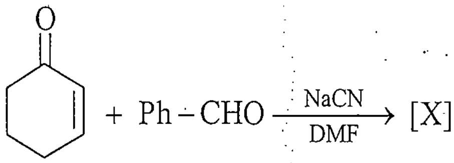
(a) 

(b) 

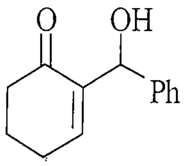
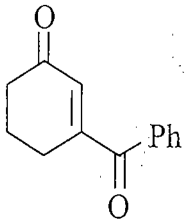
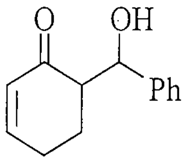
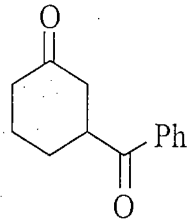
(c) 

(d) 

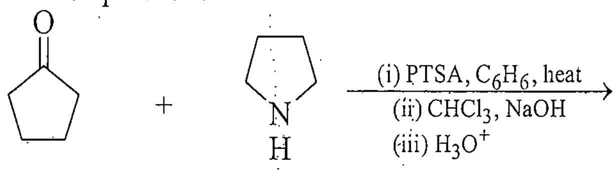
33. In the following reaction



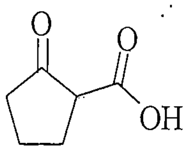
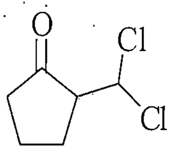
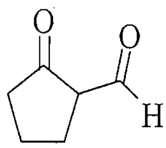
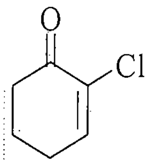
the major product [X] is

(a)  (b)  (c)  (d) 

34. In the following reaction sequence



the major product [X] is

(a)  (b)  (c)  (d) 

ANSWER KEY

EXERCISE - I

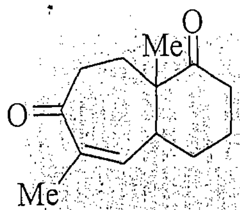
1. b	2. c	3. d	4. a	5. b	6. b	7. c
8. a	9. b	10. d	11. c	12. b	13. a	14. b
15. c	16. a	17. b	18. a	19. c	20. a	21. c
22. b	23. c	24. a	25. d	26. a	27. a	28. a
29. a	30. a	31. a	32. d	33. c	34. b	35. b
36. a	37. a	38. a	39. a	40. c	41. a	42. a
43. c	44. c	45. c	46. c	47. d	48. b	49. b
50. b	51. b	52. a	53. a	54. a	55. a	56. b
57. d	58. c	59. a	60. b			

EXERCISE - II

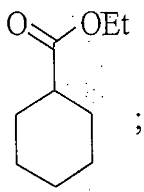
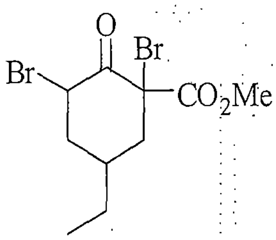
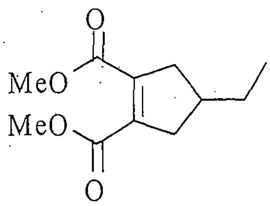
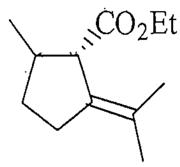
1. a,b,c,d	2. a,b	3. a,b	4. a,b

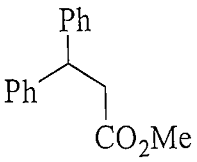
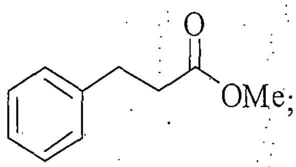
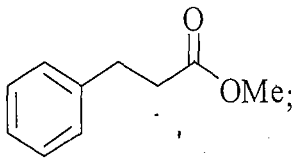
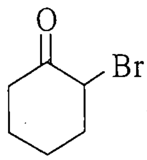
EXERCISE - III

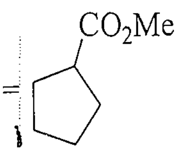
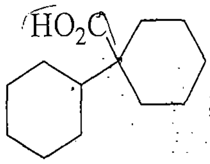
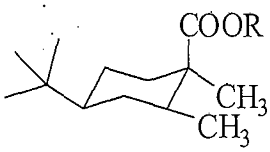
1. 1	2. 4	3. 3	4. 2	5. 3	6. 9

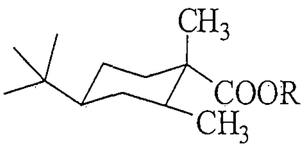
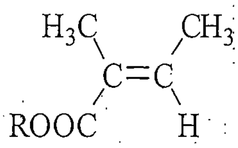
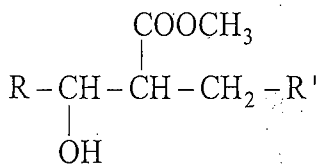
7. F =  8. 5 9. 14

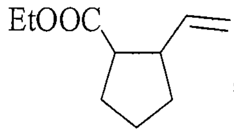
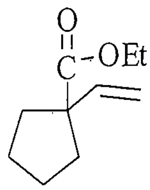
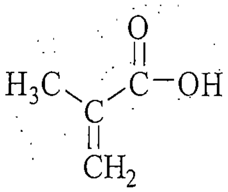
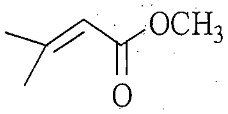
10. **FAVORSKII REACTION**

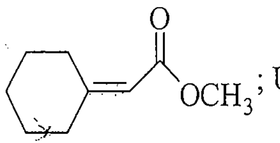
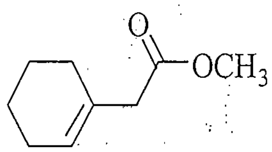
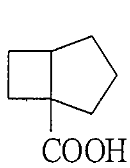
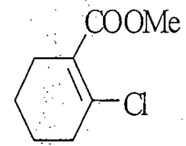
A =  ; B =  ; C =  ; D = 

E =  ; F =  ; G =  ; H =  ;

I =  ; J =  ; K = $CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-COOCH_3$; L = 

M =  ; N =  ; O = 

P =  ; Q =  ; R =  ; S = 

T =  ; U =  ; V =  ; W = 

11. CLAISEN CONDENSATION

A. $Me-\overset{\overset{O}{||}}{C}-CH_2-\overset{\overset{O}{||}}{C}-OEt$

B. $Et-\overset{\overset{O}{||}}{C}-\overset{*}{CH}(CH_3)-\overset{\overset{O}{||}}{C}-OMe$

(R / S)

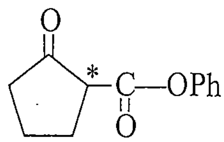
C. 6 products

D. $C_6H_5COCH_2COOC_2H_5$, $CH_3COCH_2COOC_2H_5$

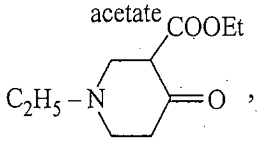
Ethyl benzolyacetate

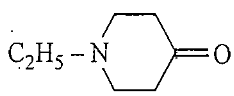
E. $C_6H_5-CH(COOC_2H_5)(COCOOC_2H_5)$

Diethyl-α-oxalyphenyl acetate

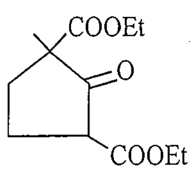
F. 

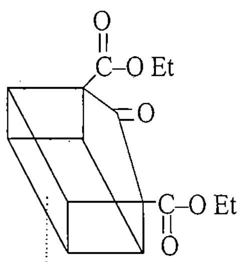
(R/S)

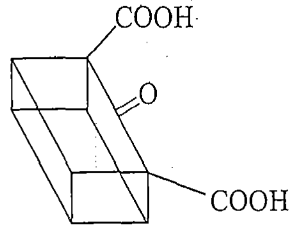
G.  ,

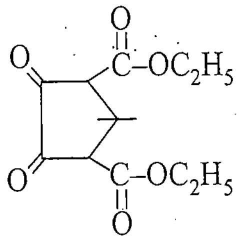
H. 

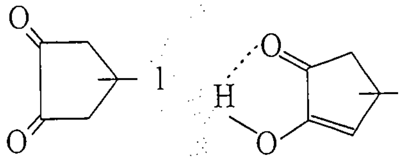
1-Ethyl-4-piperiodone

I. 

J. (J) 

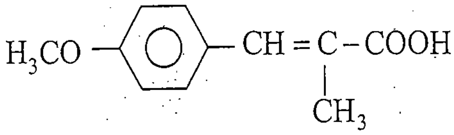
K. 

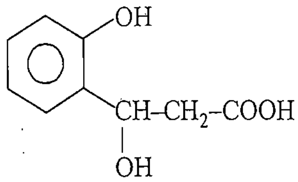
L. 

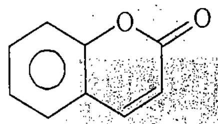
M. 

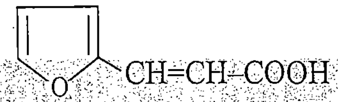
enol is more stable

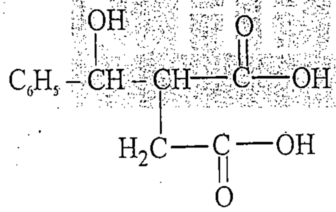
12. PERKIN CONDENSATION

A. 

B. 

C. 

D. 

E. 

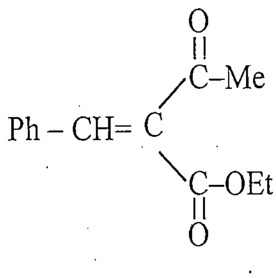
F. $Me-\overset{O}{\overset{||}{C}}-O-\overset{O}{\overset{||}{C}}-Me$

13. KNOEVENAGEL REACTION

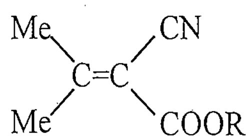
A. $CH_3-CH=CH-COOH$
Crotonic acid

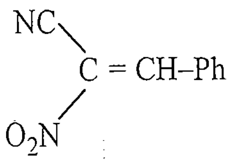
B. $C_6H_5-CH=CH-COOH$
Cinnamic acid

C. $HOOC-CH=CH-COOH$
Maleic acid

D. 

E. $Ph-CH=CH-NO_2$

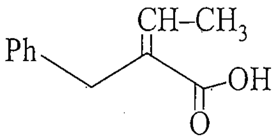
F. 

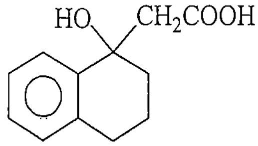
G. 

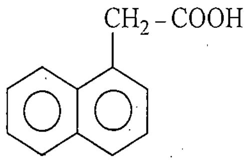
14. REFORMATSKY REACTION

A. $C_6H_5-C(CH_3)=CH-COOH$ (E/Z)

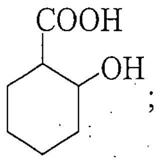
B. $Ph-CH=C(CH_3)-COOH$ (E / Z)

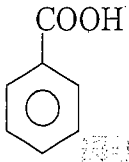
C. 

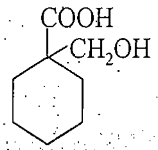
D. 

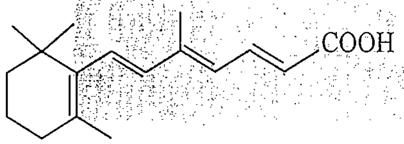
E. 

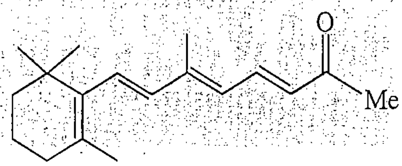
α-Naphthylacetic acid

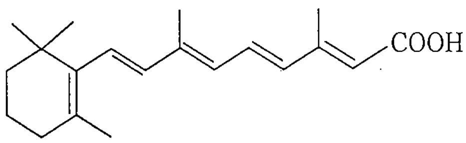
F.  ;

G. 

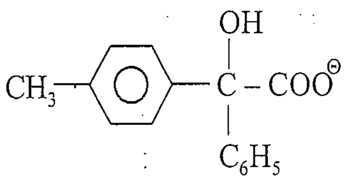
H. 

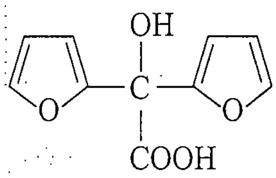
I. 

J. 

K. 

15. Benzil-BenzIlic rearrangement or Benzilic acid rearrangement

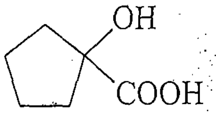
(i). 

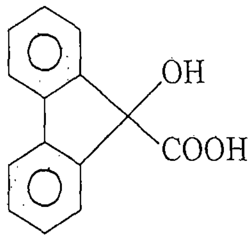
(ii). 

(Furilic acid)

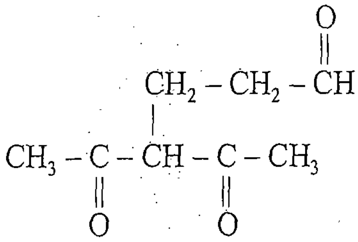
(iii). $Ph-CH_2-C(OH)(C_6H_5)-COOH$

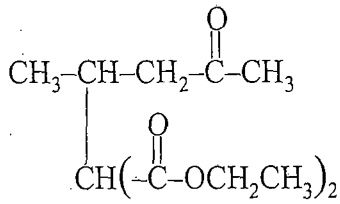
(iv). (A) $Ph-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-Ph$ (B) $Ph-C(OH)(Ph)-COOH$

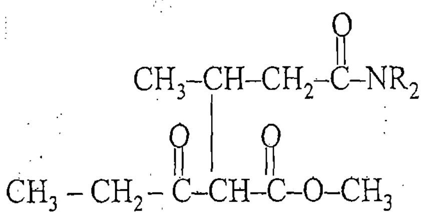
(v). 

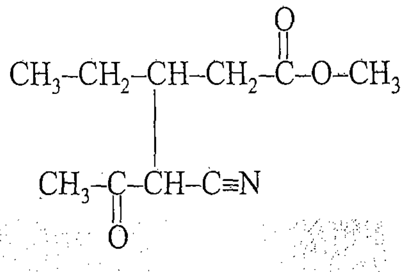
(vi). 

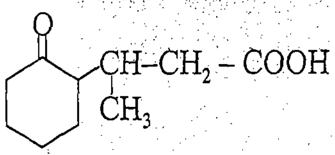
16. Michael Addition

(i). 

(v). 

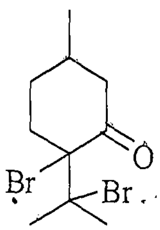
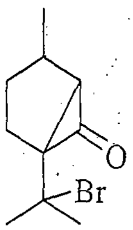
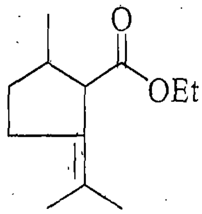
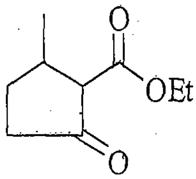
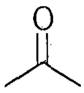
(iii). 

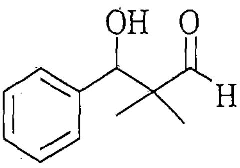
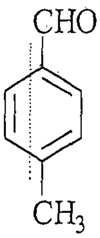
(iv). 

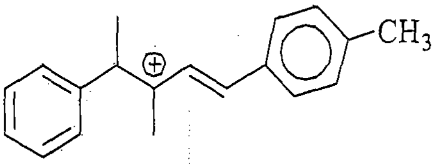
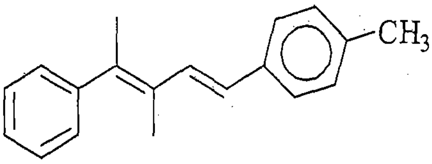
(v). 

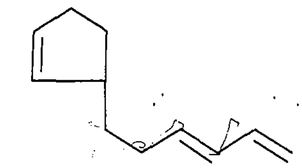
EXERCISE - IV

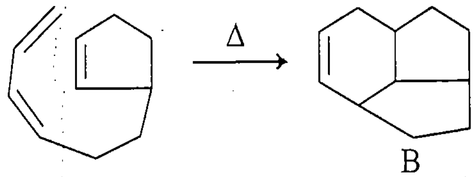
1. d 2. c 3. c 4. a 5. a,c,d 6. b 7. c
8. a 9. b

10. A =  B =  C =  D =  E = 

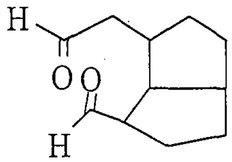
11. A =  B =  $TiCl_4/LiAlH_4$

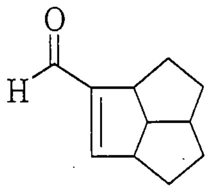
C =  D = 

12. A = 

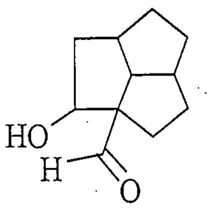


B

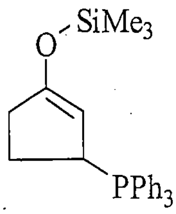
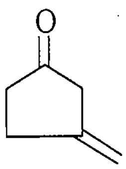
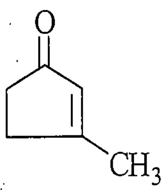
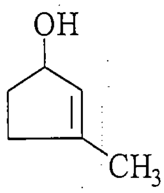
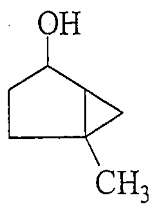
C 

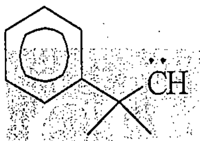


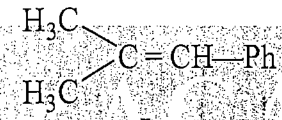
$C_{11}H_{14}O$
F



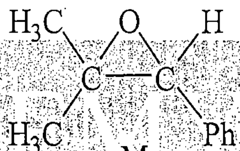
D

13. F =  G =  H =  I =  J = 

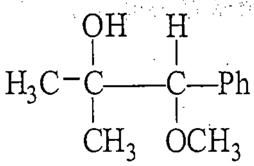
14. K = 



L

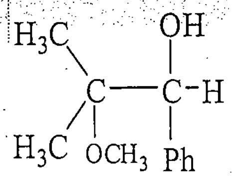


M

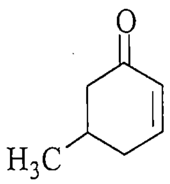
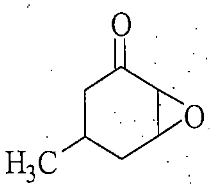
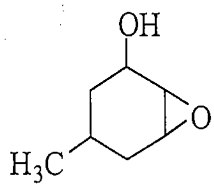


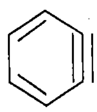
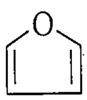
N

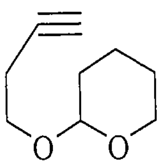
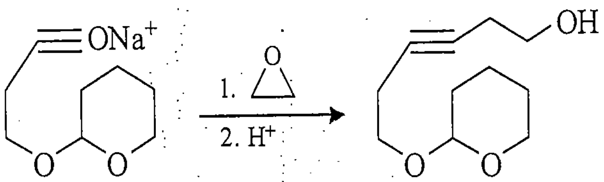
+



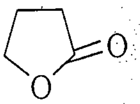
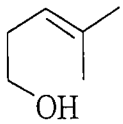
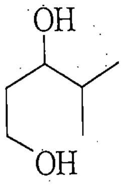
O

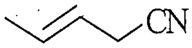
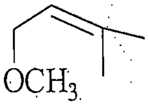
15. (a) J =  K =  L = 

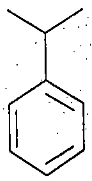
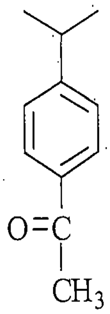
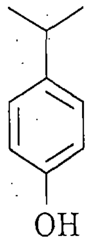
(b) M =  N = 

16. O =  P = 

Q

17. R =  S =  T = 

18. (i) S_N2  (ii) S_N1 

19. A =  B =  C = 

20. a	21. c	22. b	23. a	24. c	25. b	26. b
27. b	28. a	29. a	30. a	31. a	32. a	33. d
34. c						

CHAPTER 6

REAGENTS

Lithium Aluminium Hydride

Lithium aluminium hydride (LAH) is most powerful reducing agent.

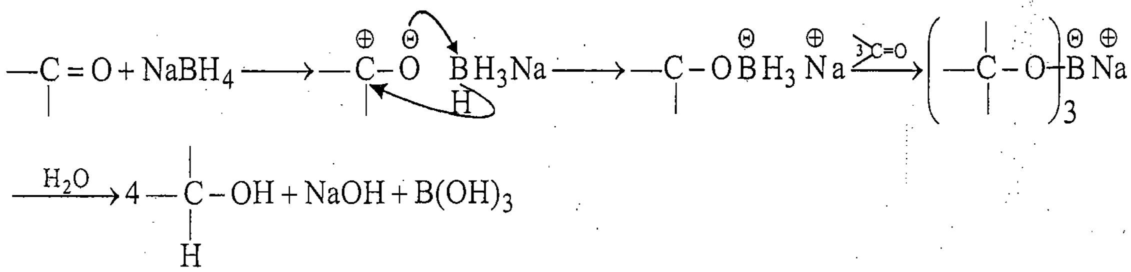
$$4\,R-\underset{\substack{|\\R'}}{C}=O + LiAlH_4 \xrightarrow{\text{Ether}} \left(R-\overset{\substack{H\\|}}{\underset{\substack{|\\R'}}{C}}-O\right)_4^{\ominus}\overset{\ominus\ \oplus}{Al\,Li} \xrightarrow[H_2O]{H_2SO_4} 4\,R-\overset{\substack{H\\|}}{\underset{\substack{|\\R'}}{C}}-OH + Al_2(SO_4)_3 + Li_2SO_4$$

(where R' = alkyl, OH, Cl, etc.)

Sodium Borohydride ($NaBH_4$)

Mechanism

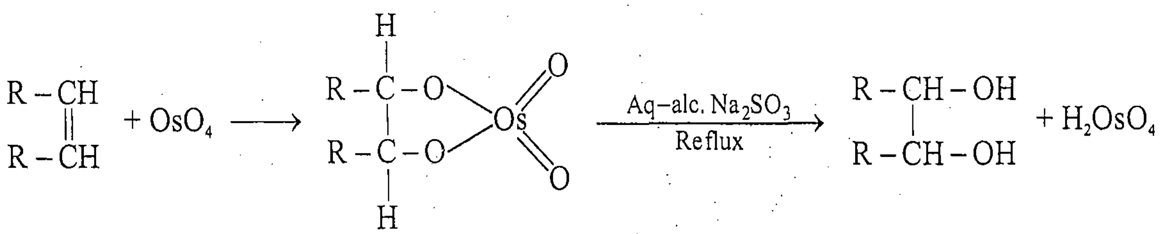
The mechanism of reduction is similar to that of $LiAlH_4$. The reaction proceeds by complexing the oxygen atom of the carbonyl group with boron and simultaneous transfer of the hydride ion to the carbonyl carbon. All the four hydrogens of the reagent are transferred to the four molecules of the substrate. Subsequent hydrolysis gives alcohols.



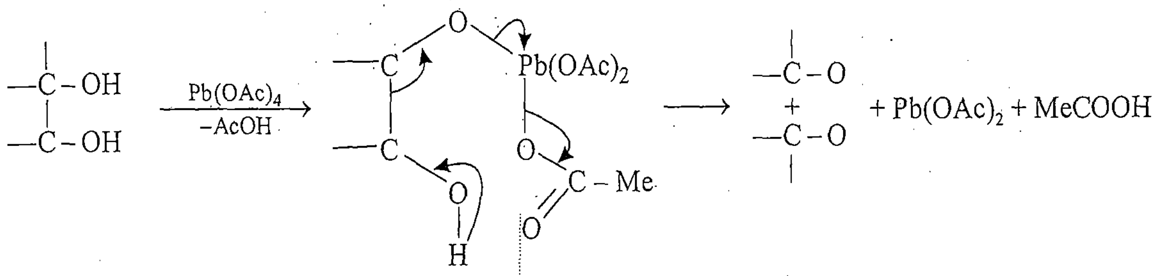
$$NaOH + B(OH)_3 \longrightarrow NaH_2BO_2 + H_2O$$

Osmium Tetroxide, OsO_4

Osmium tetroxide, like permaganate, undergoes initial cis-cycloaddition with the olefine from the less hindered side to yield cis-1, 2-diol as the final product.



Lead Tetraacetate, $(CH_3COO)_4Pb$ or $Pb(OAc)_4$



(a) **Oxidation of alcohols**

Lead tetraacetate with pyridine oxidizes alcohols to aldehydes or ketones at room temperature in good yield. The reagent in pyridine is mild enough not to oxidize aldehyde further.

$$CH_3-(CH_2)_3-CH_2OH \xrightarrow[\text{Pyridine}]{Pb(OAc)_4} CH_3-(CH_2)_3-CHO$$

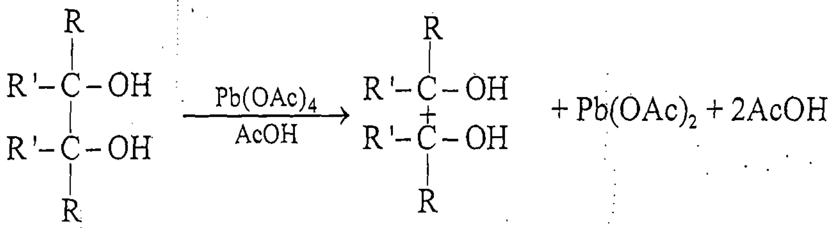
$$C_6H_5-CH=CH-CH_2OH \xrightarrow[\text{Pyridine}]{Pb(OAc)_4} C_6H_5-CH=CH-CHO$$

$$CH_3-CHOH-CH_2-CHOH-CH_3 \xrightarrow[\text{pyridine}]{Pb(OAc)_4} CH_3-CO-CH_2-CO-CH_3$$

Alcohols having hydrogen at δ-carbon may be cyclized. Tetrahydrofuran is formed in high yield from n-butanol.

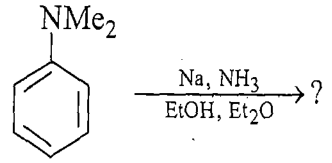
(b) **Oxidation of 1, 2-glycols**

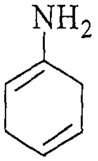
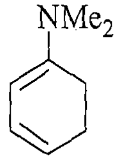
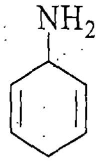
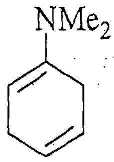
Vic-diols are oxidized by lead tetraacetate at room temperature with cleavage of bond to aldehydes, ketones or both depending upon the structure of the glycols.



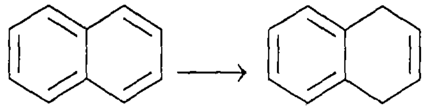
EXERCISE - 1

Single Answer Correct Type

1. 

(a)  (b)  (c)  (d) 

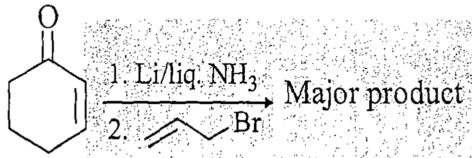
2. The reaction,

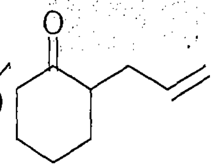
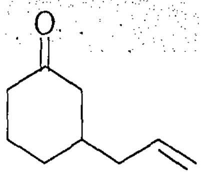
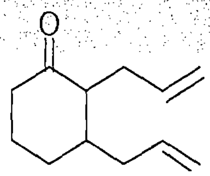


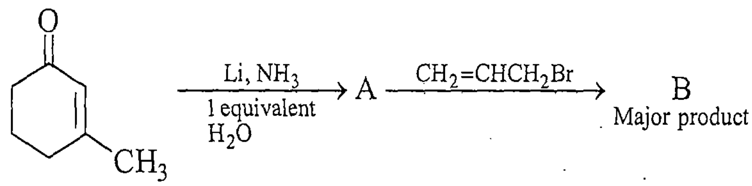
is brought about by

(a) Na/EtOH (b) Na, liquid NH_3, ethanol

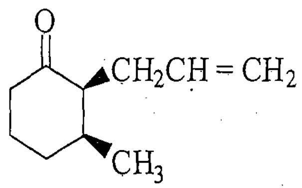
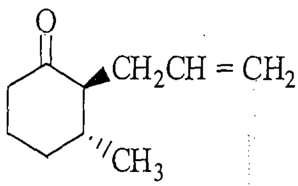
(c) H_2/Ni (d) electrolytic reduction

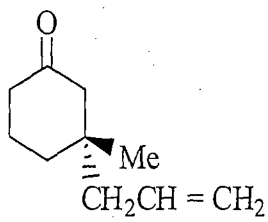
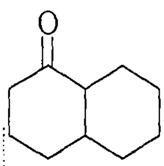
3. 

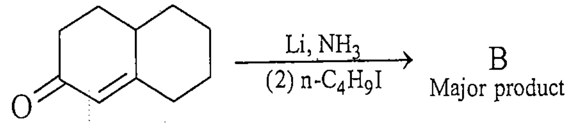
(a)  (b)  (c)  (d) None of these

4. 

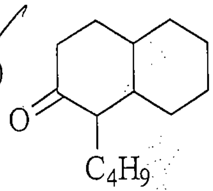
B is

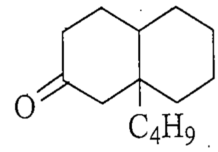
(a)  (b) 

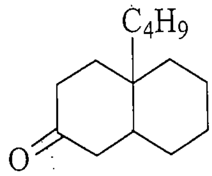
(c)  (d) 

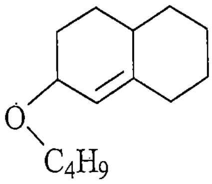
5. 

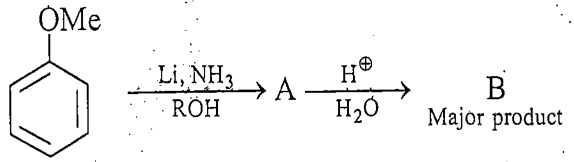
B is

(a) 

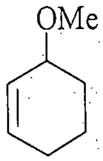
(b) 

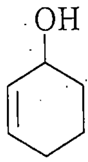
(c) 

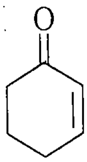
(d) 

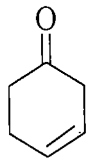
6. 

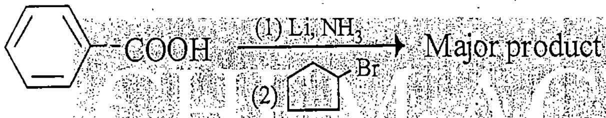
B is

(a) 

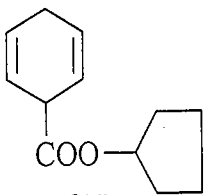
(b) 

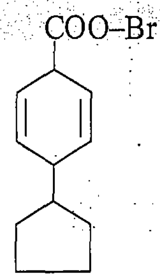
(c) 

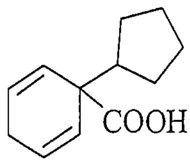
(d) 

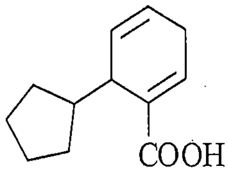
7. 

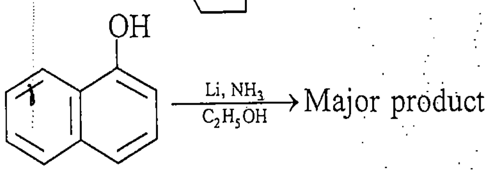
Major product is

(a) 

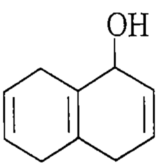
(b) 

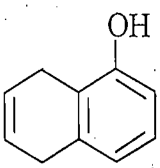
(c) 

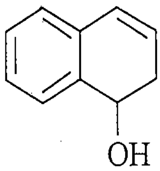
(d) 

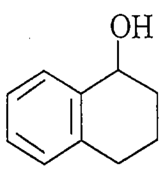
8. 

Major product is

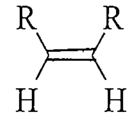
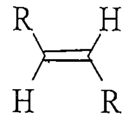
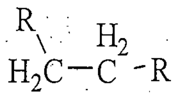
(a) 

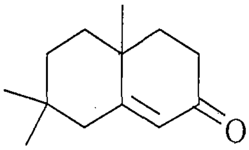
(b) 

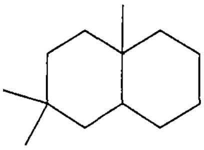
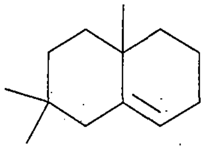
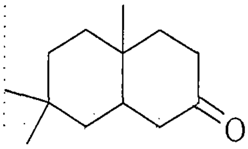
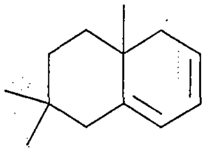
(c) 

(d) 

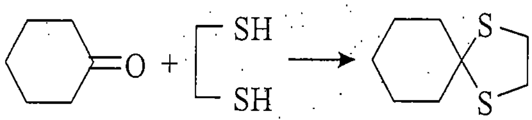
9. $R-C\equiv C-R \xrightarrow[C_2H_5OH]{Li,\ NH_3} ?$

(a)  (b)  (c)  (d) $R-CH_2-\underset{\displaystyle R}{\underset{|}{CH}}-NH_2$

10.  $\xrightarrow[HSCH_2CH_2SH]{BF_3} A \xrightarrow{Ni} B$; B is

(a)  (b)  (c)  (d) 

11. A suitable catalyst for bringing out the transformation given below is



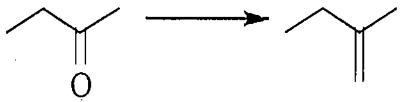
(a) $BF_3 . Et_2O$ (b) NaOEt (c) tungsten lamp (d) dibenzoyl peroxide

12. Reduction of 3-hexyne to trans-3-hexene can be effected by

(a) H_2/Lindlar's catalyst (b) Na/liq. NH_3

(c) Fe/NaCl (d) DIBAL

13. The reagent suitable for effecting the following transformation is



(a) CH_2N_2 (b) CH_3Li (c) $(CH_3)_2CuLi$ (d) $Ph_3P = CH_2$

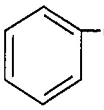
14. Cyclohexyl benzyl ether is converted to cyclohexanol using

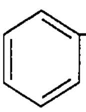
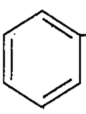
(a) 5% aq. KOH (b) hydrazine hydrate

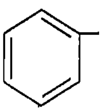
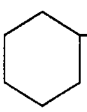
(c) H_2-Pd/C (d) tetrabutylammonium fluoride

15. The mildest reducing agent which reduces only carbonyl group in presence of nitro, carboxyl, double bond and ester groups is

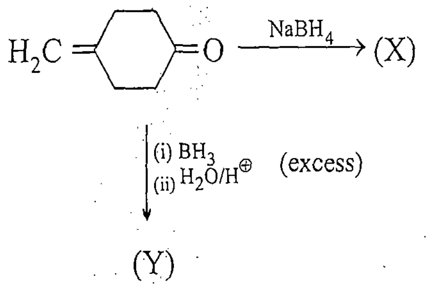
(a) $LiAlH_4$ (b) Na-NH_3 (c) $NaBH_4$ (d) H_2-Ni

16. –CH=CH–CHO $\xrightarrow{LiAlH_4}$ product is

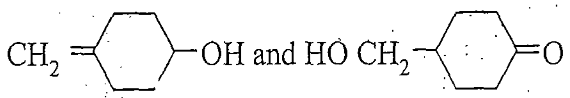
(a) –CH_2CH_2CHO (b) –$CH=CHCH_2OH$

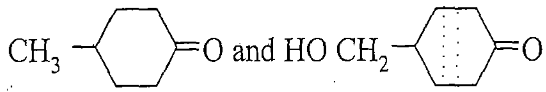
(c) –$CH_2CH_2CH_2OH$ (d) –$CH_2CH_2CH_2OH$

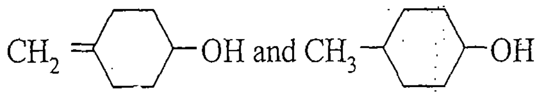
17. In the given reaction:

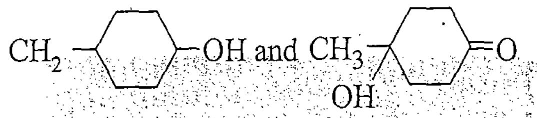


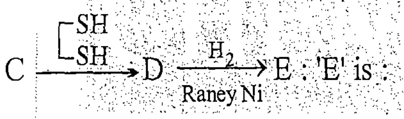
(X) and (Y) are :

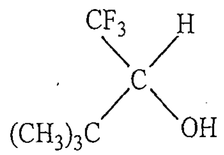
(a) 

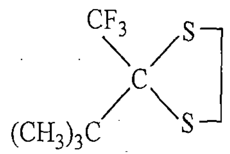
(b) 

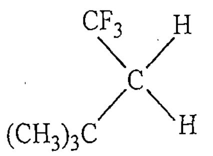
(c) 

(d) 

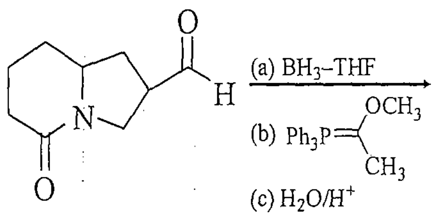
18. 

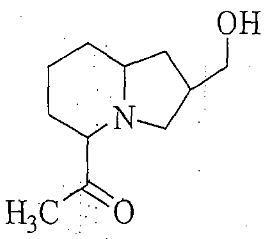
(a) 

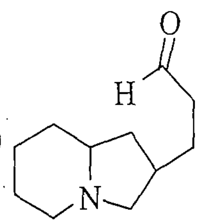
(b) 

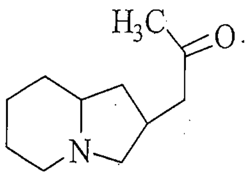
(c) 

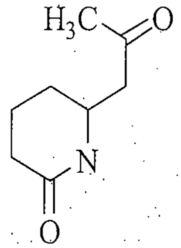
(d) $CF_3-\overset{\overset{S}{||}}{C}-S-C(CH_3)_3$

19. 

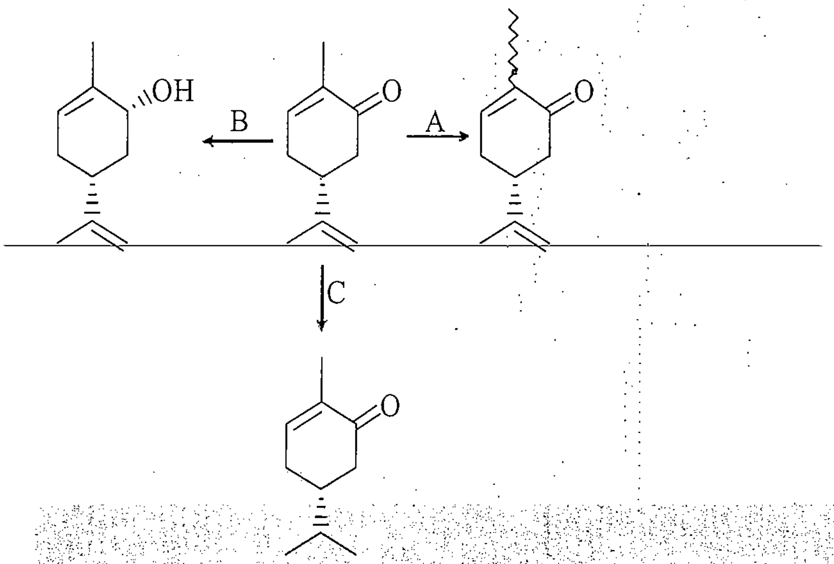
(a) 

(b) 

(c) 

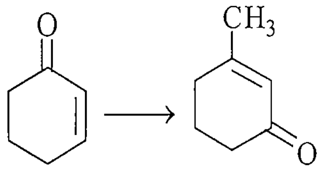
(d) 

20. The most suitable reagent combination of A-C, required in the following conversions are -

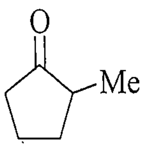


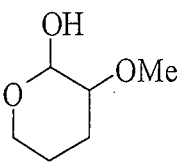
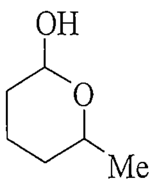
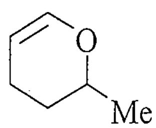
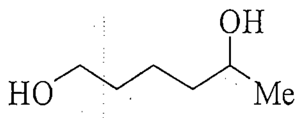
(a) A = Li/liq. NH_3; B = $NaBH_4$, $CeCl_3.7H_2O$; C = H_2, $(PH_3P)_3RhCl$
(b) A = Li/liq. NH_3; B = $NaBH_4$, $CeCl_3.7H_2O$; C = H_2, 10% Pd/C
(c) A = $NaBH_4$, $CeCl_3.7H_2O$; B = Li/liq. NH_3; C = H_2, $(Ph_3P)_3RhCl$
(d) A = $NaBH_4$, $CeCl_3.7H_2O$; B = Li/liq. NH_3; C = H_2, 10% Pd/C

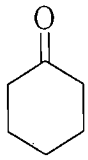
21. Correct combination of reagent which can carried out following conversion

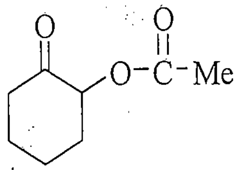
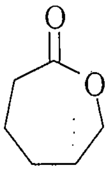
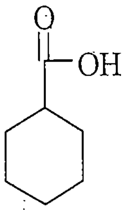
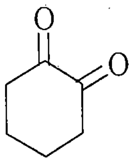


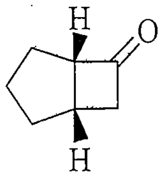
(a) (i) CH_3-MgBr then H^+ (ii) H_2SO_4 / Δ (iii) NH_2-NH_2 / KOH
(b) (i) $(CH_3)_2CuLi$ then H^+ (ii) $NaBH_4$ EtOH (iii) H_2SO_4 / Δ
(c) (i) CH_3-Li, then H^+ (ii) PCC / Δ
(d) (i) $NaBH_4 \cdot CeCl_3$ then H^+ (ii) MnO_2 (iii) CH_3-Li

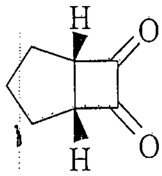
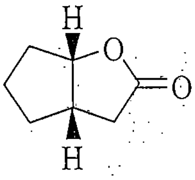
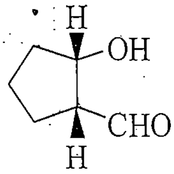
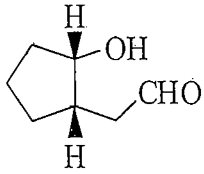
22.  $\xrightarrow[CHCl_3]{m\text{-}CPBA}$? $\xrightarrow[Et_2O]{LiAlH_4}$ X; X is

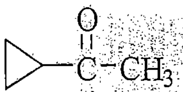
(a)  (b)  (c)  (d) 

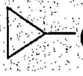
23.  $\xrightarrow{CH_3CO_3H}$ A ; A is

(a)  (b)  (c)  (d) 

24.  $\xrightarrow[CF_3CH_2OH]{H_2O_2}$ A $\xrightarrow{DIBAL-H}$ B ; B is

(a)  (b)  (c)  (d) 

25.  $\xrightarrow{CF_3COOOH}$ $\underset{\text{Major product}}{A}$ $\xrightarrow{LiAlH_4}$ B + C ; B and C are

(a) —OH & CH_3-CH_2-OH (b) —OH & $CH_3-\overset{O}{\overset{||}{C}}-CH_3$

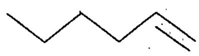
(c)  & CH_3-CH_2-OH (d)  & $CH_3CH_2-\overset{OH}{\overset{|}{C}}-CF_3$

26. Acetophenone can be converted to phenol by reaction with

(a) m-CPBA followed by base catalysed hydrolysis

(b) Conc. HNO_3 (c) iodine and NaOH

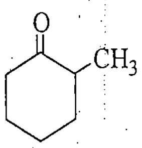
(d) Singlet oxygen followed by base catalysed hydrolysis

27.  $\xrightarrow[\text{(ii) } LiAlH_4]{\text{(i) m-CPBA}}$ Product

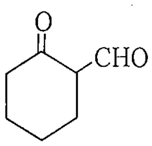
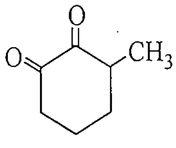
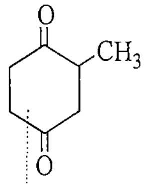
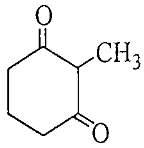
The product is

(a) racemic mixture (b) hexan-2-ol (c) hexan-1-ol (d) hexane

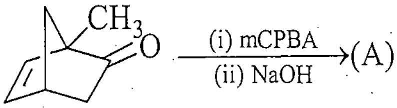
28. In the given reaction

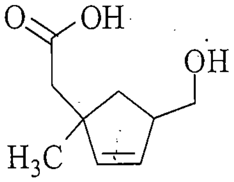
 $\xrightarrow{SeO_2}$ [X]

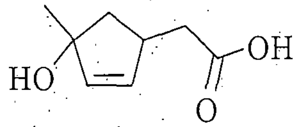
[X] will be:

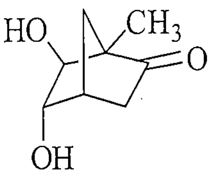
(a)  (b)  (c)  (d) 

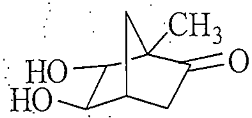
29. Major product formed in the following reaction is



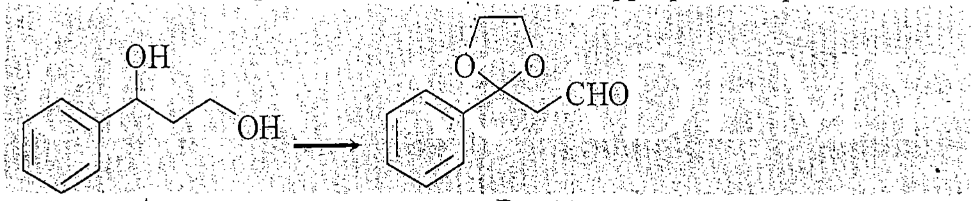
(a) 

(b) 

(c) 

(d) 

30. For the following three step conversion of A to B, the appropriate sequence of reactions is

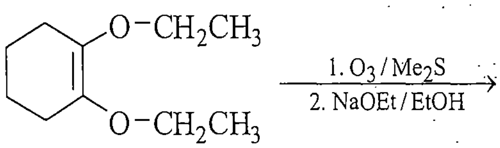


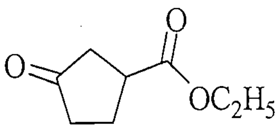
A B

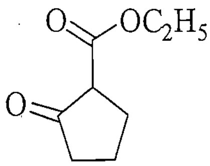
(a) MnO_2; $(CH_2OH)_2$/p-TSA; PCC (b) PCC; MnO_2; $(CH_2OH)_2$/p-TSA

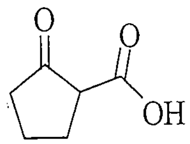
(c) PCC; $(CH_2OH)_2$/p-TSA; Jones' reagent (d) Jones' reagent; $(CH_2OH)_2$/p-TSA; MnO_2

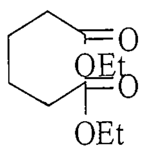
31. Major product formed in the following reaction is

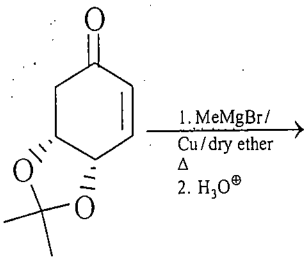


(a) 

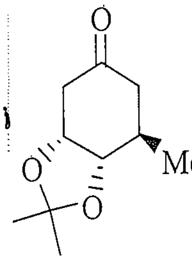
(b) 

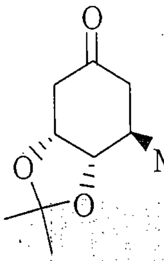
(c) 

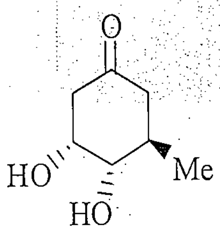
(d) 

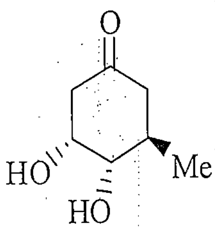
32.  Product

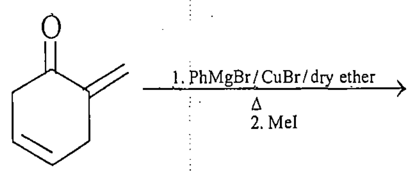
What is the major product and its selectivity of formation?

(a)  and regioselectivity

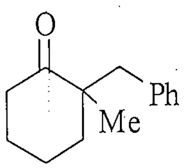
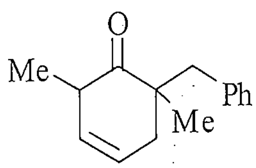
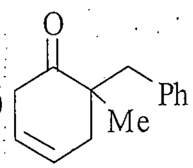
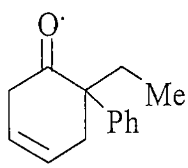
(b)  and regioselectivity and chemoselectivity both

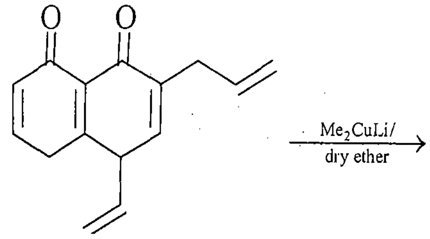
(c)  and regioselectivity and stereoselectivity both

(d)  and stereoselectivity and chemoselectivity both

33.  Major product

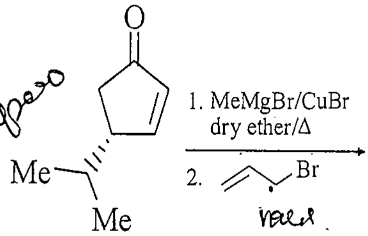
What is the major product of reaction?

(a)  (b)  (c)  (d) 

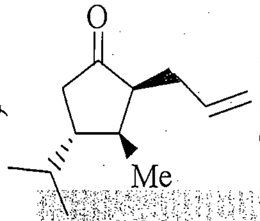
34. 

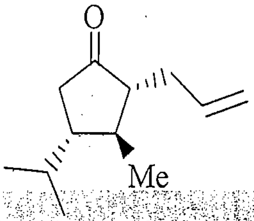
How many double bonds can give the reaction with Me_2CuLi?

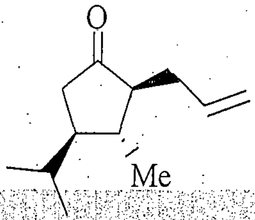
(a) 2 (b) 3 (c) 4 (d) 5

35. 

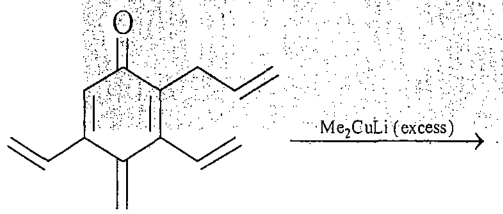
Major Product?

(a) 

(b) 

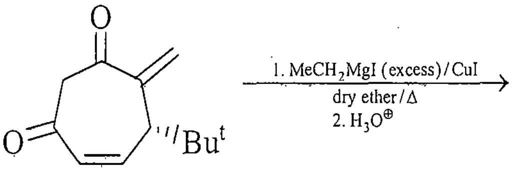
(c) 

(d) None of these

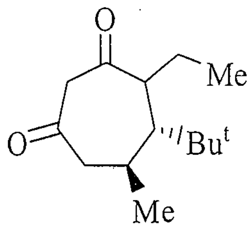
36. 

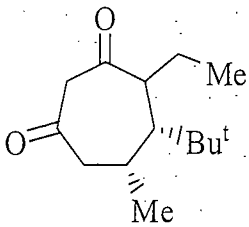
How many double bonds react with Me_2CuLi reagent?

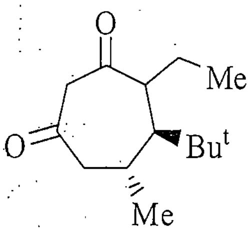
(a) 3 (b) 2 (c) 5 (d) 4

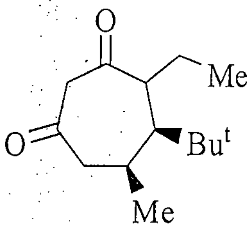
37. 

Major Product?

(a) 

(b) 

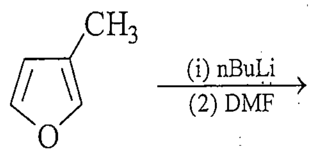
(c) 

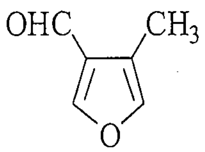
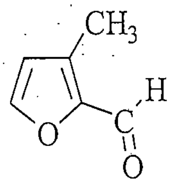
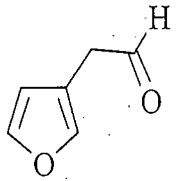
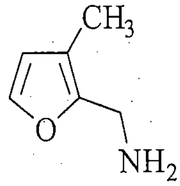
(d) 

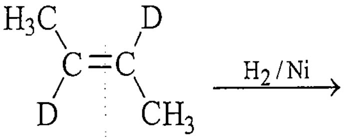
38. RR' R" OH can be prepared by the action of excess of a suitable Grignard reagent on a/an

(a) nitrile or an aldehyde
(b) ester or an alcohol
(c) aldehyde or a ketone
(d) ketone or an ester

39. Major product formed in the reaction

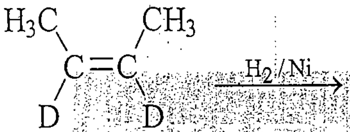


(a)  (b)  (c)  (d) 

40. 

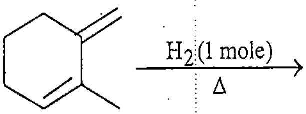
Product of above reaction will be

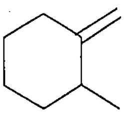
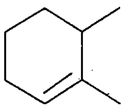
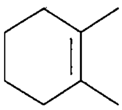
(a) racemic mixture
(b) diastereomers
(c) meso
(d) constitutional isomers

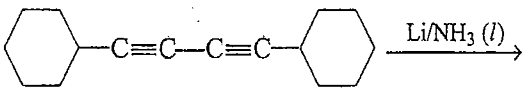
41. 

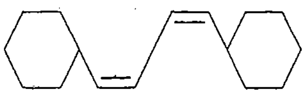
Product of above reaction will be

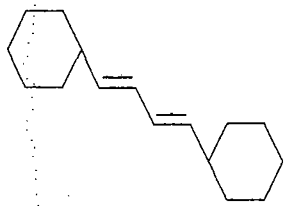
(a) racemic mixture
(b) diastereomers
(c) meso
(d) constitutional isomers

42.  Product

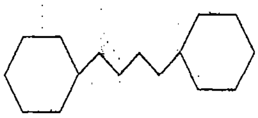
(a)  (b)  (c)  (d) None of these

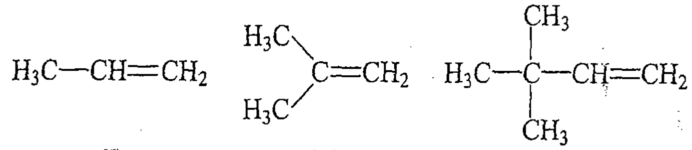
43.  Product :

(a) 

(b) 

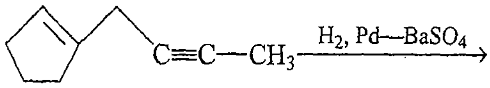
(c) Both a and b

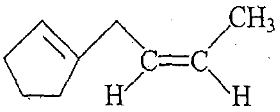
(d) 

44. 

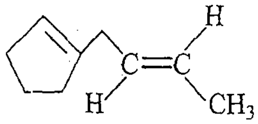
(X) (Y) (Z)

(a) an optically active compound
(b) an optically inactive compound
(c) a racemic mixture
(d) a diastereomeric mixture

45.  Major product :

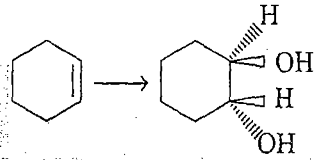
(a) 

(b) 

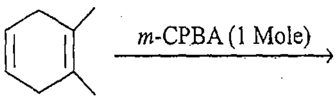
(c) 

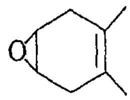
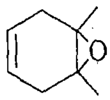
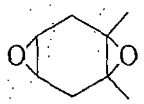
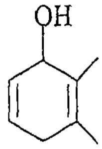
(d) None of these

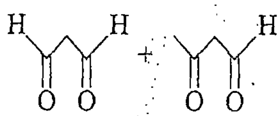
46. Give the reagent that would best accomplish the following reaction:

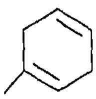
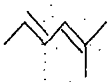
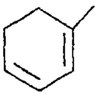


(a) Cold $KMnO_4$
(b) CF_3CO_3H, $H^{\oplus}/H_2O$
(c) O_3, $Zn-H_2O$
(d) $KMnO_4$, Δ, $\overset{\ominus}{O}H$ (Bayer reagent)

47.  (more nucleophilic double bond reacts)

(a) 
(b) 
(c) 
(d) 

48. Compound (X) $\xrightarrow{O_3,\ Zn-H_2O}$ 

(a) 
(b) 
(c) 
(d) 

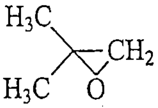
49. The conversion

$$H_3C-\overset{\overset{\displaystyle O}{||}}{C}-CH_2CH_2CO_2CH_3 \rightarrow H_3C-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2CH_2CH_2OH$$

can be effected using

(a) $LiAlH_4$ and then H^+ (b) $NaBH_4$ and then H^+

(c) H_2/Pt carbon (d) All of these

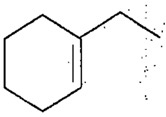
50.  $\xrightarrow{LiAlH_4}$ *A*, A is

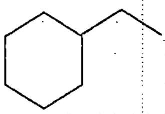
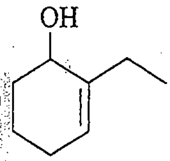
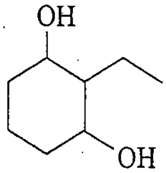
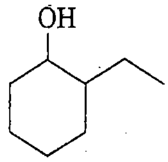
(a) CH_3CHCH_2OH with CH_3 on the second carbon ($CH_3CH(CH_3)CH_2OH$)

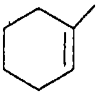
(b) $CH_3CH_2CH_2CH_2OH$

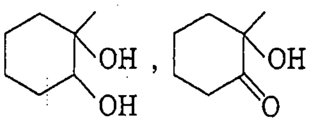
(c) $CH_3C(CH_3)_2-OH$

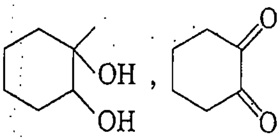
(d) No reaction

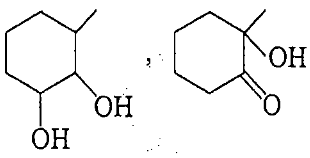
51.  $\xrightarrow{SeO_2}$ *A*, *A* is :

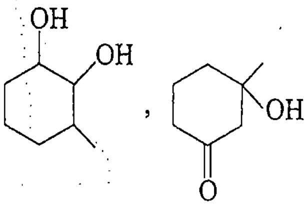
(a)  (b)  (c)  (d) 

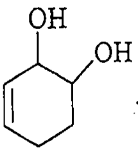
52.  $\xrightarrow{\text{cold } KMnO_4}$ *A* $\xrightarrow[AcOH]{CrO_3}$ *B*, A and B are

(a) 

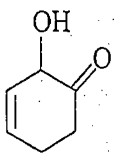
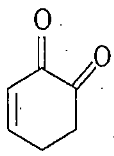
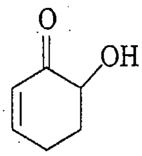
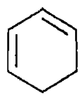
(b) 

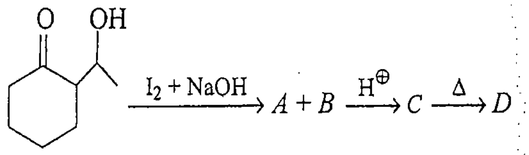
(c) 

(d) 

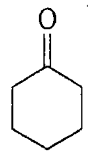
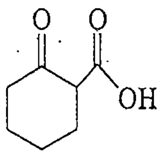
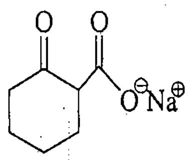
53.  $\xrightarrow{MnO_2}$ Product

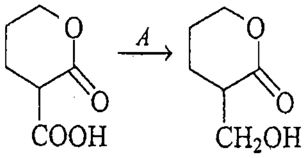
The main product is

(a)  (b)  (c)  (d) 

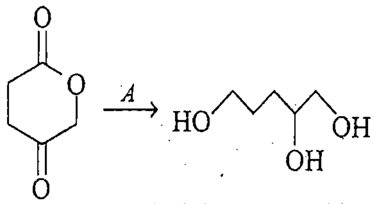
54. 

Identify product D in this reaction:

(a)  (b)  (c) CHI_3 (d) 

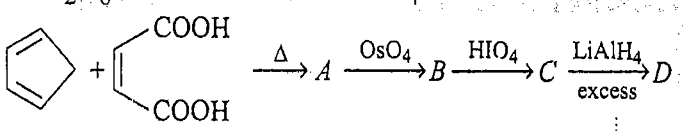
55.  ; A is:

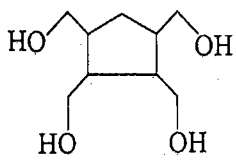
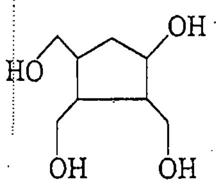
(a) B_2H_6 / H_2O (b) $LiAlH_4$ (c) CH_3OH/Na (d) P/HI

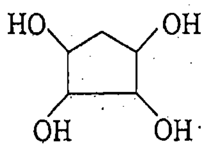
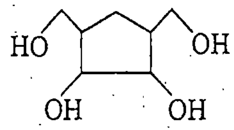
56. 

Reagent A used in this change is

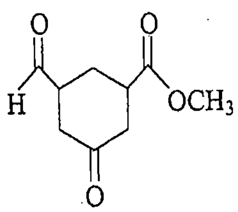
(a) B_2H_6 (b) $LiAlH_4$ (c) Sn/HCl (d) $NaBH_4$

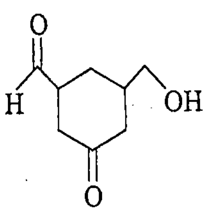
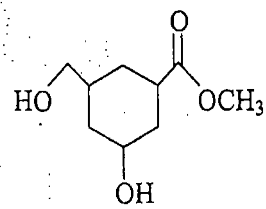
57. 

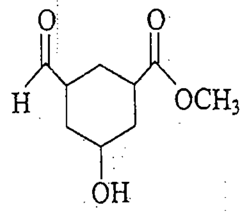
(a)  (b) 

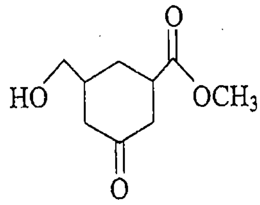
(c)  (d) 

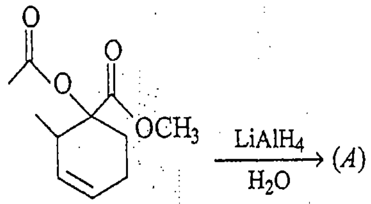
58. Find out the product when compound reacts with $NaBH_4$



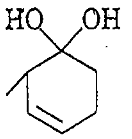
(a)  (b) 

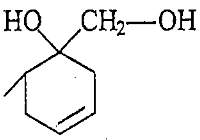
(c) 

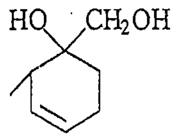
(d) 

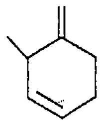
59. 

Find out 'A' of the reaction:

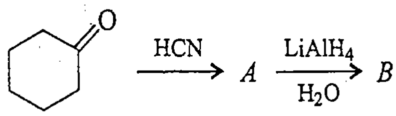
(a) 

(b) 

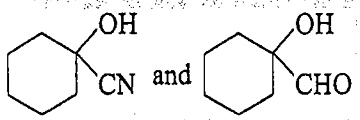
(c) 

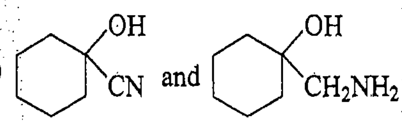
(d) 

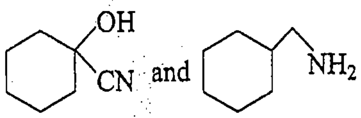
60. In the given reaction

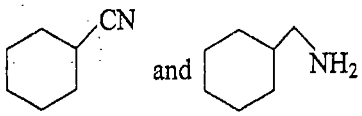


A and B will respectively be:

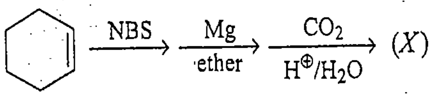
(a) 

(b) 

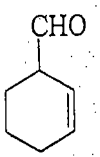
(c) 

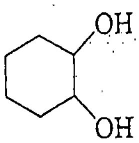
(d) 

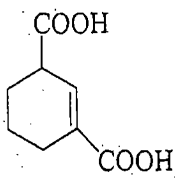
61. In the given reaction

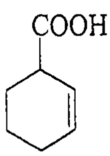


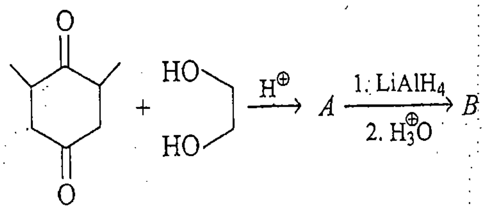
(X) will be

(a) 

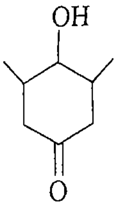
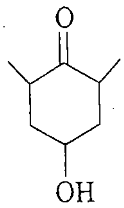
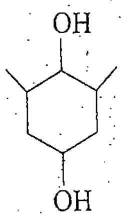
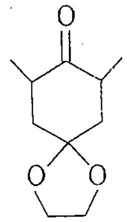
(b) 

(c) 

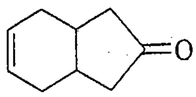
(d) 

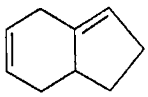
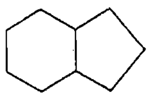
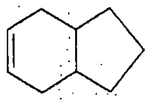
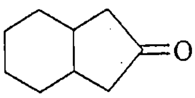
62. 

Identify structure of B:

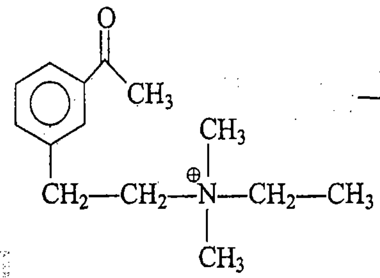
(a)  (b)  (c)  (d) 

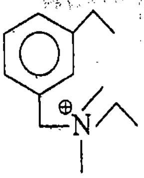
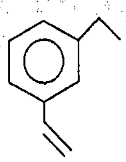
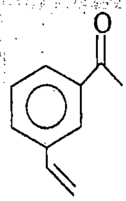
63. In the given reaction

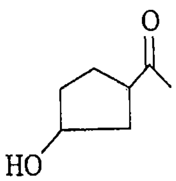
 $\xrightarrow{H_2N—NH_2/\overset{\ominus}{O}H}$ Product :

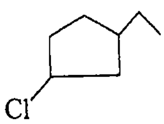
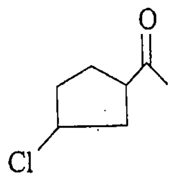
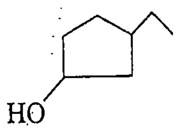
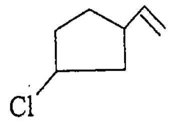
(a)  (b)  (c)  (d) 

64. Find the product of the following reaction:

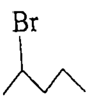
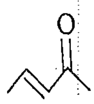
 $\xrightarrow[\Delta]{NH_2—NH_2/KOH}$

(a)  (b)  (c)  (d) None of these

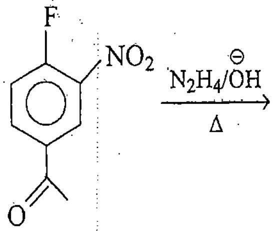
65.  $\xrightarrow[HCl]{Zn—Hg}$ Product :

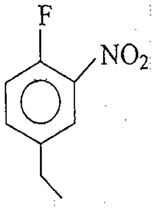
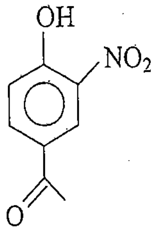
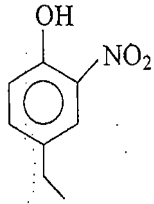
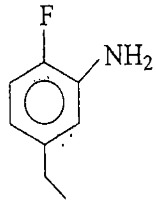
(a)  (b)  (c)  (d) 

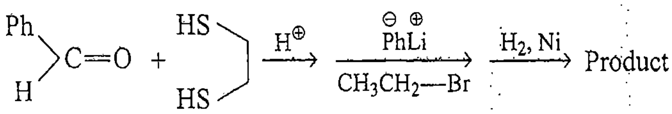
66. $CH_3—\underset{\underset{Br}{|}}{CH}—CH_2—\overset{\overset{O}{||}}{C}—CH_3 \xrightarrow[\Delta]{N_2H_4,\ \overset{\ominus}{O}H}$ Product :

(a)  (b)  (c)  (d) 

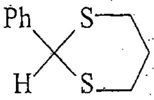
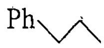
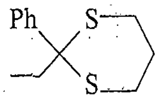
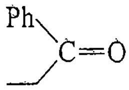
67. Find the product of the following reaction:

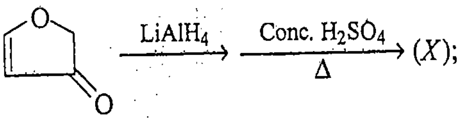


(a)  (b)  (c)  (d) 

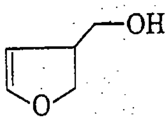
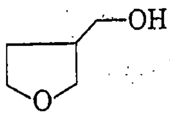
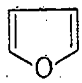
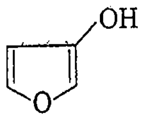
68. 

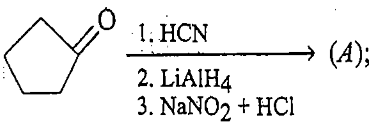
Find out final product of reaction

(a)  (b)  (c)  (d) 

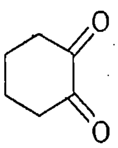
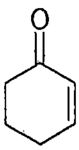
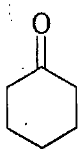
69. 

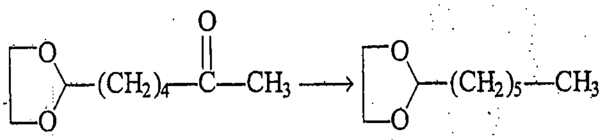
Product (X) of reaction is

(a)  (b)  (c)  (d) 

70. 

Product 'A' will be

(a)  (b)  (c)  (d) None of these

71. 

Which of the following reagents is suitable for above conversion?

(a) Zn-Hg / HCl (b) $LiAlH_4$ (c) $H_2N-NH_2/\overset{\ominus}{O}H$ (d) $NaBH_4$

acid)
change it into (in aqeuy

EXERCISE - II

One or More Than One Correct Type

1. In which of the following reactions product will be aldehyde?

(a) $CH_3-\underset{\underset{CH_3}{|}}{C}=\underset{\underset{CH_3}{|}}{C}-C_2H_5 \xrightarrow[(ii)H_2O]{(i)O_3}$

(b) $CH_3-CH=CH_2 \xrightarrow[\Delta]{CO/H_2/CO_2(CO)_8}$

(c) $CH_3-C\equiv CH \xrightarrow[NaOH, H_2O_2]{B_2H_6}$

(d) $CH_3-C\equiv CH \xrightarrow{HOH/HgSO_4/H_2SO_4}$

2. Which of the following alcohols can be oxidised by K_2CrO_4?

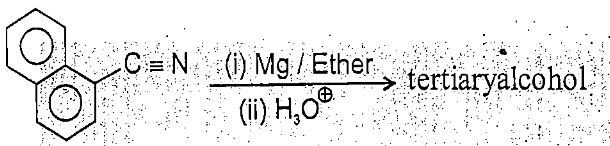
(a) Ethanol (b) Tert butyl alcohol

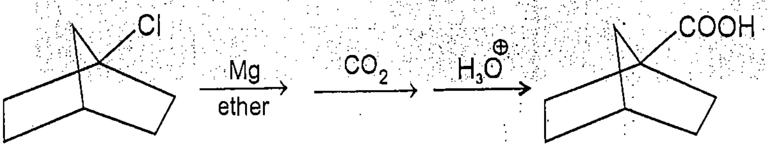
(c) Isopropyl alcohol (d) Allyl alcohol

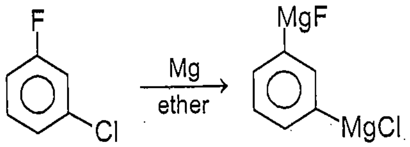
3. Which one of the following reagent(s) is/are used for the conversion of ketone into hydrocarbons?

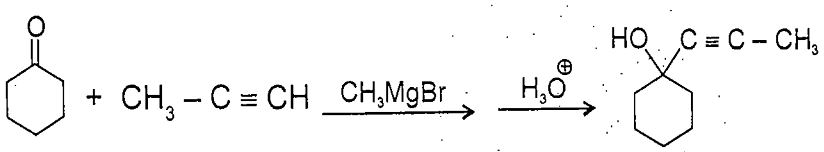
(a) LAH (b) N_2H_4/H_2O_2 (c) $Mg/Hg\ H_2O$ (d) Zn-Hg/HCl

4. Which reaction is/are correct.

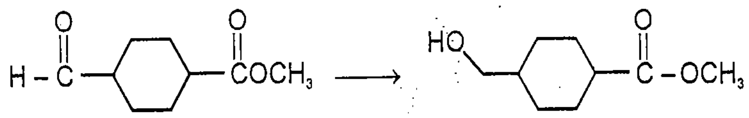
(a) 

(b) 

(c) 

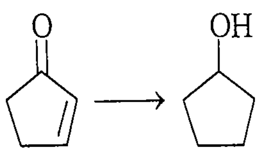
(d) 

5. Which reducing agent, would you cannot use to carry out the following transformation.



(a) $LiAlH_4$ (b) $NaBH_4$ (c) Na/NH_3 (d) B_2H_6/THF

6. Correct combination of following reagents which can give the following product



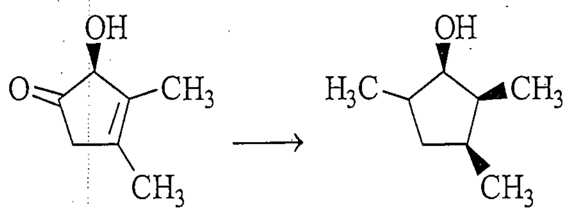
(a) (i) $NaBH_4 \cdot CeCl_3$ (ii) H_2, $Rh[P(Ph)_3]_3Cl$

(b) (i) H_2 / Pd / C (ii) $NaBH_4$ – EtOH

(c) (i) H_2 / Pd / C (ii) NH_2 –NH_2 / KOH

(d) (i) DIBALH – 78°C (ii) H_2, Pd / C

7. Appropriate reagent for the following conversion is



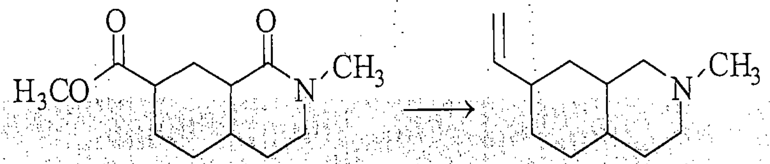
(a) (i) $NaBH_4$ (ii) H_2 Pd/C (iii) H_2SO_4 / Δ

(b) (i) H_2 / Pd / C (ii) $CH_2 = PPh_3$ (iii) $Rh(PPh_3)_3Cl$ / H_2

(c) (i) Na / Liq. NH_3 (ii) $CH_2 = PPh_3$

(d) (i) $CH_2 = PPh_3$ (ii) H_2 Pd / C excess

8. Correct sequence of reagents carried but the following conversion is/are



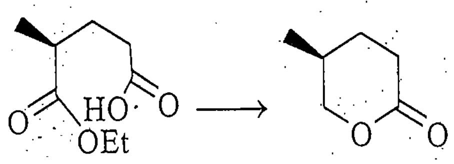
(a) (i) BH_3–THF (ii) DIBALH – 78°C (iii) CH_2= PPh_3

(b) (i) $LiBH_4$ (ii) BH_3–THF (iii) PCC (iv) CH_3=PPh_3

(c) (i) $LiAlH_4$ (ii) PCC (iii) $CH_2 = PPh_3$

(d) (i) BH_3–THF (ii) NaOH / H_2O (iii) CH_2N_2

9. Incorrect sequence of reagents for the following coversion.



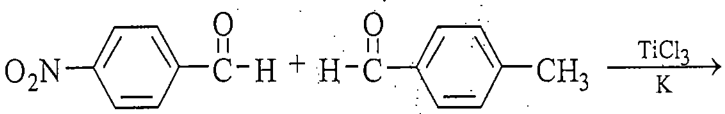
(a) (i) BH_3 THF (ii) H^+ / H_2O (b) (i) $LiBH_4$ (ii) H^+/H_2O

(c) $LiAlH_4$ (ii) H^+/H_2O (d) (i) $NaBH_4$ (ii) H^+/H_2O

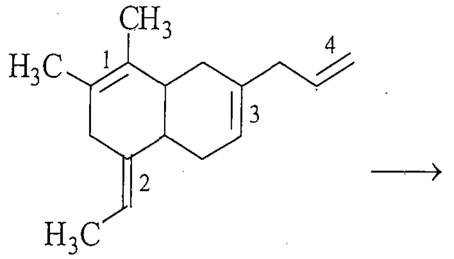
EXERCISE - III

Numerical Answer Type

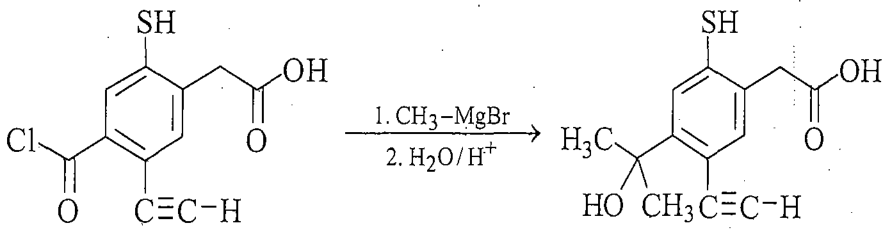
1. How many product formed in the given reaction

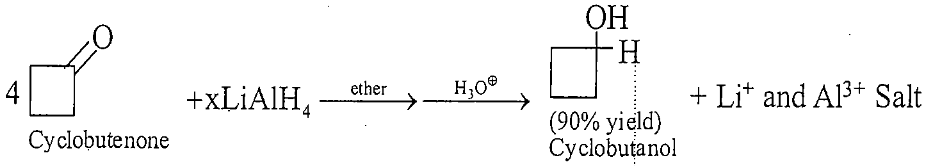


2. Double bond which is most reactive for hydrogenation reaction with willkinson catalyst.



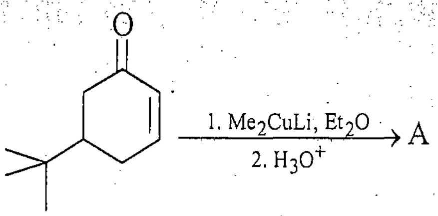
3. How many mole of RMgX required for the following reaction is



4. 

Value of x in above reaction is

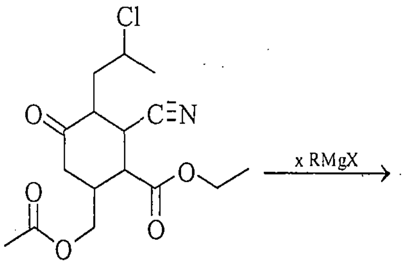
5. The major product formed in the reaction given below is



How many stereocenters are present in A?

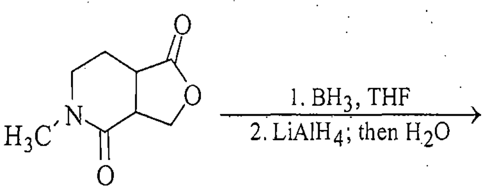
6. How many isomer of C_4H_8O when reacts with CH_3MgBr followed by acidification to give 2° alcohol (only consider carbonyl isomers)? (Including stereoisomers)

7. Total number of RMgX are consumed in the following reaction

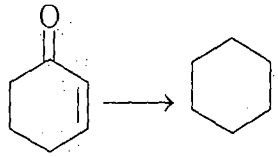


8. How many isomers of $C_4H_{10}O$ reacts with CH_3MgBr to evolve CH_4 gas? (Excluding stereoisomer)

9. How many –OH group will form in the given reaction is



10. How many reagents can carried out the followng conversion:



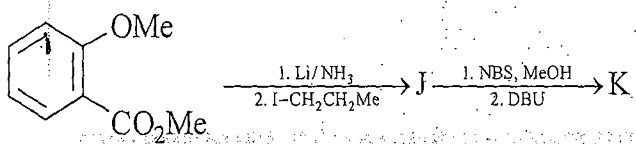
(i) DIBALH – 78°C then H_2 / Pd / C (ii) (a) H_2 / Pd / C (b) Zn-Hg, HCl

(iii) (a) Na / Liq. NH_3 (b) $NH_2 - NH_2$/KOH (iv) (a) $NaBH_4.CeCl_3$ (b) H_2 / Pd / C

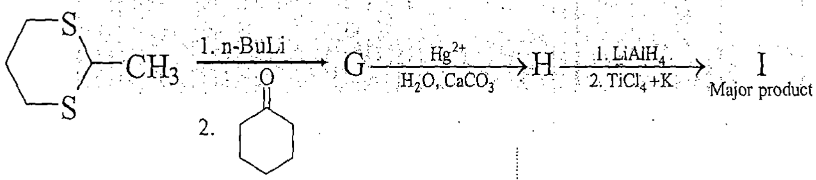
11. 4.6 g of a polyhydric alcohol was treated with an excess of methy magnesium bromide to produce 3.36 litre of CH_4 at STP. Calculate number of –OH group present in the alcohol.
(molecular weight of alcohol = 92)

12. How many possible product formed in the given reaction

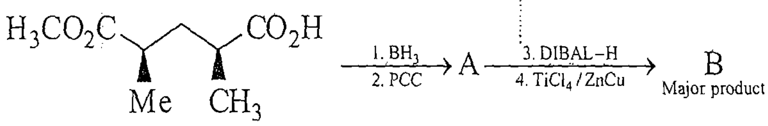
$$Ph-\overset{O}{\overset{\|}{C}}-H + Ph-\overset{O}{\overset{\|}{C}}-Ph \xrightarrow[LiAlH_4]{TiCl_3}$$

13. 

Find the structure of K

14. 

Find the structure of I

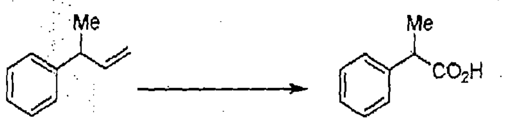
15. 

Find the structure of B.

EXERCISE - IV

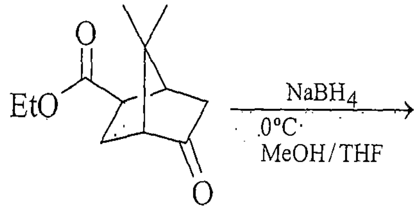
Previous Year Questions

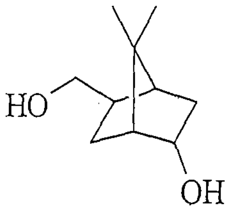
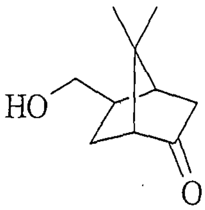
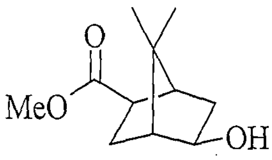
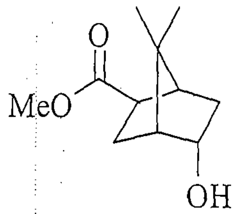
1. The following conversion is carried out using



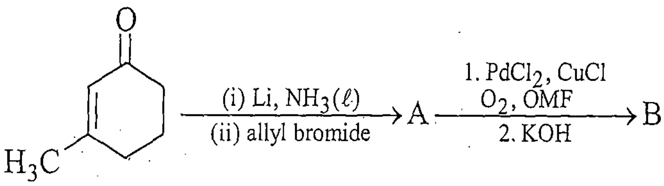
(a) hydroboration oxidation followed by Jones oxidation
(b) Wacker oxidation followed by haloform reaction
(c) oxymercuration-determination followed by Jones oxidation
(d) ozonolysis followed by haloform reaction

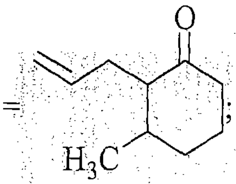
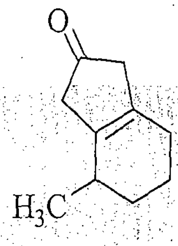
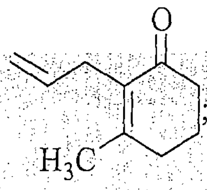
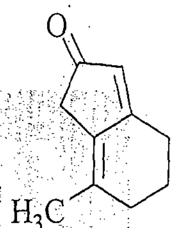
2. The major product formed in the following

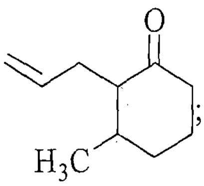
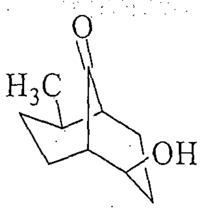
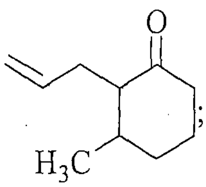
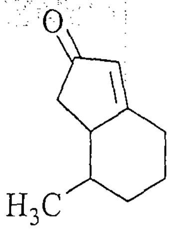


(a)  (b)  (c)  (d) 

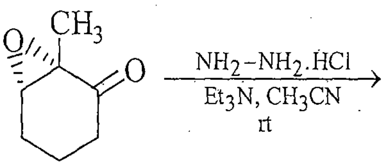
3. The major products A and B formed in the following reaction sequences are

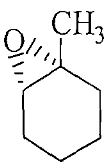
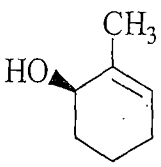
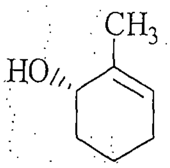
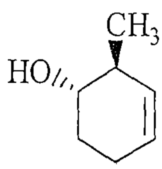


(a) A =  ; B =  (b) A =  ; B = 

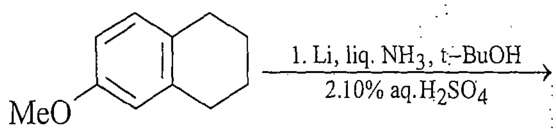
(c) A =  ; B =  (d) A =  ; B = 

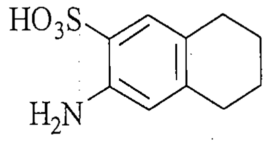
4. The major product formed in the following reaction is

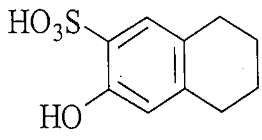


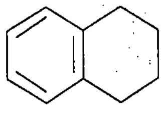
(a)  (b)  (c)  (d) 

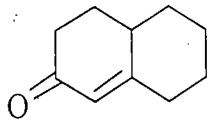
5. The compound formed in the following reaction sequence is



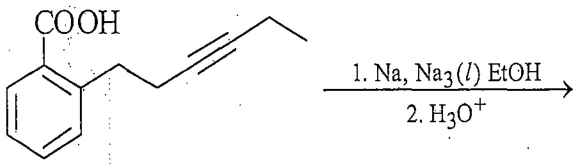
(a) 

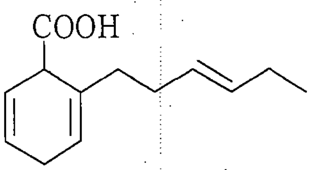
(b) 

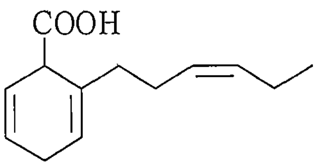
(c) 

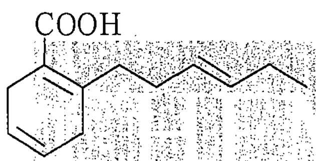
(d) 

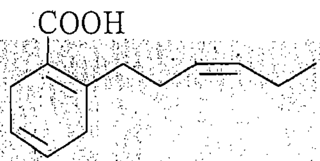
6. The major product of the following reaction is



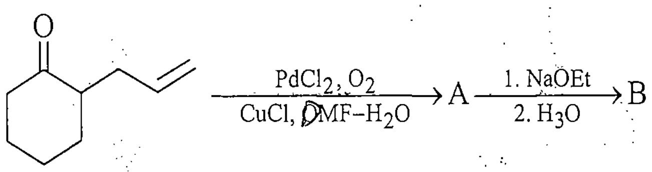
(a) 

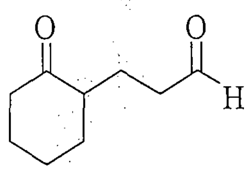
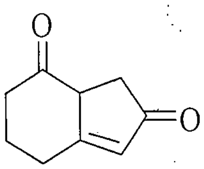
(b) 

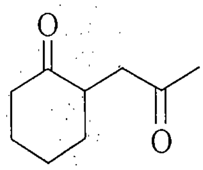
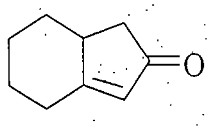
(c) 

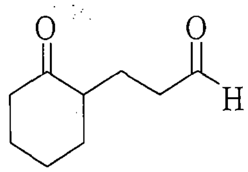
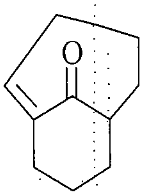
(b) 

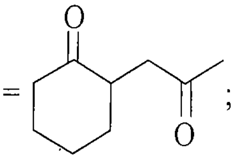
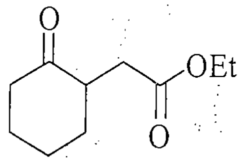
7. The products A and B in the following reaction sequence are



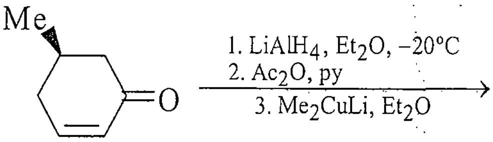
(a) A =  ; B = 

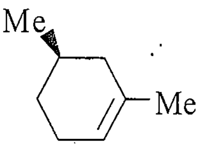
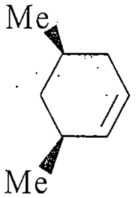
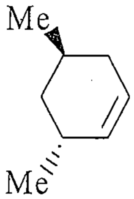
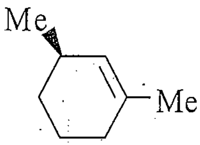
(b) A =  ; B = 

(c) A =  ; B = 

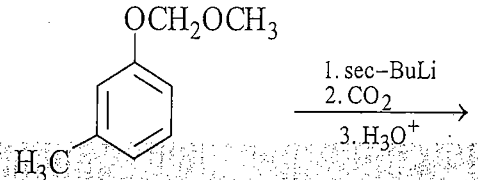
(d) A =  ; B = 

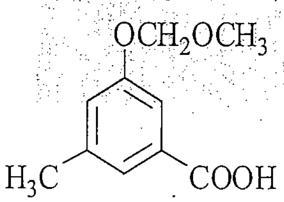
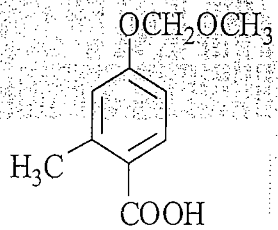
8. The major product formed in the following reaction sequence is

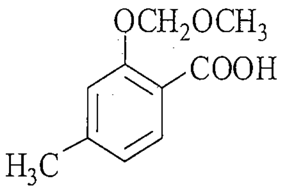
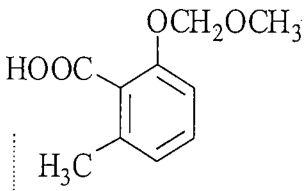


(a)  (b)  (c)  (d) 

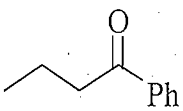
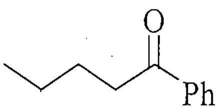
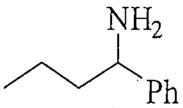
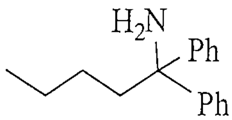
9. The major product formed in the following reaction is



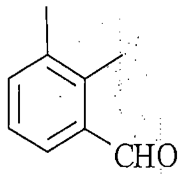
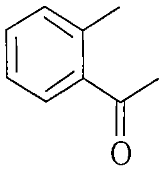
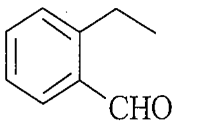
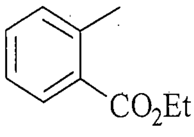
(a)  (b) 

(c)  (d) 

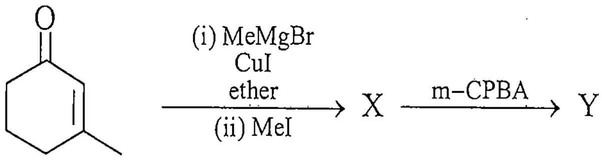
10. The major product formed in the reaction of butanenitrile with phenylmagnesium bromide followed by acidification is

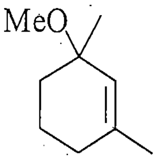
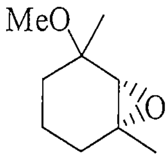
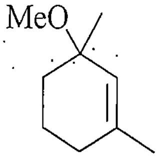
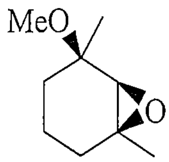
(a)  (b)  (c)  (d) 

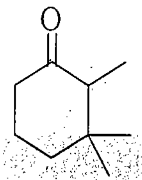
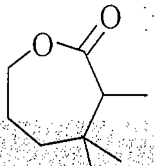
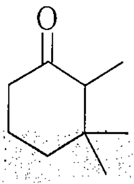
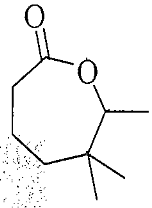
11. An organic compound on reaction with 2,4-dinitrophenylhydrazine (2,4-DNP) gives a yellow precipitate. It also gives silver mirror on reaction with ammoniacal $AgNO_3$. It gives an alcohol and sodium salt of a carboxylic acid on reaction with concentrated NaOH. It yields benzene-1,2-dicarboxylic acid on heating with alkaline KMnO4. The structure of the compound among the following is

(a)  (b)  (c)  (d) 

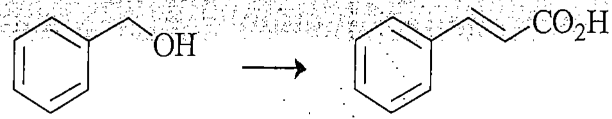
12. The major products **X** and **Y** in the following reaction sequence are



(a) X =  Y =  (b) X =  Y = 

(c) X =  Y =  (d) X =  Y = 

13. The appropriate reagents required for carrying out the following transformation are



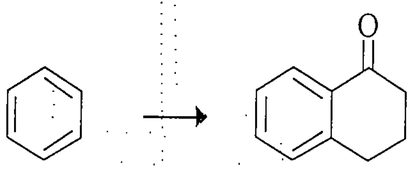
(a) (i) PCC, CH_2Cl_2; (ii) $Ph_3P{=}CHCO_2Et$; (iii) aq. NaOH, heat, then acidify

(b) (i) CrO_3, H_2SO_4, aq. acetone (ii) Ac_2O, NaOAc

(c) (i) MnO_2; (ii) $CH_2(CO_2H)_2$, piperidine, pyridine

(d) (i) PCC, CH_2Cl_2; (ii) $BrCH_2CO_2C(CH_3)_3$, Zn (iii) H_3O^+, heat

14. The appropriate reagents required for carrying out the following transformation are



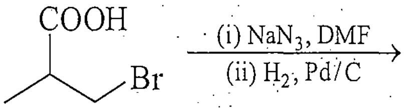
(a) (i) succinic anhydride, $AlCl_3$; (ii) Zn/Hg, HCl; (iii) polyphosphoric acid

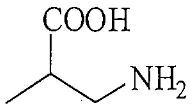
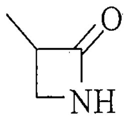
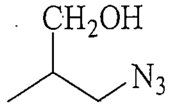
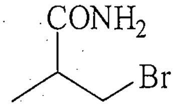
(b) (i) maleic anhydride, $AlCl_3$; (ii) $H_2N\text{-}NH_2$, KOH; (iii) H_2SO_4

(c) (i) succinic anhydride, $FeCl_3$; (ii) $LiAlH_4$; (iii) H_2SO_4

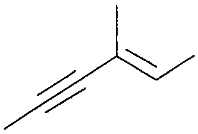
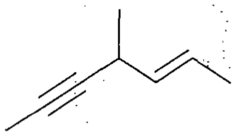
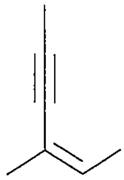
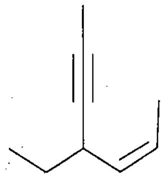
(d) (i) phthalic anhydride, $F_3B{\cdot}OEt_2$; (ii) $HS(CH_2)_2SH$, H^+; (iii) Raney Ni;
(iv) polyphosphoric acid

15. The major product formed in the following reaction is

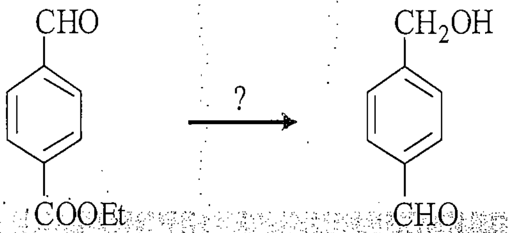


(a)  (b)  (c)  (d) 

16. The ene-yne that produces a chiral compound upon treatment with Lindlar's catalyst is

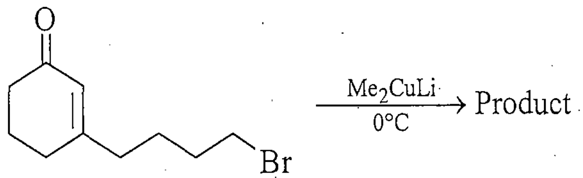
(a)  (b)  (c)  (d) 

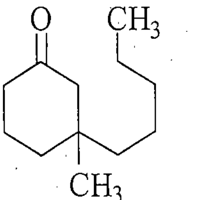
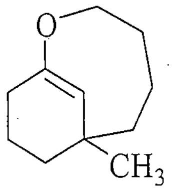
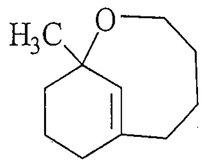
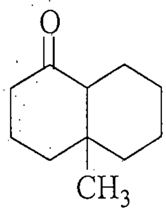
17. Identify the correct reagents required for the following transformation



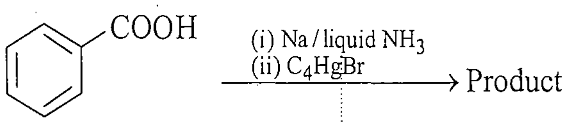
(a) (i) $NaBH_4$; (ii) H_3O^+
(b) (i) $LiAlH_4$; (ii) H_3O^+
(c) (i) $HOCH_2CH_2OH$, H^+; (ii) $LiAlH_4$; (iii) H_3O^+
(d) (i) $HSCH_2CH_2SH$, H^+; (ii) $LiAlH_4$; (iii) H_3O^+

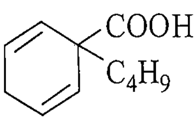
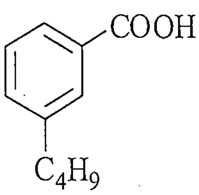
18. The structure of the major product in the following reaction is

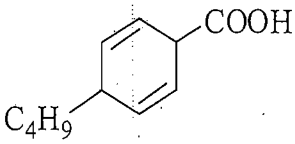


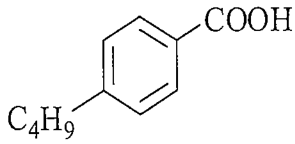
(a)  (b)  (c)  (d) 

19. The major product formed in the following reaction is :

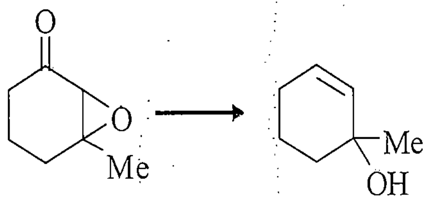


(a)  (b) 

(c) 

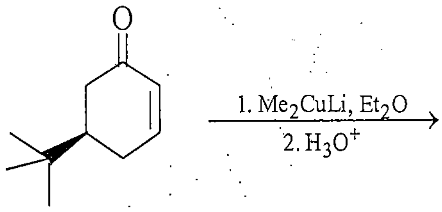
(d) 

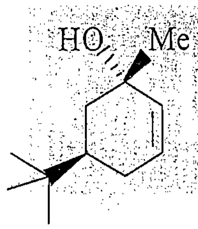
20. The most suitable reagent(s) to effect the following transformation is

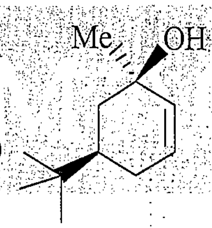


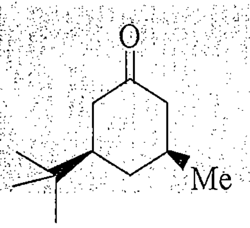
(a) N_2H_4, KOH, heat
(b) $TsNHNH_2$, CF_3COOH
(c) $LiAlH_4$
(d) Na, liq. NH_3

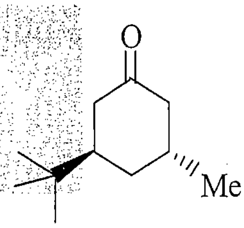
21. The major product formed in the reaction given below is



(a) 

(b) 

(c) 

(d) 

ANSWER KEY

EXERCISE - I

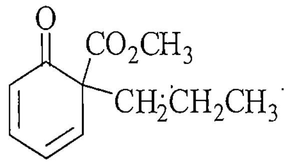
1. b	2. b	3. b	4. b	5. a	6. c	7. c
8. b	9. b	10. b	11. a	12. b	13. d	14. c
15. c	16. c	17. c	18. c	19. c	20. a	21. c
22. d	23. b	24. d	25. a	26. a	27. b	28. b
29. b	30. a	31. b	32. c	33. a	34. b	35. b
36. c	37. a	38. d	39. b	40. a	41. c	42. b
43. b	44. b	45. a	46. b	47. b	48. a	49. b
50. c	51. b	52. a	53. c	54. a	55. a	56. b
57. a	58. b	59. c	60. b	61. d	62. a	63. c
64. b	65. a	66. c	67. c	68. d	69. c	70. c
71. c						

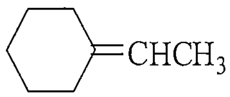
EXERCISE - II

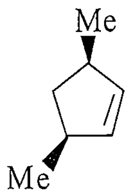
1. b,c	2. a,c,d	3. d	4. b,d	5. a,c,d	6. a,b,d	7. b,d
8. a,b,c	9. a,c,d					

EXERCISE - III

1. 6	2. 4	3. 5	4. 1	5. 2	6. 2	7. 7
8. 4	9. 2	10. 2	11. 3	12. 4		

13. K = 

14. I = 

15. B = 

EXERCISE - IV

1. b	2. c	3. d	4. c	5. d	6. a	7. b
8. c	9. c	10. a	11. b	12. d	13. a,c,d	14. a
15. a	16. b	17. c	18. d	19. a	20. a	21. d

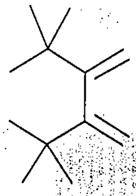
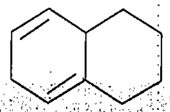
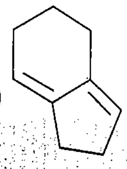
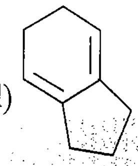
CHAPTER 7

Pericyclic Reactions

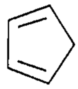
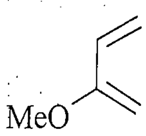
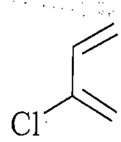
EXERCISE - I

Single Answer Correct Type

1. Diene which can give Diel's alder reaction is

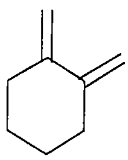
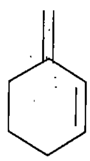
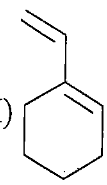
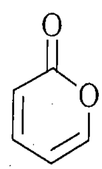
(a)  (b)  (c)  (d) 

2. Correct order of the reactivity of Diene in Diel's Alder reaction is

(I)  (II)  (III)  (IV) 

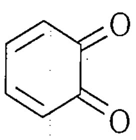
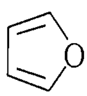
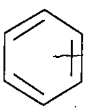
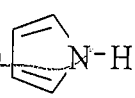
(a) I > II > III > IV (b) I > III > IV > II (c) I > III > II > IV (d) II > II > I > IV

3. Diene which can give Diel's Alder reaction

(I)  (II)  (III)  (IV) 

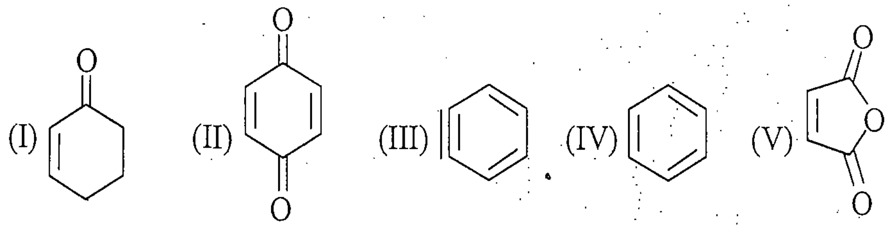
(a) I and IV (b) I, III and IV (c) I and III (d) II and IV

4. Diene which can not given Diel's Alder reaction

(I)  (II)  (III)  ~~(IV)~~ 

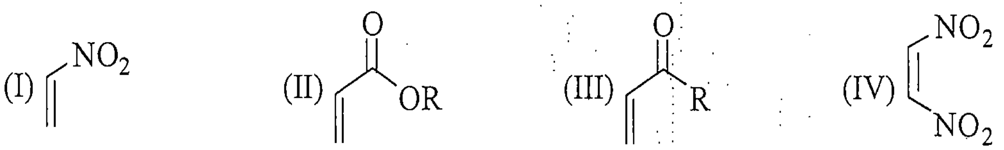
(a) I and III (b) II, III and IV (c) III and IV (d) I, III and IV

5. Compound which can't be use as dienophile



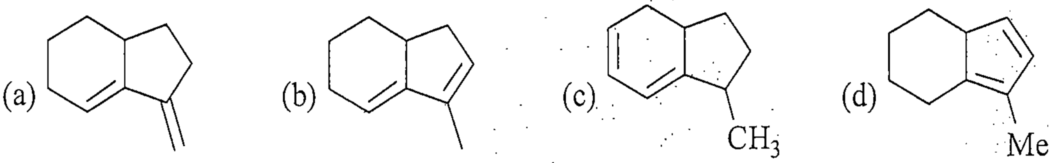
(a) I, V (b) III, II (c) III and IV (d) Only IV

6. Correct order of reactivity of Dienophile is

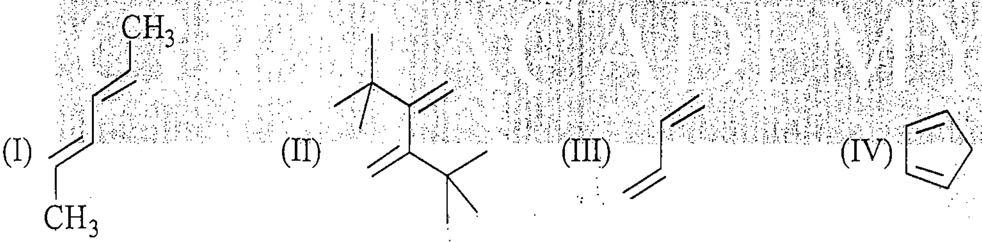


(a) IV > I > II > III (b) IV > II > I > III (c) I > IV > III > II (d) IV > I > III > II

7. Amongst the following, the compound that does not act as diene in Diel's Alder reaction is

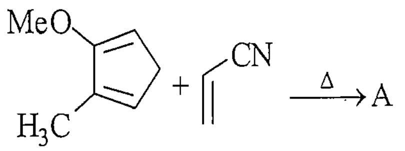


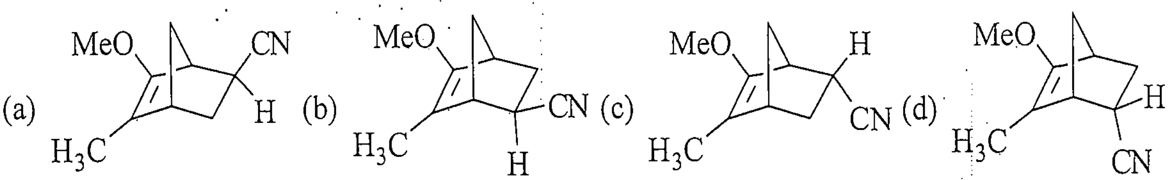
8. Correct order of the reactivity of diene is



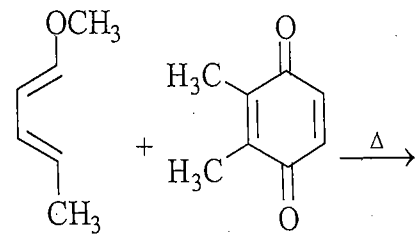
(a) I > II > III > IV (b) IV > III > I > II (c) IV > I > II > III (d) IV > I > III > II

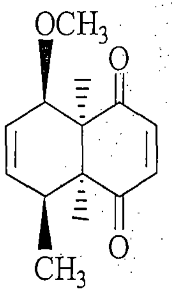
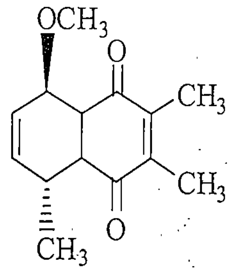
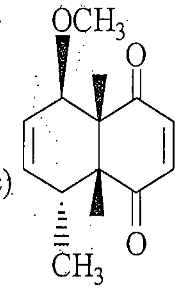
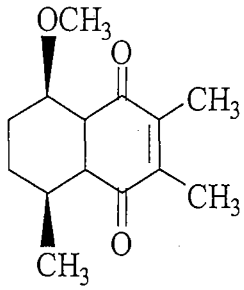
9. Major product formed in the given reaction is





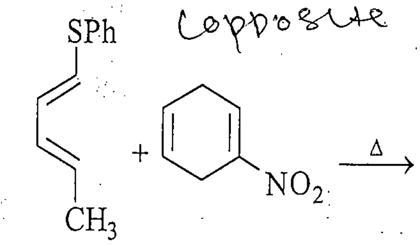
10. Major product formed in the given reaction is

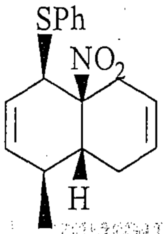
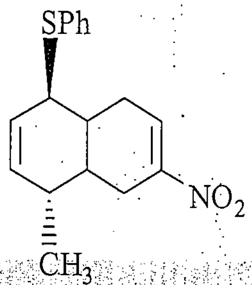
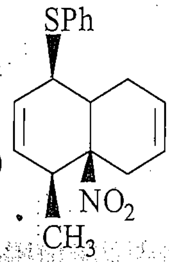
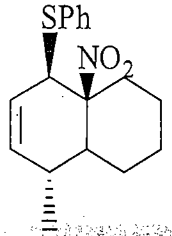


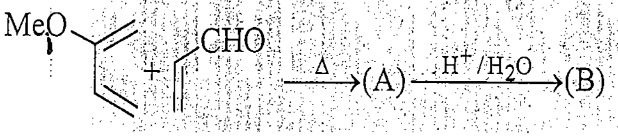
(a)  (b)  (c)  (d) 

11. Major product formed in the given reaction is

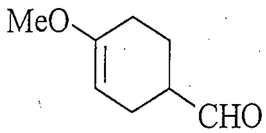
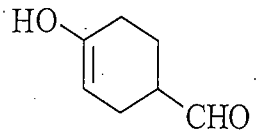
(opposite side) → cis

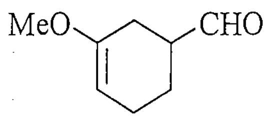
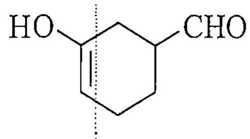


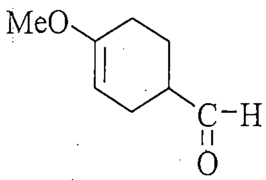
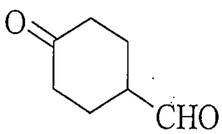
(a)  (b)  (c)  (d) 

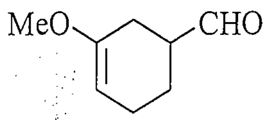
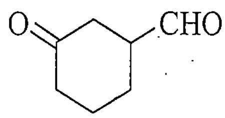
12. 

Product A and B are

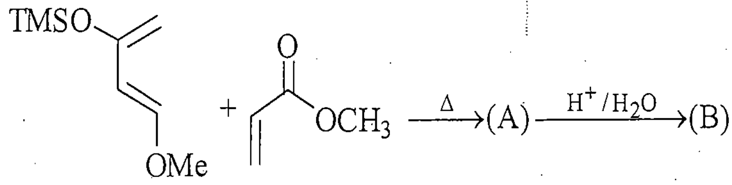
(a) A =  ; B = 

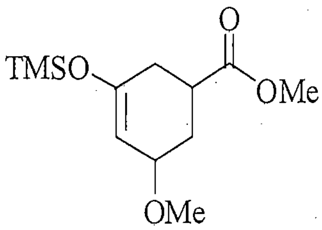
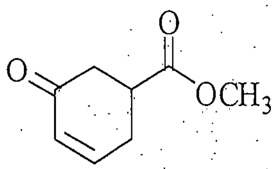
(b) A =  ; B = 

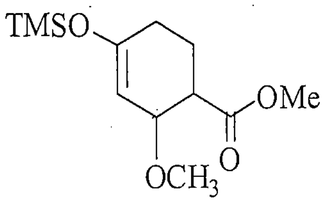
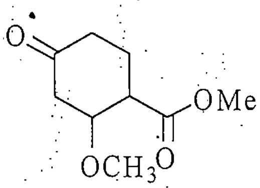
(c) A =  ; B = 

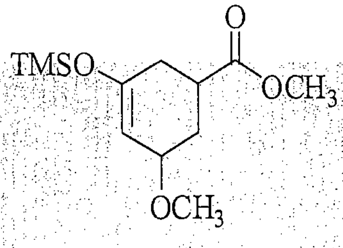
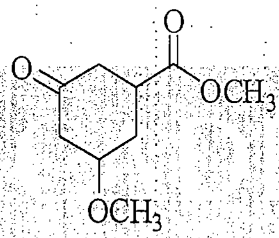
(d) A =  ; B = 

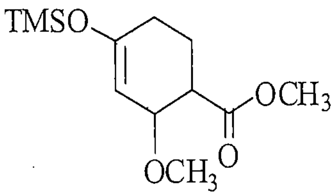
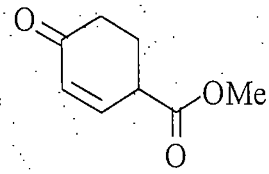
13. Major product A and B formed during the given reaction is

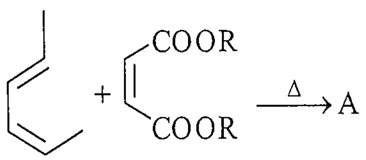


(a) A =  ; B = 

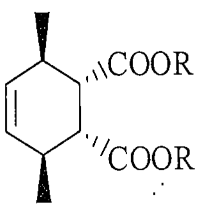
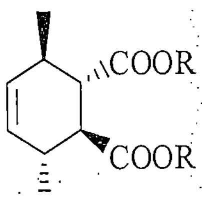
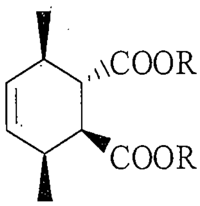
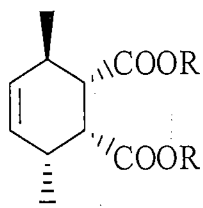
(b) A =  ; B = 

(c) A =  ; B = 

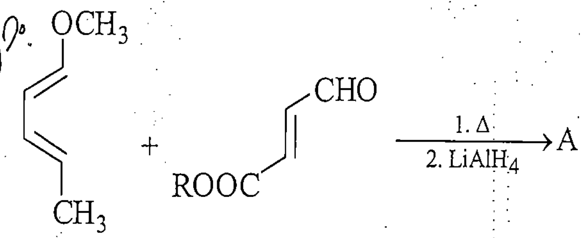
(d) A =  ; B = 

14. 

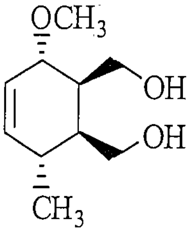
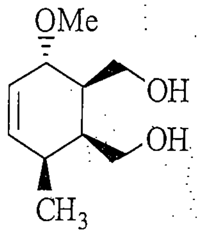
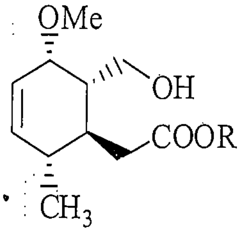
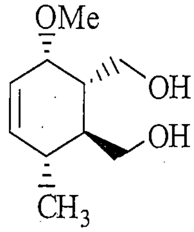
Major product A formed in the given react is

(a)  (b)  (c)  (d) 

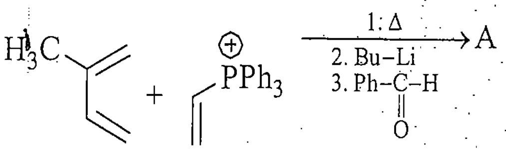
Impo.

15. 

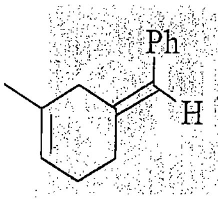
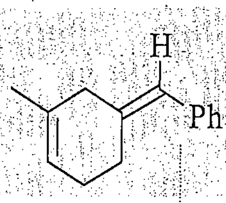
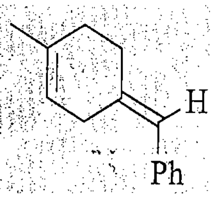
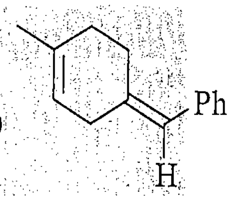
Major product A formed in the given reaction is

(a)  (b)  (c)  (d) 

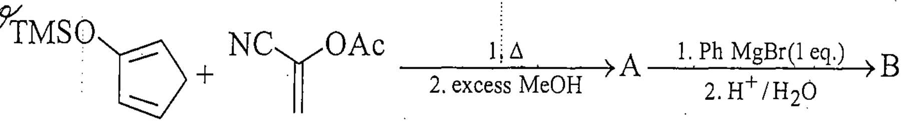
Impo.

16. 

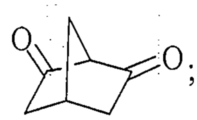
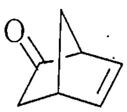
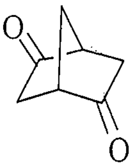
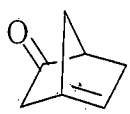
Major product A formed in the given reaction is

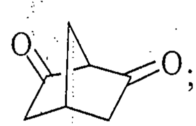
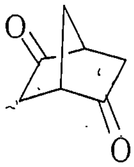
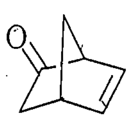
(a)  (b)  (c)  (d) 

check once.

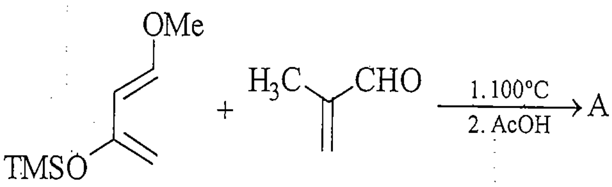
17. 

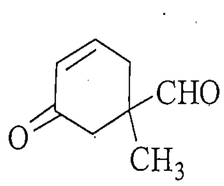
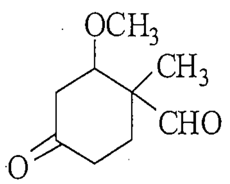
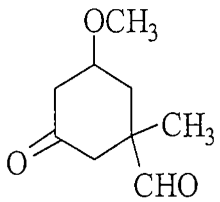
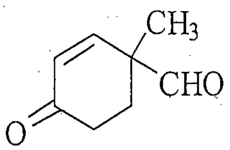
Major product A and B in the following reaction

(a) A = ; B =  (b) A = ; B = 

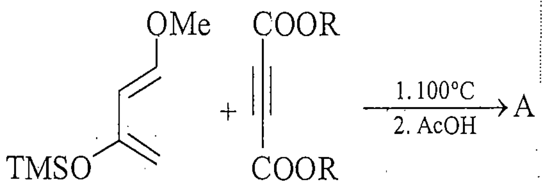
(c) A = ; B =  (d) A = ; B = 

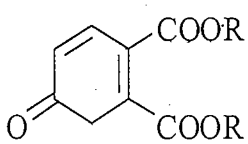
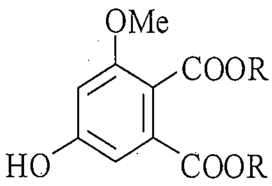
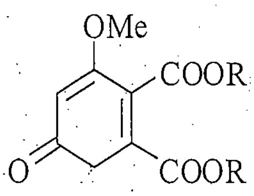
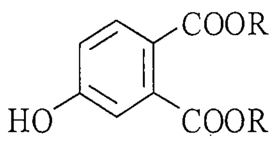
18. Major product formed in the following reaction is



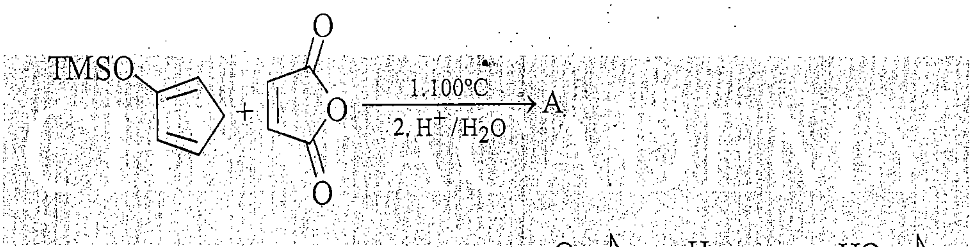
(a)  (b)  (c)  (d) 

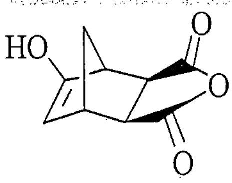
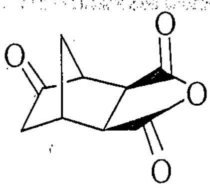
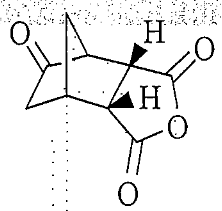
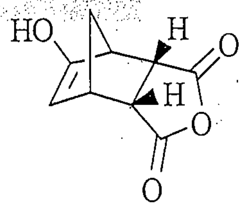
19. Major product formed in the following reaction is



(a)  (b)  (c)  (d) 

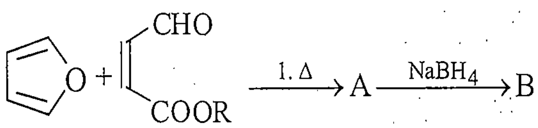
20. Major product A formed in the given reaction

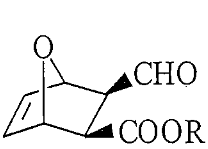
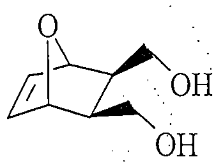


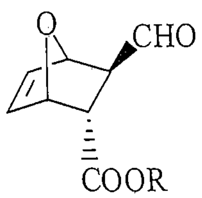
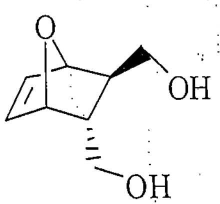
(a)  (b)  (c)  (d) 

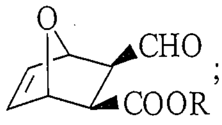
Good

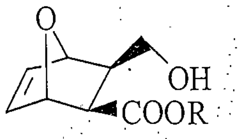
21. Major product formed during the given reaction is

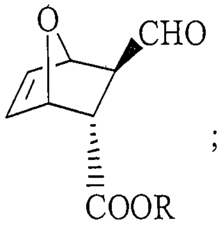


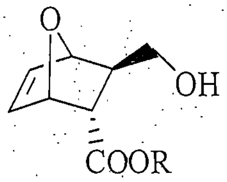
(a) A =  ; B = 

(b) A =  ; B = 

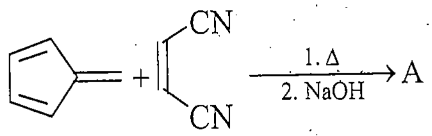
(c) A = 

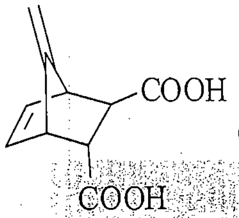
; B = 

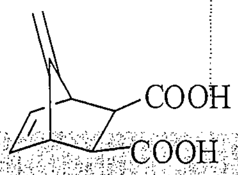
(d) A = 

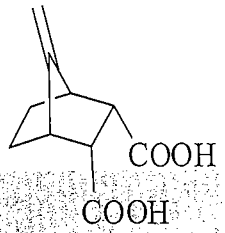
; B = 

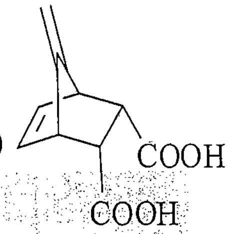
22. Major product formed during the given reaction is



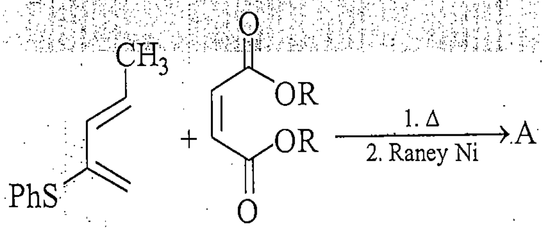
(a) 

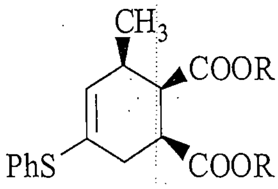
(b) 

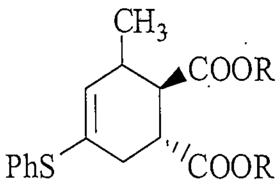
(c) 

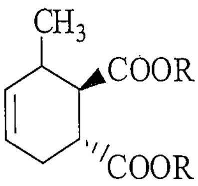
(d) 

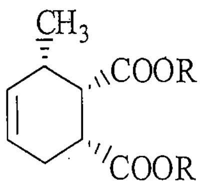
23. Product A in the given reaction is



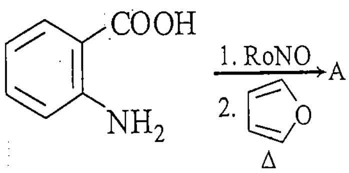
(a) 

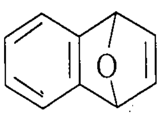
(b) 

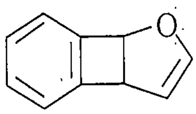
(c) 

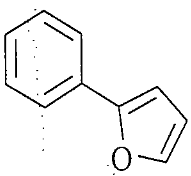
(d) 

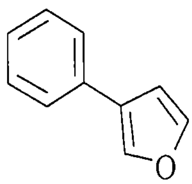
24. Major product A formed in the given reaction is



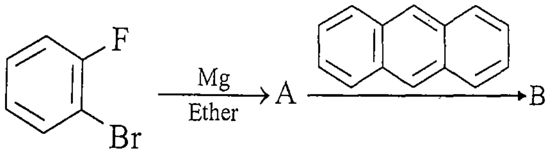
(a) 

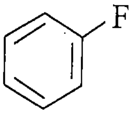
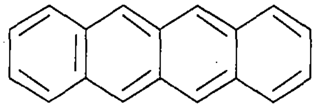
(b) 

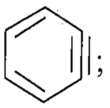
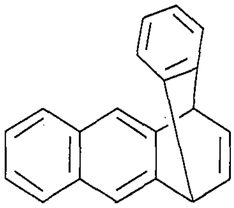
(c) 

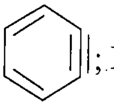
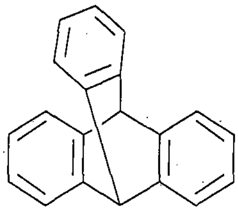
(d) 

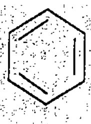
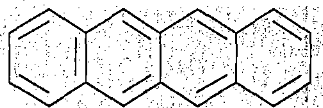
25. Major product formed in the given reaction is



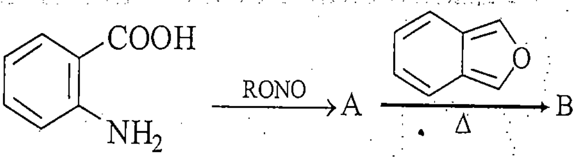
(a) A =  ; B = 

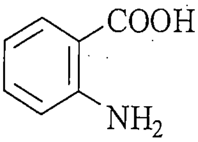
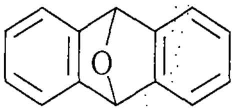
(b) A =  ; B = 

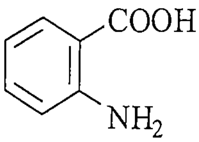
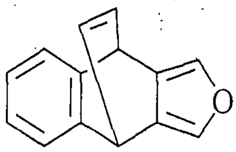
(c) A =  ; B = 

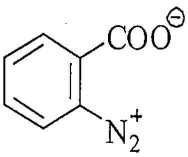
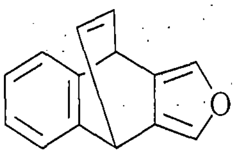
(d) A =  ; B = 

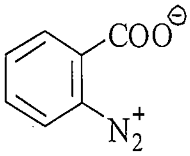
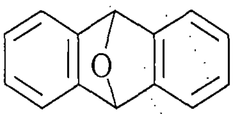
26. Major product A formed in the given reaction is



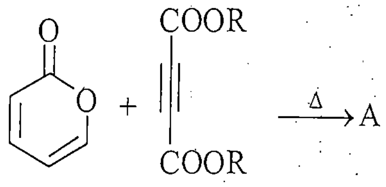
(a) A =  ; B = 

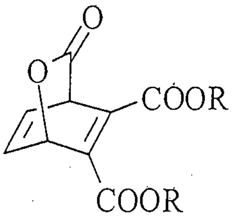
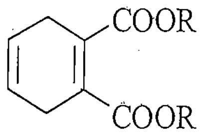
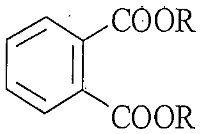
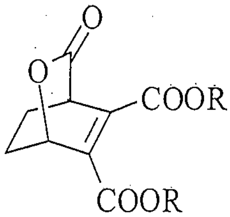
(b) A =  ; B = 

(c) A =  ; B = 

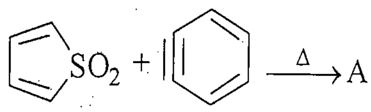
(d) A =  ; B = 

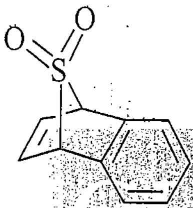
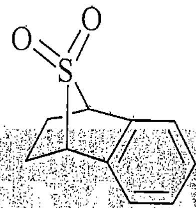
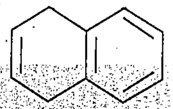
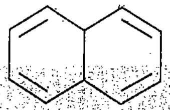
27. Major product formed in the following reaction is



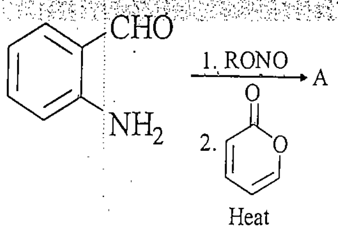
(a)  (b)  (c)  (d) 

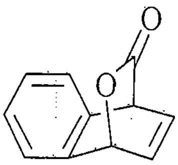
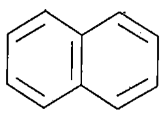
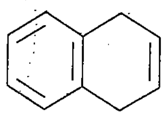
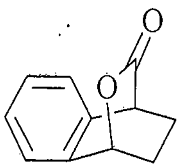
28. Major product formed



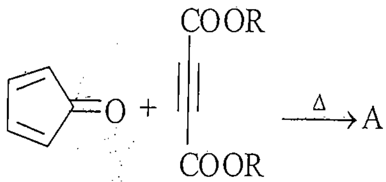
(a)  (b)  (c)  (d) 

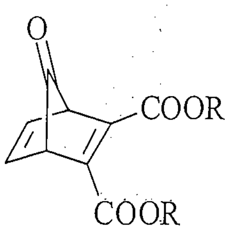
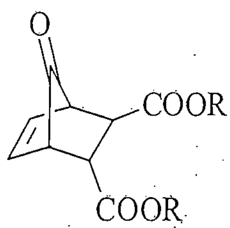
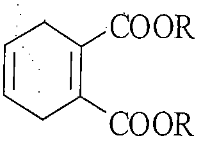
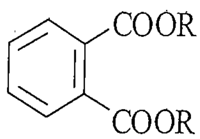
29. Major product A formed



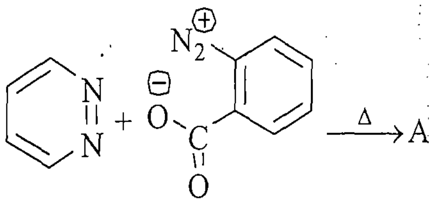
(a)  (b)  (c)  (d) 

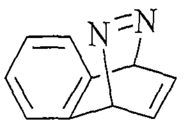
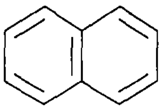
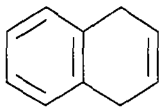
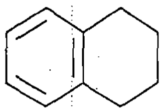
30. Major Product



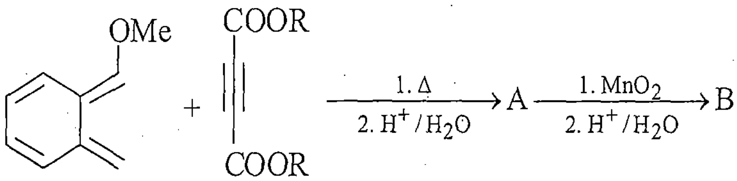
(a)  (b)  (c)  (d) 

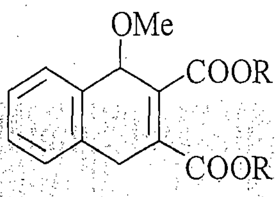
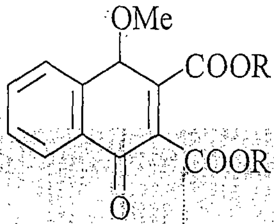
31. Major product

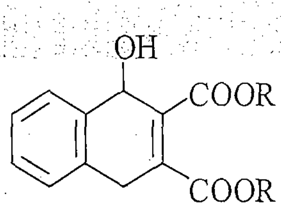
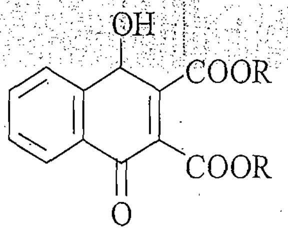


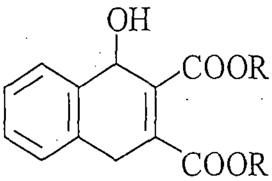
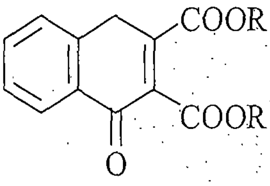
(a)  (b)  (c)  (d) 

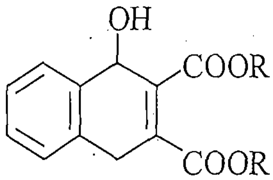
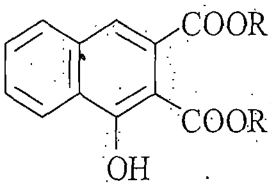
32. Major Product

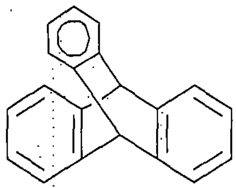


(a) A =  ; B = 

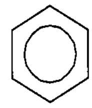
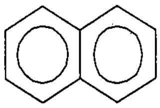
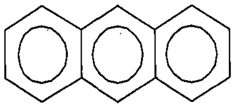
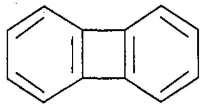
(b) A =  ; B = 

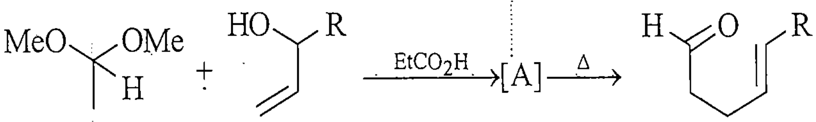
(c) A =  ; B = 

(d) A =  ; B = 

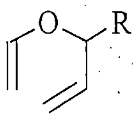
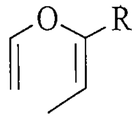
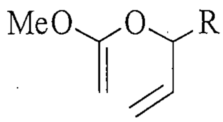
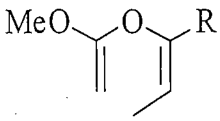
33. Anthranilic acid $\xrightarrow{\text{RONO}}$ [Intermediate] $\xrightarrow{\text{A}}$ 

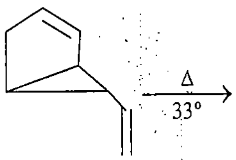
In the above reaction, the species involved A is

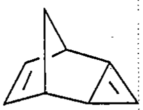
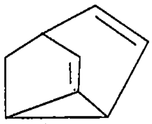
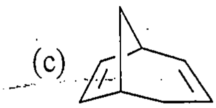
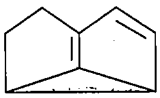
(a)  (b)  (c)  (d) 

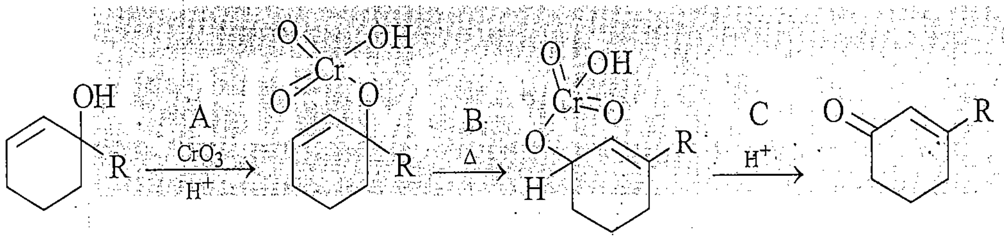
34. 

The intermediate A is

(a)  (b)  (c)  (d) 

35. 

(a)  (b)  (c)  (d) 

36. 

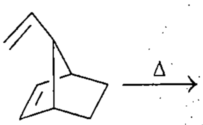
In the above reaction, Step B proceeds through a

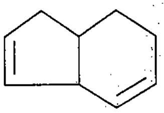
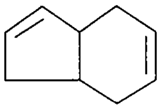
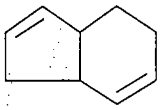
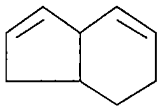
(a) [1, 3]-sigmatropic rearrangement

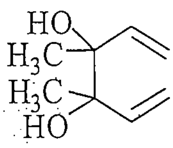
(b) [2, 3]-sigmatropic rearrangement

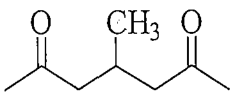
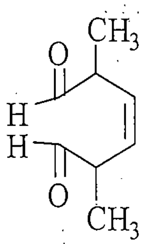
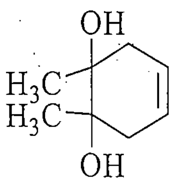
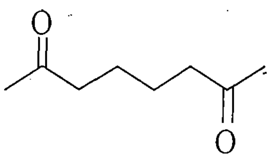
(c) [3, 3]-sigmatropic rearrangement

(d) [3, 5]-sigmatropic rearrangement

37. 

(a)  (b)  (c)  (d) 

38. On heating  rearranges to give

(a)  (b)  (c)  (d) 

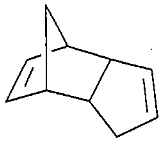
39. The major product formed in Diels-alder reaction is endo-adduct. This is due to

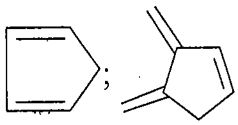
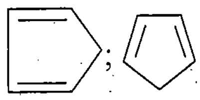
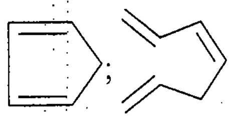
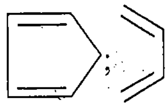
(a) Higher stability of the product

(b) Faster formation constant of the endo product

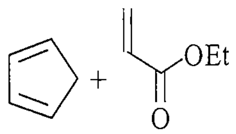
(c) Steric hindrance

(d) Secondary orbital interactions between a diene and a dienophile

40. For the synthesis of  using diels-alder reaction, the reactants required are

(a)  (b)  (c)  (d) 

41. In the given reaction:



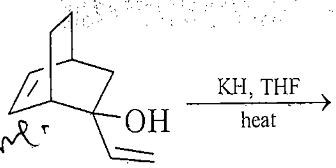
the interacting frontier orbitals are:

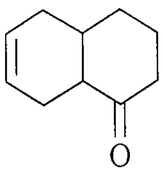
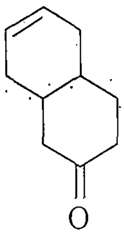
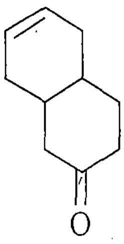
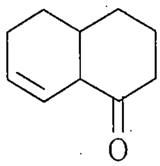
(a) HOMO of a Diene and LUMO of a dienophile

(b) HOMO of a Dienophile and LUMO of a diene

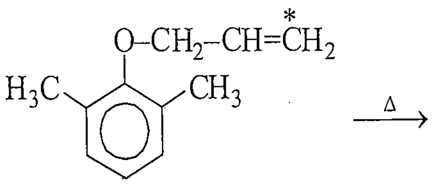
(c) HOMO of a diene and HOMO of a dienophile

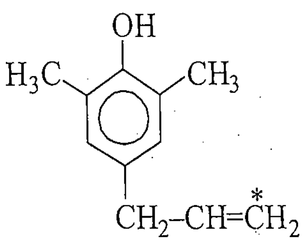
(d) LUMO of a diene and LUMO of a dienophile

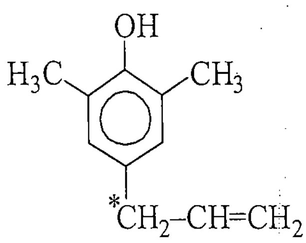
42. 

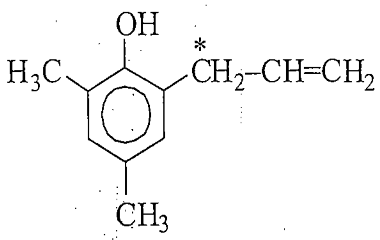
(a)  (b)  (c)  (d) 

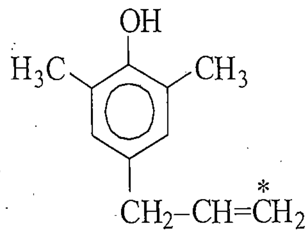
a/d

43. 

(a) 

(b) 

(c) 

(d) 

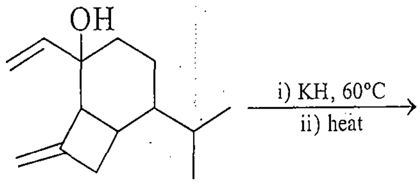
44. Which of the following statement about sigmatropic rearrangements is false?

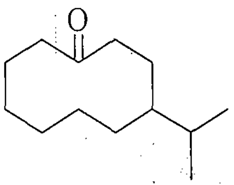
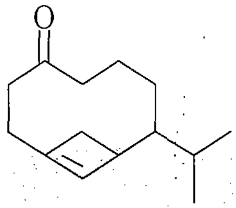
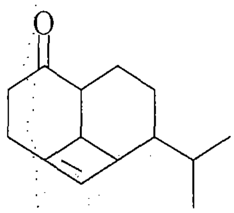
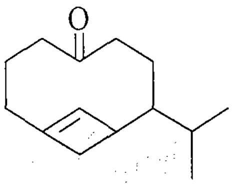
(a) Concerted intermolecular rearrangements

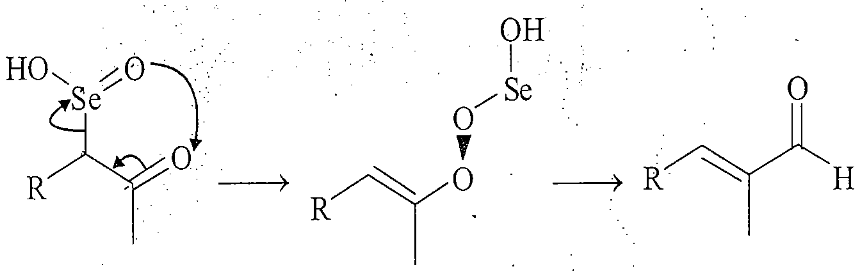
(b) In these an atom (or a group of atoms) shifts from one position to another.

(c) Involves breaking of a bond and formation of a new bond.

(d) All of the above

45. 

(a)  (b)  (c)  (d) 

46. 

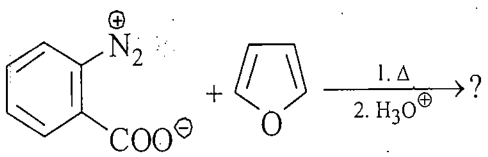
The above reaction proceeds through a

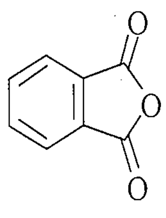
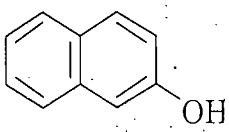
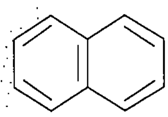
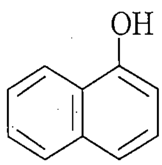
(a) [1, 3]-sigmatropic rearrangement

(b) [2, 3]-sigmatropic rearrangement

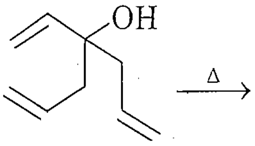
(c) [3, 3]-sigmatropic rearrangement

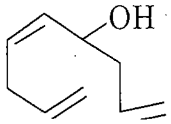
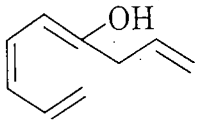
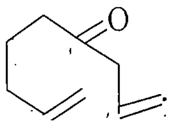
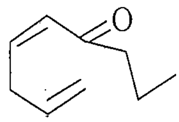
(d) [3, 5]-sigmatropic rearrangement

47. 

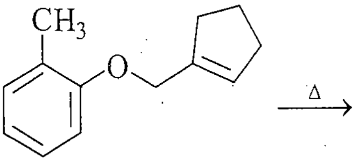
(a)  (b)  (c)  (d) 

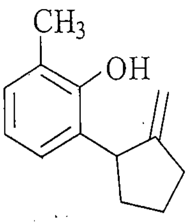
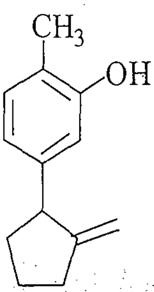
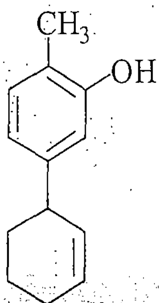
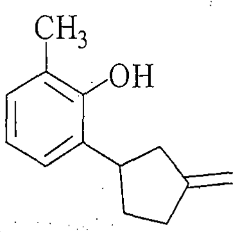
48. Give the product of the reaction



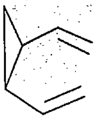
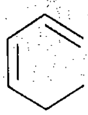
(a)  (b)  (c)  (d) 

49. Give the product of the reaction

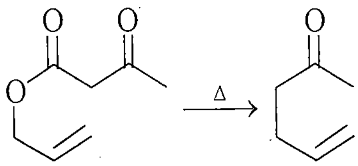


(a)  (b)  (c)  (d) 

50. Which of the following reactants do not undergoes cope rearrangement?

(a)  (b)  (c)  (d) 

51. The following reaction involves

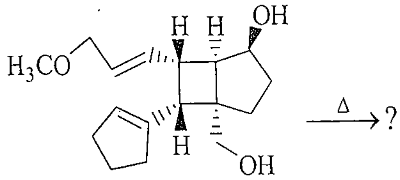


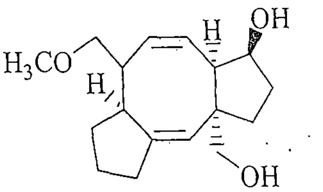
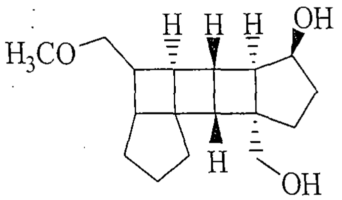
(a) Keto-enol tautomerism, [3, 3] sigmatropic rearrangement & decarboxylation

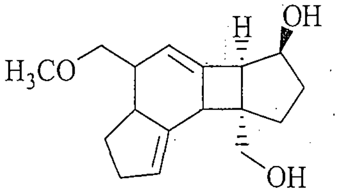
(b) Ketoenol tautomerism followed by electrocyclisation and decarbonylation.

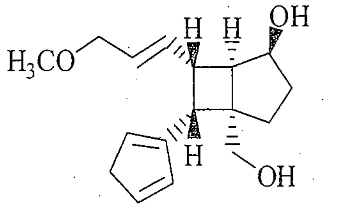
(c) [3, 3] sigmatropic rearrangement & decarboxylation

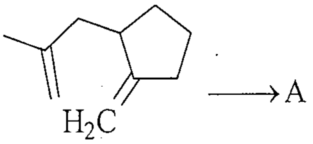
(d) Keto-enol tautomerism followed by cope rearrangement & de carboxylation.

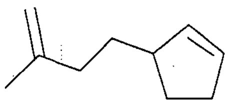
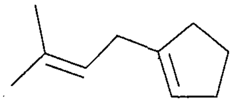
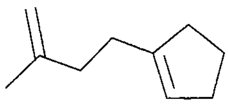
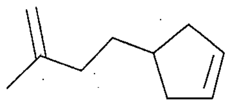
52. 

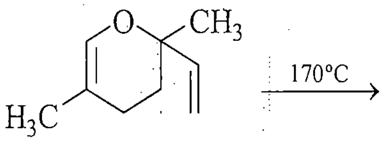
(a)  (b) 

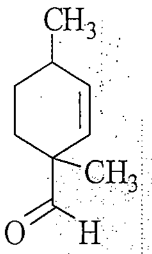
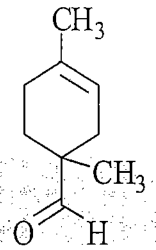
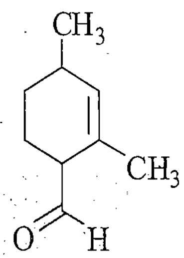
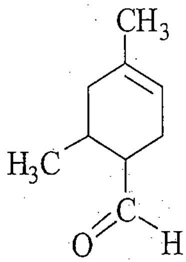
(c) 

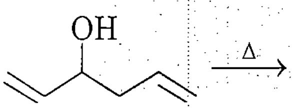
(d) 

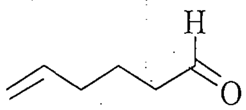
53. 

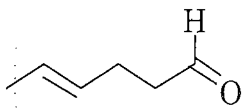
(a)  (b)  (c)  (d) 

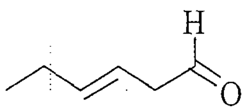
54. 

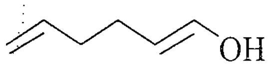
(a)  (b)  (c)  (d) 

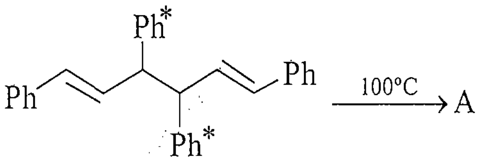
55. 

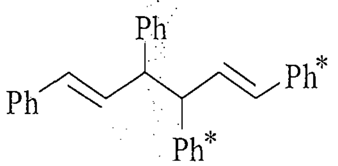
(a) 

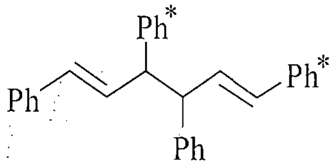
(b) 

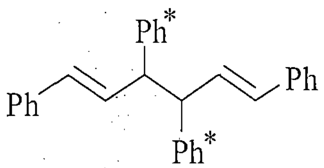
(c) 

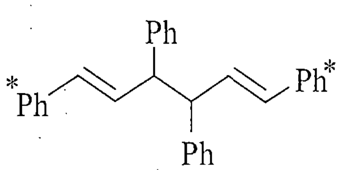
(d) 

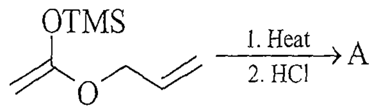
56. 

(a) 

(b) 

(c) 

(d) 

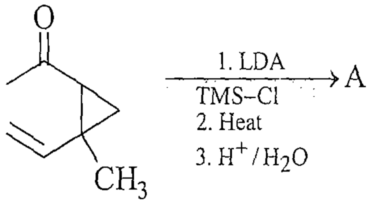
57. 

(a) $HO-\overset{O}{\overset{\|}{C}}-CH_2-CH=CH-CH_3$

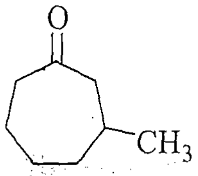
(b) $HO-\overset{O}{\overset{\|}{C}}-CH=CH-CH_2-CH_3$

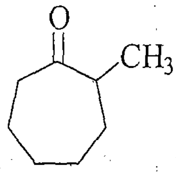
(c) $HO-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH=CH_2$

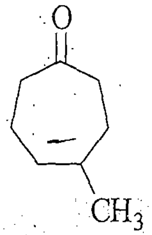
(d) $TMSO-\overset{O}{\overset{\|}{C}}-CH_2-CH=CH-CH_3$

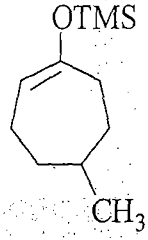
58. 

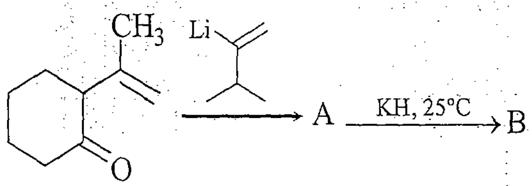
Check

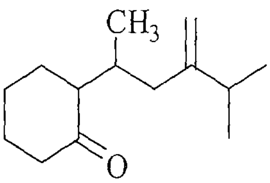
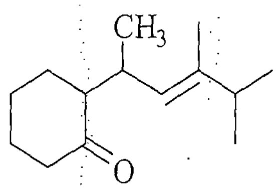
(a) 

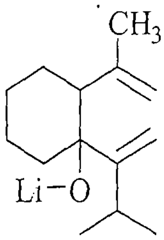
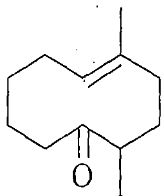
(b) 

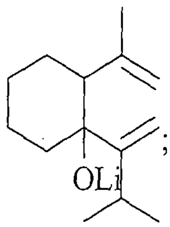
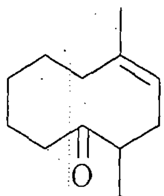
(c) 

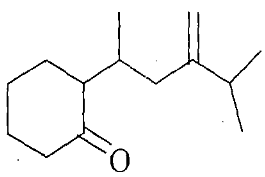
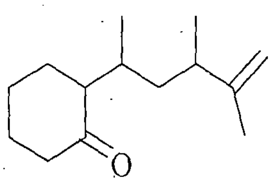
(d) 

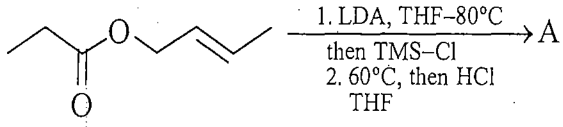
59. 

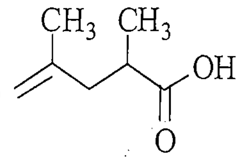
(a) A =  ; B = 

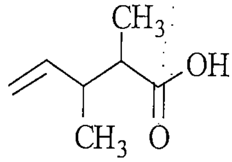
(b) A =  ; B = 

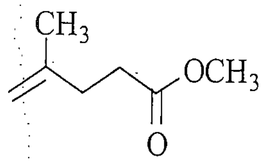
(c) A =  ; B = 

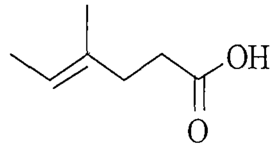
(d) A =  ; B = 

60. 

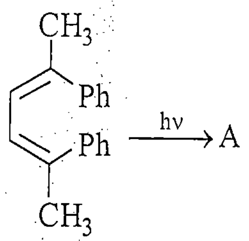
(a) 

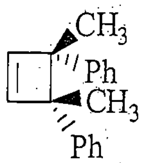
(b) 

(c) 

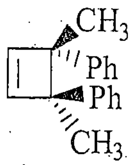
(d) 

61. Major product formed in the given reaction and mode of rotation is

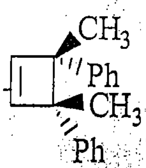


(a) 

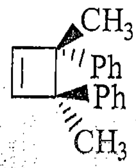
; conrotatory

(b) 

; Conrotatory

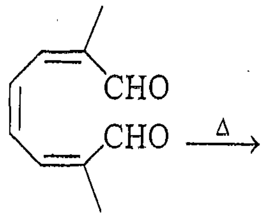
(c) 

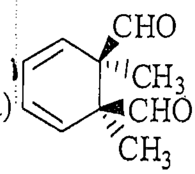
; Disrotatory

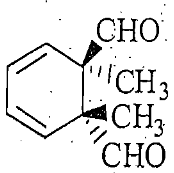
(b) 

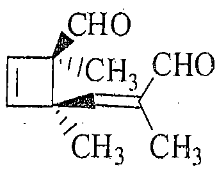
; Disrotatory

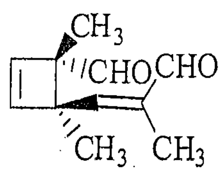
62. Major product formed in the following reaction is

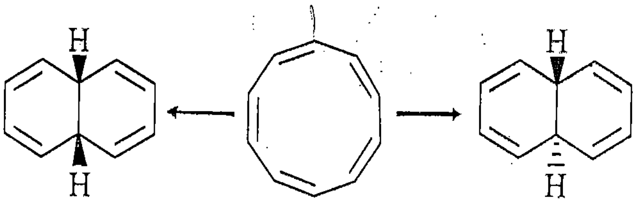


(a) 

(b) 

(c) 

(d) 

63. 

(A) (B)

Correct statement about formation of A and B are

(1) Product A formed in presence of ($h\nu$ – con)

(2) Product B formed in presence of (Δ – dis)

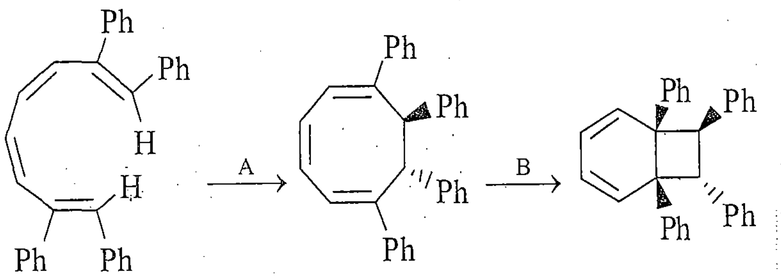
(imp.) Check cover of P.S. KALSi – CSIR NET eligibility

(3) Product A formed in presence of (Δ – dis)

(4) Product B formed in presence of ($h\nu$ – con)

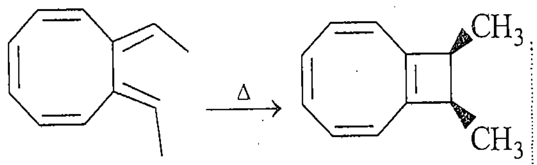
(a) 1 and 2 (b) 2 and 3 (c) 3 and 4 (d) 1 and 4

64. The condition A – B required for the following pericyclic reaction are



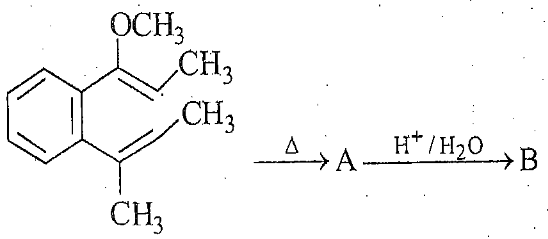
(a) A – Δ, B – $h\nu$ (b) A – $h\nu$, B – $h\nu$ (c) A – $h\nu$, B – Δ (d) A – Δ, B – Δ

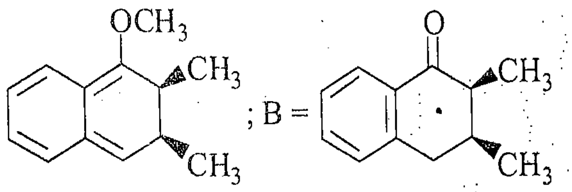
65. The number of π electrons participating and the pericyclic mode in the following reaction are

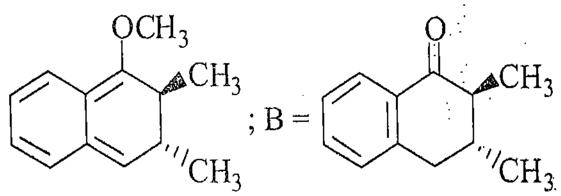


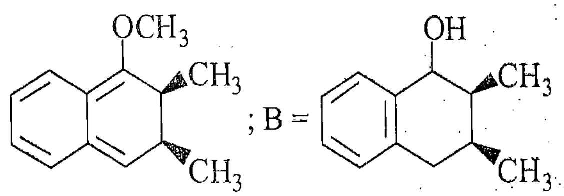
(a) 4 and con (b) 10 and con (c) 4 and dis (d) 10 and dis

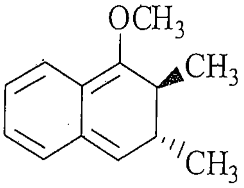
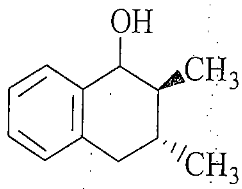
66. The major products A and B in the following reaction sequences are:



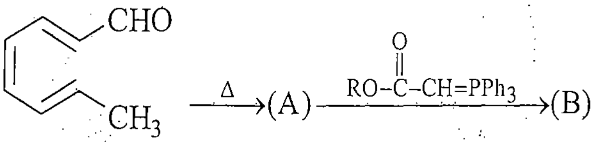
(a) A = 

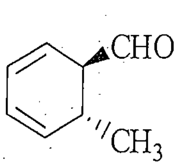
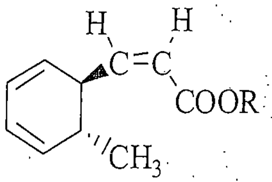
(b) A = 

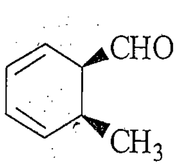
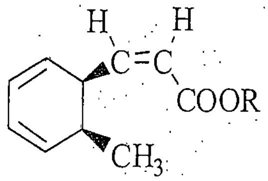
(c) A = 

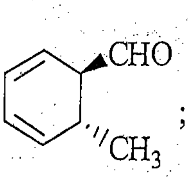
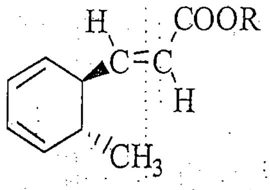
(d) A =  ; B = 

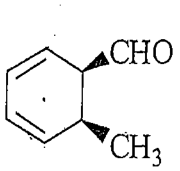
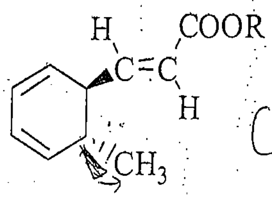
67. Major product A and B in the following reaction sequence is

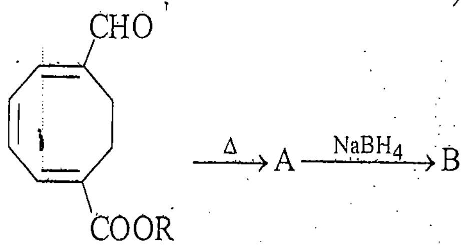


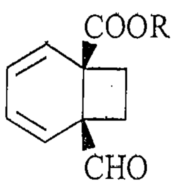
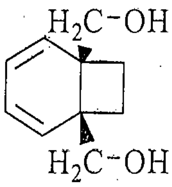
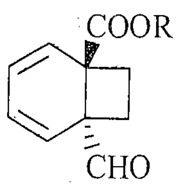
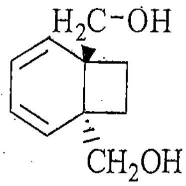
(a) A =  ; B = 

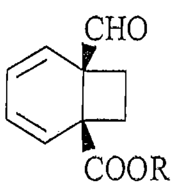
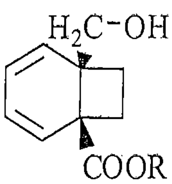
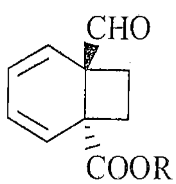
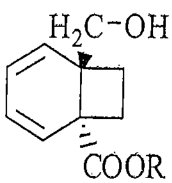
(b) A =  ; B = 

(c) A =  ; B = 

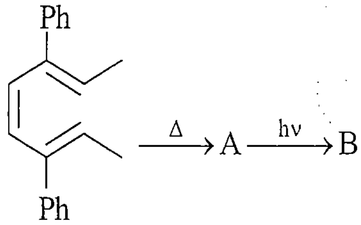
(d) A =  ; B = 

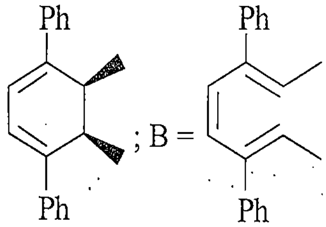
68. 

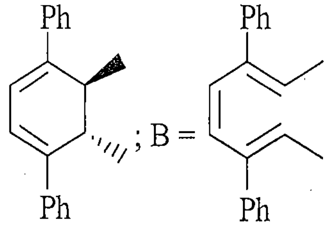
(a) A =  ; B = 
(b) A =  ; B = 

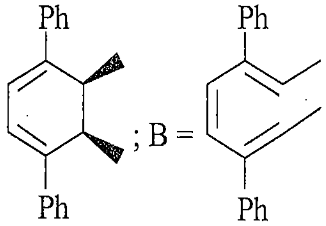
(c) A =  ; B = 
(d) A =  ; B = 

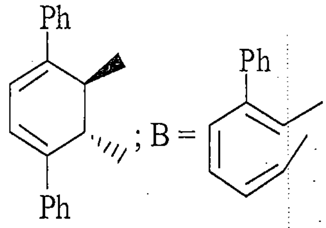
69. The major product formed during given reaction is



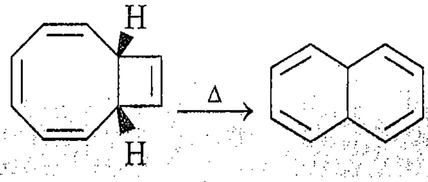
(a) A = ; B = 

(b) A = ; B = 

(c) A = ; B = 

(d) A = ; B = 

70. The following transformation proceeds through two consecutive electrocyclic process, which are

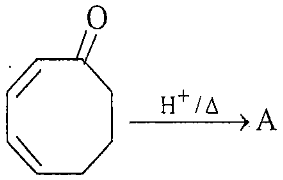


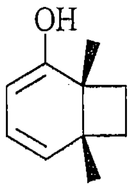
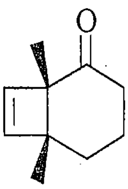
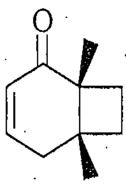
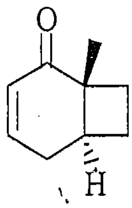
(a) 4π con-rotatory and 6π con-rotatory (b) 4π Dis-rotatory and 6π con-rotatory

(c) 4π con-rotatory and 6π Dis-rotatory (d) 4π Dis-rotatory and 6π Dis-rotatory

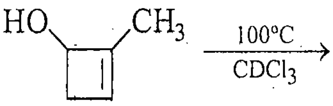
71. Major product A formed during the given reaction is

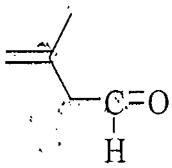
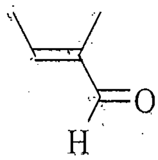
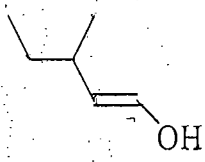
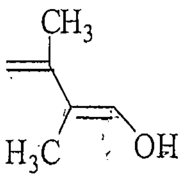
Check,

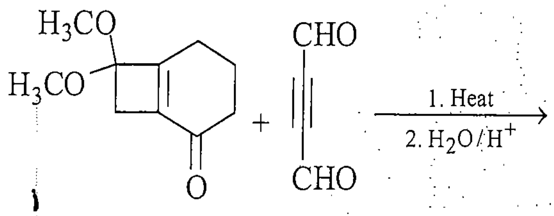


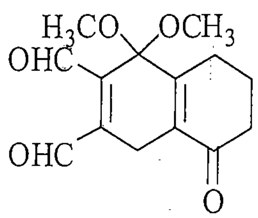
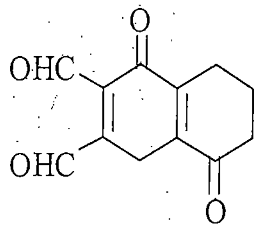
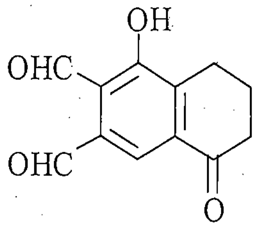
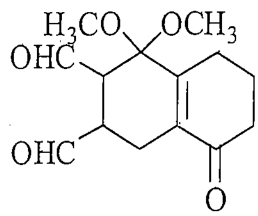
(a)  (b)  (c)  (d) 

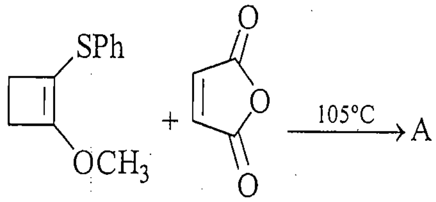
Check, new double protonation

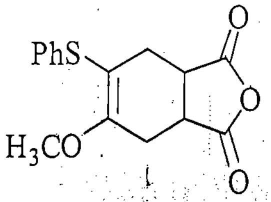
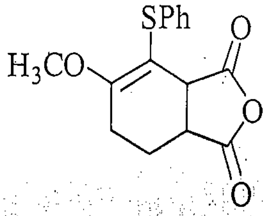
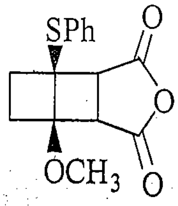
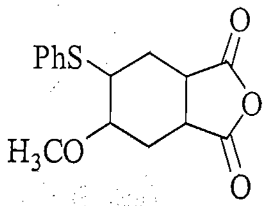
72. 

(a)  (b)  (c)  (d) 

73. 

(a)  (b)  (c)  (d) 

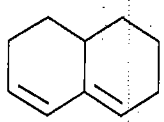
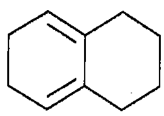
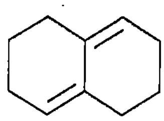
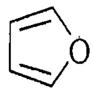
74. 

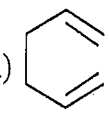
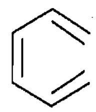
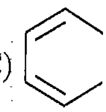
(a)  (b)  (c)  (d) 

EXERCISE - II

One or More Than One Correct Type

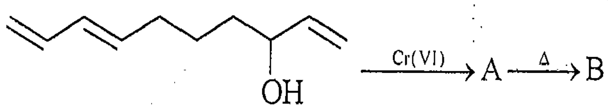
1. Which of the following diene give/given diels-Alder Reaction

(a)  (b)  (c)  (d) 

2. (A)  (B)  (C) 

The true statement for above compound is

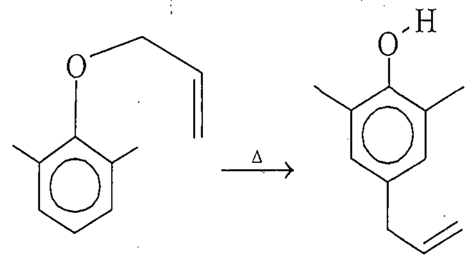
(a) A can gives sigmatropic reaction
(b) B can gives sigmatropic reaction
(c) C can gives diels alder reaction
(d) B can gives electrocyclic reaction

3. 

(a) B has only one π bond
(b) Degree of unsaturation of B is 4
(c) B can give 2, 4-DNP test
(d) Conversion of A to B is Diels Alder reaction

4. Which of the following statement is true
(a) All SN^2 reaction is concerted reaction
(b) Pericyclic reactions are concerted reaction
(c) All pericyclic reaction is SN^2 reaction
(d) All SN^2 is pericyclic reaction

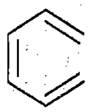
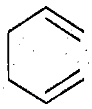
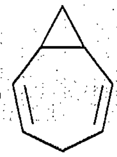
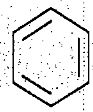
Chap Pericyclic Rxn (Thermal) Modern Physical organic Chemistry By Eric Ansyln Dennis Dougherty

5. 

above reaction involves
(a) Cope rearrangement
(b) Claisen rearrangement
(c) Sigmatropic rearrangement
(d) $\Delta\sigma$ is 0.

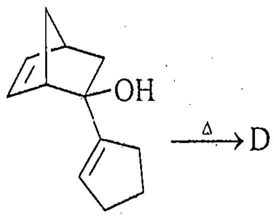
6. The true statement is/are
(a) No. of electrons present in the HOMO of pentadienyl radicals is 1.
(b) No. of Nodes present in the ψ_3^* of allyl free radical is 2.
(c) Reaction of cyclopentadiene with meleic anhydride on heat give endo product majority.
(d) Transition states of Diels Alder reaction is always aromatic.

7. Which of the following is/are degenerate cope rearrangement?

(a)  (b)  (c)  (d) 

EXERCISE - III

Numerical Answer Type

1. 

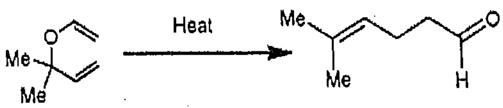
Number of 5 membered rings in the compound D is ______

2. How many nodes are present in the HOMO of 2,4,6-heptatrienyl system.
3. Change in the π bonds takes place when diels alder reaction occurs is_____

EXERCISE - IV

Previous Years Questions

1. The following conversion(s) is/are example(s) of



(a) oxy-Cope rearrangement (b) Sigmatropic rearrangement

(c) Claisen rearrangement (d) Pericyclic reaction

2. The incorrect statement(s) among the following is/are

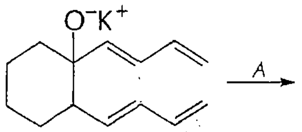
(a) $[4\pi + 2\pi]$ cycloaddition reactions are carried out in presence of light

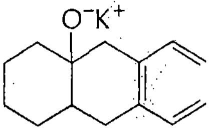
(b) $[2\pi + 2\pi]$ cycloaddition reaction between a keto group and an alkene is photochemically allowed.

(c) $[4\pi + 2\pi]$ cycloaddition reactions are thermally allowed

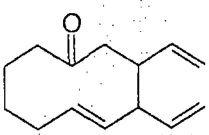
(d) Transoid dienes undergo Diels-alder reactions

3. The product formed and the process involved in the following reaction are

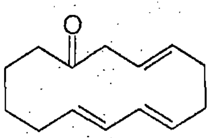


(a) 

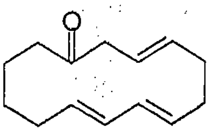
; [3, 3] sigmatropic rearrangement

(b) 

; [1, 3] sigmatropic rearrangement

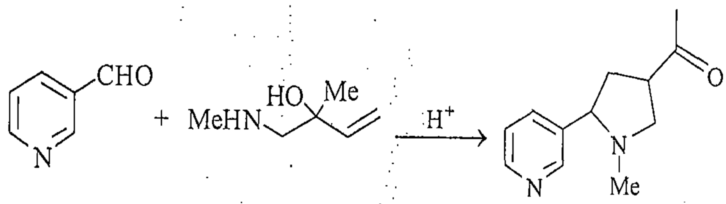
(c) 

; [5, 5]-sigmatropic rearrangement

(d) 

; [1, 5] sigmatropic rearrangement

4. The following transformation involves



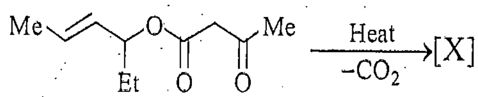
(a) an iminium ion, [3,3]-sigmatropic shift and Mannich reaction.

(b) a nitrenium ion, [3,3]-sigmatropic shift and Michael reaction.

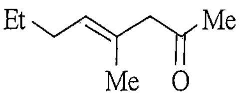
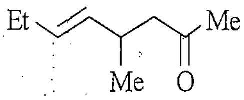
(c) an iminium ion, [1,3]-sigmatropic shift and Mannich reaction.

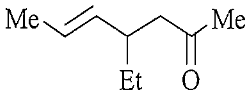
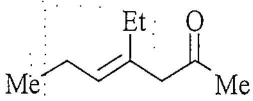
(d) a nitrenium ion [1,3]-sigmatropic shift and Michael reaction.

5. In the following reaction,

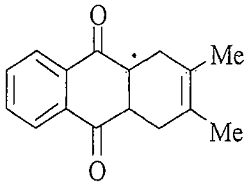


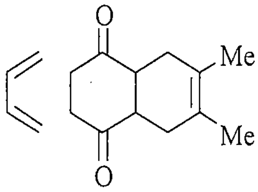
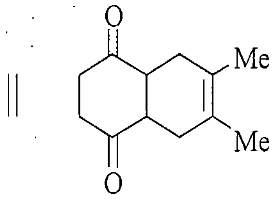
the major product [X] is,

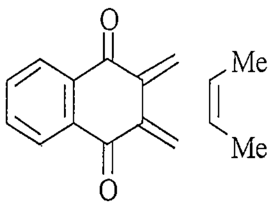
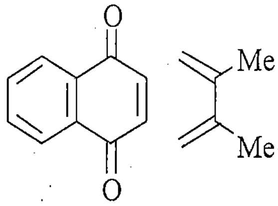
(a) 
(b) 

(c) 
(d) 

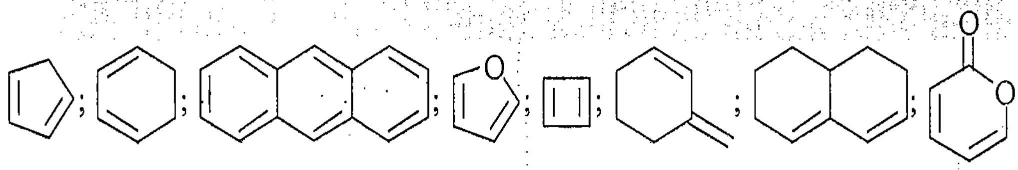
6. The most appropriate materials for one step synthesis of the compound (I) are



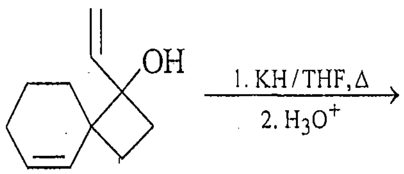
(a) 
(b) 

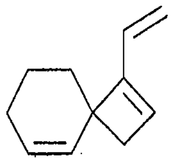
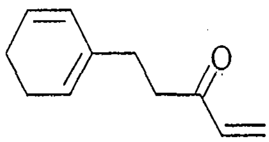
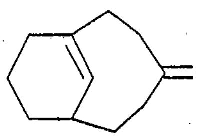
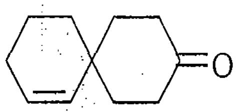
(c) 
(d) 

7. Among the following, the number of compounds, which can participate as 'diene' component in a Diels-Alder reaction is ____.

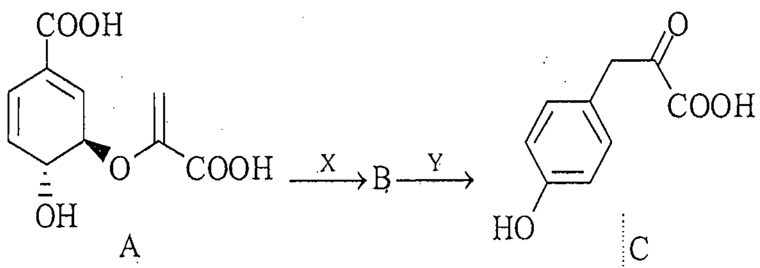


8. The major product formed in the following reaction is



(a) 
(b) 
(c) 
(d) 

9. With respect to the following biogenetic convertion of chorismic acid (A) to 4-hydroxyphenylpyruvic acid (C), the correct statement is



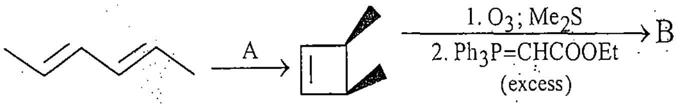
(a) X is Claisen rearrangement; Y is oxidative decarboxylation

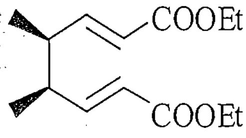
(b) X is Fries rearrangement; Y is oxidative decarboxylation

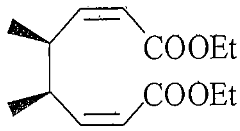
(c) X is Fries rearrangement; Y is dehydration

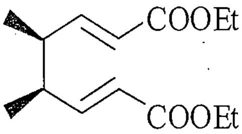
(d) X is Claisen rearrangement; Y is dehydration

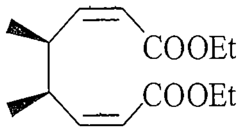
10. Predict the condition A and the structure of the major product B in the following sequence



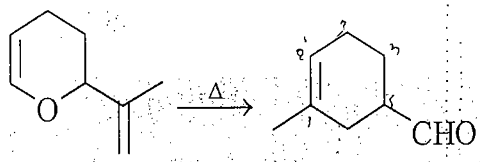
(a) A is $h\nu$ B is 

(b) A is $h\nu$ B is 

(c) A is ΔB is 

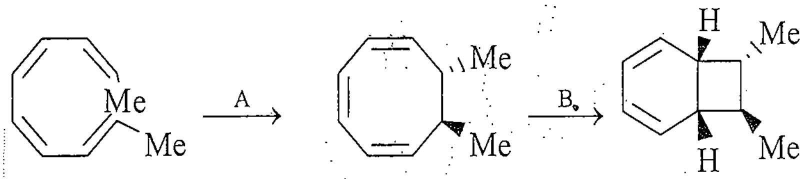
(d) A is ΔB is 

11. The following reaction proceeds through a



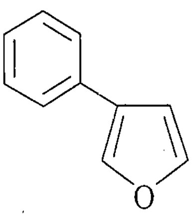
(a) 1, 3-sigmatropic rearrangement
(b) 2, 3-sigmatropic rearrangement
(c) 3, 3-sigmatropic rearrangement
(d) 3, 5-sigmatropic rearrangement

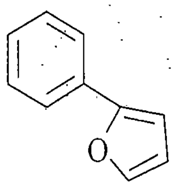
12. The conditions A-B, required for the following pericyclic reactions are

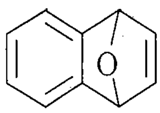


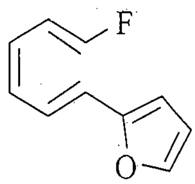
(a) $A-\Delta; B-\Delta$ (b) $A-h\nu; B-\Delta$ (c) $A-h\nu; B-h\nu$ (d) $A-\Delta; B-h\nu$

13. The reaction of 1-bromo-2-fluorobenzene with furan in the presence of one equivalent of Mg gives

(a) 

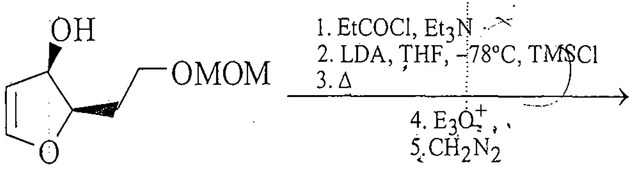
(b) 

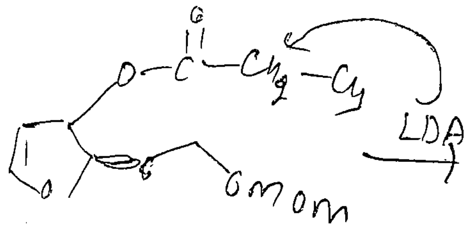
(c) 

(d) 

Smpoo

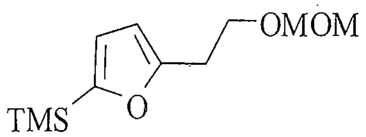
14. The major product formed in the following reaction sequence is

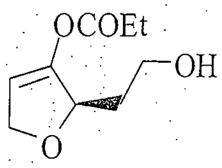


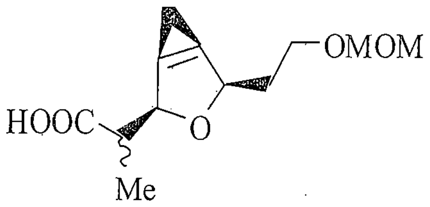


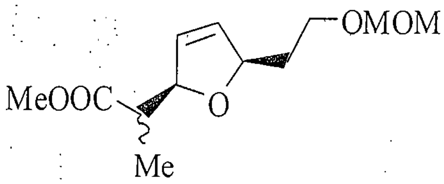
The process with

(3,3) - Sigmatropic

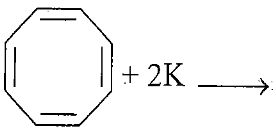
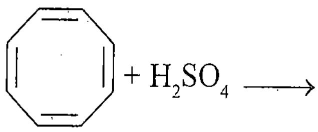
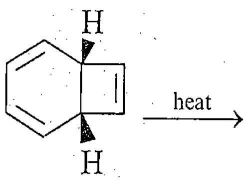
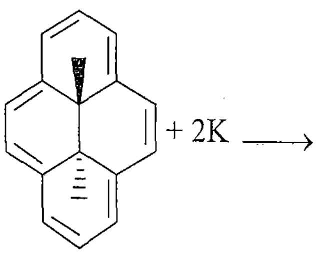
(a) 

(b) 

(c) 

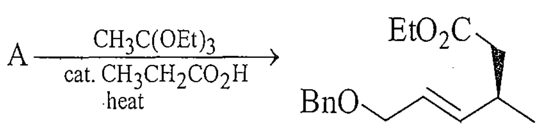
(d) 

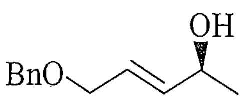
15. Correct match for the products of the reactions in column A with the properties in column B is

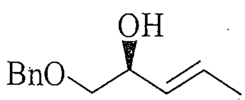
Column A	Column B
(i) 	P. aromatic
(ii) 	Q. antiaromatic
(iii) 	R. non-aromatic
(iv) 	S. homoaromatic

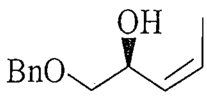
(a) i-P, ii-S, iii-R, iv-Q
(b) i-P, ii-R, iii-Q, iv-S
(c) i-Q, ii-R, iii-S; iv-P
(d) i-S, ii-Q, iii-R, iv-P

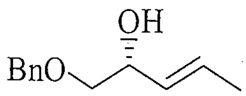
16. The correct starting compound A in the following reaction is



(a) 

(b) 

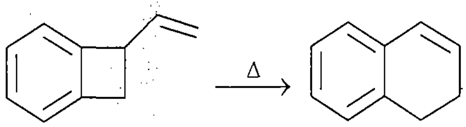
(c) 

(d) 

Hint resonatic structure.

most imp

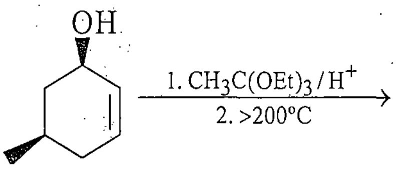
17. The following transformation proceeds through two consecutive electrocyclic processes, which are

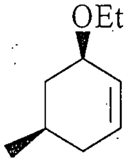


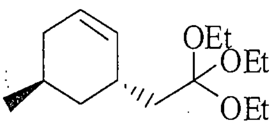
(a) 4π conrotatory and 6π conrotatory (b) 4π disrotatory and 6π conrotatory

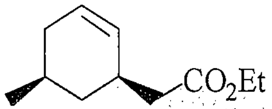
(c) 4π conrotatory and 6π disrotatory (d) 4π disrotatory and 6π disrotatory

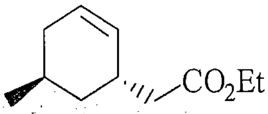
18. The major product formed in the following reaction is



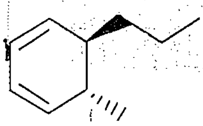
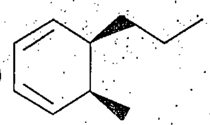
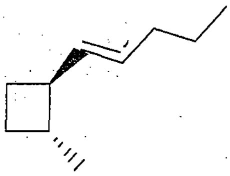
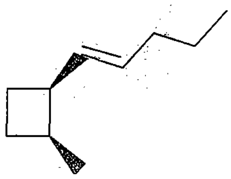
(a) 

(b) 

(c) 

(d) 

19. The major product formed by photochemical reaction of (2E, 4Z, 6E)-decatriene is

(a)  (b)  (c)  (d) 

ANSWER KEY

EXERCISE - I

1. d	2. c	3. b	4. c	5. d	6. d	7. b
8. d	9. d	10. d	11. a	12. c	13. d	14. d
15. d	16. c	17. d	18. d	19. d	20. c	21. c
22. b	23. d	24. a	25. c	26. d	27. c	28. d
29. b	30. d	31. b	32. d	33. c	34. a	35. c
36. c	37. c	38. d	39. d	40. b	41. a	42. b
43. a	44. a	45. d	46. b	47. d	48. c	49. a
50. d	51. a	52. a	53. c	54. b	55. a	56. d
57. c	58. c	59. b	60. b	61. c	62. a	63. c
64. d	65. a	66. b	67. d	68. c	69. c	70. c
71. c	72. b	73. c	74. a			

EXERCISE - II

1. b,d	2. a,c,d	3. b,c,d	4. a,b	5. a,b,c,d	6. a,b,c,d	7. b,c

EXERCISE - III

1. 2	2. 2	3. 2

EXERCISE - IV

1. b,c,d	2. a,d	3. c	4. a	5. b	6. d	7. 6
8. c	9. a	10. a	11. c	12. b	13. c	14. d
15. a	16. b	17. c	18. c	19. a		

CHAPTER 8

Biomolecules & Natural Products

CARBOHYDRATES

1. Introduction

Carbohydrates are derived from their general formula $C_x(H_2O)_y$ structurally, they are polyhydroxy aldehydes or ketones that exist primarily in cyclic hemiacetal or acetal forms.

(A) Classification

Carbohydrates

monosaccharides | Oligosaccharides | Polysaccharides

Monosaccharide

A carbohydrate that cannot be hydrolyzed to a simpler structure.

Disaccharide

A carbohydrate that can be hydrolyzed to two monosaccharide molecules, not necessarily the same.

Example : $\underset{\text{one mole}}{\text{Maltose}} \xrightarrow[H_2O]{H_3O^+} \underset{\text{two moles}}{\text{Glucose}}$

Oligosaccharide

A carbohydrate that can be hydrolyzed to a small number (up to 10) of monosaccharide molecules, sometimes of three or more types.

Polysaccharide

A carbohydrate that can be hydrolyzed to a large number of monosaccharide molecules, often of three or more types.

$$\underset{\text{a polymeric molecule}}{\text{Starch}} \xrightarrow[H_2O]{H_3O^+} \underset{\text{many moles}}{\text{Glucose}}$$

Aldose A carbohydrate that contains an aldehyde group

Ketose A carbohydrate that contains a ketone group

Triose A carbohydrate having three carbons

Tetrose A carbohydrate having four carbons

Aldopentose A five-carbon carbohydrate that contains an aldehyde group

Ketohexose A six-carbon carbohydrate that contains a ketone group

D-Glucose (an aldohexose and the most abundant monosaccharide) is oxidized by enzymes in the first step of a process that produces energy at the cellular level :

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{Energy}$

glucose

Excess glucose is stored ~~in anim~~als as a polymer called glycogen. Plants convert glucose into a storage polymer called starch or into the structural polymer cellulose.

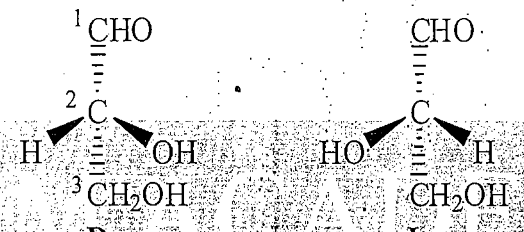
2. (+)-Glucose

Glucose had been obtained from natural sources such as fruits. It is somewhat less sweeter than sucrose (common table sugar). It precipitates as a white solid in two forms: (α mp 146°C, and β, mp 148-155°C). The two froms show different (and unusual) rotatory power, although both are dextrorotatory.

3. D and L conventions

Fischer select the enantiomers of glyceraldehyde as stereochemical references and arbitrarily assigned configurations around the single stereocentre to the dextro- and levorotatory isomers.

D/L assignment subsequetly made by Rosanoff for Fischer's glyceraldehyde reference choices:



D for (+)-isomer L for (–)-isomer

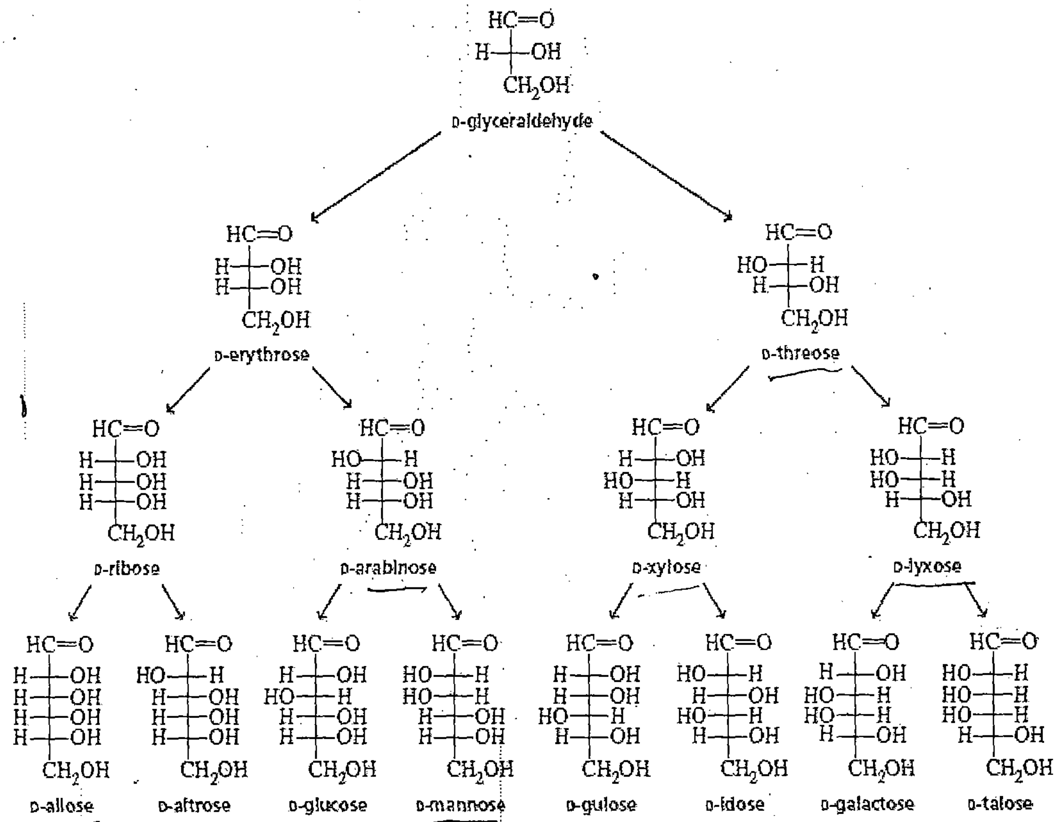
D designation come to mean that the hydroxy group on the highest numbered chiral atom is on the right in a fischer projection, and an L designation that the hydroxyl group there is on the left.

[D/L designations (like (R/S) designations) give no indication about ~~dextro-vs. le~~vorotatory nature.]

In the Cahn-lngold-Prelog convention, the "D" configruations is (R) and the "L" configuration is (S).

The D and L Families of Monosaccharides

The common sugars have chain lengths of 3 to 6 C's though longer ones are known. Using D-(+)-glyceraldehyde as the starting point and adding new chiral HCOH groups adjacent to the carbonyl gives this progression (depicted using original Fischer cross projections) :



4. **Benedict's Fehling's and Tollen's Reagents**

These are classic, mild oxidizing agent used in tests for sugars. Aldehydes and α-hydroxy ketones, inlcuding aldoses and ketoses, give positive tests, whether in open-chain or hemiacetal form.

In the **Tollen's test** the oxidant is $Ag(NH_3)_2^+$, prepared from $AgNO_3$ and aqueous NH_3.

$$\mathrm{R\overset{\displaystyle O}{\overset{\|}{C}}H} \xrightarrow[H_2O]{Ag(NH_3)_2^+} \mathrm{R\overset{\displaystyle O}{\overset{\|}{C}}O^-}\ \text{Ag (as a silver mirror)}$$

$$\mathrm{R\overset{\displaystyle OH}{\overset{|}{C}}H\overset{\displaystyle O}{\overset{\|}{C}}R'} \xrightarrow[H_2O]{Ag(NH_3)_2^+} \mathrm{R\overset{\displaystyle O}{\overset{\|}{C}}—\overset{\displaystyle O}{\overset{\|}{C}}R'}$$

In the **Benedict's test** the alkaline reagent contains a copper citrate complex as oxidant, and in the **Fehling test** the alkaline reagent contains a copper tartrate complex as oxidant. In both cases, a positive test is the appearance of a brick-red Cu_2O precipitate in the blue test solution.

$$Cu^{2+}\ [\text{complexed}] + \underset{\text{aldose}}{\begin{array}{c} CHO \\ | \\ (CHOH)_n \\ | \\ CH_2OH \end{array}} \quad \text{OR} \quad \underset{\text{ketose}}{\begin{array}{c} CH_2OH \\ | \\ C=O \\ | \\ (CHOH)_n \\ | \\ CH_2OH \end{array}} \longrightarrow Cu_2O \downarrow + \text{oxidation products}$$

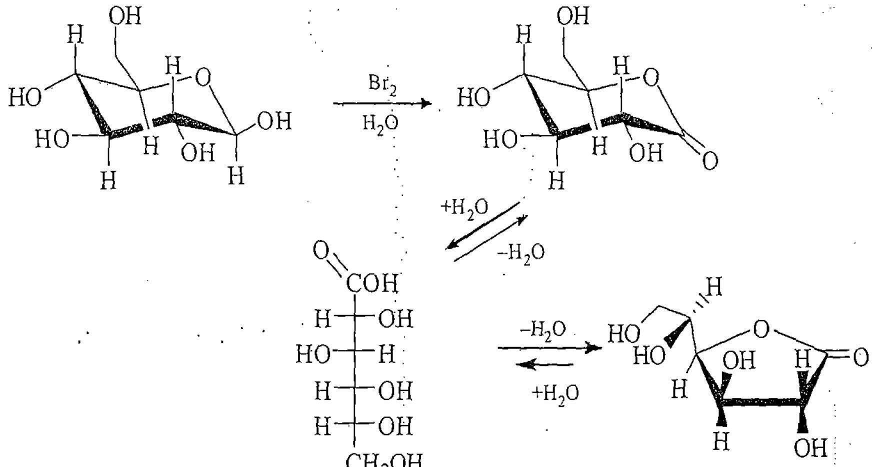
Since these reagents are all alkaline, and since acetals are stable in alkaline media, acetal-type sugars like the typical glyconsides do not react in these oxidation tests. Thus sugars can be classified as reducing or non-reducing.

5. Oxidising Agents in Carbohydrate Chemistry

(a) Bromine Water : The Synthesis of Aldonic Acid

Bromine water (Br_2/H_2O) is mild oxidant that selectively oxidizes aldoses to carboxylic acids called **aldonic acids.**

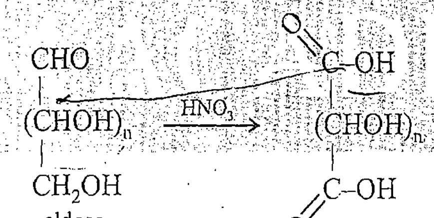
The course of the reaction, in more details, is this :



D-Glucono-γ-lactone [Predominat form of the oxidation product]

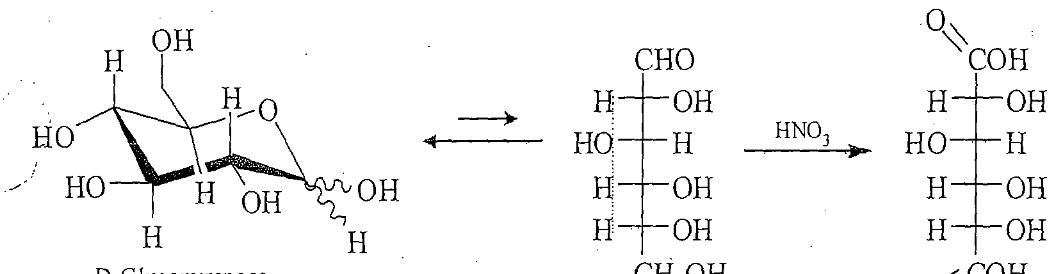
(b) Nitric Acid oxidation : Aldaric Acids

Nitric acid is a strong oxidant that converts aldoses to dicarboxylic acids called **aldaric acids.**



aldose aldaric acid

Like other-hydroxy acids, the aldaric acids readily form lactones by intramolecular esterification. Since esterifications is acid-catalyzed and aldanic acids are prepared using an acidic oxidant, lactones may be involved in the oxidation process.



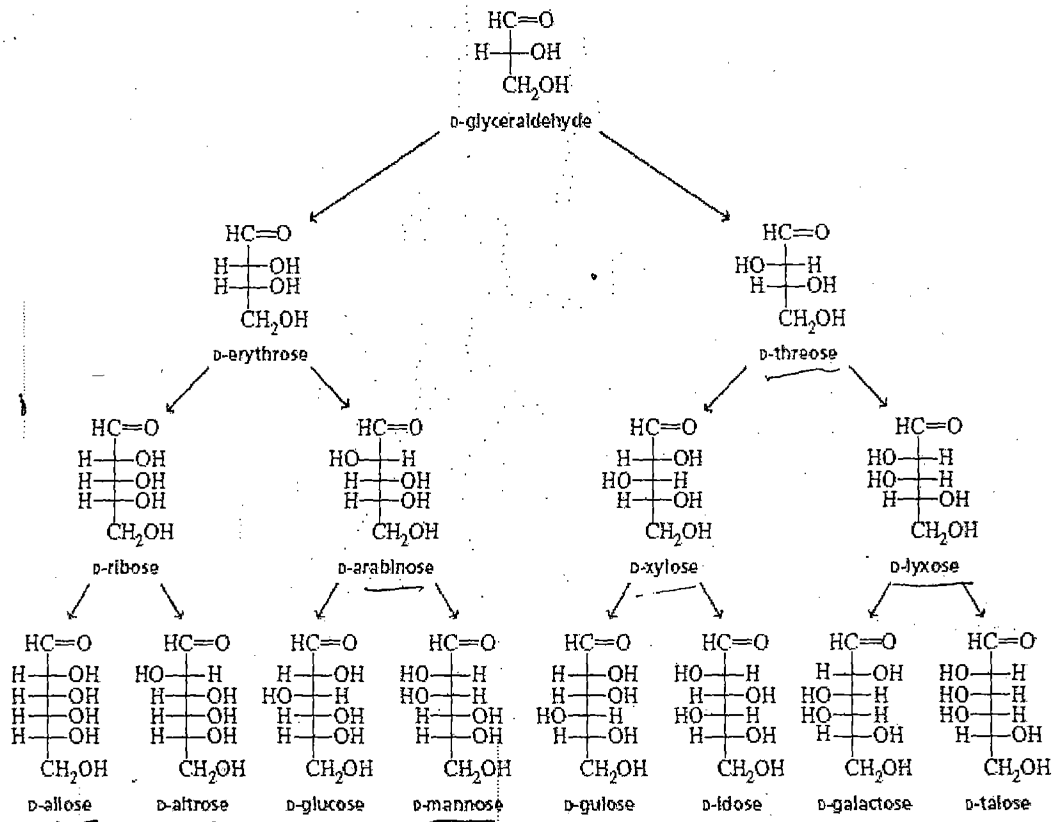
D-Glucopyranose open chain D-glucose D-glucose acid

(c) Periodate Oxidation:

Oxidative Clevage of Polyhydroxy Compounds

Compounds with hydroxy groups or hydroxyl and aldehyde/ketone functions on adjacent carbons undergo oxidative **clevage** reactions with aqueous periodic acid (HIO_4).

The reactions is though to proceed by way of a cyclic periodate intermediate (similar to the cyclic intermediates in syn hydroxylation with permanganate or osmium tetroxide):



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$$RCH(OH)C(=O)R' \xrightarrow[H_2O]{Ag(NH_3)_2^+} RC(=O){-}C(=O)R'$$

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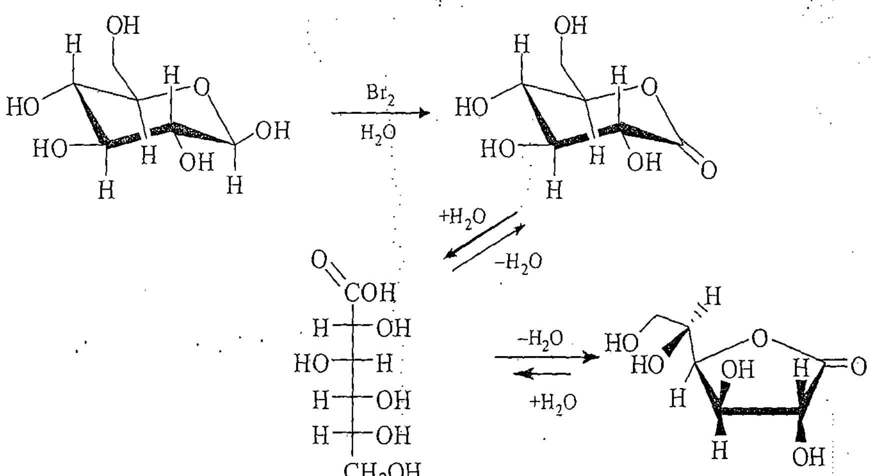

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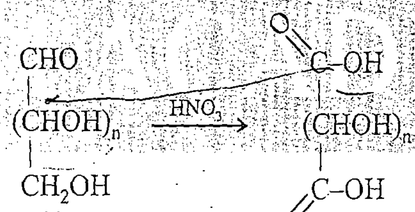

aldose   aldaric acid

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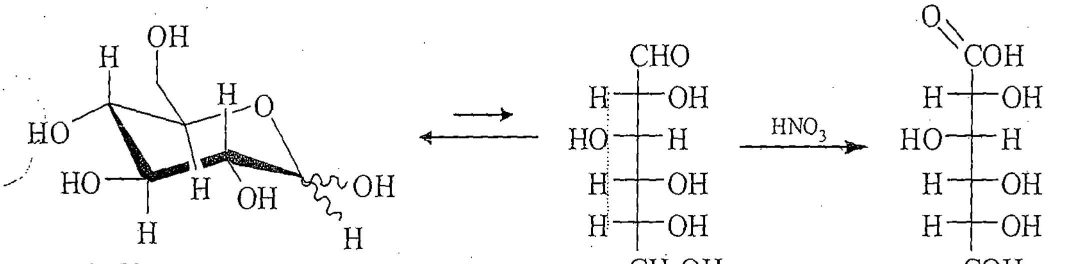

D-Glucopyranose   open chain D-glucose   D-glucose acid

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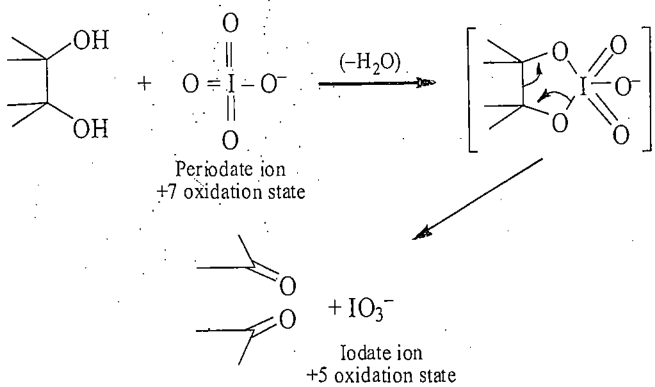
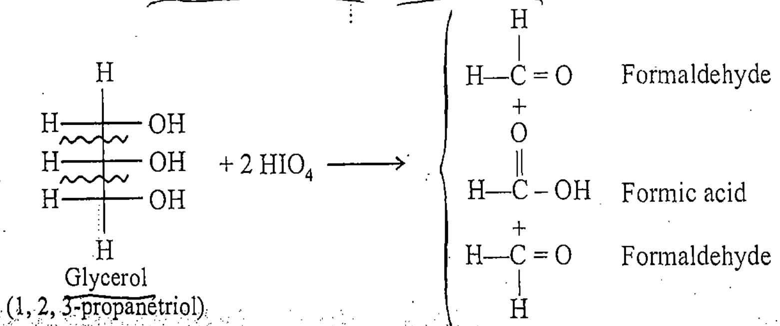


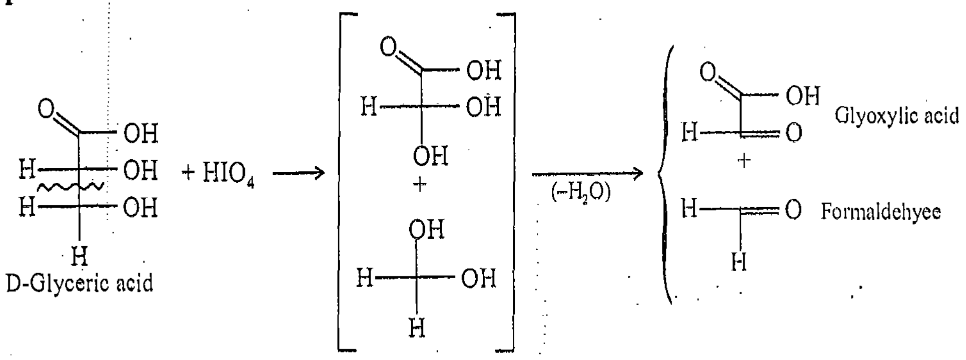
(i) Structure-Clevage Relationships using Periodate Oxidation:

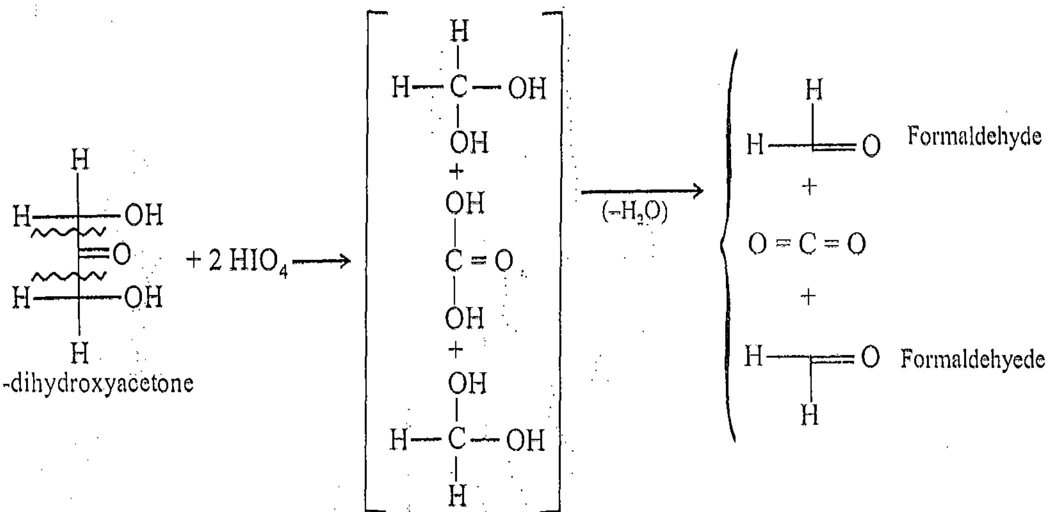
When there are three or more continous "active functions" (–OH or aldehyde/ketone C = O), multiple bond clevages occur. Carbonyl groups of carboxylic acids or esters are not "active".



The products of the periodate reaction may be predicted by replacing each **cleaved** C–C bond with OH groups on the carbons. Water is then removed as needed to give carbonyl functions (since having two, worse three hydroxyl groups on the carbon atom is rarely stable).

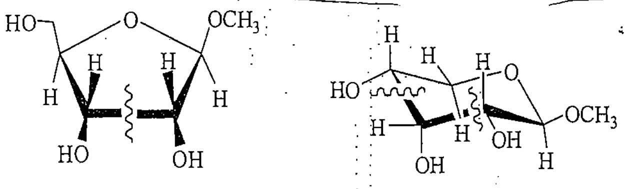
Examples





(ii) Qualitative Analysis

Because the periodic acid oxidative clevage reaction usually is very efficient, it is possible to use the number of molar equivalent of HIO_4 consumed as a tools in structure analysis.

(A) 

(A) (B)

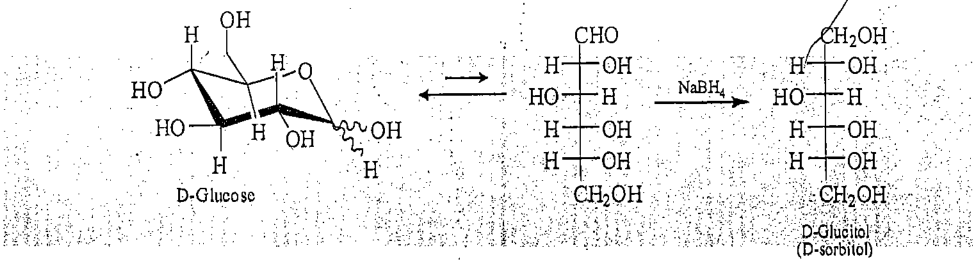
Q. $C_6H_{12}O_5$ methyl riboside is knwon to be one or the other of the above isomrs. On quantitative IO_4^- oxidation, it is found to consume 2.0 m molof IO_4^- per mol of glycoside. Which isomer is it?

Ans. It is the pyranoside, B, which has two sites subject to oxidation while the furanoside, A, has only one (and so would consume only 1.0 mmol of IO_4^- per mmol of glycoside).

The consumption of IO_4^- can be followed either titrimetrically or spectrophotomerically.

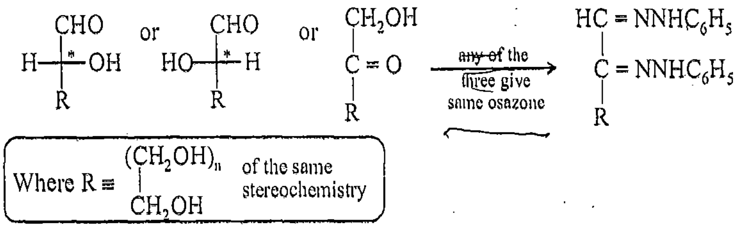
6. Reducing Agents in Carbohydrate Chemistry

Sodium borohydride, or hydrogen with a catalyst like platinum, will reduce the carbonyl groups of either aldoses or ketones. The resuting alditols are produced via reduction of the low concentration of open-chain sugar present at equilibrium with hemiacetals.

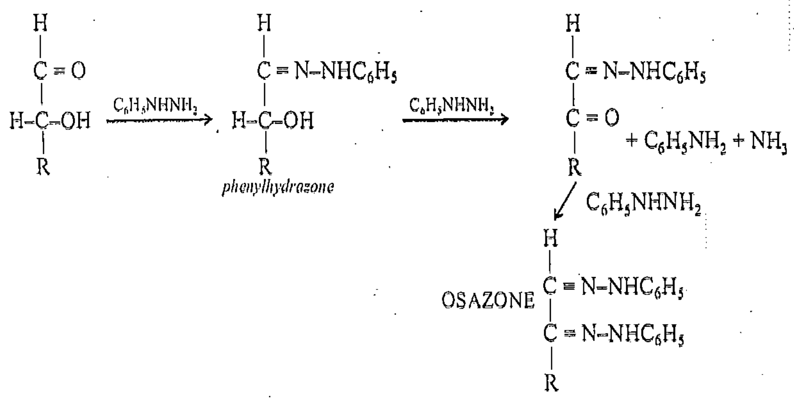


7. Osazone Formation

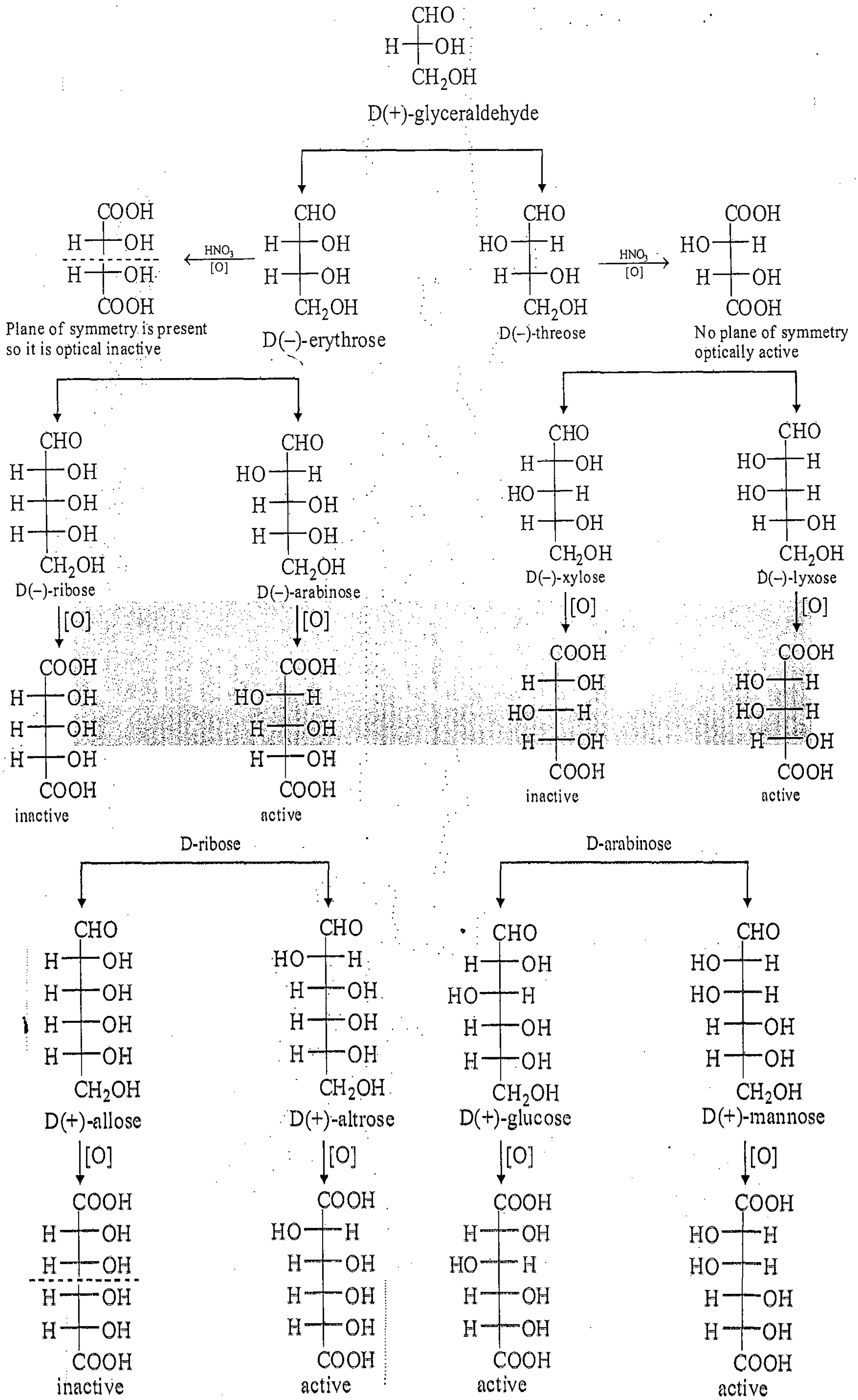
This reaction of sugars with phenylhydrazine can identify isomers that differ in configuration only at C2, or in the location of the carbonyl group at C1/C2. [Stereoisomers that differ in configuration at only one of two or more chirality centres are called **epimers.**]

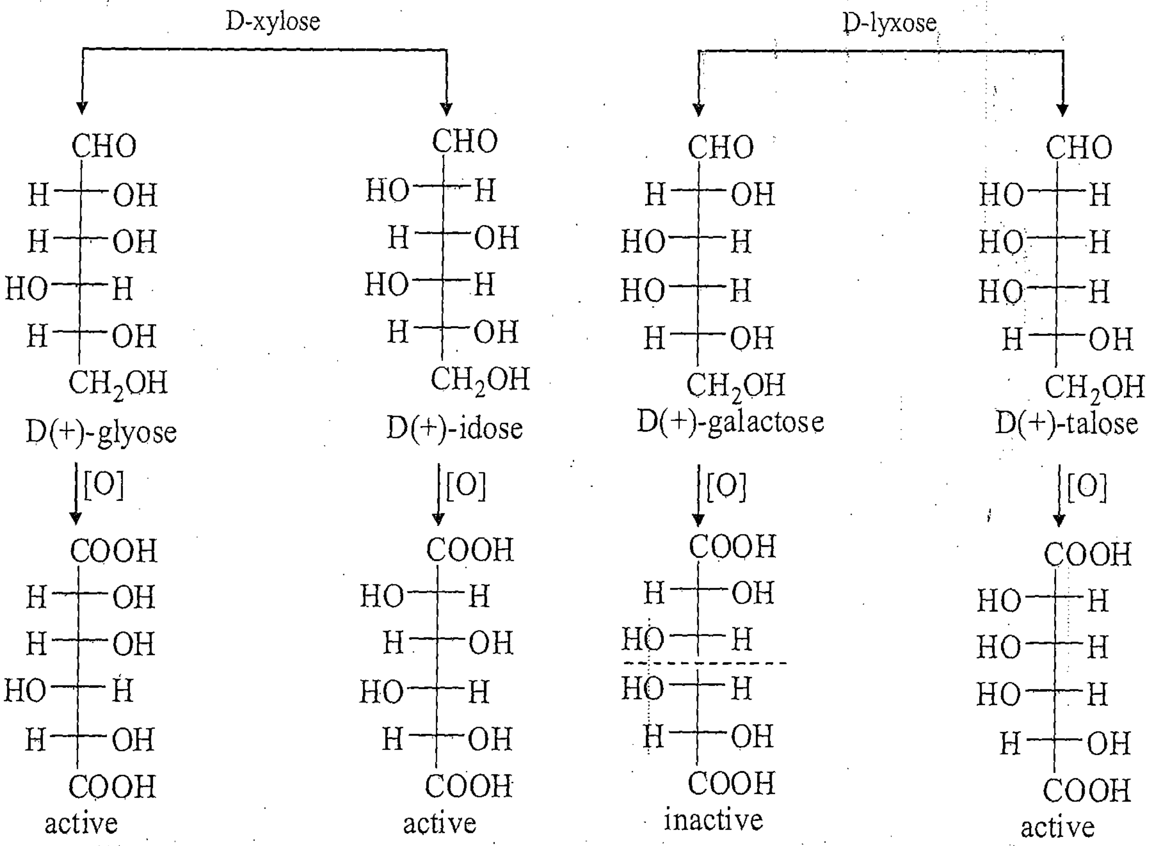


Osazone formation proceeds stepwise :



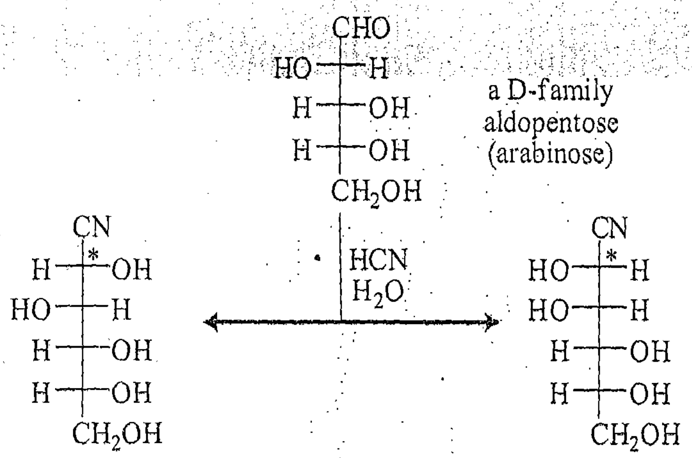
8. Optical Activity in Carbohydrate



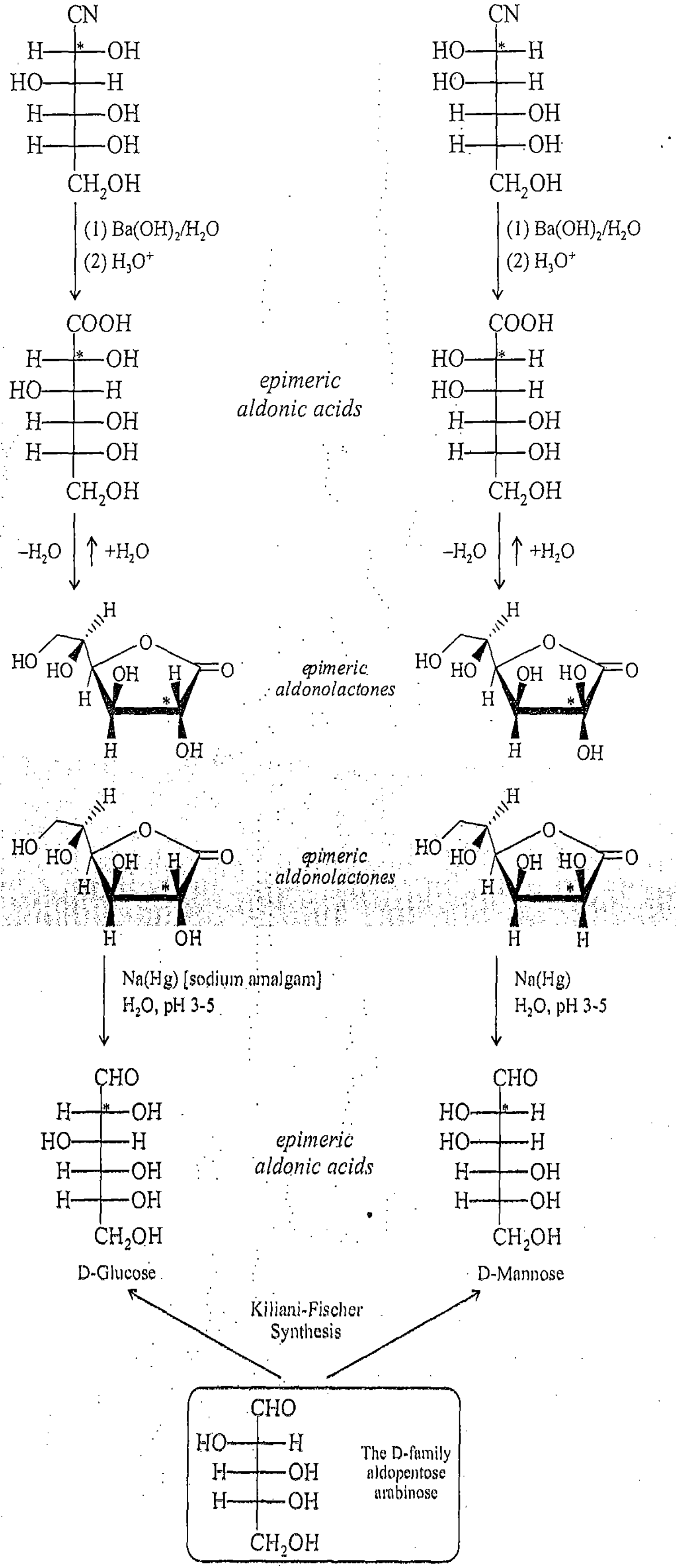


9. **The Kiliani-Fischer synthesis : Chain lengthening**

A method was developed to lengthen carbochain of an aldose while preserving its stereochemistry.

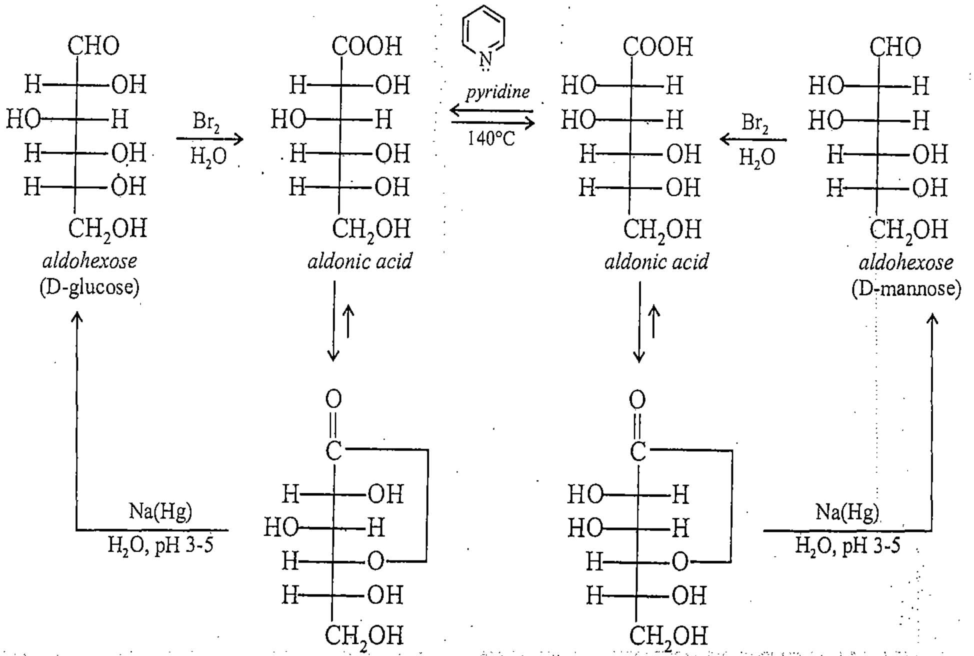


Cyanohydrin products are formed that are epimeric at C2. These diastereomers are separated and the synthesis continues.


(1) Ba(OH)2/H2O
(2) H3O+
epimeric aldonic acids
epimeric aldonolactones
Na(Hg) [sodium amalgam] H2O, pH 3-5
D-Glucose
D-Mannose
Kiliani-Fischer Synthesis
The D-family aldopentose arabinose

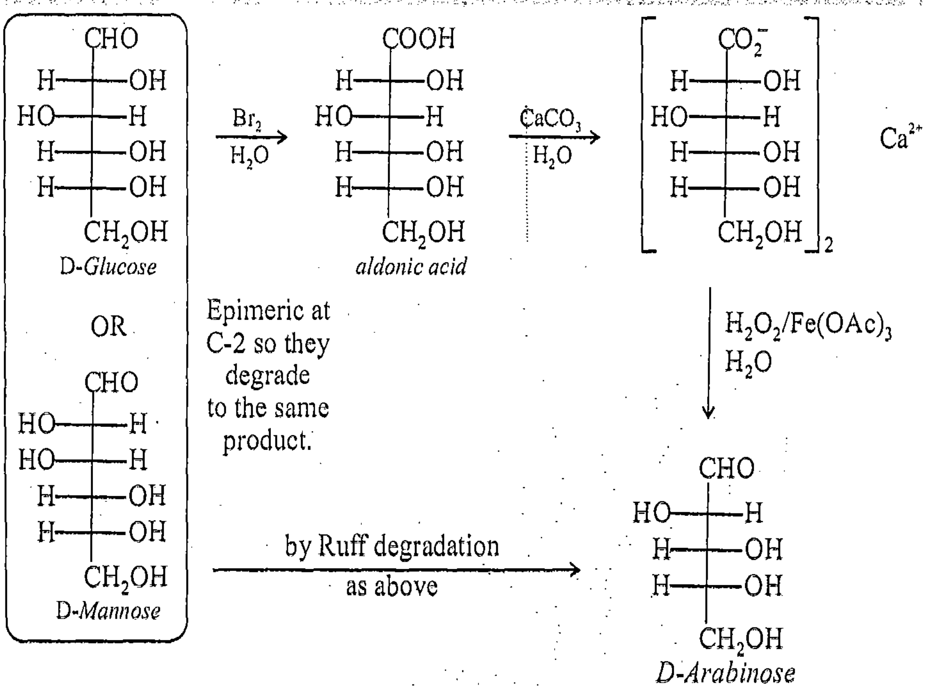
10. Epimerization of Aldonic Acids at C2

The aldonic acids that are epimeric at C2 may be interconverted by heating in pyridine (an amine base). By this reaction, C2 epimeric pairs of aldonic acids (and therefore their parents aldos, as well) may be identified.



11. The Ruff Degradation : Chain shortening

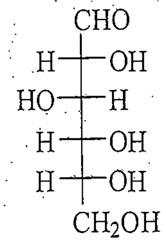
A method was develped to shorten an aldos carbon chain by loss of C1. This allows stereochemical information from one aldose family to be correlated with that of a second, shorte-chain aldose family.



12. **Some Problems with the Open-Chain (Fischer)**

(a) Structure for D-(+)-Glucose

The open-chain aldose structures is not consistent with some of the chemcial and physical properties of glucose.



(1) Certain standard aldehyde reactions, such as bisulfite addition, do not occur. Also the Schiff reagent test (a colour test based on the easy oxidation of the aldehyde function) fails.

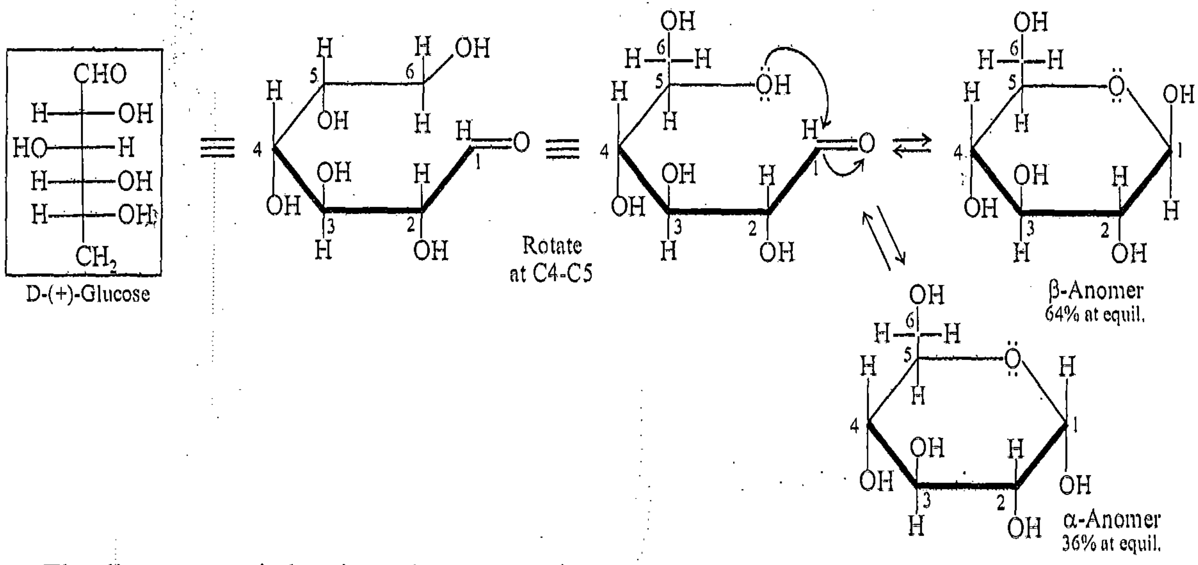
(2) D-(+)-Glucose as usually prepared, has a mp of 146°C (dec.) This form, dissolved in water, has an initial specific rotation of $[\alpha] = +112°$. But over time, the specific rotation drops to $[\alpha] = +52.7°$. This change in rotatory power is called mutarotation. A trace of acid or base accelerates mutatoration.

(3) A second form of D-(+)-glucose can be isolated that shows an initial $[\alpha] = +19°$ in water. Over time, the specific rotation of this solution changes to $[\alpha] = +52.7°$.

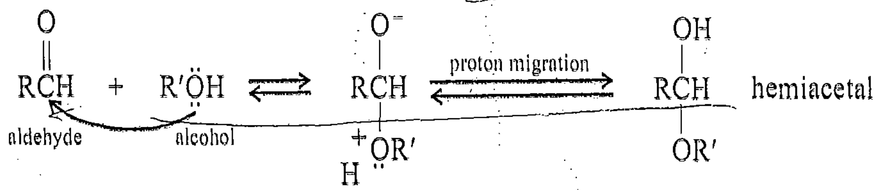
Since both forms ultimately come to the same final $[\alpha]$ value, it appears likely that an equilibrium is reached between them.

(b) The Cyclic Hemiacetal Structures

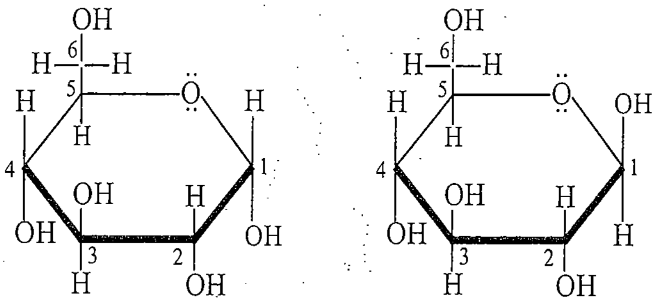
This behaviour or D-(+)-glucose is not consistent with the simple aldose structure. It soon become clear that glucose and other sugars are in reversible equilibrium with cyclic **hemiacetal structure.** These isomeric strucures often dominate in the equilibrium, as they do with glucose.



The diastereomeric hemiacetals (anomers) interconvert by way of these equilibruia :



13. Haworth Projection Formulas



α-Anomer
α-D-(+)-Glucopyranose

β-Anomer
βa-D-(+)-Glucopyranose

Howorth showed that the equilibrium forms of glucose, the above cyclic hemiacetal structure (anomers), contain a six-membered ring. These cyclic structures are drawn in a convention called Haworth projection formulas. If, as here, the ring is six-membered it is called a pyranose ring; if it is five-membered it is called a **furanose** ring. Thse terms are made a part of the name of the compound, as shown above. The α and β cyclic hemiacetals are **epimers** (diastereomers that differ at only one chiral center). In carbohydrate chemistry, diasteromeric structures are called **anomers** if they are epimeric at the originally carbonyl carbon (here, C1). In the α-**anomer,** the hydroxyl on the anomeric carbon is *trans* to the hydroxymethylene group (here on C5). In the β-**anomer,** it is *cis.*

14. Conformational Formulas

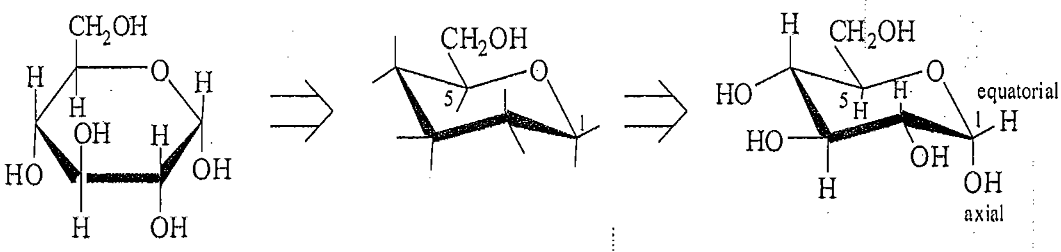
The existence of cyclohexane in the chair conformation was shown in the 1930's to explain the nearly strain free structure of this cycloalkane. The same analysis applies to the cyclic structures of the pyranose sugars. Conformational representations more accurately show the stereochemical features of these compounds.

To proceed from a Haworth formula to the corresponding conformational formula :

(1) Draw a chair representation as shown below.

(2) Place the large hydroxymethyl group at C5 in the equatorial position.

(3) Place the hydroxy groups at C1 through C4 cis and trans, as required.

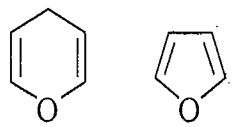


α-D-(+)-Glucopyranose

15. Nomenclature of the Monosaccharide Hemiacetals

All carbohydrates cyclize to six-membered hemiacetal rings. Five-membered rings are also common. The size of the ring can be indicated in the name of the carbohydrate.

The method is based on the names of these oxygen heterocycles :

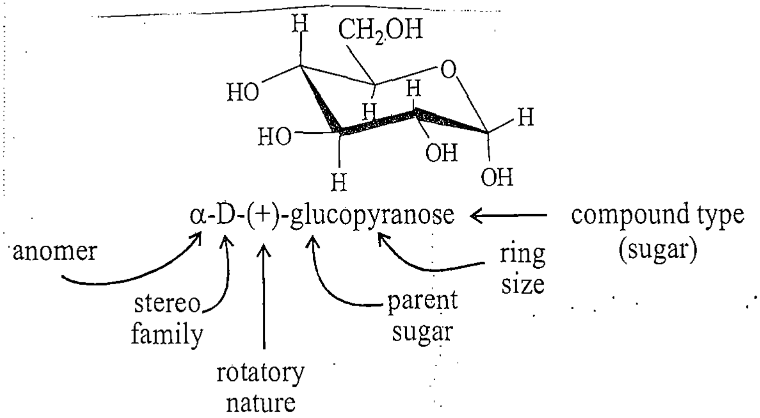


pyran furan

A six-membered sugar hemiacetal is a **pyranose.**

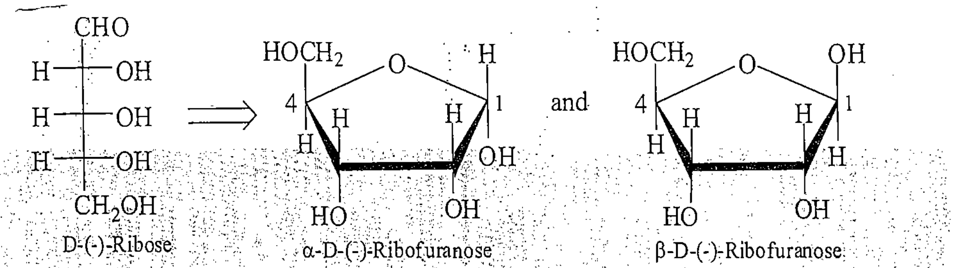
A five-membered sugar hemiacetal is a **furanose.**

The full descriptive name of this hemiacetal is comprised of these parts :



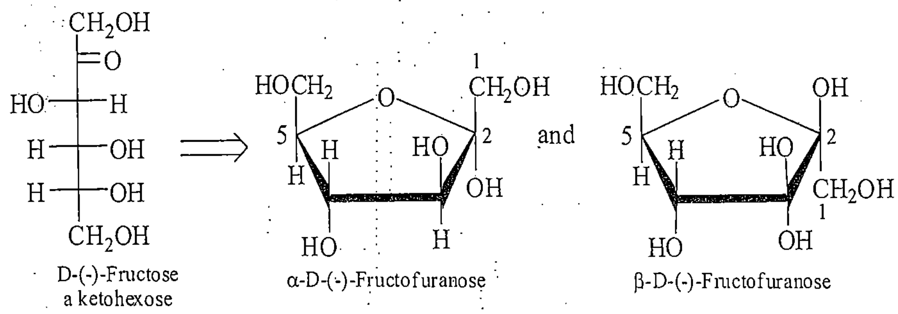
Examples :

Aldopentoses commonly cyclize to five-membered hemiacetals (furanoses). The cyclization process maybe described using the step-by-step procedure that gives howorth projection formula. Applying this to D-ribose gives this result :



[Pyranose forms are also known.]

Applying the same step-by-step procedure to D-fructose, the most common ketohexose, gives this result:



16. Mutarotation

Ordinary D-(+)-glucose has mp 146°C. But when D-(+)-glucose is crystallized from an aqueous solution kept above 98°C, a second form of D-(+)-glucose is obtained with a somewhat broad mp of about 150°C.

In aqueous solution, the following are observations.

(1) Initially, water solutions of the two forms of D-(+)-glucose have different specific rotations.

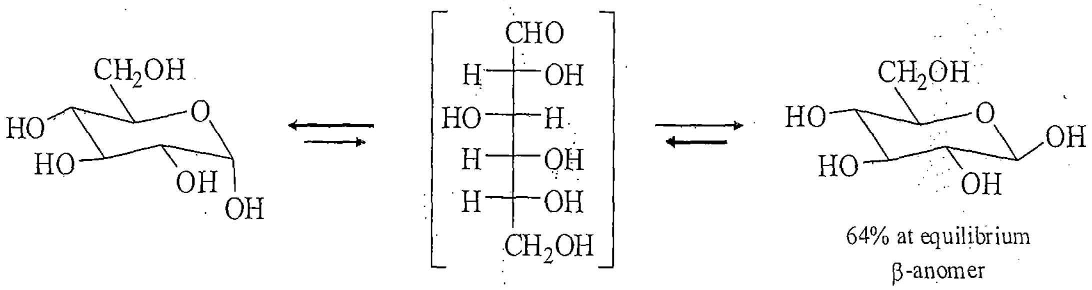
$$\text{Form A} \; \begin{matrix} \text{mp } 146^\circ \\ [\alpha]_D^{25} = +112 \end{matrix} \qquad \text{From} \; \begin{matrix} \text{mp } 150^\circ \\ [\alpha]_D^{25} = +18^\circ \end{matrix}$$

(2) On standing, an aqueous solution of either form of glucose undergoes a change in specific rotation, ending with the same final value of $[\alpha]_D^{25} = +52.7°$

This change in rotatory power is called **mutarotation.**

(3) Either acids or bases **speed up** the rate of mutarotation.

Mutarotation is due to the interconversion of the α- and β- anomers of D-(+)-glucopyranose through the aldohexose form. The two isolated forms of D-glucose, with their different physical properties, are the two anomers. The final rotatory power of an aqueous solution of D-glucose (+52.7° at 25°C) results from an equilibrium mixture that contains almost exclusively the two anomers.



64% at equilibrium
β-anomer
mp 150°C, $[\alpha]_D^{25}$ + 18.7°

In the solid state, D-glucose exists as one or the other of the above anomers, which preferentially crystallize from solution under different conditions of temperature and solvent. In the abvoe equilibrium, only a trace amount of the open chain and α- and β-furanose anomeric isomers are present.

The reason that the β-pyranose is more abundant at equilibrium is that **it has all ring substituents** equatorial positions. This likely is also why glucose is the most abundant of the sugars in nature.

17. Glycosides : Sugar Acetals

Hemiacetals and Acetals

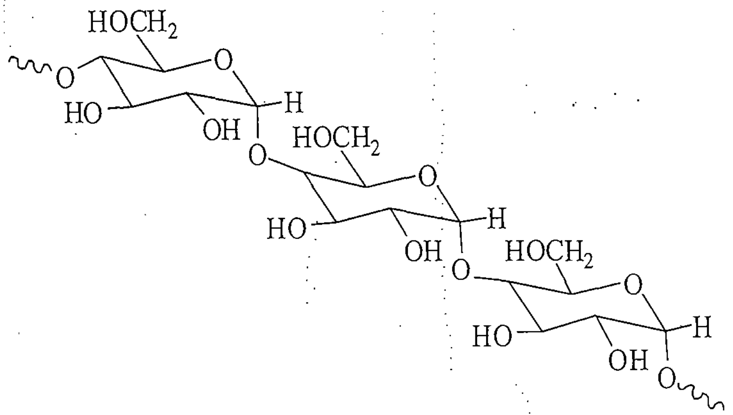
Two equivalents of an alcohol reversibily add to an aldehyde in the presence of an acid catalyst to form a hemiacetal and then an acetal :

$$R\overset{\overset{O}{\|}}{C}H + R'OH \overset{H^+}{\rightleftharpoons} R\underset{OR'}{\overset{OH}{C}}H \overset{H^+,\, R'OH}{\rightleftharpoons} R\underset{OR'}{\overset{OR'}{C}}H + H_2O$$

18. Starch

Starch is found in the roots, tubers,and seeds of plants. Important sources for human diets are potatoes, wheat and rice. Starch is a mixture of polyglucose structures, approximately 20% **amylose** and 80% **amylopectin.**

Amylose is made up of > 1000 D-glucopyranosyl units linked by α-linkage between C1 to one unit and C4 of the next unit.



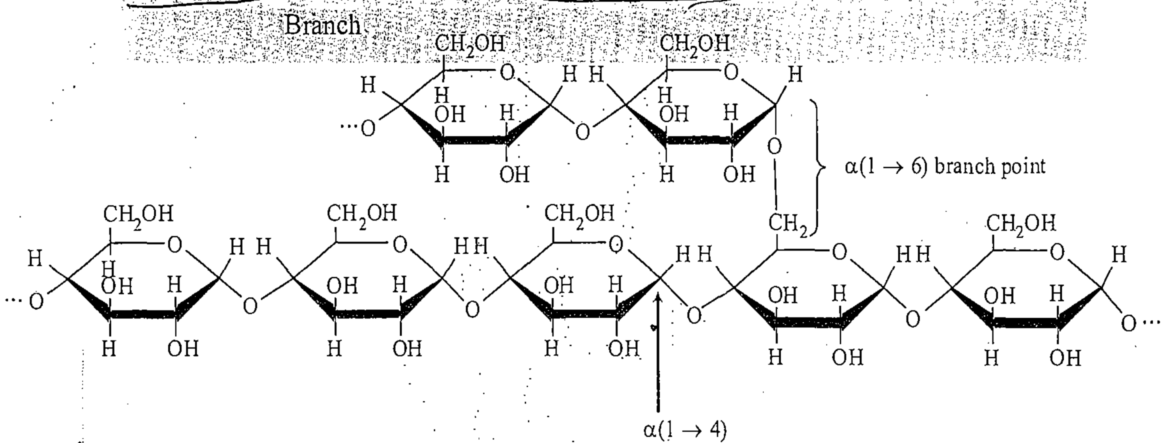
(a) Amylose

Amylose forms colloidal dipersions in water. When iodine (I_2) is added to these solutions, an intense blue-black colour is formed. The non-polar I_2 migrates in to the low polarity core of the helix, which assembles with the surrounded groups on the exterior where they can hydrogen bond with the surrounding water. This is a commonly used test for the presence of starch (or of I_2).

The hydrolysis of starch can be followed by periodicaly testing samples with a dilute iodine solution. As the starch is broken into smaller fragments, there is a colour change from **blue-black → blue → purple → pink → colourless.**

(b) Amylopectin

Amylopectin has a structure similar to amylose except that it has polyglucose side branches attached at an intervals of 20-25 glucose units by α1-O-6 acetallinks. All other acetal links are like those of amylose, α1-O-4. Amylopectin is larger in size, contaning 6000-35,000 glucose units.



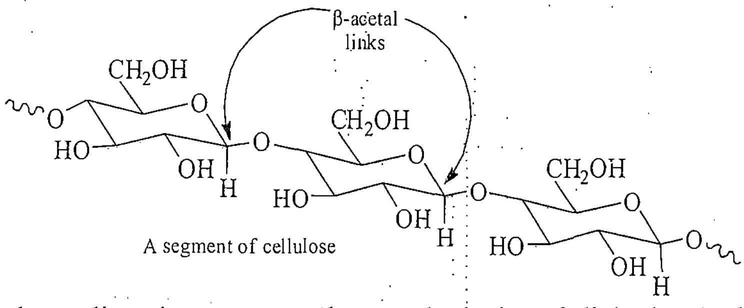
19. Glycogen

Glycogen is much like amylopectin, but it may contain as many as 600,000 glucose units and is also much more highly branched. Branches are attached as often as every 10-12 glucose units.

Just as amylopectin is the reserve carbohydrate for plants, glycogen is the reserve carbohydrate for animals. the highly branched nature of glycogen is advantageous in that this makes many end groups available to the enzyme that release glucose as needed, permitting faster release of glucose units than from a more linear structure.

20. Cellulose

Cellulose is another polyglucoside, made up of 10 to 15 thousand D-glucopyranose units per strand, but here the linakge are of β1-O-4 type. these β-acetal linkages permit the polysaccharide chain to be linear rather than helical. The chains aggregate in parallel fashion through inter-chain hydrogen bonds, leading to a highly insoluble, rigid, and fibrous polymer structure. This, and the cementing together of the cellulose fibers by lignin (a complex polymer derived from variously oxygenated phenylpropane monomers), accounts for the strength of plant materials, especially wood.



A segment of cellulose

Humans do not have digestive enzymes that can hydrolyze β-linked polyglucosides in contrast to the case of α-linked ones like starch.

Consequently the cellulose of plants and wood cannot serve as food, except for termites and cows, which have symbiotic bacteria in their guts that provide β-glucosidases.

Cellulose Derivatives

Cellulose triacetate as a derivative that has all three of the hydroxyl groups on each glucose unit esterified by use of acetic anhydride. It can be made into fibers and woven into the fabric "Arnel." Cellulose trinitrate is an explosive called "gun cotton."

The ester derivatives above are soluble in organic solvents, but cellulose itself in soluble in almost all solvents. Another way that it can be solubilized is by converting the free hydroxyl groups into xanthate groups as follows :

$$\underset{\text{(insoluble)}}{\text{cellulose-OH}} \underset{H_3O^+}{\overset{HO^-}{\rightleftharpoons}} \text{cellulose-O}^- \underset{H_3O^+,\ H_2O}{\overset{S{=}C{=}S}{\rightleftharpoons}} \underset{\substack{\text{cellulose exanthate} \\ \text{(water soluble)}}}{\text{cellulose-O}-\overset{\overset{S}{\|}}{C}-S^-}$$

Treatment of the aqueous solution of the xanthate with acid regenerates insoluble cellulose, which can be obtained in the form of fibers (rayon) or sheets (cellophane).

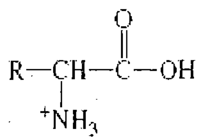
AMINO ACIDS, PEPTIDES AND NUCLEIC ACIDS

1. Introduction

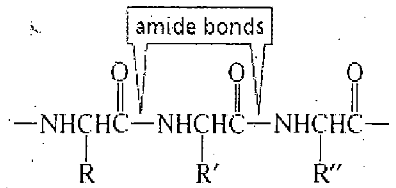
Proteins catalyze and regulate chemical reactions at the cellular level, control body movement as muscles and tendons, provide protection of life forms as skin and hair, transport oxygen as hemoglobin, and protect against diseases as antibodies.

2. Proteins are Polyamides

They all are polymers of α-amino acids. The amino acid units are held together by amide bonds, so proteins are polyamides.



α-aminocarboxylic acid
an amino acid



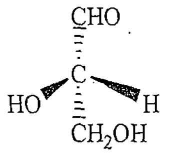
amino acids are linked together by amide bonds

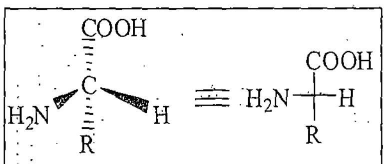
The α-amino acids differ in the structure of their R groups. There are 22 different important amino acids in nature. In a protein, the sequence of amino acids along the polyamide chain is called the primary structure. The attractive interactions and instrinsic folding of the polyamide chain are responsible for the secondary and tertiary structures.

3. **Stereochemistry**

Glycine (2-aminoacetic acid), the simplest of the α-amino acids has two hydrogen on its αC, which is therefore not a chiral centrecenter.

All of the other natural amino acids have a chiral αC of L configuration (usign the Fischer notation). Drawing the carbon chain vertically, Fischer fashion, show the amino acids (having a chiral αC are analogous with the L-enantiomer of glyceraldehyde, the reference compound for D vs. L designations.


L-glyceraldehyde (S)


L-α-amino acid (usually S)

4. **Essential Amino acids**

Some higher animals cannot synthesize all the amino acids required for proteins. The ones that must be obtained through the diet are called essential amino acids. In adult humans, eight amino acids are essential.

5. **Amino Acids Dipolar Ions**

The properties of amino acids indicate they exist as dipolar ions (zwitterions) in the solid state and in solution in water.

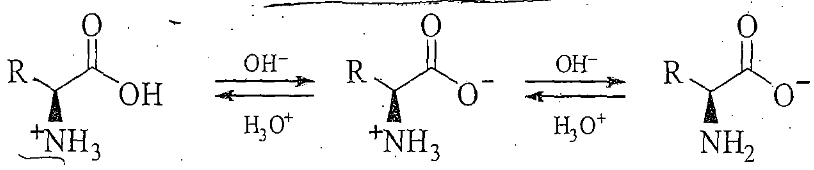
(1) Amino acids are non volatile, crystalline solids with high melting points.

(2) They are soluble in water and insoluble in nonpolar solvents.

(3) Aqueous solution of amino acids behave like solution of high ionic strength.

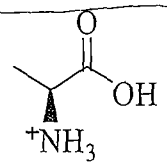
(4) Acidicity and basicity constant (K_a and K_b) are consistent with zwitterionic structures.

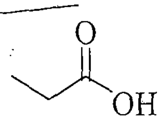
The structure of the species in solution depends on the pH :


Cationic form (predominant at low pH) — Dipolar ion (no net charge) — Anionic form (predominant at high pH)

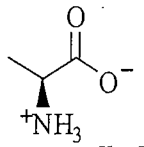
At some intermediate pH, called the isoelectric point (pl), the concentration of the dipolar form is at maximum and the concentrations of the cationic and anionic forms are equal :

Consider the case of alanine, the simplest chiral amino acid. The pK_a of its cationic form is appreciably lower than that of the simpler analog propanoic acid.

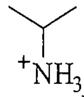
Alanine 
pK_{a1} 2.3

 Propanoic acid
pK_a 4.89

The inductive effect of the ammonium ion makes alanine more acidic. The pK_a of the dipolar ion shows that it is more acidic than it analog isopropylaminium ion. This is contrary to expectation and is likely due to a difference in the effectiveness of stabilization by solvation.



pK_{a2} 9.7



pK_a 10.73

6. **Isoelectric Point pI**

In the presence of an electric field, chemical species with a net charge migrate towards the pole of the electric field with opposite charge. This is the basis of a separation procedure called electrophoresis that is applicable to both amino acids and proteins.

$$\underset{\substack{\text{cationic form}\\ \text{migrates towards cathode}}}{H_3\overset{+}{N}\underset{\substack{|\\ R}}{C}HCO_2H} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\substack{\text{dipolar ion}\\ \text{(no net charge)}}}{H_3\overset{+}{N}\underset{\substack{|\\ R}}{C}HCO_2^-} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\substack{\text{anionic form}\\ \text{migrates towards anode}}}{H_3\overset{+}{N}\underset{\substack{|\\ R}}{C}HCO_2^-}$$

As some pH unique to the amino acid or protein being studied, it will have no net ionic charge and will not migrate under the influence of an electric field. This pH is defined as the pI for the compound studied. When applying electrophoresis to a mixture of dipolar species, at any given pH some will be present with an excess of cationic forms, some with an excess of anionic forms, and if the pH is equal to the pI of some component it will not migrate.

(a) The Henderson-Hasselbalch Equation

This is a variant of the more familiar equation and can be derived from it when needed.

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

(1) Solve for $[H^+]$ $\quad [H^+] = K_a \dfrac{[HA]}{[A^-]}$

(2) Invert $\quad \dfrac{1}{[H^+]} = \dfrac{1}{K_a} \cdot \dfrac{[A^-]}{[HA]}$

(3) Write in log form

$$\log \frac{1}{[H^+]} = \log \frac{1}{K_a} + \log \frac{[A^-]}{[HA]}$$

(4) Recall that $\log x = -\log 1/x$

Therefore $\log \dfrac{1}{[H^+]} = pH$, and $\log \dfrac{1}{K_a}\ pK_a$

(5) Rewriting gives the Henderson-Hasslbalch equation : $pH = pK_a + \log \dfrac{[A^-]}{[HA]}$

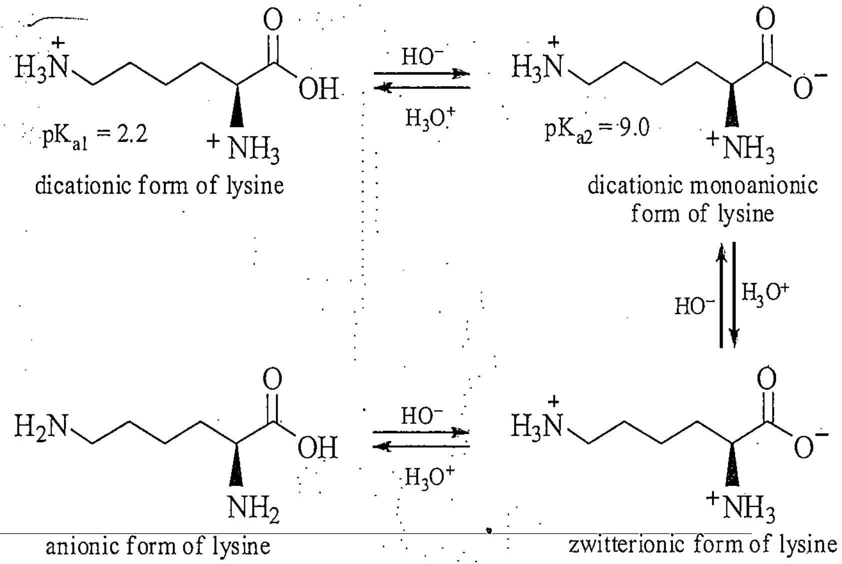
(6) Form this, it is seen that when $[A^-] = [HA]$ the last term becomes

The log of 1, which is 0, and thus at this condition

$pH = pK_a$

(b) Additional Observation on Isolectric Points

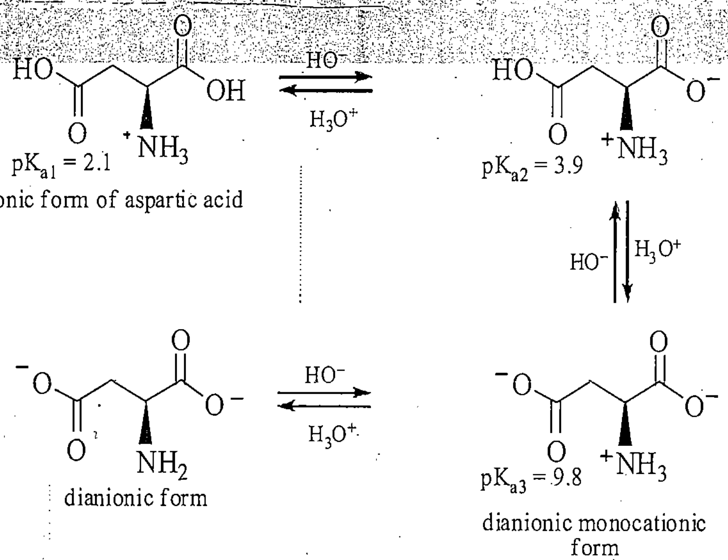
Lysine has one carboxyl and two amino functions. At low pH, it has three acidic functions that deprotonate in order of their acid strengths as OH^- is added.



The isoelectric point of lysine is the average of pK_{a2} and pK_{a3}: $pI = \dfrac{9.1 + 10.5}{2} = 9.8$

At pH = 9.8, the domaint lysine species in solution is the zwitterionic form just above.

Aspartic acid has one amino and two carboxyl functions. at low pH, it has three acidic functions that deprotonate in the order of their acid strengths as OH^- is added.



The isoelectric point of lysine is the average of pK_{a1} and pK_{a2}: $pI = \dfrac{2.1 + 3.5}{2} = 3.0$

At pH = 3.0, the dominant form of aspartic acid is neutral zwitterionic.

7. Synthesis of α-Amino Acids

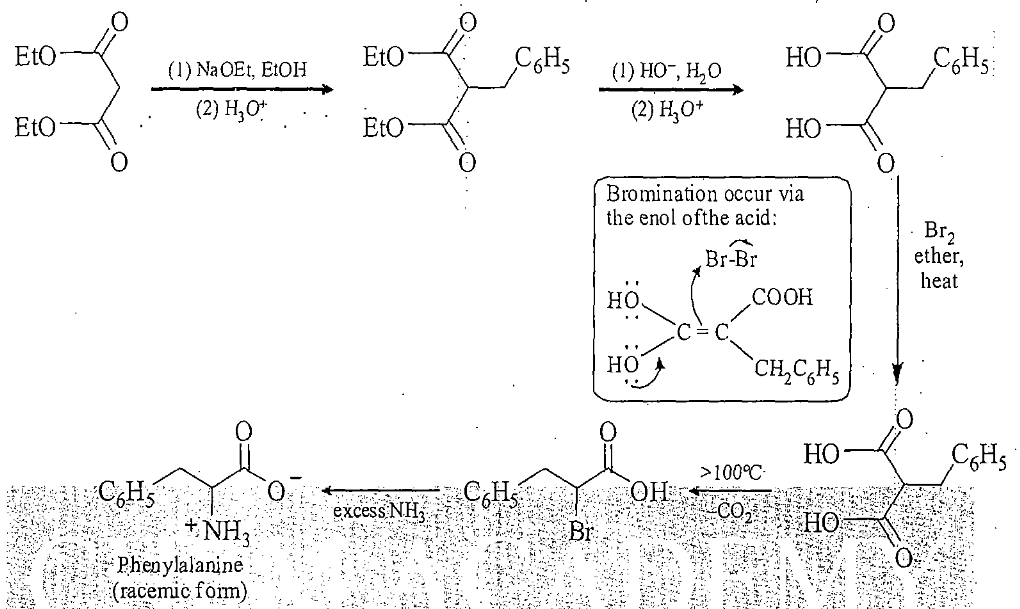
There are several standard syntheses of α-amino acids.

(a) Direct Ammonolysis of α-Halo Acids

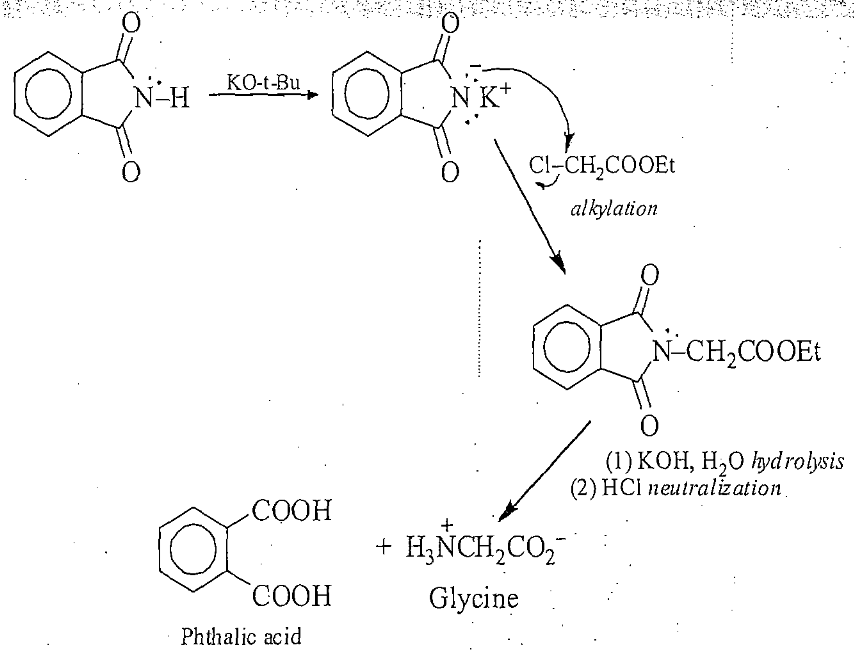
$$\underset{\text{Propanoic acid}}{CH_3CH_2COOH} \xrightarrow[(2)\ H_2O]{(1)\ Br_2,\ P} \underset{\displaystyle Br}{CH_3\overset{}{C}HCOOH} \xrightarrow{\text{excess } NH_3} \underset{\displaystyle {}^{+}NH_3}{CH_3CHCO_2^-}$$

This is the method of amine or, as here, ammonia alkylation that is difficult to limit to monoalkylation, which is why an excess of ammonia is used.

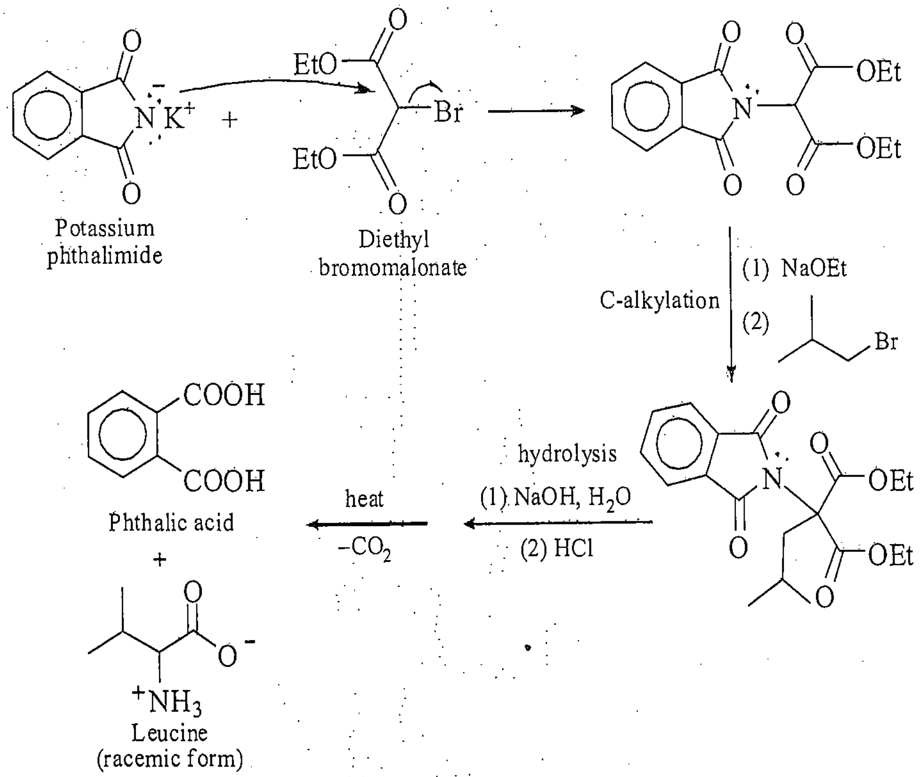
(b) The Malonic Ester synthetic Route



(c) The Gabriel Synthesis : Potassium Phthalimide



(d) The Malonic Ester Variation of the Gabriel Synthesis



(e) The Strecker Synthesis

α-Amino acids may be prepared by reaction of an aldehyde, ammonia and hydrogen cyanide, followed by hydrolysis of the α-aminonitrite produced.

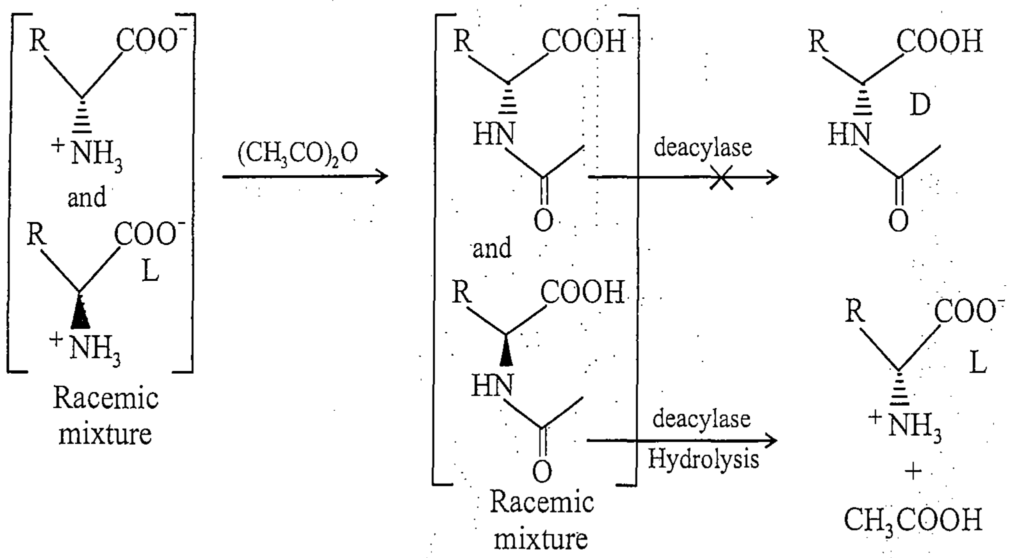
$$\mathrm{RCH(=O) + NH_3 + HCN \longrightarrow \underset{\alpha\text{-aminonitrile}}{RCH(NH_2)CN} \xrightarrow[\text{heat}]{H_3O^+} \underset{\alpha\text{-amino acid}}{RCH(NH_3^+)CO_2^-}}$$

A Mechanism for the Strecker Synthesis

$$\mathrm{RCH(=O) + {:}NH_3 \overset{\text{addition}}{\rightleftharpoons} RCH(O^-)(NH_3^+) \rightleftharpoons \underset{\text{addition product}}{RCH(OH)(NH_2)} \overset{-H_2O}{\rightleftharpoons} \underset{\text{imine}}{RCH{=}NH}}$$

$$\mathrm{RCH{=}NH \xrightleftharpoons[\text{2) } H^+]{\text{1) } :C\equiv N^- \text{ addition}} \underset{\alpha\text{-aminonitrile}}{RCH(NH_2)C\equiv N}}$$

$$\mathrm{\underset{\alpha\text{-aminonitrile}}{RCH(NH_2)C\equiv N} \xrightarrow[H_2O]{H_3O^+,\ heat} \underset{\alpha\text{-amino acid}}{RCH(CO_2^-){-}NH_3^+} \equiv \underset{\alpha\text{-amino acid}}{RCH(NH_3^+)CO_2^-}}$$



8. Asymmetric Syntheses of Amino Acids

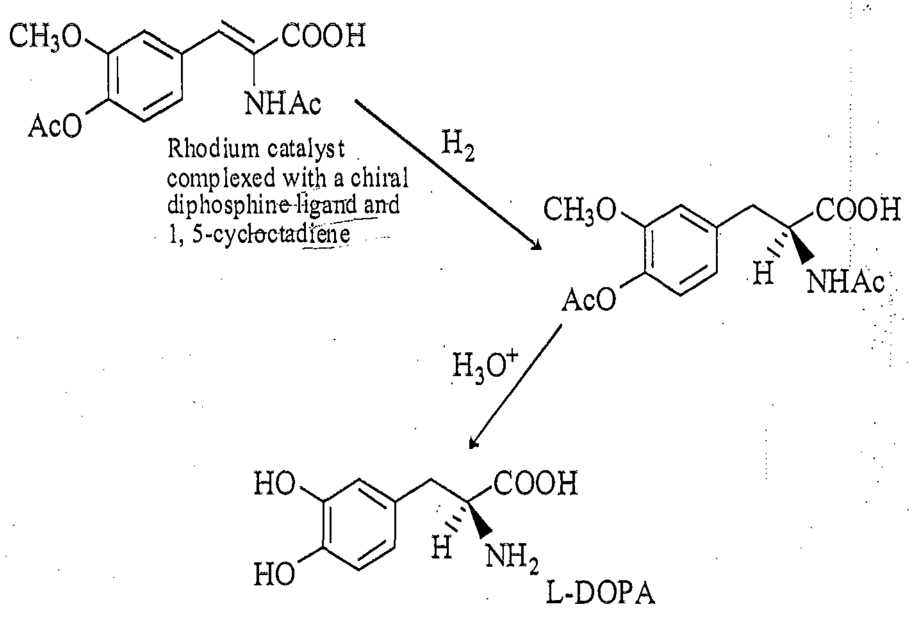
Optical rotation measurements can be reported as the enantiomeric excess (ee), expressed in percent:

$$\%\ \text{ee} = \frac{\text{observedy specific rotation}}{\text{specific rotation of the pure enantiomer}} \times 100\%$$

Successful asymmetric synthesis of amino acids has been achieved by hydrogenation methods that employ catalysts complexed with enantiomerically pure ligands. Some are of great commerical value.

Example of Enantioselective Hydrogenation

This is the method developed by W. Knowles and co-workers at Monsanto Corporation for the synthesis of L-DOPA [(S)-3, 4-dihydroxyphenylalanine], a drug used for treatment of Parkinson's disease.



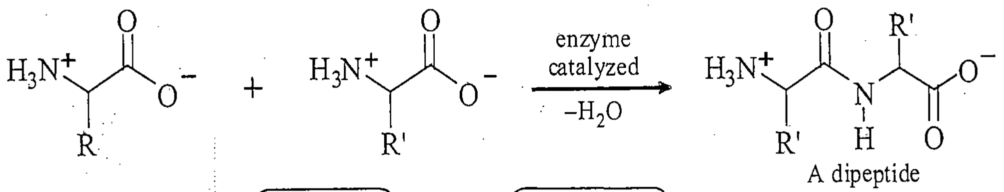
(S)-3, 4-dihydroxyphenylalanine

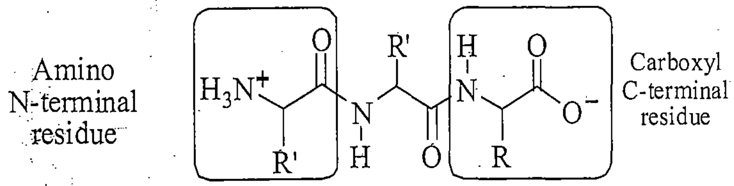
9. Polypeptides and Proteins

Peptides consist of two or more amino acids linked by amide bonds, which in this context are commonly referred to as 'peptide bonds." peptides are designated dipeptides, tripeptides, etc.

depending on the number of linked amino acids. At the decapeptide size, polypeptides are called proteins, which may contain hundereds of amino acid units, sometimes in more than one polypeptide chain.

Polypeptides are linear condensation polymers :





A dipeptide

As in this tripeptide, the amino end is written first, one the left, and the carboxyl end last.

10. Primary Structure of Polypeptides and Proteins

The approach to structure determination of a polypeptide or protein is similar to that used with small molecules :

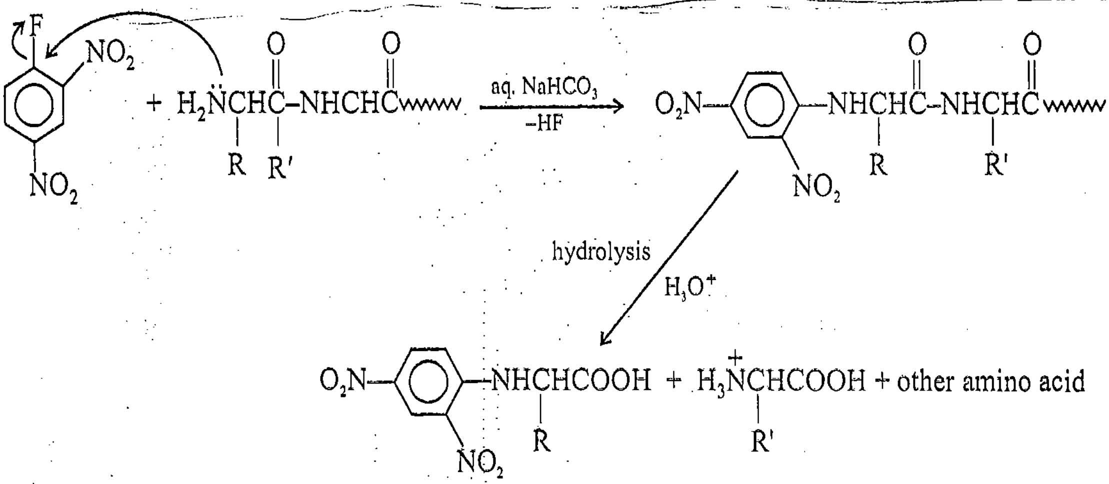
(1) The molecular weight (in amu or Daltons) may be determined by several physical measurements such as ultracentrifugation, light scattering, gel electrophoresis, or mass spectroscopy.

(2) The amino acid composition (analogous to elemental composition for small molecules) may be determined by classical chemical methods, which may employ either partial or complete hydrolysis, derivatization, and separation.

(3) The sequence of amino acids may be determined by older automated chemical, or newer mass spectroscopic, methods. The amino acid sequence of a polypeptide is the primary structure. Important break-through in techniques in recent years (such as electrospray ionization) have made mass spectroscopy a powerful and almost routine methodology for structure determination.

(a) Sanger N-Terminal Analysis

This method identifies the N-terminal amino acid in a polypeptide by attaching a 2, 4-dinitrophenyl label prior to complete hydrolysis. The labeling is done under slightly basic condition so the N-terminal group is in its free base form, permitting its nucleophilic attack on the aryl fluoride reagent.



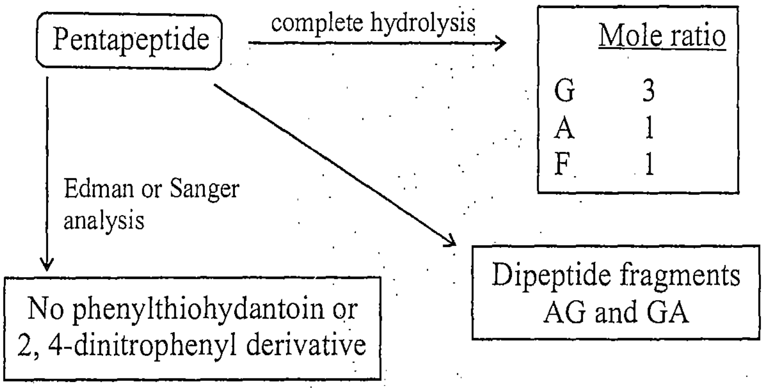
The hydrolysis mixture is separated by chromatography and the labeled N-terminal residue (orange red) is identified spectrophotometrically.

(b) Partial Hydrolysis

Often very large proteins are partially hydrolyzed by acids and enzymes into smaller polypeptide fragment that are analyzed by the Edman method. After the polypeptide fragments have been sequenced, the fragments are pieced together to give a unique sequence for the original protein. The approach can be eased by used for site-specific cleavage e.g., by the enzyme trypsin, which cleaves peptide bonds one the C-terminal side of arginine and lysine.

(c) A Simple Example of Sequencing

An unknown pentapeptide gives the following results :



(d) Conclusions

(1) There is no N-terminus, so this must be a cyclic pentapeptide.

(2) since there is only one α amino acid unit, the isolated dipeptide fragments indicate there is the sequence –GAG–.

(3) There is not enough information to assign a unique structure, but the two possibilities are :

GAGFG and GAGGF

(e) Examples of Polypeptide and Protein

(i) Primary Structure

Primary structure is simply the sequence of amino acid residues. It does not take into account bond angles and other features that determine the true three-dimensional picture of a polypeptide or protein.

(ii) Directed Coupling

The synthesis of a dipeptide by the coupling of two amino acids illustrates this problem. Since amino acids are bifunctional, coupling can occur to produce two differnet mixed dipeptides. The possibility of an amino acid coupling with itself and with newly formed dipeptides are additional problems.

$$\underset{\substack{| \\ R}}{H_2NCHCOOH}\ (A) + \underset{\substack{| \\ R'}}{H_2NCHCOOH}\ (B) \longrightarrow$$

$$\underset{AB}{H_2N\underset{\substack{| \\ R}}{CH}\overset{\substack{O \\ \|}}{C}NH\underset{\substack{| \\ R'}}{CH}COOH} + \underset{BA}{H_2N\underset{\substack{| \\ R'}}{CH}\overset{\substack{O \\ \|}}{C}NH\underset{\substack{| \\ R}}{CH}COOH} + AA + BB + ABA + BAB \text{ etc.}$$

11. Protecting Groups

Directed coupling is achieved by using a protecting group (Q) to block reaction at one of the nucleophilic amino groups.

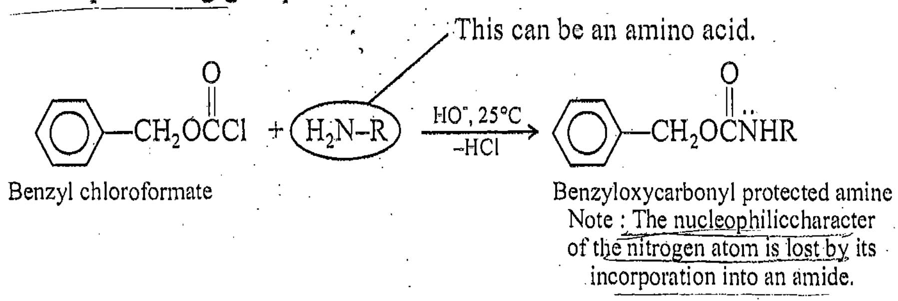
$$QH\ddot{N}\underset{\substack{| \\ R}}{CH}COOH + H_2\ddot{N}\underset{\substack{| \\ R'}}{CH}COOH \xrightarrow[-H_2O]{\text{directed coupling}} QH\ddot{N}\underset{\substack{| \\ R}}{CH}\overset{\substack{O \\ \|}}{C}\ddot{N}H\underset{\substack{| \\ R'}}{CH}COOH$$

$$\xrightarrow{\text{removal of Q}} H_2\ddot{N}\underset{\substack{| \\ R}}{CH}\overset{\substack{O \\ \|}}{C}\ddot{N}H\underset{\substack{| \\ R'}}{CH}COOH$$

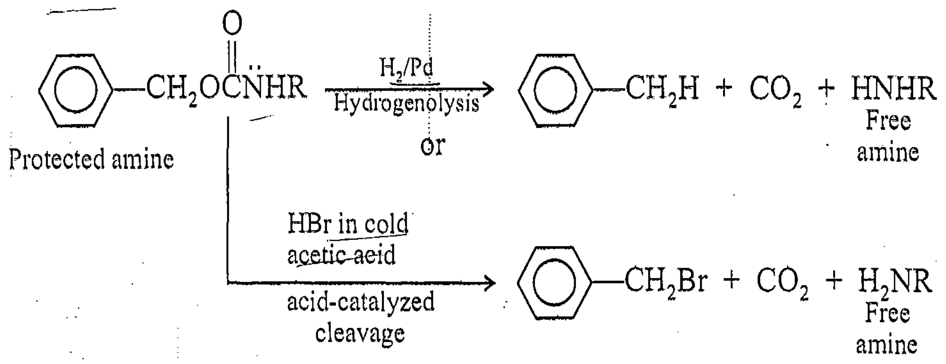
There are two widely used protecting groups for polypeptide synthesis. Both function by eliminating the nucleophilic character of an attached amino group, which explains why the above approach works. Good protecting groups are easy to put on and easy to take off.

(a) Benzyl Chloroformate

(1) Addition of protecting group

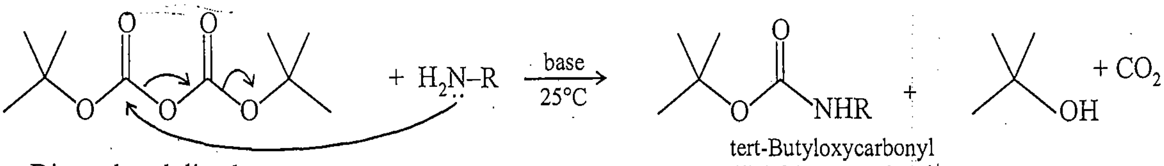


(2) Removal of Q



(b) Di-*tert*-Butyl Dicarbonate

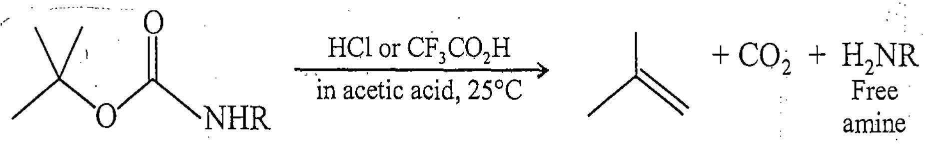
(1) Addition of protecting group



Di-*tert*-butyl dicarbonate

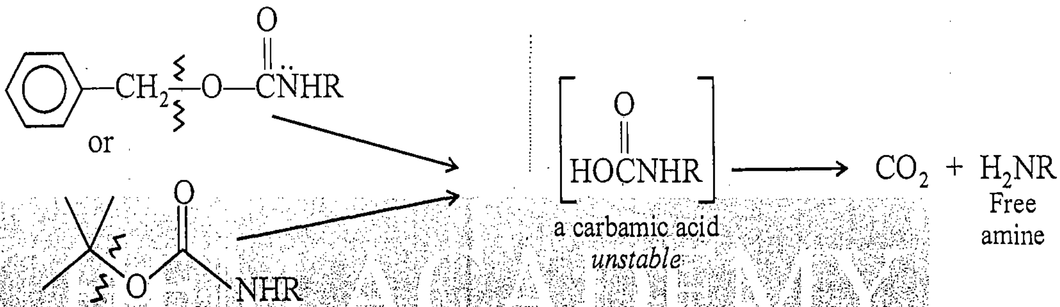
tert-Butyloxycarbonyl or "BOC" protected amine

(2) Removal of BOC group



tert-Butyloxycarbonyl or "BOC" protected amine

The removal of either the benzyloxycarbonyl or BOC protecting group produces unstable carbamic acids that rapidly decarboxylate.



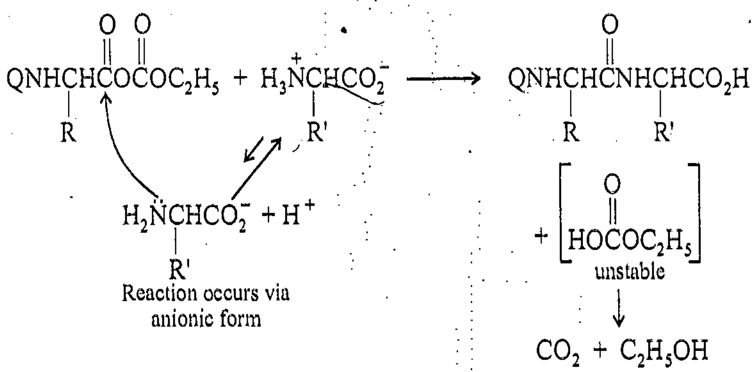
(c) Activation of the Carboxyl Group

The coupling reacting between amino acids may be promoted by chemically modifying the carboxyl function to make its hydroxyl component a better leaving group, as shwon in the example below.

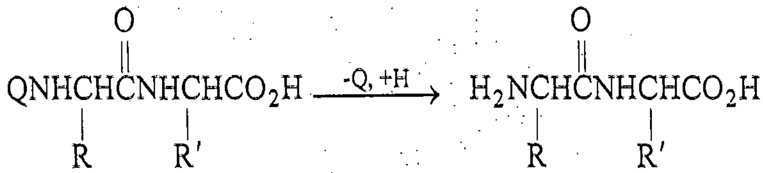
(d) Mixed Anhydrides

A protecting amino acid is reacted with ethyl chlorocarbonte, producing a mixed anhydride.

Reacting with a second amino acid lead to directed coupling, facilitated by the group leaving group.

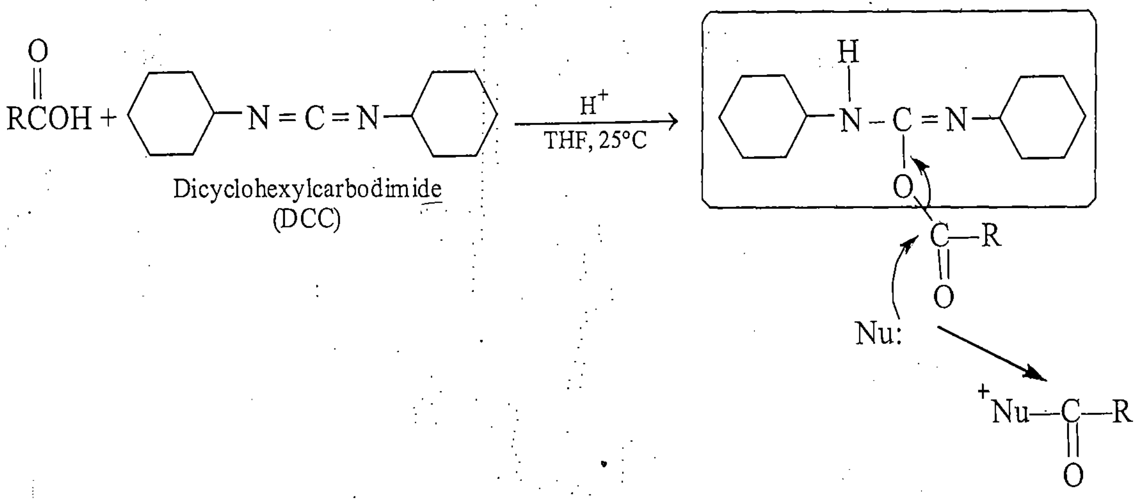


Deprotecting yields the dipeptide :



(e) Dicyclohexylcarbodiimide (DCC).G An Important Coupling Reagnet

DCC reacts with carboxylic acids under very mild conditions (H^+ catalyst in THF at 25°C) to produce intermediate with a carboxyl function activated towards nucleophilic substitution.



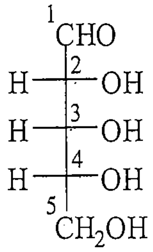
A variety of derivative of a carboxylic acid may be synthesized from the reaction of the carboxylic acid with the DCC reagent and nucleophiles.

NUCLEIC ACIDS

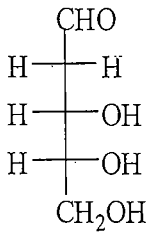
1. Introduction

- The nucleic acids DNA and RNA are high molecular weight polymers composed of billions of glycosylamine units linked as phosphate diesters.
- DNA consists fo two polymers strands held together in the famous helix arrangement by hydrogen bonds. It is coiled and bundle into the **chromosome,** of which in humans there are 23 pairs.
- **Genes** are those varying length segments of a DNA strand that code for (serve as a template for) assembly of specific proteins. The genetic information coded in the DNA of an organism is its **genome.**
- The set of proteins produced under the direction of the geneme is called its **proteome.**
- In the deoxynucleic acids (DNA's) and the ribonucleic acids (RNA's), the units in the polymers chains are **nucleosides** linked via phosphate diester groups that run from the C3' hydroxyl group of one nucleoside to the C4' hydroxyl group of the next nucleoside unit.
- A nucleoside is, its suffix indicates, a glycoside. In ribonucleic acids, the sugar is D-ribose, and in the deoxynucleic acids it is 2-deoxy-D-ribose. In both cases, the sugar moiety present in the nucleoside is in the **furanose form.**

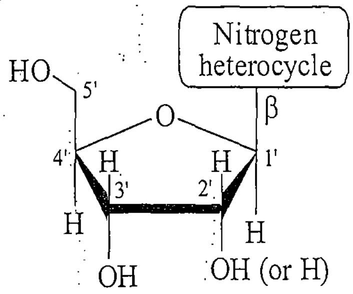
2. Nucleotides and Nucleoside



D-Ribose



2-Deoxy-D-ribose

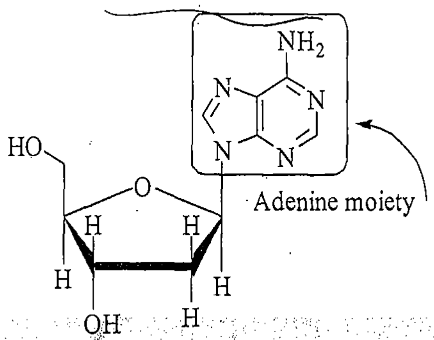


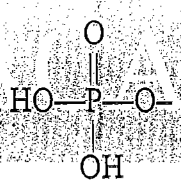
General formula for nucleosides

[Since the atoms of the nitrogen base are also numbered, the atoms of the sugar moiety are assigned prime numbers]

In all cases, the nuclesides are β-glycosides.

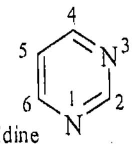
An example of a nucleoside, 2'-deoxyadenosine :



Nucleotide have a phosphate ester unit  attached at either C3' or C5'.

* **The heterocyclic Nitrogen bases of DNA and RNA**

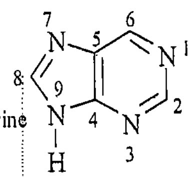
They are derivatives of



Pyrimidine

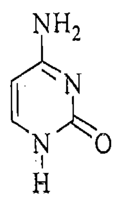
Has standard numbering

OR derivatives of

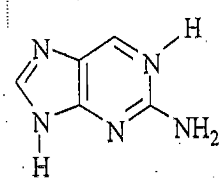


Purine

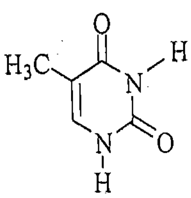
Has unique numbering



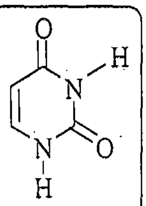
Cytosine (C)



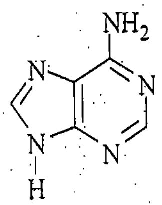
Guanine (G)



Thymine (T)

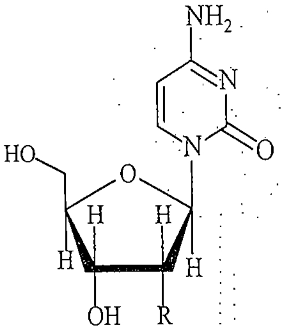


Uracil (U) [Replaces thymine in RNA]

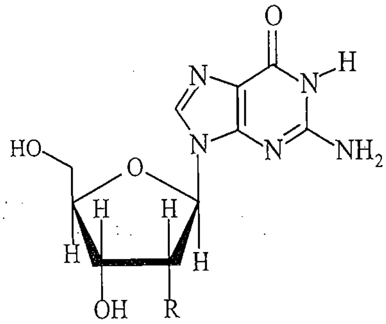


Adenine (A)

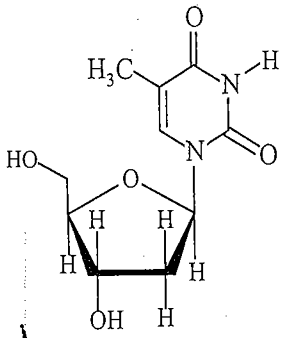
The Nucleosides of DNA and RNA



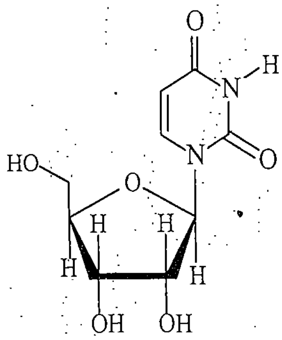
R = OH, Cytidine
R = H, 2'-Deoxycytidine



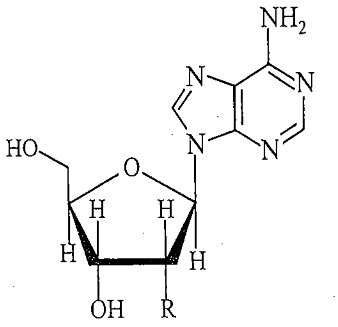
R = OH, Guanosine
R = H, 2'-Deoxyguanosine



2'-Deoxythymidine



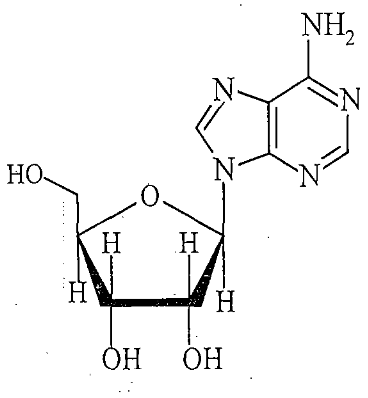
Uridine
[Replaces
2'-deoxythymidine in
RNA



R = OH, Adenosine
R = H, 2'-Deoxyadenosine

Nucleotides

Examples of nucleotide structures and naming :



$R = \mathrm{P(=O)(OH)-OH}$, Adenylic acid or AMP or adenosine monophosphate

$R = \mathrm{O-P(=O)(OH)-O-P(=O)(OH)-OH}$, ADP or adenosine diphosphate

$R = \mathrm{O-P(=O)(OH)-O-P(=O)(OH)-O-P(=O)(OH)-OH}$, ATP or adenosine triphosphate

In the cases of all of the names above, they may be preceded by "5'-" (usually just assumed) if there is need to be explicit (or by 2' - or 3'- for the other positional isomers).

3. **Deoxyribonucleic Acid : DNA**

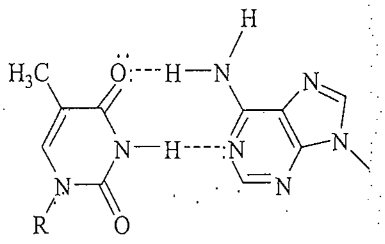
(a) Primary Structure

The units are of four types of 2'-deoxynucleosides and the connecting links are phosphate diester groups that connect the C5' hydroxyl of one nucleoside to the C3' hydroxyl of the next.

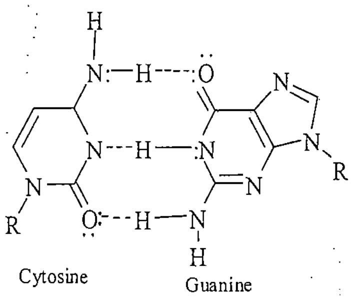
The order in which the deoxynucleosides are connected expalin the difference between organism.

(b) Secondary Structure

The Secondary Structure consist of hydrogen-bonded pairs of nitrogen bases, **adenine always bridging to thymine and guanine to cytosine.**



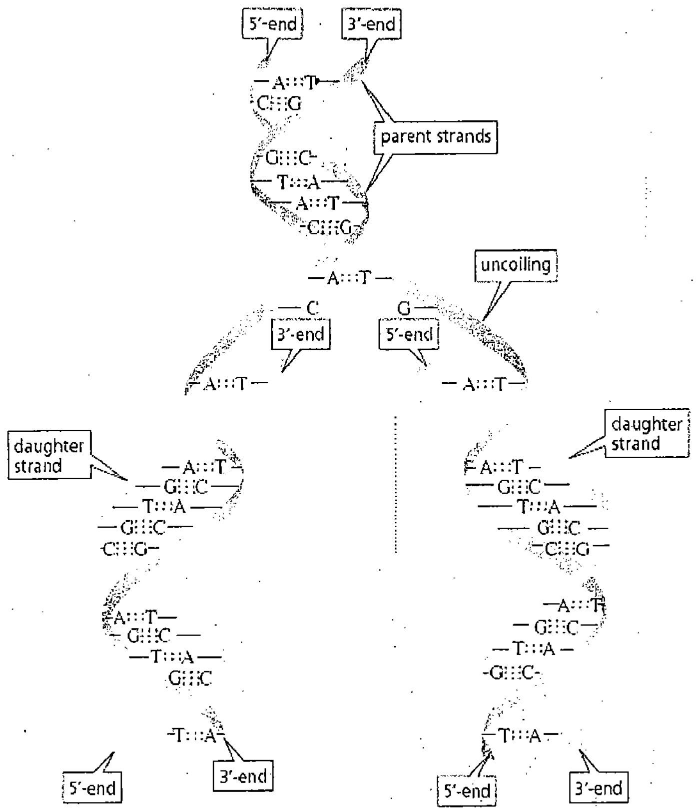
Thymine Adenine



Cytosine Guanine

4. Replication of DNA

- Cell division begins with a partial unwinding of the two strands of the helix. Each of the separate polymer ends then act as a template for the building of a complement to each of the strands.
- When replication is complete, there are two identical new DNA strands, one for each of the daughter cells.



5. RNA and Protein Synthesis

- Each gene of a DNA molecule directs the synthesis of a single protein or polypeptide.
- The first step, **transcription,** occurs in the cell nucleus. It involves transfer of the DNA genetic information of messenger RNA (mRNA).
- The second step, translation, takes place inthe surrounding cytoplasm and involves two other forms of RNA, **ribosomal RNA (rRNA)** and **transfer RNA (tRNA).**

(a) Messenger RNA Synthesis Transcription

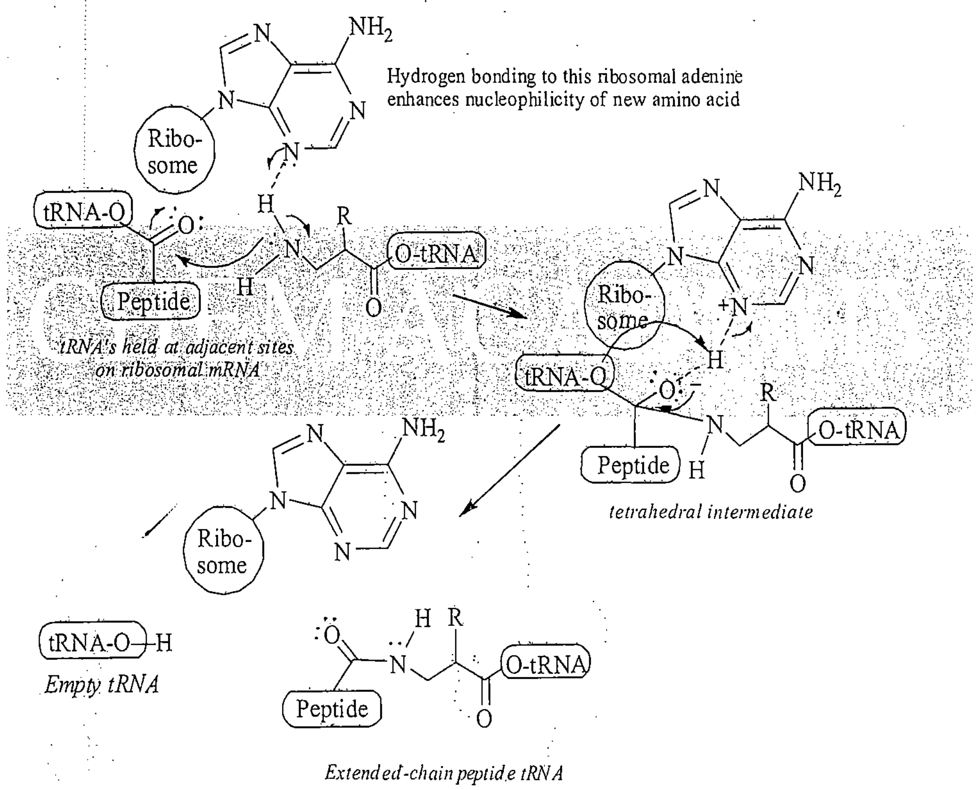
- The "**DNA chain of gene**" is a short selection of DNA helix that has unwound enough to act as a template.

  The top ribonucleotide is delivering a **uridine** to pair with the DNA strand's **adenine** instead of thymine since it is an RNA chain that is being assembled.

(b) Ribosomes rRNA

- Ribosome are **ribozymes,** RNA and protein complexes that catalyze peptide bond formation. The RNA consiss of two subunits, the smaller (designated 30S) mediates the binding of the protein template mRNA, and the larger (50S) catalyzes peptide bond formation.
- A third, smaller type of ribonucleic acid, **transfer RNA (tRNA),** holds the growing peptide chain in place on the mRNA that is acting in concert with the ribosome. The mRNA also is coded to attract to an adjacent site a second tRNA that carries the next amino acid to be attached to the growing chain.

Mechanism for Ribosome-Catalyzed Peptide Bond Formation



Extended-chain peptide tRNA

(c) Transfer RNA

- tRNA is a comparatively low molecular weight type of polynucletide, but one that contains a greater variety of nitrogen heterocyclic bases in its nucleotide units.
- Its function is to carry amino acids to the proper points on ribosomal mRNA for linking to a growing peptide chain.

  The amino acid is carried by attachment as an ester of the C3' hydroxyl of the terminal adenylic acid unit shown at the top of this diagram.

- There are one or more tRNA's for each amino acid. Each tRNA is directed to its proper place on ribosomal rRNA by its **anticodon,** a sequence of three nucleotides (in this example, **IGC**) that will associate only with its codon counterpart in the mRNA.

anticodon

The unusual nucleosides in this tRNA include on in the anticodon, inosine (I), whose heterocyclic bases is : it offers the appart advantage of being able to pair with U, A, or C.

6. Summary

5'...TCA...3' Informational DNA strand

↑ REPLICATION

5'...AGT...3' Template DNA strand

↓

[RNA complement] TRANSCRIPTION

↓ *Introns removed*

5'...UCA...3' mRNA (codon)

↓ *via AGU anticodon of tRNA* TRANSLATION

SERIES

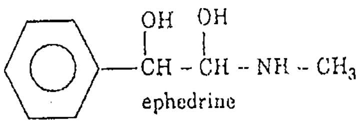
ALKALOIDS & TERPENES

1. Introduction

An alkaloid is an organic compound of plant origin which has a structure containing one or more basic nitrogen, possibly in heterocyclic rings and can induce pronounced physiological activity to animals and man. (Some authors specify alkaloids obtained from plants and plant alkaloids or vegetable alkaloids.)

The above definition of the alkaloids is by no means perfect and does not cover all compounds classed as alkaloids.

1. Piperine, the alkaloid of pepper, is not basic and has practically no physiological activity.
2. Purines such as caffeine (in coffee and tea) and theobromine (in cocoa bean), which stimulate the nervous system, and are heterocycle containing nitrogen, conform to the definition of alkaloids but are frequently not included in this class.
3. Opium (containing the alkaloid morphine) and hashish or bhang, are both habit-forming drugs, yet the active principle of the latter does not contain nitrogen.
4. Ephedrine is a straight-chain alkaloid that is produced by animal glands, and has marked physiological activity.


ephedrine

2. Classification

Various groups of alkaloids, based on the nucleus present and structures of some of the alkaloids of each group are listed below:

(i) Phenylethylamine group

(ii) Pyrrolidine group

(iii) Pyridine and piperidine groups

(iv) Pyrrolidine-pyridine group

(v) Quinoline group

(vi) Isoquinoline group

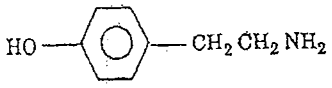
(vii) Phenanthrene group

(viii) Indole group

(i) **Phenylethylamine group**

$$C_6H_5CH(OH)\underset{\displaystyle NHCH_3}{\underset{|}{CH}}-CH_3$$

D(–)ephedrine



β-p-hydroxyphenylethylamine
(tyramine)

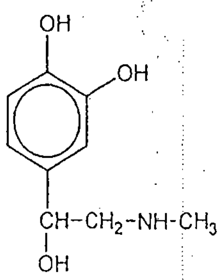
Adrenaline:

Molecular formula $C_9H_{13}NO_3$.

Non-steroid hormone.

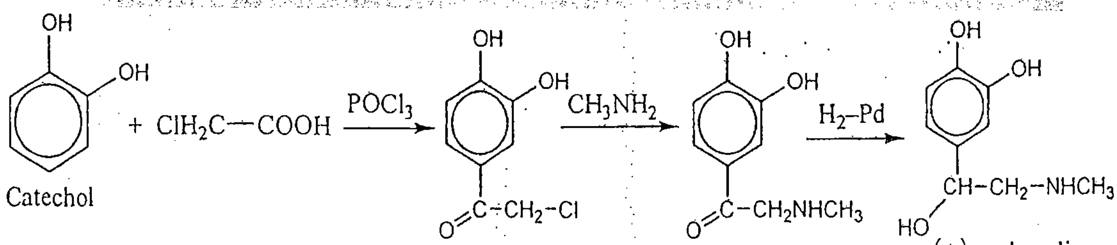
1st hormone to be isolated in a cystalline form.

It raises the blood-pressure, and is used locally to stop haemorrhage.



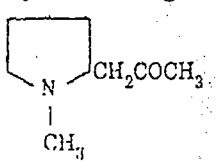
(±) adrenaline

Synthesis:



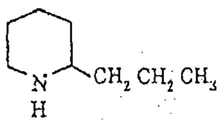
(±) – adrenaline

(ii) **Pyrrolidine group**



Hygrine

(iii) **Pyridine and piperidine groups**

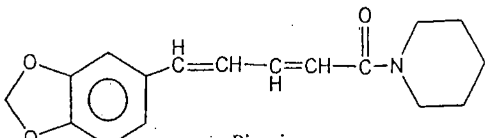


Coniine

Piperine:

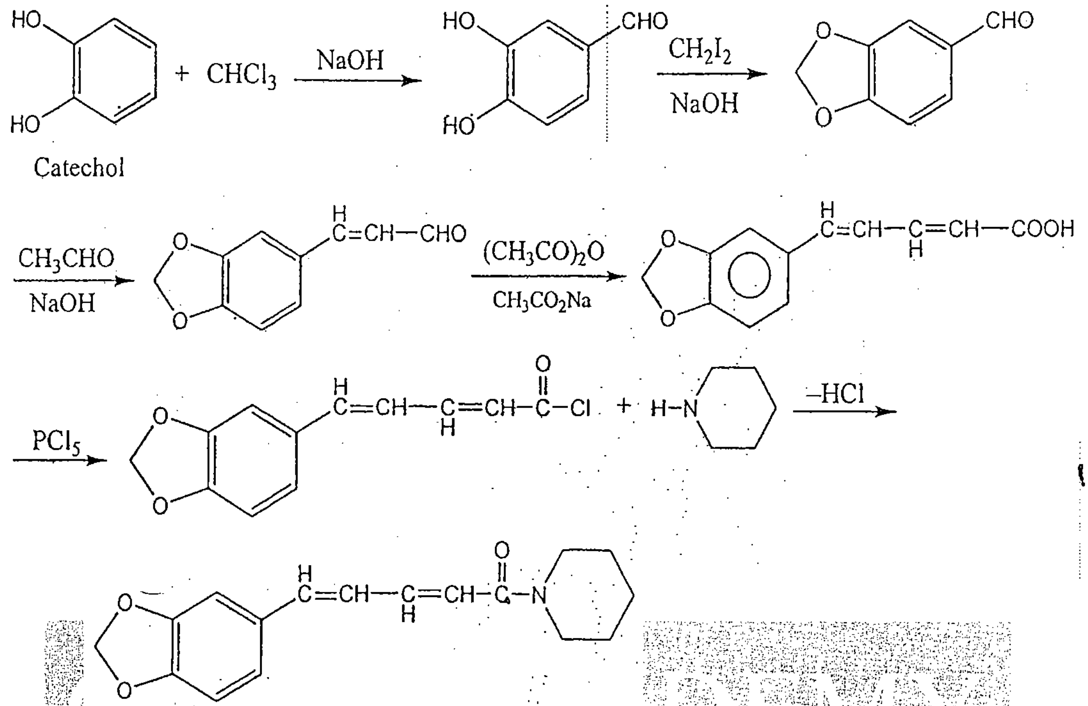
Molecular formula – $C_{17}H_{19}NO_3$, M.P. 128 – 129.5°C

This occur in pepper, especially black pepper.

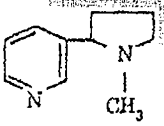


Piperine

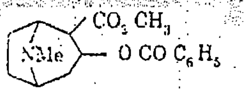
Synthesis:



(iv) **Pyrrolidine-pyridine group**



Nicotine (Tobacco alkaloid)



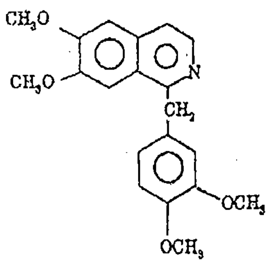
Cocaine
(Coca alkaloid)

(v) **Isoquinoline group**

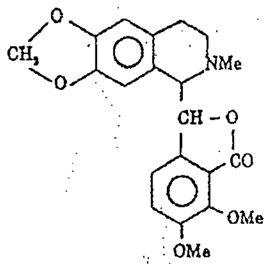
Opium alkaloids – many alkaloids isolated from opium – they are divided into:

(a) Isoquinoline group e.g. Papaverine, laudanosine etc.

(b) Phenanthrene group e.g. morphine.

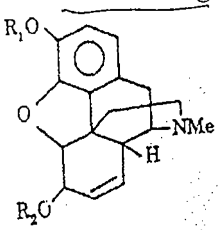


Papaverine



Norcotine

(vi) **Phenanthrene group**



morphine

$R_1 = R_2 = H$ – morphine, $R_1 = Me$, $R_2 = H$ – codeine

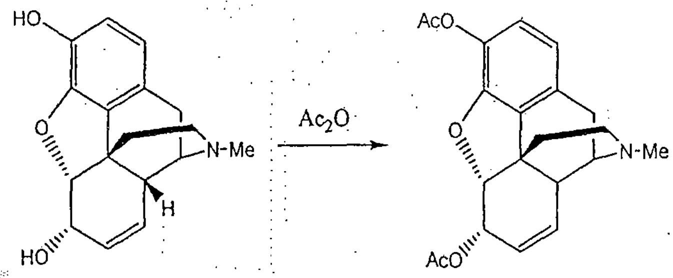
$R_1 = R_2 = CH_3$ – thebaine, R_1, $R_2 = COCH_3$ – heroin

Morphine:

Molecular formula. $C_{17}H_{19}NO_3$, M.P. 254°C

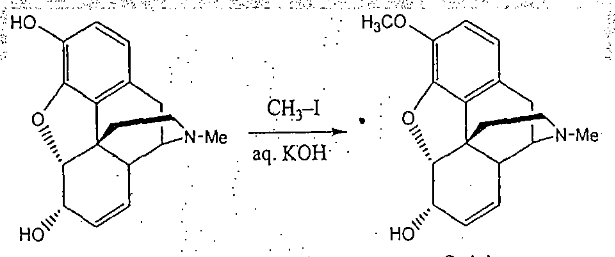
Morphine is the chief alkaloid in opium.

The diacetyl derivative of morphine is known as Heroin.



Heroine

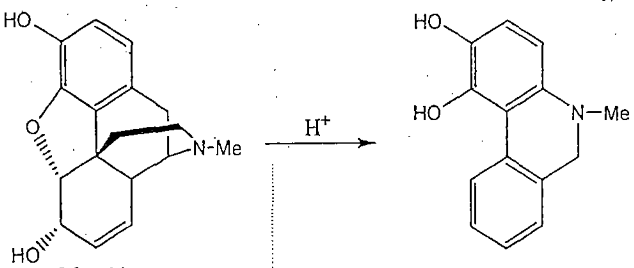
When heated with methyl iodide in the presence of aqueous potassium hydroxide, morphine methylated to give codeine.



Codeine

Morphine when heated with concentrated hydrochloride undergoes rearrangement to form apomorphine.

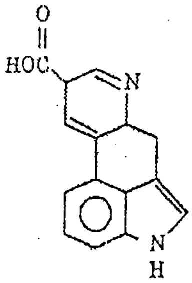
This rearrangement occurs with the loss of the elements of water ($C_{17}H_{19}NO_3 \rightarrow C_{17}H_{17}NO_3$)



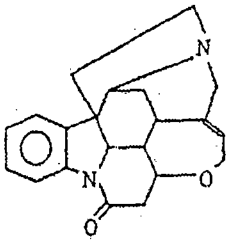
Morphine Apomorphine

The details of the mechanism are uncertain.

(viii) Indole group

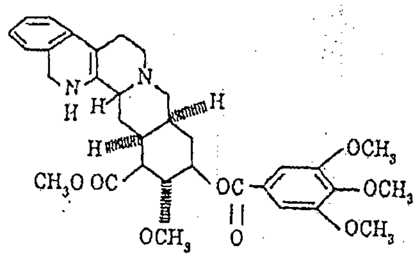


Lysergic acid (Part of LSD)



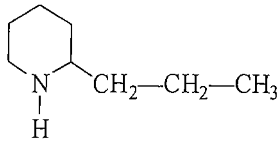
Strychnine

(Dimethylamide of lysergic acid = LSD)

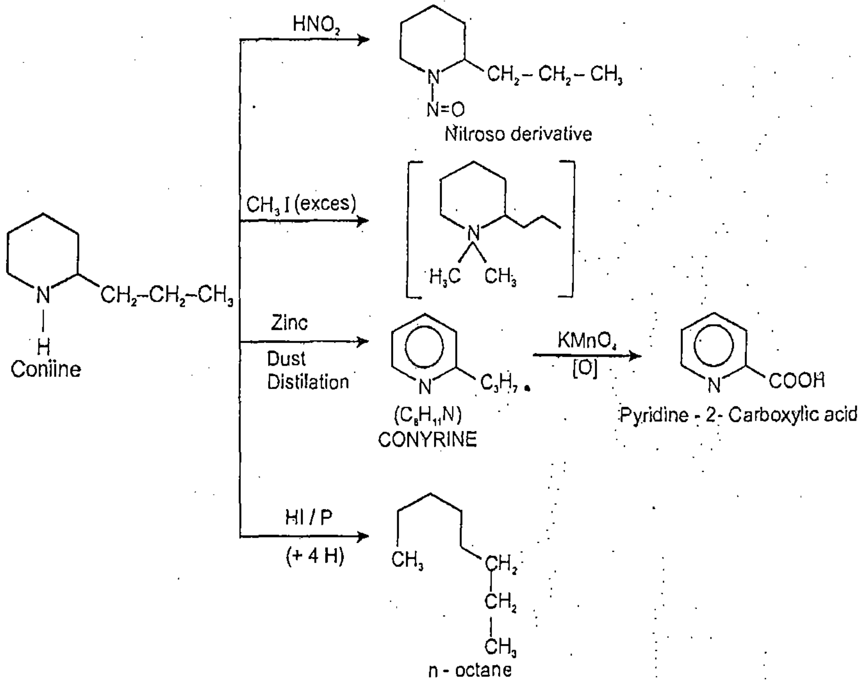


3. CONIINE

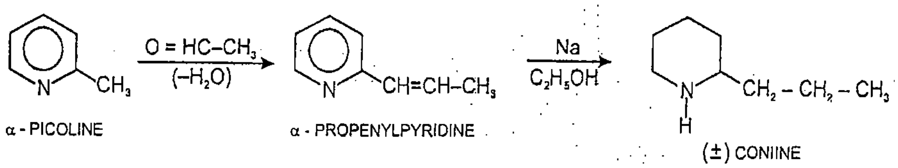
Molecular formula – $C_8H_{17}N$

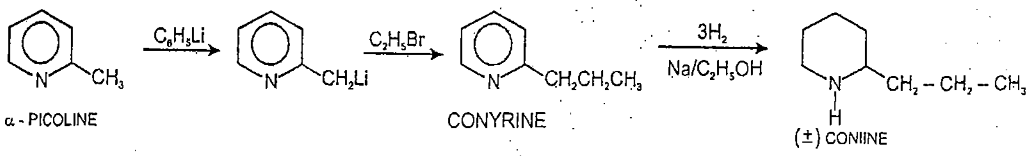
Structural formula – 

Chemical reactions



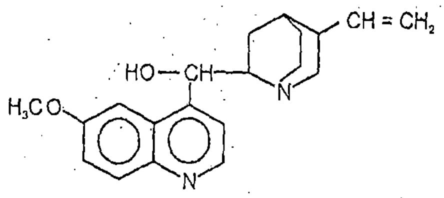
Synthesis



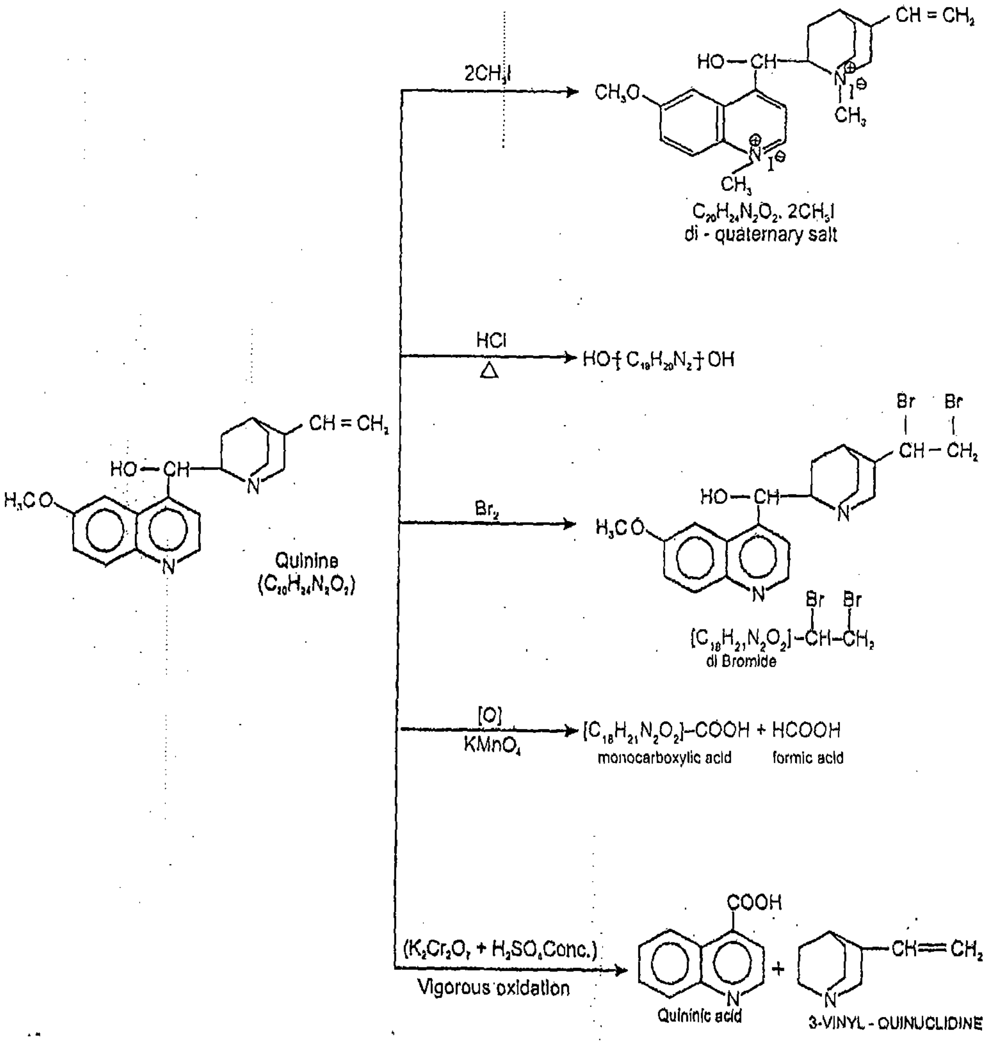


4. QUININE

Molecular formula: $C_{20}H_{24}N_2O_2$

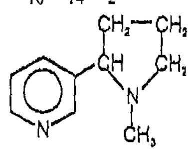
Structural formula: 

Chemical Properties



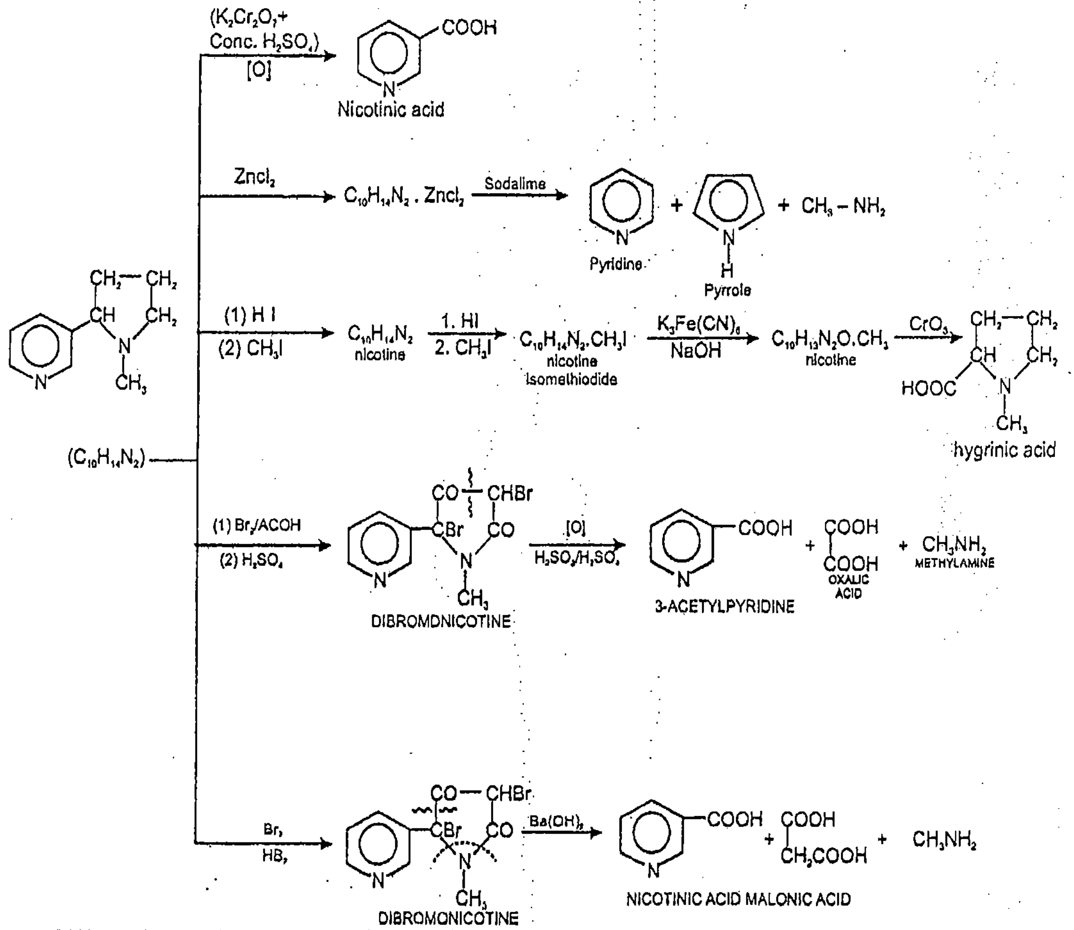
5. NICOTINE

Molecular formula: $C_{10}H_{14}N_2$

Structural formula: 

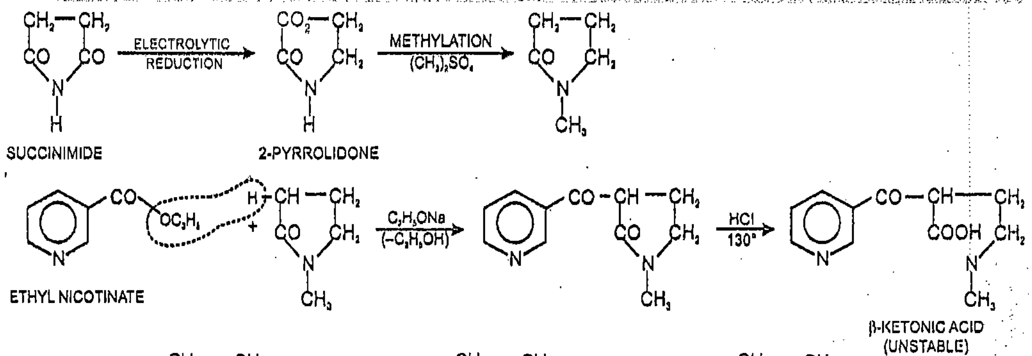
(±) – Nicotine

Chemical Properties

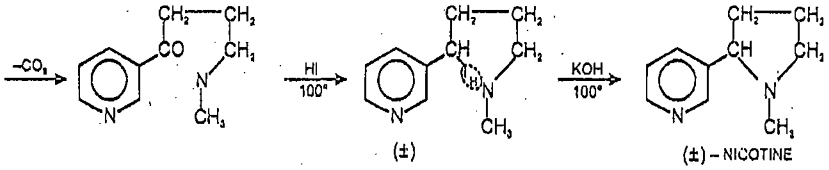


Synthesis:

(i)



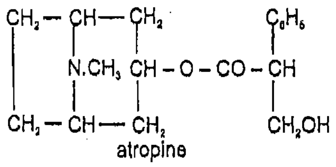
(ii)



6. ATROPINE

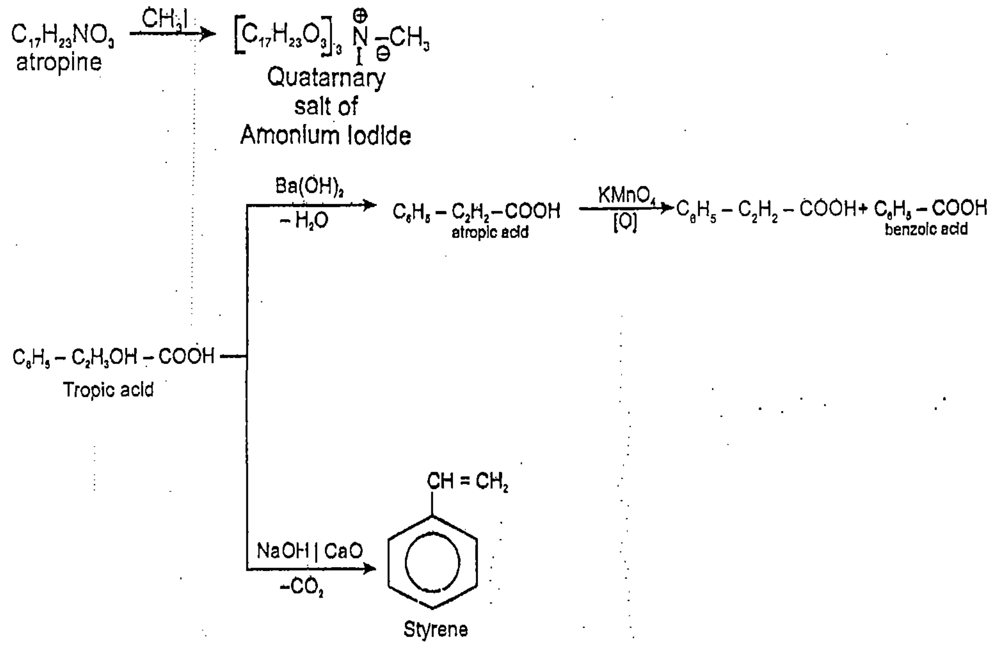
Molecular formula: $C_{17}H_{23}NO_3$

Structural formula:



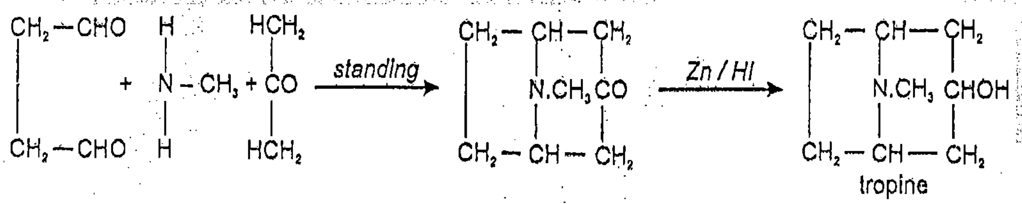
(1) $$\underset{\text{atropine}}{C_{17}H_{23}NO_3} + H_2O \xrightarrow[130^\circ]{H^+} \underset{(\pm)\text{-tropic acid}}{C_9H_{10}O_3} + \underset{\text{tropine}}{C_8H_{15}NO}$$

(2)

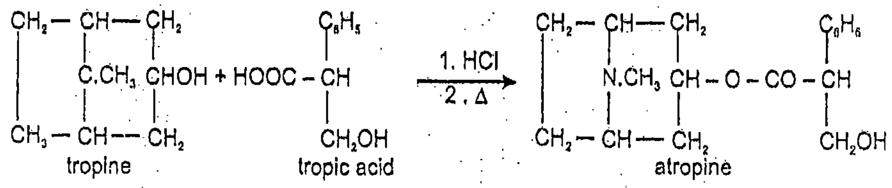


Robinson Synthesis

Step 1



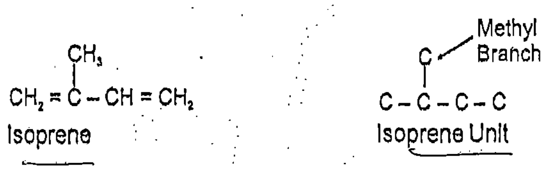
Step 2



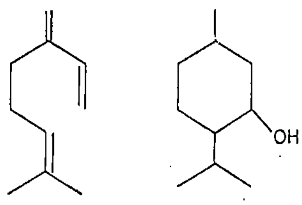
TERPENES

1. Introduction

Terpenes are plant – produced compounds which contain one or more isoprene units in their carbon skeleton.



Examples:



Myrcene Menthol

Points to Remember

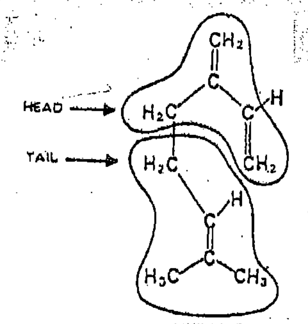
1. Terpenes are isolated from plants
2. An isoprene unit is a chain of four carbons with one carbon attached to the second carbon of the four carbon chain.
3. All terpenes contain 2, 3, 4, 5, 6 or 8 isoprene units.
4. The structure of terpenes are frequently represented with Ene formulas. A corner is meant to represent a carbon atom with appropriate number of hydrogens. A line branching off the structure represents a methyl branch, not a hydrogen.

2. Isoprene rule

The isoprene rule states that: the molecules of all terpenes are composed of two or more isoprene units, usually joined in a head - to - tail fashion.

$$\text{(Head) } C-\underset{}{\overset{C}{\overset{|}{C}}}-C-C \text{ (tail)}$$

The head - to tail arrangement of two isoprene units in myrcene is shown below:



MYRCENE

3. Classification

Terpenes are classified according to the number of isoprene units (C_5) in the molecule.

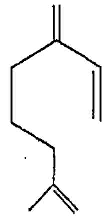
Monoterpenes:	2 Isoprene unite
Sesquiterpenes:	3 Isoprene unite
Diterpenes:	4 Isoprene unite
Triterpenes:	6 Isoprene unite
Tetraterpenes:	8 Isoprene unite

These classes are further subdivided according to the number of rings in the molecule:

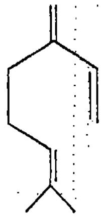
Acyclic:	No Rings (Straight-chain)
Monocyclic:	1 Ring
Bicyclic	2 Ring
Tricyclic	3 Rings

Then terpenes are classified on the basis whether they are pure hydrocarbons or oxygenated derivatives aldehydes, Ketones, ethers, or alcohols.

Acyclic Monoterpenes

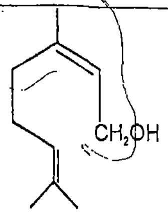


Ocimene

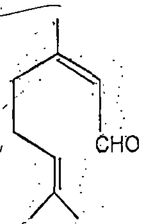


Myrcene

Acyclic Oxygenated Monoterpenes

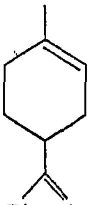


Geraniol

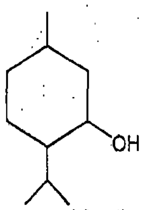


Citral

Monocyclic Monoterpenes

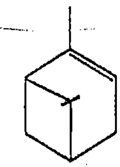


Dipentene

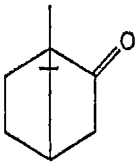


Menthol

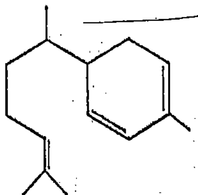
Bicyclic Monoterpenes



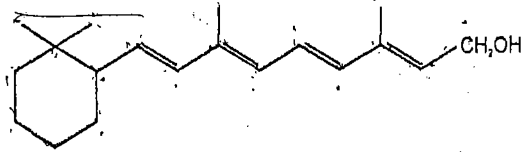
a-Pinene



Camphor

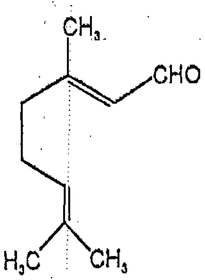


Zingiberene (Sesquiterpene)

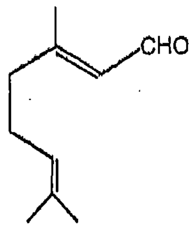


Vitamin-A (Diterpene)

4. **CITRAL**

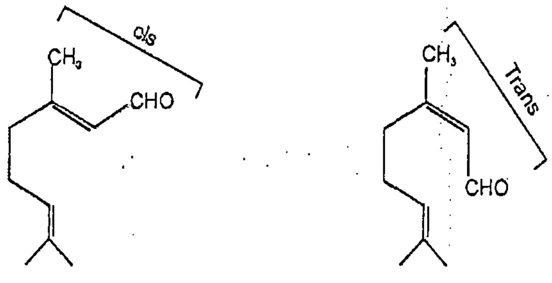


Canbe Written as



Geometrical Isomerism

The cis- isomer is known as citral - α. The trans-isomer is known as citral-β.



Citral-α   Citral-β

Constitution of citral

(a) Molecular formula of citral is $C_{10}H_{16}O$.

(b) There are two carbon-carbon double bonds in citral

Citral adds two molecules of bromine to form a tetrabromide. This shows the presence of two carbon-carbon double bonds.

$$C_{10}H_{16}O + 2Br_2 \rightarrow C_{10}H_{18}OBr_4$$

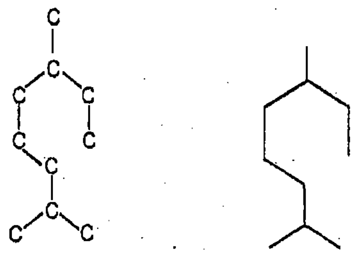
(c) There is an aldehyde group in citral

Citral undergoes oxidation with silver oxide to give geranic acid without loss of any carbon. This shows the presence of –CHO group.

$$\underset{\text{Citral}}{(C_9H_{15})-\overset{\overset{O}{\|}}{C}-H} + [O] \xrightarrow{Ag_2O} \underset{\text{Geranic acid}}{(C_9H_{15})-\overset{\overset{O}{\|}}{C}-OH}$$

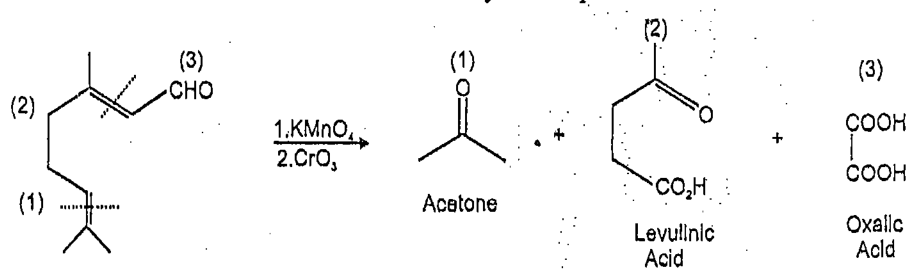
(d) Carbon skeleton of citral

The two isoprene units are joined head - to - tail in citral (Isoprene rule) and its carbon skeleton was



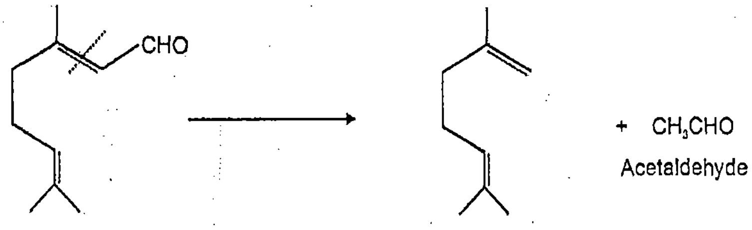
(e) Location of carbon-carbon double bonds in citral

Oxidation of citral with alkaline $KMnO_4$, followed by chromic acid, gives acetone, levulinic acid and oxalic acid. This is accountable only if the position of the double bonds is as shown below



Citral
(Prorosed structure)

The above structure of citral is supported by the hydrolysis of citral with aqueous Na_2CO_3 to give methylheptanone + acetaldehyde.



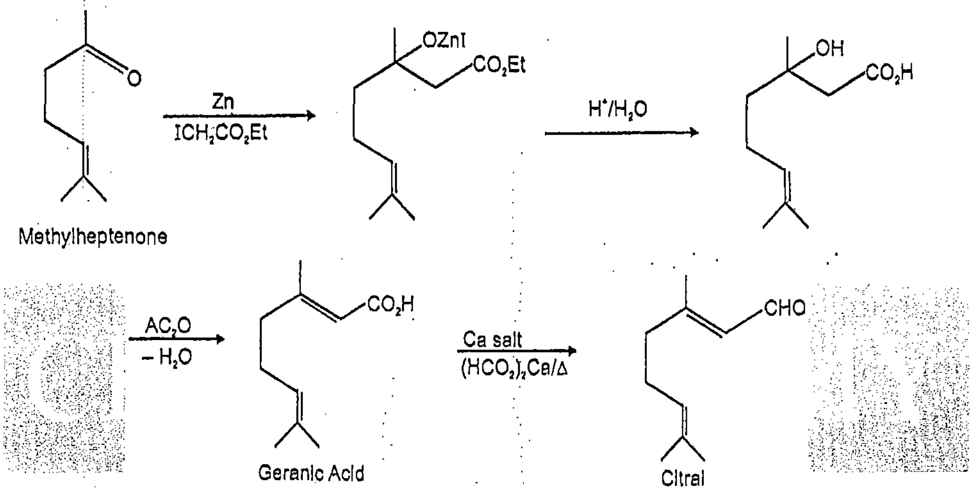
Citral Methylheptenone

(f) Synthetic Proof

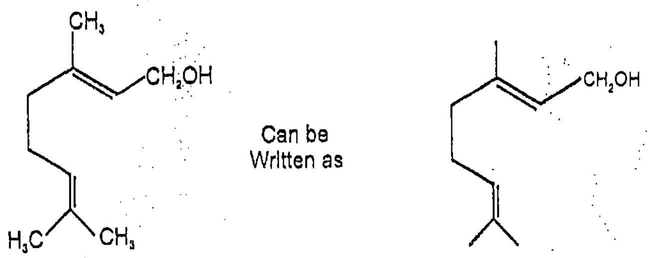
The structure of citral has been confirmed by the following synthesis.

Reminder

The first step is the reformatsky reaction

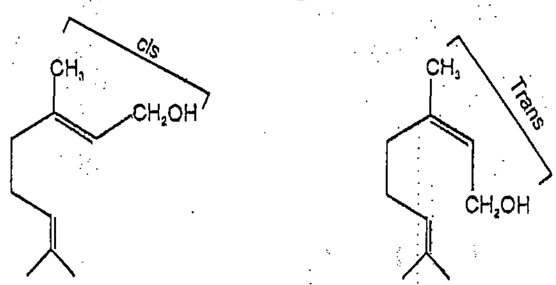


5. GERANIOL



Geometrical Isomerism

The cis isomer is known as geraniol. The transisomer is known as nerol.



Geraniol (Cis - From) Nerol (Trans-Form)

(a) Molecular formula of geraniol is $C_{10}H_{18}O$.

(b) There are two carbon-carbon double bonds in geraniol

Geraniol adds two bromine molecules and two hydrogen molecules on catalytic hydrogenation. This show the presence of two carbon-carbon double bonds.

$$C_{10}H_{18}O + 2Br_2 \rightarrow C_{10}H_{18}OBr_4$$

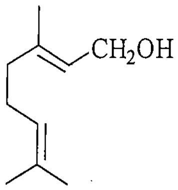
$$C_{10}H_{18}O + 2H_2(Ni) \rightarrow C_{10}H_{22}O$$

(c) There is a $-CH_2OH$ group in geraniol

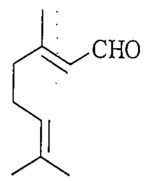
When geraniol is oxidised it first forms citral – α (an aldehyde) and then geranic acid (a carboxylic acid) containing the same number of carbon atoms as geraniol

$$\underset{\text{Geraniol}}{(C_9)CH_2OH} \xrightarrow{[O]} \underset{\text{Citral}-\alpha}{(C_9)CHO} \xrightarrow{[O]} \underset{\text{Geranic acid}}{(C_9)COOH}$$

This shows that geraniol is a primary alcohol and the arrangement of carbon atoms and the positions of the two double bonds are the same as citral-a. Knowing the structure of citral-α, geraniol is given the following structure.



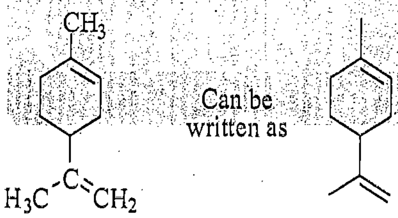
Geraniol



Citral-a
(cis-from)

6. **DIPENTENE**

Structural Formula



Occurrence

Dipentene, also known as (±). Limonene occurs in terpentine oil.

Use

Constitution of Dipentene

Dipentene is used as a flavouring agent in dental and shaving creams. It is also used in the manufacture of p-cymene, p-menthane and synthesit resins.

(a) Molecular formula of dipentene is $C_{10}H_{16}$

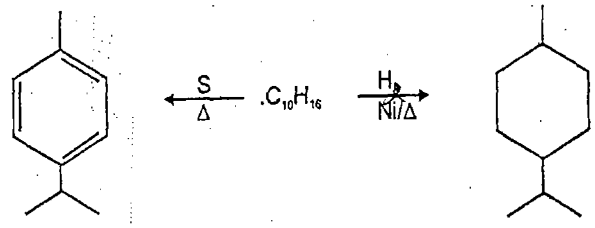
(b) There are two carbon-carbon double bonds in dipentene

Dipentene adds two molecules of bromine to give a tetrabromide. This shows the presence of two carbon-carbon double bonds.

$$C_{10}H_{16} + 2Br_2 \rightarrow C_{10}H_{16}Br_4$$

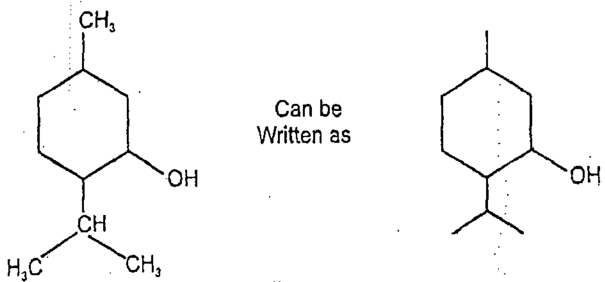
(c) Carbon skeleton in dipentene

Dipentene undergoes dehydrogenation over heated suphur to give p-cymene. It also undergoes catalytic hydrogenation to give p-menthane. These reactions show the nature of the carbon frame work in dipentene.



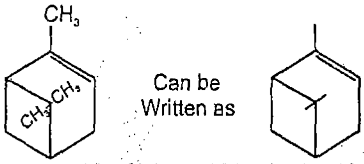
P-Cymone P-methane

7. **MENTHOL**

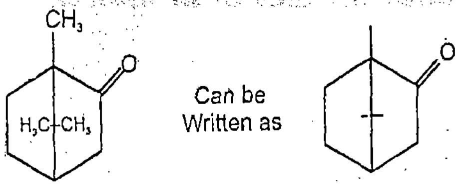


Menthol occurs in peppermint oil.

α-Pinene

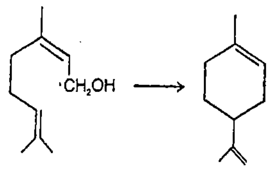


Camphor

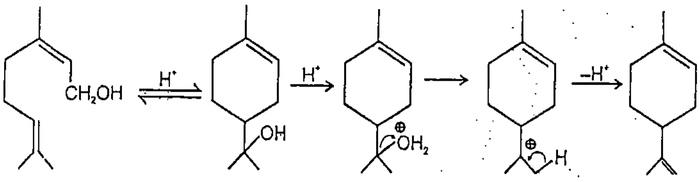


SOLVED EXAMPLES

1. Give a mechanism of following conversion



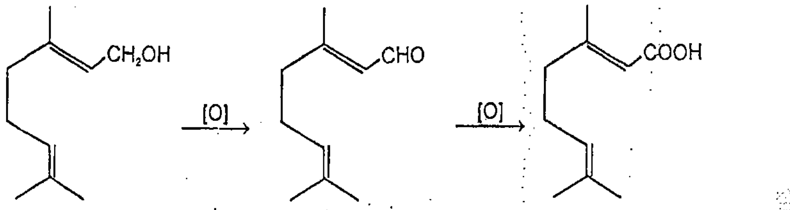
Sol.



2. (a) What happens when geraniol is subjected to vigorous oxidation?

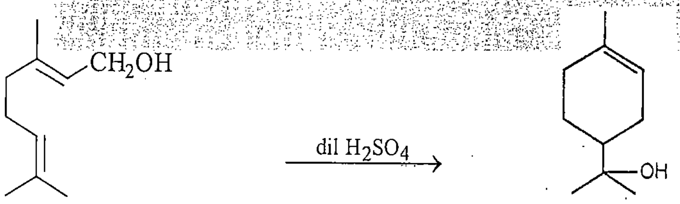
(b) What happens when geraniol is treated with dilute sulphuric acid?

Sol. (a) This is a 2-step reaction. Geraniol is first converted to citral - α and then to geranic acid.



Geraniol Citral -a Geranic acid

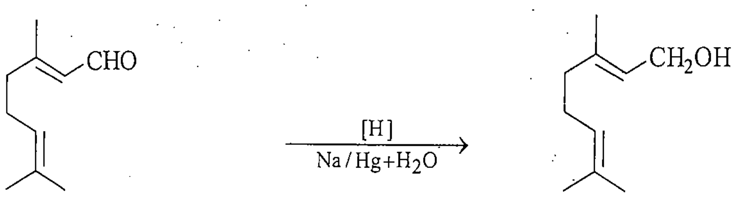
(b) a-Terpineol is formed.



Geraniol α- Terpineol

3. How will you synthesis geraniol from citral?

Sol.



Citral Geraniol

EXERCISE - I

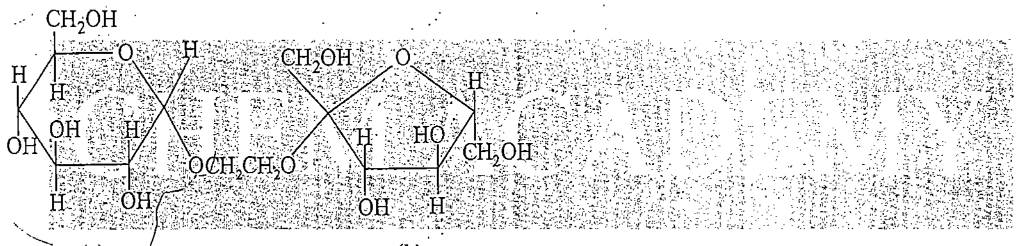
Single Answer Correct Type

1. Which of the following pairs give positive Tollen's test?
(a) Glucose, sucrose (b) Glucose, fructose
(c) Hexanal, Acetophenone (d) Fructose, sucrose

2. Two forms of D – glucopyranose, are called.
(a) Enantiomers (b) Anomers (c) Epimers (d) Diastereomers

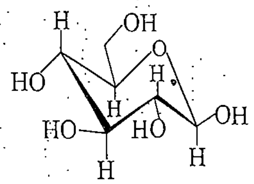
3. **Statement-1 :** Glucose gives a reddish-brown precipitate with Fehling's solution.
because
Statement-2 : Reaction of glucose with Fehling's solution gives CuO and gluconic acid.
(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

4. The correct statement about the following disaccharide is



(a) Ring **(a)** is pyranose with α-glycosidic link.
(b) Ring **(a)** is furanose with α-glycosidic link
(c) Ring **(b)** is furanose with α-glycosidic link
(d) Ring **(b)** is pyranose with β-glycosidic link

5. The following carbohydrate is



(a) a ketohexose (b) an aldohexose (c) an α-furanose (d) an α-pyranose

6. The term anomers of glucose refers to
(a) Isomers of glucose that differ in configurations at carbons one and four (C–1 and C-4)
(b) A mixture of (d)-glucose and (L)-glucose
(c) Enantiomers of glucose
(d) Isomers of glucose that differ in configuration at carbon one (C–1)

7. Which of the following is an example of aldopentose?
(a) Erythrose (b) Ribose (c) Fructose (d) Dihydroxyacetone

8. Which pair is different for reaction with Fehling solution:
(a) Glucose, Fructose (b) HCHO, CH_3CHO
(c) CH_2COCH_3, C_6H_5CHO (d) Glucose, Sucrose

9. Glucose contains in addition to aldehyde group
(a) One secondary OH and four primary OH groups
(b) One primary OH and four secondary OH groups
(c) Two primary OH and three secondary OH groups
(d) Three primary OH and two secondary OH groups

10. Naturally occuring (+) - sucrose is :
(a) α-D-glucopyronoside-β-D-fructofuranoside
(b) α-D-glucopyronoside-α-D-fructofuranoside
(c) β-D-glucopyronoside-α-D-fructofuranoside
(d) β-D-glucopyronoside-β-D-fructofuranoside

11. When methyl D-glucopyranoside is treated with HIO_4 how many moles of HIO_4 are consumed with per mole of the sugar ?
(a) 2 (b) 3 (c) 4 (d) 5

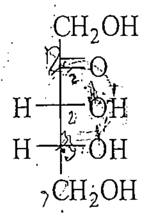
12. The configuration of the C-2 epimer of D-glucose is-
(a) 2R, 3S, 4R, 5S (b) 2S, 3S, 4R, 5R (c) 2S, 3R, 4S, 5R (d) 2R, 3S, 4R, 5R

13. Same osazone derivative is obtained in case of D-glucose, D-Mannose and D-Fructose due to
(a) the same configuration at C-5 (b) the same constitution.
(c) the same constitution at C-1 and C-2
(d) The same constitution and same configuration at C-3, C-4, C-5 and C-6 but different constitution and configuration at C-1 and C-2 which becomes identical by osazone formation.

14. Amylose and cellulose both are linear polymers of glucose. The difference between them is:
(a) Amylose has β (1 → 4') linkage and cellulose has α (1 → 4') linkage
(b) Amylose has α (1 → 4') linkage and cellulose has β (1 → 4') linkage
(c) Amylose has α (1 → 4') linkage and cellulose has α (1 → 6') linkage
(d) Amylose has β (1 → 4') linkage and cellulose has β (1 → 6') linkage

15. The colour of the precipitate formed when a reducing sugar is heated with Fehling solution is:
(a) Brown (b) Red (c) Blue (d) Green

16. The absolute configurations at the two chiral centers in D-Ribulose are



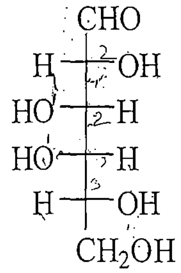
3R

4R

D-Ribulose

(a) 3R, 4R (b) 3R, 4S (c) 3S, 4R (d) 3S, 4S

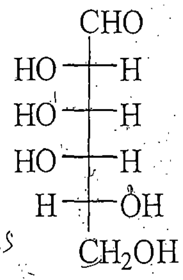
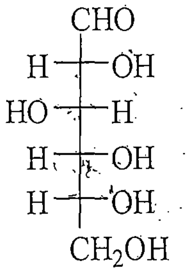
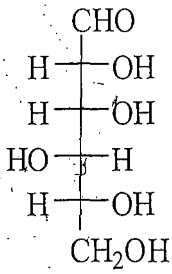
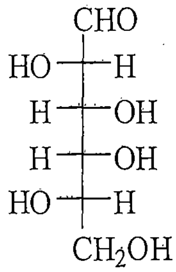
17. The structure of D-galactose is



3S

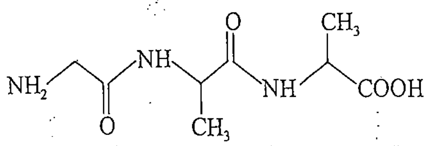
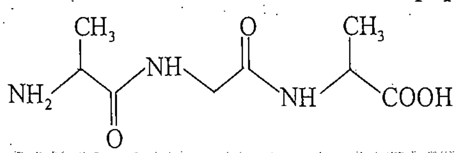
S

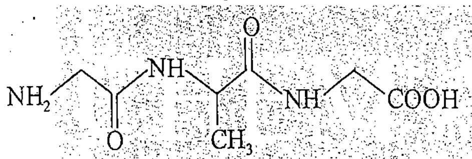
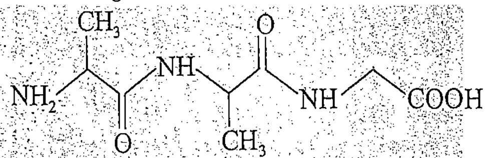
which one of these structures is L-galactose?

(a)  (b)  (c)  (d) 

4S

18. A tripeptide is written as Glycine-Alanine-Glycine. The correct structure of the tripeptide is

(a)  (b) 

(c)  (d) 

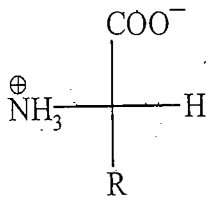
19. Which compound can exist in a dipolar (zwitter ion) state

(a) $C_6H_5CH_2CH(N=CH_2)COOH$ (b) $(CH_3)_2CH \cdot CH(NH_2)COOH$

(c) $C_6H_5CONHCH_2COOH$ (d) $HOOC \cdot CH_2CH_2COCOOH$

– COOH is more acidic But NH2 is less Basic

Nucleus

20. The pH of the solution containing following zwitter ion species is 

(a) 4 (b) 6 (c) 8 (d) 9

21. Peptide linkage is -

(a) $-\overset{O}{\overset{\|}{C}}-O-$ (b) $-\overset{O}{\overset{\|}{C}}-NH_2$ (c) $-\overset{O}{\overset{\|}{C}}-NH-$ (d) $-\overset{O}{\overset{\|}{C}}-NH-NH_2$

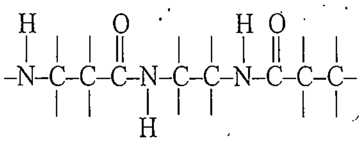
22. Test used to identify peptide linkage in protein is:

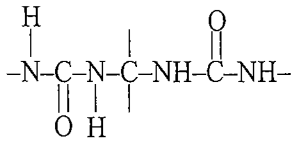
(a) Biuret (b) Ninhydrin test (c) Molisch test (d) 2,4-DNP test

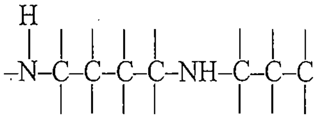
Identify -C-NH-   All proteins   Carbohydrates

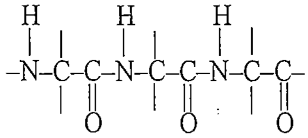
Quickly

23. Which one of the following structures represents the peptide chain:

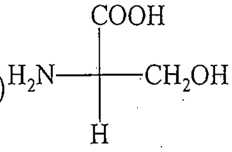
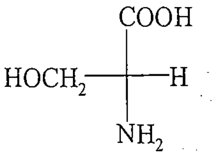
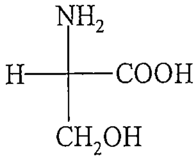
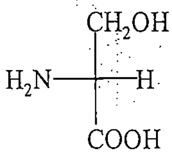
(a) 

(b) 

(c) 

(d) 

24. Among the following L-serine is:

(a) 
(b) 
(c) 
(d) 

25. Which substance is not present in nucleic acid?

(a) Cytosine (b) Adenine (c) Thymine (d) Guanidine

26. To identify the N-terminal amino acid of peptide 1-fluoro-2, 4-dinitrobenzene (DNFB) is used. This is called

(a) van-Slyke reagent (b) Sorenson reagent (c) Sanger reagent (d) None of these

pH = pKa

27. CH_2COOH [$pK_a = 2.34$] ; NH_2 ⟵ [$pK_b = 4.40$] Hence, isoelectric point is

Hence $\boxed{pK_a + pK_b = 14}$

(a) 3.37 (b) 10.63 (c) 5.97 (d) 8.03

28. Which reagent is used in the Edman degradation for N-terminal group analysis of peptides?

(a) Phenyl isothiocyanate (b) Di-t-butyl dicarbonata
(c) Dicyclohexyl carbodiimide (d) Benzyl chloroformate

29. A nucleoside on hydrolysis gives

(a) an aldopentose and orthophosphoric acid (b) an aldopentose and a heterocyclic base
(c) an aldopentose, a heteroccyclic base and orthophosphoric acid
(d) a heterocyclic base and orthophosphoric acid

30. In DNA, the complementary bases are

(a) Uracil and adenine; cytosine and guanine (b) Adenine and thymine; guanine and cytosine
(c) Adenine and thymine; guanine and uracil
(d) Adenine and guanine; thymine and cytosine

31. The process by which synthesis of protein takes place based on the genetic information present in m-RNA is called

(a) messenger hypothesis (b) replication
(c) transcription (d) translation

32. The complementary strand of DNA for the following single stranded DNA sequence, 5'-A-T-C-A-T-G-C-3' is
(a) 5'-A-T-C-A-T-G-C-3' (b) 5'-T-A-G-T-A-C-G-3'
(c) 5'-G-C-A-T-G-A-T-3' (d) 5'-C-G-T-A-C-T-A-3'

33. Match the isoelectric points with the amino acids

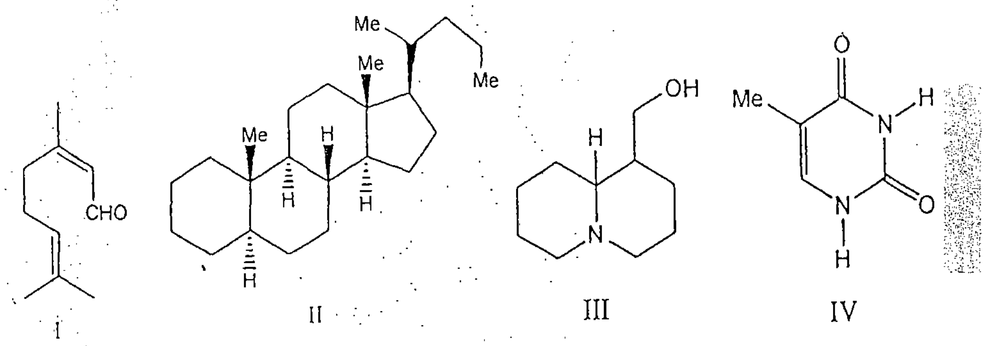
Amino acid		Isoelectric point
(X) H_2NCH_2COOH	(I)	9.5
(Y) $HOOCCH_2CH_2CH(NH_2)COOH$	(II)	6.0
(Z) $H_2N(CH_2)_4CH(NH_2)COOH$	(III)	3.1

(a) X-II, Y-III, Z-I (b) X-III, Y-I, Z-II (c) X-I, Y-II, Z-III (d) X-II, Y-I, Z-III

34. Caffeine, present in tea leaves and coffee seed, is an example of
(a) alkaloids (b) steroid (c) terpenoid (d) vitamin

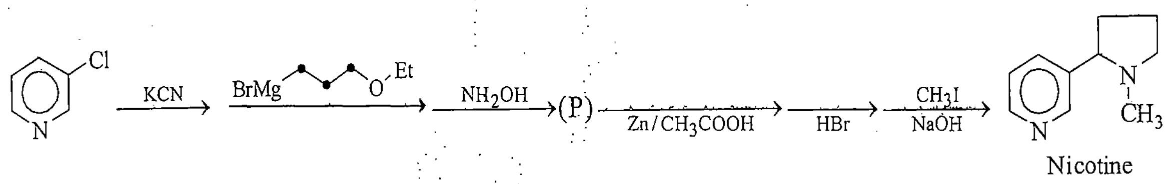
35. Mevalonic acid is a biogenetic precursor for
(a) carbohydrates (b) proteins (c) terpenoids (d) alkaloids

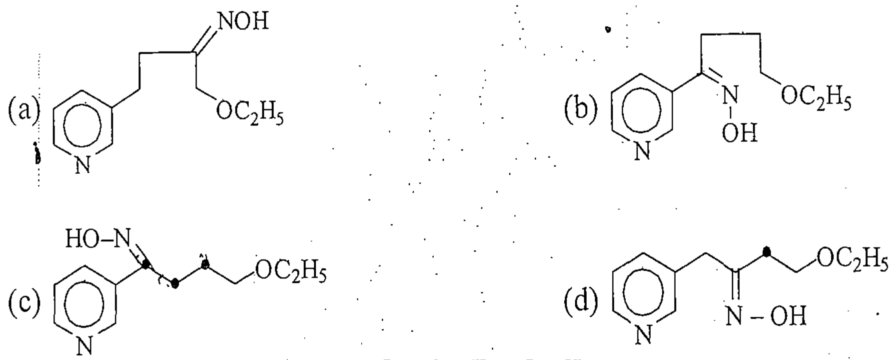
36. Match the following compounds with their respective classes.



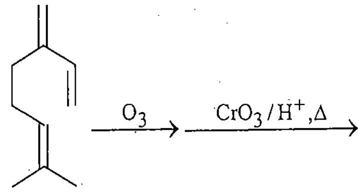
(a) I : Steroid; II : terpenoid; III : alkaloid; IV : DNA base
(b) I : terpenoid; II : steroid; III : alkaloid; IV : DNA base
(c) I : terpenoid; II : steroid; III : DNA base; IV : alkaloid
(d) I : steroid; II : terpenoid; III : DNA base; IV : alkaloid

37. The intermediate product (P) obtained in synthesis of Nicotine are



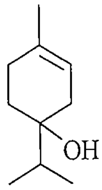
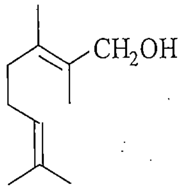
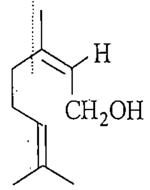
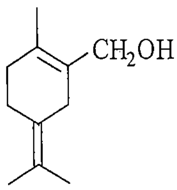


38. The ozonolysis and oxidation products of terpenoid myrcene are

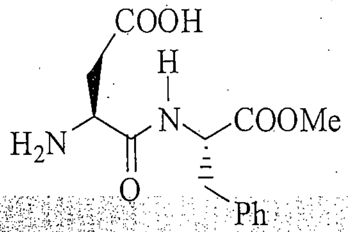


(a) Pimelic acid + $5CO_2$ + CH_3COOH (b) Glutaric acid + $6CO_2$ + CH_3COOH
(c) Adipic acid + $4CO_2$ + CH_3COOH (d) Succinic + $4CO_2$ + CH_3COOH

39. Geraniol ($C_{10}H_{18}O$ Terpenoid) has structure

(a)  (b)  (c)  (d) 

40. The amino acid constituents of artificial sweetener given below are

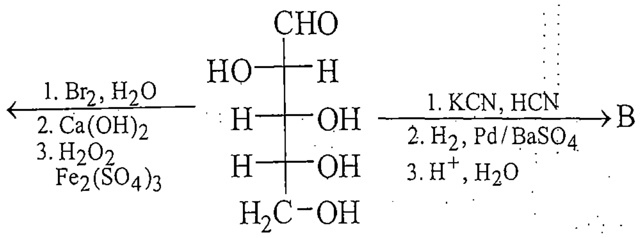


(a) D-Glutamic acid and L-phenylglycine (b) L-Glutamic acid and L-Phenylalanine
(c) L-Arpartic acid and L-Phenylalanine (d) L-Arpartic acid and L-Tyrosine

41. Among the following which can differntiate between glucose and fructose
(a) Tollen's reagent (b) B_2^+, H_2O (c) 2, 4.DNP (d) Zn + HCl

42. The configurations of carbon atoms C3 and C4 in D-ribose, respectively are
(a) R and S (b) S and R (c) R and R (d) S and S

43. The major product A and B in the following reaction sequences are

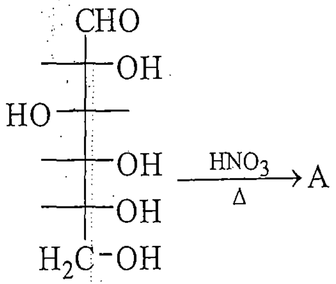


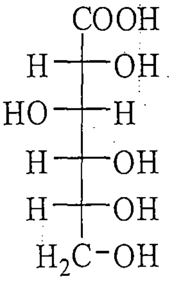
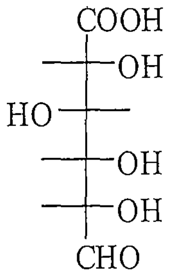
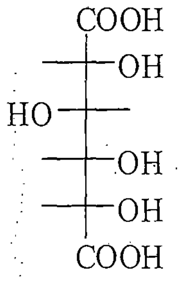
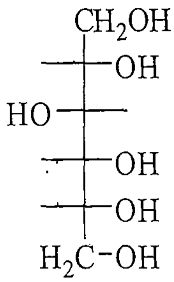
(a) A = D-threose; B = D-glucose (b) A = D-erythrose, B = D-glucose + D-mannose
(c) A = D-threose; B = D-glucose + D-mannose
(d) A = D - tartaric acid; B = D-glucose

44. Compolementary strand form by transcription of DNA to RNA
5′-A–G–G–A–C–G
(a) 5′-U–G–C–U–G–C-3′ (b) 5′-T–G–C–T–G–C-3′
(c) 5′-C–G–U–C–G–U–3′ (d) 5′–C–G–T–C–G–T-3′

45. Reagent which are used in Ruff degradation is
(a) H_2O / Fe^{+3} (b) H_2O_2 / Fe^{+2} (c) H_2O_2 / Fe^{+3} (d) H_2O / Fe^{+2}

46. Major product formed in the following reaction is

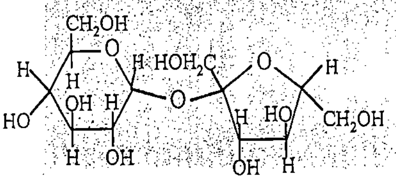


(a)  (b)  (c)  (d) 

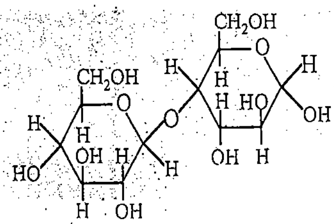
EXERCISE - 2

One or More Than One Correct Answer Type

1. The correct statement(s) about the following sugars X and Y is(are)



(X)



(Y)

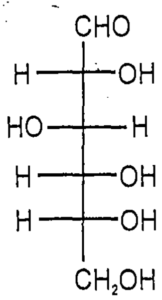
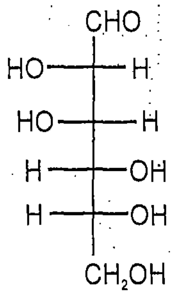
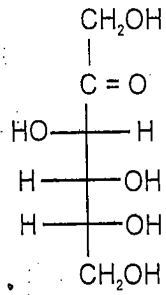
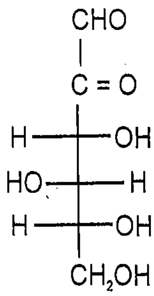
(a) X is a reducing sugar and Y is a non-reducing sugar

(b) X is a non-reducing sugar and Y is a reducing sugar

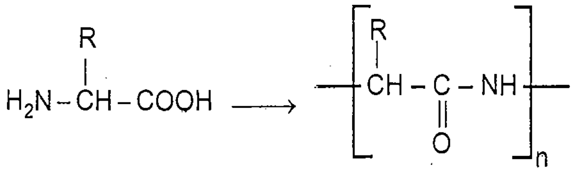
(c) The glucosidic linkages in X and Y are α and β, respectively.

(d) The glucosidic linkages in X and Y are β and α, respectively.

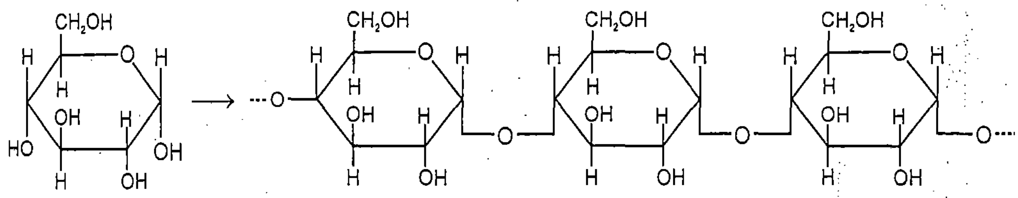
2. When D-Glucose is placed in basic aqueous solution an equilibrium mixture of three compounds is obtained. Which of the following will be present in equilibrium mixture.

(a)  (b)  (c)  (d) 

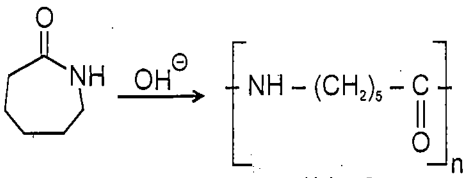
3. Which of the following polymerisation reaction can not have branched polymers also.

(a) 

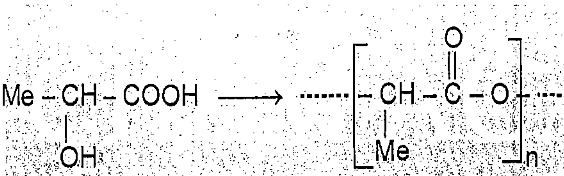
A polypeptide

(b) 

(polysaccharide)

(c) 

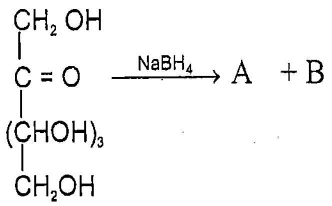
Nylon-6

(d) 

Polylactic acid

4. Which of the following is /are reducing sugar

(a) Sucrose (b) Glucose (c) Fructose (d) methylmaltoside

5. 

Fructose

The product A and B in the above reaction are

(a) Diastereomers (b) C - 2 epimers

(c) Anomers (d) Optically active hexahydroxy compounds

6. Which of the following pairs is (are) correctly matched

(a) α- D (+) glucose and β-D(+) glucose → C - 2 epimers

(b) Glucose and fructose → C - 3 epimers

(c) Glucose → mutarotation

(d) Sucrose → Glucose + fructose

7. Which of these are polysaccharides of glucose ?

(a) Starch (b) Cellulose (c) Sucrose (d) Lactose

8. The correct structure of glycine at given pH are :

(a) $H_3\overset{\oplus}{N}CH_2-\underset{\underset{O}{\|}}{C}-OH$ at pH = 2.0 (b) $H_3\overset{\oplus}{N}CH_2-\underset{\underset{O}{\|}}{C}-O^{\ominus}$ at pH = 6.0

(c) $H_2NCH_2-\underset{\underset{O}{\|}}{C}-O^{\ominus}$ at pH = 9 (d) $H_2NCH_2-\underset{\underset{O}{\|}}{C}-OH$ at pH = 12

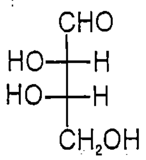
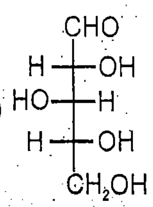
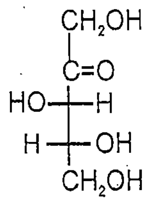
9. The correct statement (s) about starch

(a) It is a pure single compound

(b) It is mixture of two polysaccharides of glucose

(c) It involves the ($C_1 - C_4$) α - glycosidic linkage between two α - D glucose units

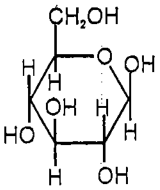
(d) It involves branching by ($C_1 - C_6$) glycosidic linkage

10. (I)  (II)  (III) 

The correct statement about the sugars given above are

(a) I and II are L-Sugars (b) II and III above D-Sugar

(c) I and III are D-sugars (d) I is L-sugar

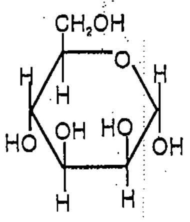
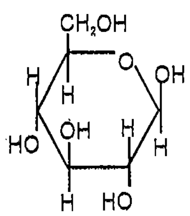
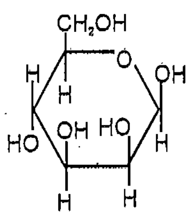
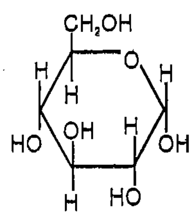
11.  Glucose

The correct statements about above structure of glucose are :

(a) It is a Pyranose form (b) It is a furanose form

(c) It is a β-anomer (d) It is a D -sugar

12. D-Mannose differs from D-glucose in its stereochemistry at C-2. The pyranose form of D-Mannose is

(a)  (b)  (c)  (d) 

13. The correct statements about anomers are

(a) Anomers have different stereochemistry at C-1(anomeric carbon)

(b) α-D-glucopyranose and β-D-glucopyranose are anomers

(c) Both anomers of D-glucopyranose can be crystallised and purified.

(d) When pure α-D-glucopyranose is dissolved in water its optical rotation slowly changes

14. The correct statements about peptides are

(a) A dipeptide has one peptide link between two amino acids.

(b) By convention N-Terminus is kept at left and C- terminus at right in the structure of a peptide

(c) If only one amino group and one carboxylic acid, group are available for reaction, then only one dipeptide can forms.

(d) A polypeptide with more than hunderd amino acid recidues (mol. mass > 10,000) is called a protein

15. Among the following, the correct statement(s) about ribose is/are

(a) On reduction with $NaBH_4$, it gives optically inactive product

(b) On reduction with Br_2-$CaCO_3$ water it gives optically inactive product

(c) It gives positive tollen's test

(d) It is reducing sugar

16. The Correct statement about Lactose is/are

(a) It gives two molecules of glucose on hydrolysis

(b) It gives D-galactose and D-glucose on hydrolysis

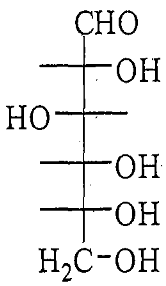
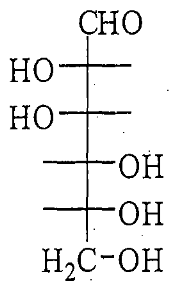
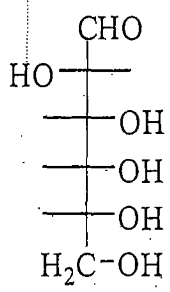
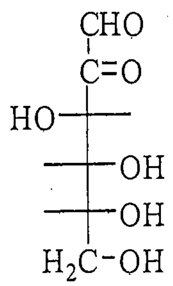
(c) Subunits are joined through β-1,4′glycosidic linkage

(d) It is non reducing sugar.

17. Compound which are reducing sugar

(a) Lactose (b) Sucrose (c) Maltose (d) Glucose

18. Compound which give acid on the reaction with Br_2/H_2O is/are

(a) 
(b) 
(c) 
(d) 

EXERCISE - 3

Numerical Answer Type

1. For $HOOC-(CH_2)_2-\underset{\overset{|}{^{\oplus}NH_3}}{CH}-COOH$ Glutamic acid value of pKa_1, pKa_2, pKa_3 are 2.00, 4.65 and 9.98 respectively. At which pH Glutamic acid will not be obtained during electrophoresis at any one of the electrodes.

2. In fructose the possible optical isomers are

3. The specific rotation of two glucose anomers are $\alpha = +110^\circ$ and $\beta = +19^\circ$ and for the constant equilibrium mixtures is $+52.7^\circ$. Calculate the percentage compositions of the anomers in the equilibrium mixture.

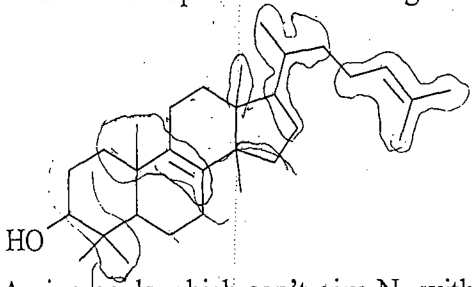
4. Calculate the specific rotation ~~of invert sugar~~, given that

   $[\alpha]_D = +52.7^\circ$ for D-glucose and

   $[\alpha]_D = -92.4^\circ$ for D-fructose

5. Number of isoprene units present in carotenoid is ________.

6. Number of isoprene units in the given compound is ________



7. Amino acids which can't ~~give N_2~~ with HNO_2 (Proline)

   Phe, Ala, Gly, Arp, Pro, His, Arg, Lys

8. How many aromatic amino acids amongst the following

   Ala, Phe, His, Tyr, Typ, Gly, Lys

9. From which position bases are joined to sugar unit in DNA

10. How many fragments are formed after hydrolyzing a sample of the given peptide with chymotrypsin.

    Ala – Lys – Phe – Gly – Asp – Trp – Ser – Arg – Tyr – Leu – His

11. How many product formed between reaction with fructose with Tollen's reagent?

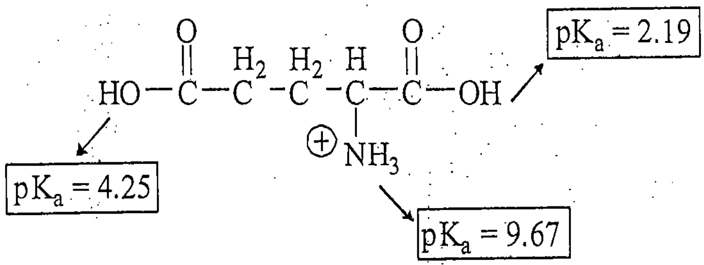
12. Specific rotation of α-anomer of glucose when dissolve in H_2O.

13. D-galactose is C-x epimer of D-glucose. Cube x is

14. How many fragments of peptide bond will form on reaction with $BrC\equiv N$.

    Ala – Lys – Phe – Gly – Arg – Net – Val – Arg – Lys – Net – Gly – Lys – Arg

15. Isoelectronic point value of the given compound is



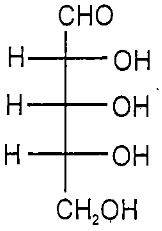
16. How many amino acid containing heterocyclic aromatic ring

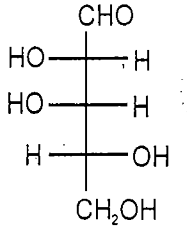
    Phe, Tyr, Pro, His, Trp, Gln, Lys, Asp

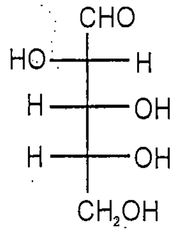
EXERCISE - IV

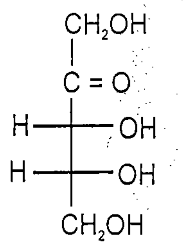
Previous Year Questions

1. Which of the following will form same product (osazone) on reaction with $PhNHNH_2$ (excess).


(X)


(Y)


(Z)

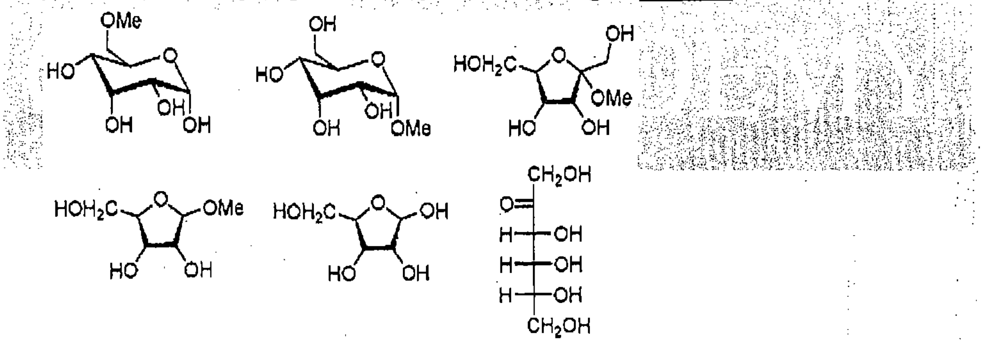

(W)

(a) X (b) Y (c) Z (d) W

2. Among the following the correct statement(s) is/are
(a) Guanine is a purine nucleobase
(b) Glycine and proline are achiral amino acids
(c) DNA contains glycosidic bonds and pentose sugars
(d) Sucrose is a non-reducing sugar

3. The maximum number of dipeptides that could be obtained by reaction of phenylalanine with leucine is ______

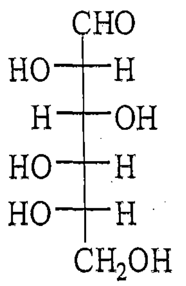
4. The number of reducing sugars among the following is ______

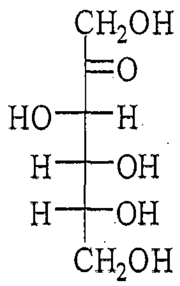


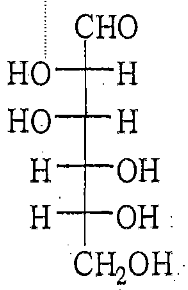
5. Consider the following reaction:

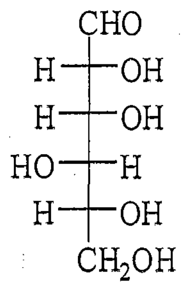
$$\text{(D)-glucose} \xrightarrow[\text{cat. } H^+]{\text{Ph-NH-NH}_2 \text{ (3 equiv)}} X$$

Among the following, the compound(s) whose osazone derivative(s) will have the same melting point as that of X is(are)

(a) 

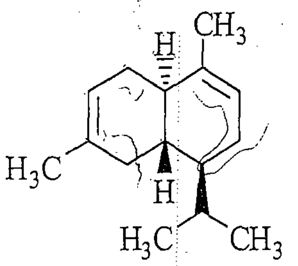
(b) 

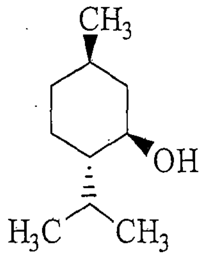
(c) 

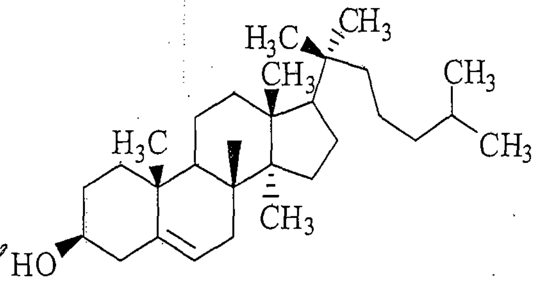
(d) 

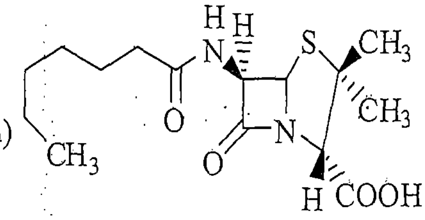
6. Tollen's test will be negative for:
(a) Glucose (b) Mannose (c) Sucrose (d) Galactose

7. Which one among the following is a sesquiterpene?

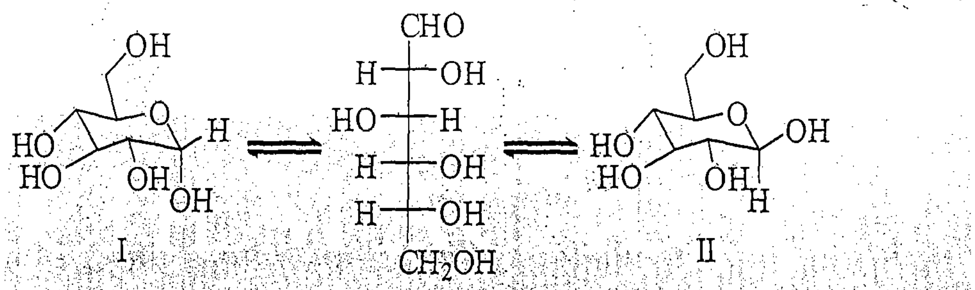
(a) 

(b) 

(c) 

(d) 

8. Specific rotations of freshly prepared aqueous solutions of I and II are +112 and +18.7, respectively. On standing the optical rotation of aqueous solution of I slowly decreases to give a final value of +52.7 due to equilibrium with II. Under this state of equilibrium, what is the ratio II : I?



$[\alpha]_D^{25} = +112$ $[\alpha]_D^{25} = +18.7$

(a) 0.57 (b) 1.00 (c) 1.75 (d) 5.9

9. Which one of the following statements is Correct?

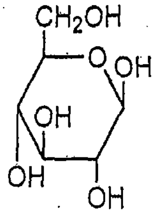
(a) Naturally occuring DNA has B-configuration.

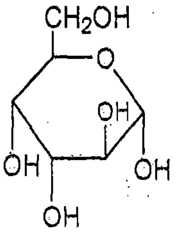
(b) Nucleic acids are derived from proteins.

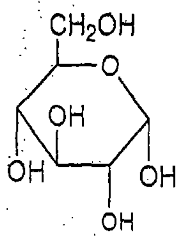
(c) Proteins store genetic information

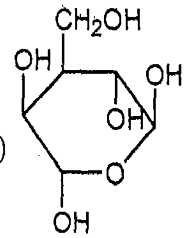
(d) Vitamins generally act as enzymes

10. The Haworth projection for α-anomer of D-glucose is

(a) 

(b) 

(c) 

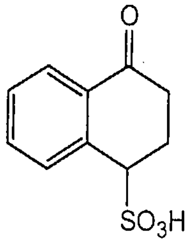
(d) 

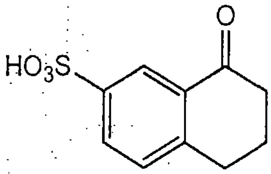
11. The complementary DNA sequence of the given DNA 5'-G-A-A-T-T-C-3' is:

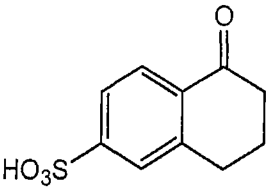
(a) 5'-C-T-T-A-A-G-3' (b) 5'-C-U-U-A-A-G-3'

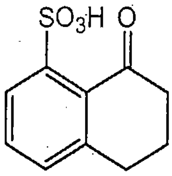
(c) 3'-C-T-T-A-A-G-5' (d) 3'-G-A-A-T-T-C-5'

12. The major mono-sulfonation product of α-tetralone is

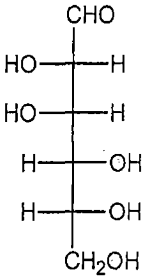
(a) 

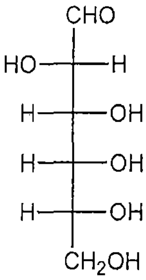
(b) 

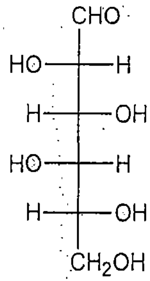
(c) 

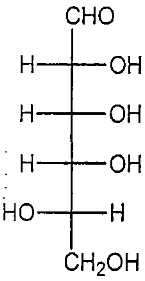
(d) 

13. The correct epimeric pair of the following is


P

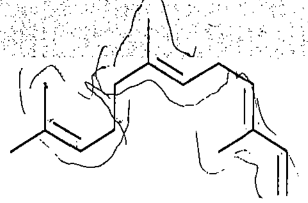

Q


R


S

(a) P and Q (b) R and Q (c) Q and S (d) R and S

14. α-Farnesene shown below is a



(a) diterpene having two isoprene units (b) triterpene having three isoprene units
(c) triterpene having four isoprene units (d) Sesquiterpene having three isoprene units.

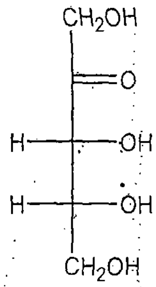
15. The correct relationship within each pair of the natural products is:

(a) Camphor – terpene; insulin – protein; nicotine – alkaloids; streptomycin – carbohydrate
(b) Camphor – terpene; insulin – carbohydrate; nicotine – alkaloid; streptomycin – lipid
(c) Camphor – alkaloid; insulin – protein; nicotine – terpene; streptomycin – carbohydrate.
(d) Camphor – carbohydrate; insulin – protein; nicotine – alkaloid; streptomycin – terpene.

16. The INCORRECT statement in the following is:

(a) The nucleobase pairs are aligned perpendicular to the helical axis in DNA.
(b) RNA contains uracil and thymine, but DNA contains only thymine.
(c) All naturally occuring amino acids with the exception of glycine are chiral
(d) All enzymes are proteins, but all proteins are not necessarily enzymes.

17. The absolute configurations at the two chiral centers in D-Ribulose are



D-Ribulose

(a) 3R, 4R (b) 3R, 4S (c) 3S, 4R (d) 3S, 4S

18. The complementary strand of DNA for the following single stranded DNA sequence, 5′–A–T–C–A–T–G–C–3′ is

(a) 5′–A–T–C–A–T–G–C–3′ (b) 5′–T–A–G–T–A–C–G–3′

(c) 5′–G–C–A–T–G–A–T–3′ (d) 5′–C–G–T–A–C–T–A–3′

ANSWER KEY

EXERCISE - I

1. b	2. b	3. c	4. a	5. b	6. d	7. b
8. d	9. b	10. a	11. a	12. b	13. d	14. b
15. b	16. d	17. d	18. c	19. b	20. b	21. c
22. a	23. d	24. c	25. d	26. c	27. c	28. a
29. b	30. b	31. d	32. c	33. c	34. a	35. c
36. b	37. b	38. d	39. b	40. c	41. b	42. c
43. b	44. c	45. c	46. c			

EXERCISE - II

1. b,c	2. a,b,c	3. a,c,d	4. b,c	5. a,b,d	6. c,d	7. a,b
8. b,c	9. b,c,d	10. b,d	11. a,c,d	12. a,c	13. a,b,c,d	14. a,b,c,d
15. a,c,d	16. a,d	17. a,c,d	18. a,b,c			

EXERCISE - III

1. 3.325	2. 8
3. α–anomer = 37.2%, β–anomer = 62.8%	4. Specific rotation : – 19.9°.
5. 4	6. 6
7. 1	8. 4
9. 9	10. 4
11. 2	12. 52.7
13. 4	14. 3
15. 3.22	16. 3

EXERCISE - IV

1. a,c,d	2. a,c,d	3. 8 or 2	4. 3	5. a,b,c	6. c	7. a
8. c	9. a	10. c	11. c	12. b	13. a	14. d
15. a	16. b	17. a	18. c			

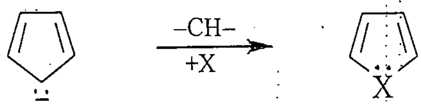
CHAPTER 9

Hetrocyclic Compound

CLASSIFICATION

(1) Five-membered Aromatic Heterocycles

These are structurally considered to be derived from cyclopentadienyl anion by replacement of one or more —CH group(s) by heteroatom(s).

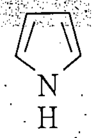


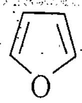
Cyclopentadienyl anion X = NH, O, S

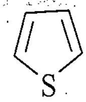
Five membered aromatic heterocycles are further classified as

(i) With one heteroatom

Replacement of one –CH group of cyclopentadienyl anion by heteroatom.


pyrrole

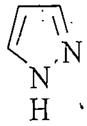

furan

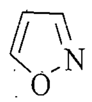

thiophene

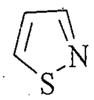
(ii) With two heteroatoms

Replacement of two –CH– group by two heteroatom.

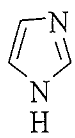
(a) Replacement from 1, 2-positions

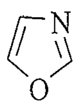

pyrrole

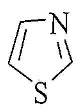

isoxazole


isothiazole

(b) Replacement from 1, 3-positions

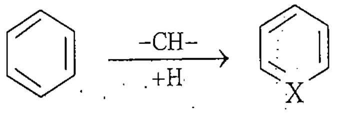

imidazole


oxazole


thiazole

(2) Six-membered Aromatic Heterocycles

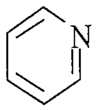
These are considered to be structurally derived from benzene by replacement of –CH– group(s) by heteroatom(s).



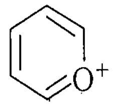
$(X = N, \overset{+}{O} \text{ and } \overset{+}{S})$

(i) With one heteroatom

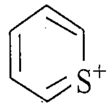
Replacement of one –CH– group by one heteroatom :



pyridine



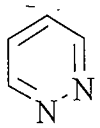
pyryllium



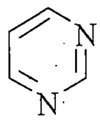
thiopyryllium

(ii) With two heteroatoms

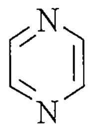
Replacement of one –CH– groups by two heteroatom :



pyridazine



pyrimidine

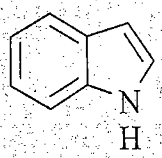


pyrazine

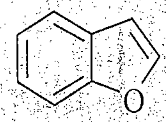
(3) Condensed Aromatic Heterocycles

These heterocycles contain two or more fused rings. The fused rings may be partly carbocyclic or partly heterocyclic.

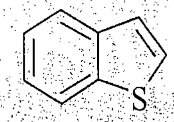
(i) Benzo-fused five-membered heterocycles



benzo[b]pyrrole (Indole)

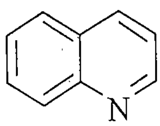


benzo[b]furan

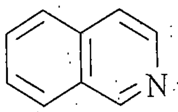


benzo[b]thiophene

(ii) Benzo-fused six-membered heterocycles

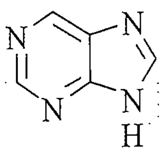


quinoline

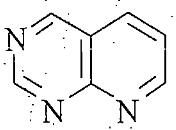


isoquinoline

(iii) Fusion of two heterocyclic rings



purine



pteridine

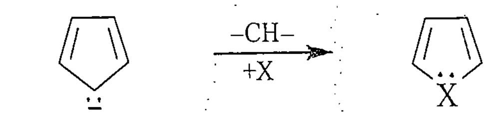
CLASSIFICATION BASED ON CHEMICAL BEHAVIOUR

On the basis of chemical behaviour, aromatic heterocycles are classified as :

(1) π-Excessive heterocycles (2) π-Deficient heterocycles

(1) π-Excessive heterocycles

(i) Five-membered aromatic heterocycles are considered structurally to be derived from cyclopentadienyl anion by replacement of –CH– group by heteroatom.



Cyclopentadienyl anion

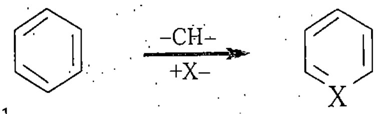
X = NH; pyrrole
O; furan
S; thiophence

(ii) In these heterocycles, six π-electrons are distributed over five atoms. Therefore, each atom has approximately (6/5 = 1.2) electron density as compared to (6/6 = 1) in benzene on each carbon atom. These heterocycles are, therefore, referred to as π-excessive heterocycles.

(iii) These heterocycles are susceptible towards electrophilic attack and undergo electrophiic substitutions very easily.

(2) π-Deficient heterocycles

(i) These heterocycles are considered structurally to be derived from benzene by replacement of –CH– group by heteroatom.



benzene X = N; pyridine

(ii) In these heterocycles, six π-electron are distributed over six atoms. Therefore, each atom is expected to have one electron density. But in the heterocyclic ring, the heteroatom is more electronegative than the ring carbon atoms and attracts electron towards itself. As a result of which the electron density on each ring carbon atom will be less than one. These heterocycles are, therefore, referred to as π-deficient heterocycles.

(iii) These heterocycles are susceptible towards nucleophilic attack and undergo nucleophilic substitution reactions.

NOMENCLATURE

Monocyclic heterocycles are named by systematic nomenclature system (Hantzsch-Widman system). This nomenclature system specifies the ring size, type and position of heteroatom. The following rules are adopted for five and six-membered monocyclic heterocycles.

(i) Combination of prefix and stem

Monocyclic heterocycle is named by combining prefix with stem.

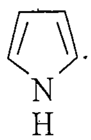
Prefix

The prefix indicates the heteroatom present in the ring. The prefixes for heteroatoms in decreasing order of priority are as follows

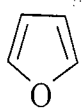
Stem

(i) The stem indicates the size of the ring and the saturation and unsaturation in the ring.

(ii) If the stem begins with vowel, the terminal 'a' of prefix is dropped.



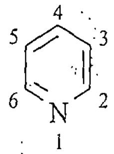
prefix = aza (for nitrogen)
stem = ole (for five-membered ring)
aza + ole = azole (pyrrole)



prefix = oxa (for oxygen)
stem = ole
oxa + ole = oxole (furane)

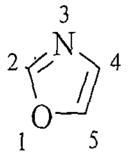
(iii) Trivial names have also been retained in the systematic nomenclature system by IUPAC such as; pyrrole, furane, thiophene, pyridine etc.

(iv) The atoms in the ring are numbered in such a way that heteroatom gets lowest number.



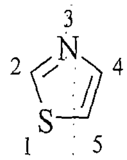
(v) If two or more heteroatoms are present in the ring, the numering starts from the heteroatoms with highest preference. (oxygen takes precedence over sulphur and sulphur over nitrogen)

(vi)If two or more different heteroatoms are present in the ring, the prefixes of heteroatoms are combined in order of preference.



oxa + aza + ole

= 1, 3 - oxazole

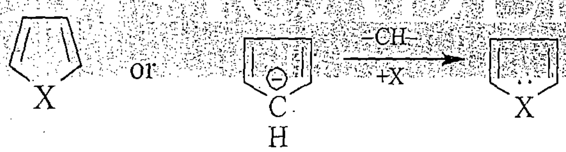


thia + aza + ole

= 1, 3-thiazole

FIVE-MEMBERED HETEROCYCLES

Five-membered aromatic heterocycles with one heteroatom; pyrrole, furan and thiophene are considered structurally to be derived from cyclopentadienyl anion by replacement of one –CH– group by heteroatom.

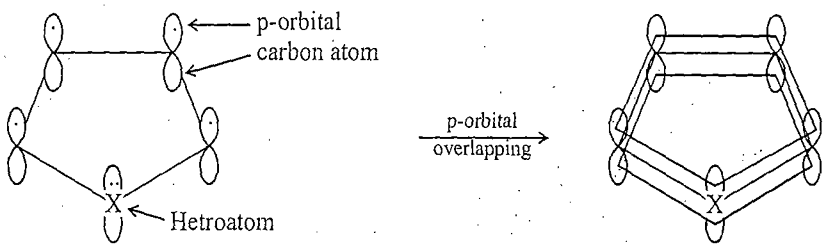


cyclopentadienylanion

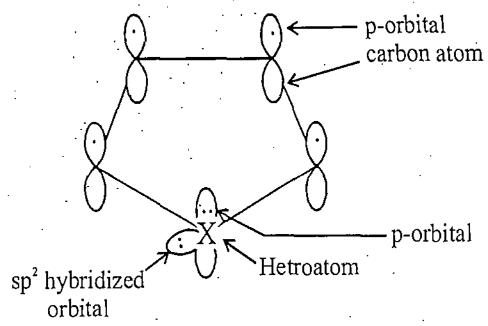
These heterocycles exhibit special characteristics associated with aromaticity.

Structure of Aromaticity

These are cyclic planar molecules with sp^2 hybridized atoms. One p-orbital on each carbon with one electron and p-orbital on heteroatom containing two electrons overlap to form p-electron cloud below and above the plane of the ring and results an aromatic sextet. Thus six p-electrons are distributed over five sp^2 hybridized atoms. Each carbon contributes one electron to the aromatic sextet, while the heteroatom contributes two electrons and essentially imparts aromatic character to the heterocyclic system.

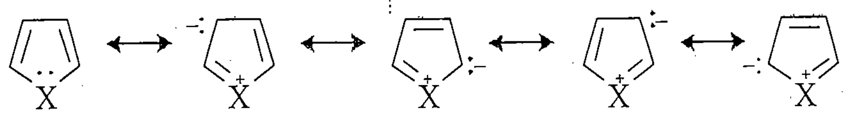


Five-membered heterocycles have three pairs of delocalized electrons. Two pairs of π-electrons are shown as two π-bonds and one pair is shown as lone pair on heteroatom, which is a part of π-cloud (aromatic sextet). But furan and thiophene have second pair of lone pair (non-bonding electrons) which is in sp^2-hybridized orbital (perpendicualr to π-cloud) and is not a part of π-electron cloud (aromatic sextet).



(X = O, S)

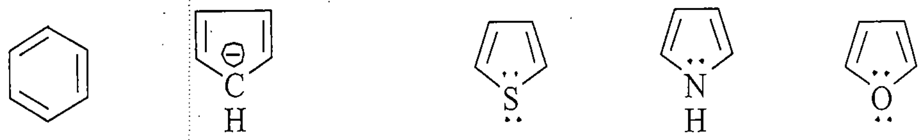
The structure of these heterocycles in terms of valence bond descripton are considered to be resonance hybrid of following resonating structures



Thus the lone pair on heteroatom is delocalized over ring carbon atom due to which the carbon atoms acquire negative charge. These heterocycles are, therefore, cyclic planar molecules with cyclically delocalized $(4n + 2)\pi$ electrons. Hence, each heterocycles (pyrrole, furan and thiophene) fulfils the criteria of aromaticity.

Resonance Stabilization

These heterocycles are associated with high resonance stabilization energy. But the resonance energies of pyrrole, furan and thiophene are not as high as resonance energy of benzene or the compound for which the resonance contributors are all equivalent.

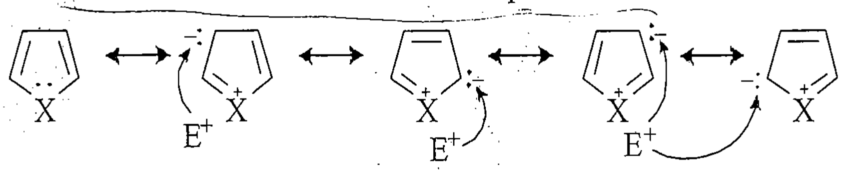


36 k cal	27 k cal	29 k cal	21 k cal	16 k cal
(benzene)	(cyclopentadienyl anion)	(thiophene)	(pyrrole)	(furan)

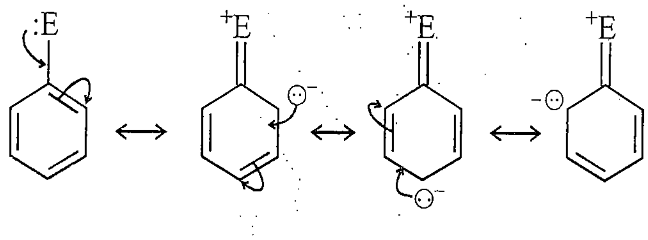
Thiophene with least electronegative heteroatom (sulphur) has highest resonance energy among the three five-membered aromatic heterocycles, but furan with most electronegative heteroatom (oxygen) has the lowest resonance energy.

Electrophilic substitution

(i) Reactivity: Five-membered heterocycles (pyrrole, furan and thiophene) are π-excessive and are characterized by their ability to undergo electrophilic substitution reactions on the ring carbon atoms. The partial positive charge on heteroatom hinders the attack of electrophile, while negatively charged carbon atoms facilitate the attack of electrophile.



(ii) Resemblance with phenol and aniline: The reactivity of five-membered aromatic heterocycles is comparable with that of aromatic compound containing electron releasing substituents (–OH, –NH_2). This is because the electron releasing substitutent gives electron pair to the ring and makes the ring carbon atoms electron rich for electrophilic attack.



(iii) Reactivity Order: The order of reactivity among the five-membered aromatic heterocycles is :

pyrrole > furan > thiophene > benzene

(a) the five-membered heterocycles; pyrole, furan and thiophene, are aromatic and more reactive than benzene. These are also known as **"superaromatic compounds".**

(b) The reason for more reactivity of pyrrole, than furan is that as compared to oxygen the nitrogen can accommodate positive charge more easily because nitrogen is less electronegative than oxygen.

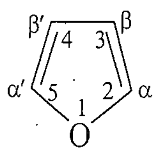
(c) Thiophene is less reactive than furan becaue of the larger size of sulphur than that of oxygen. The electron-releasing tendency (+M effect) of sulphur is, therefore, smaller than that of oxygen in furan.

(iv) Orientation: Five-membered heterocycles undergo electrophilic substitution reactions preferentially at α-position (C-2 or C-5 (α-position) is rationalized by the stabilization of transition states (intermediate carbocation) resulting from the attack of electrophile at C-2 or C-5 (α-posiiton) and C-3 or C-4 (β-position).

FURAN

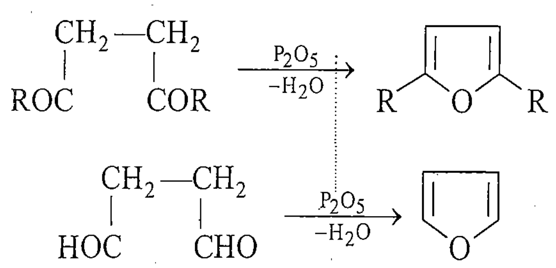
Furan is a five membered heterocyclic compound with oxygen atom as the hetero atom.

The numbering in furan ring system can be given as follows :

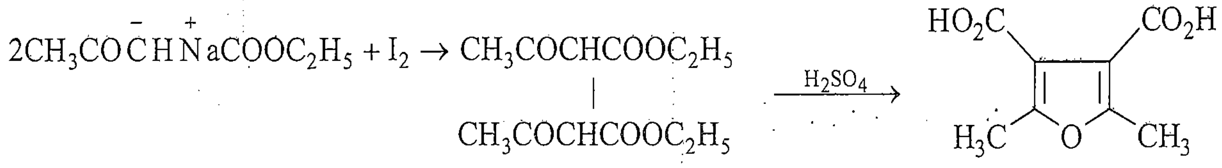


Synthesis of furan derivatives

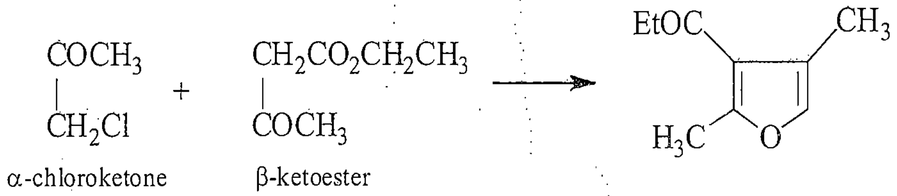
(i) These can be prepared by dehydrating 1, 4-diketones or aldehydes with phosphorus pentoxie or sulphuric acid.



(ii) These can be prepared from ethyl acetoacetate as follows.

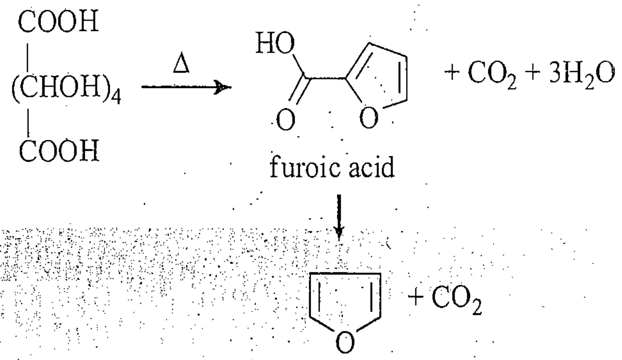


(iii) These can be pprepared by the Feist-Benary synthesis.



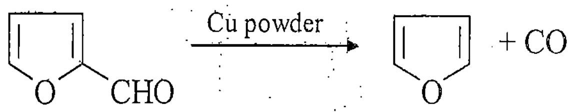
Synthesis of Furan : Furan can be obtained by the distillation of pine-wood.

It can be prepared by the dry distillation of mucic acid and heating the product, furoic acid.



Furoic acid can be conveniently decarboxylated in quinoline in the presence of copper powder.

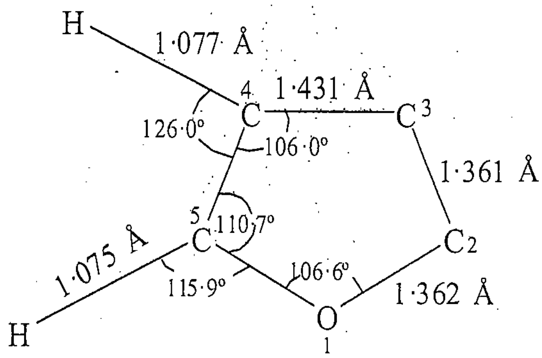
Furan can be manufactured by the catalytic decomposition of furfural in steam in the presence of an oxide catalyst.



Physical Properties

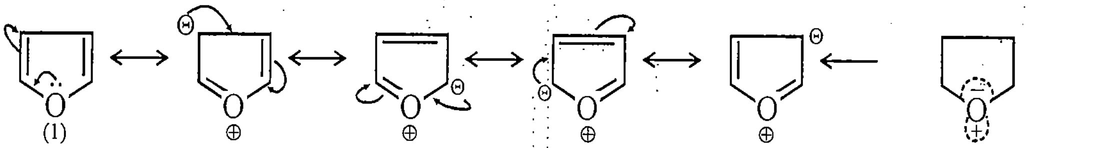
- Colourless liquid, b.p. 31·36°C with chloroform like smell.
- It is slightly soluble in water but it is miscible with most organic solvent.

Structure of Furan



Furan is an aromatic $(4n + 2)\pi$ system. It is a monocyclic planar molecule. Furan is π excessive aromatic system.

Out of the above 5 structures, structures 3 and 4 contribute more to the resonance hybrid than the strucures 2 and 5. Hence electron density is more at positions 2 and 5 than at 3 and 4 (position 2 and 5 are equal, similarly position 3 and 4 are equal). Hence electrophilic substitution occurs at position 2 (or 5).

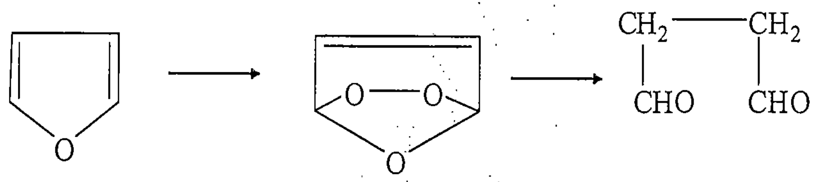


(1) (2) (3) (4) (5) (Resonance Hybrid)

Chemical Properties

1. Addition reactions of furan

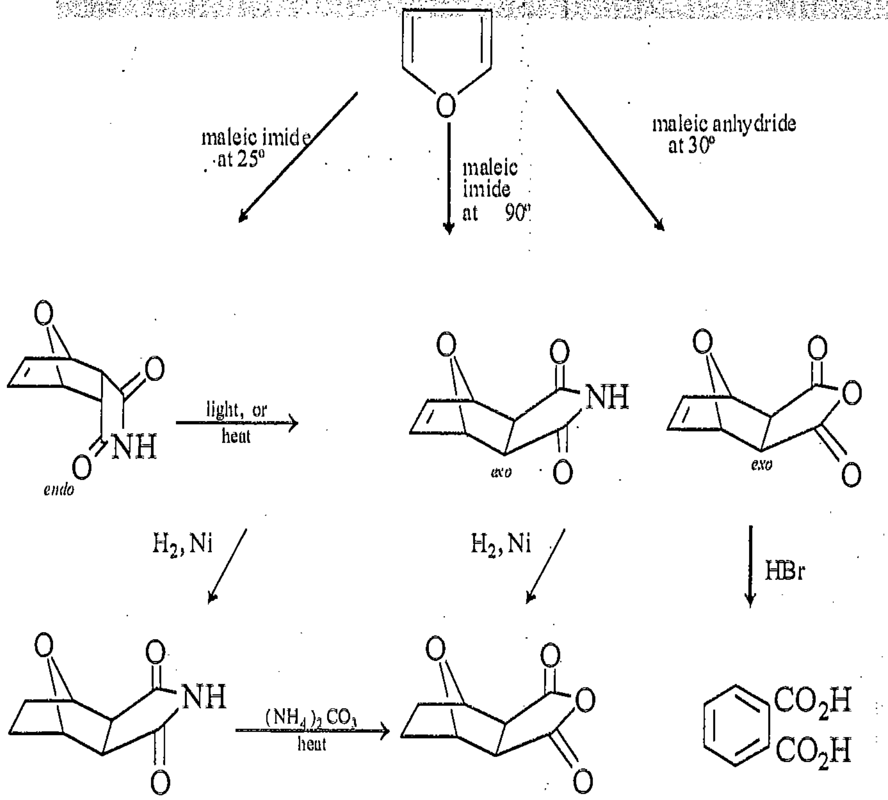
Furan itself is not stable in the presence of air or oxygen and is usually stabilized by the addition of small quantities of hydroquinone. Aerial oxidation takes place by2, 5-addition first to a peroxide (a),



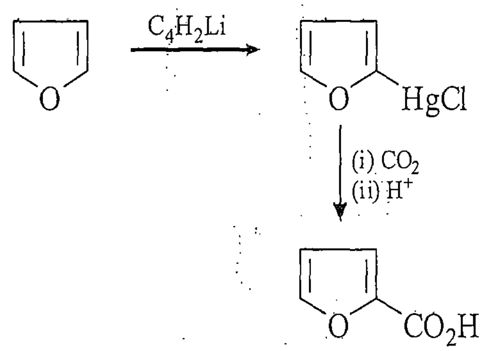
(a)

which has been isolated, and then through a free-radical polymerization to a resin. Hydrogenation of the peroxide gives succindialdehyde. Furan is completely oxidized by potassium permanganate.

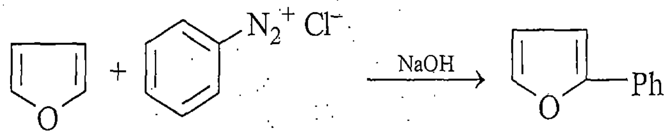
2. Furan undergoes **Diels-Alder** reaction with maleic anhydride



3. Furan forms 2-lithium derivative on heating with n-butyl lithium. This butyl lithium undergoes many reactions. e.g. with CO_2.

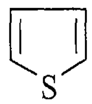


4. Furan undergoes Gomberg reaction with diazoium salts in alkaline solution as follows :

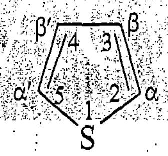


THIOPHENE

Thiophene is a five membered heterocyclic compound with sulphur atom as the hetero atom (sulphur analogue of furan). The structure of thiophene is as follows :

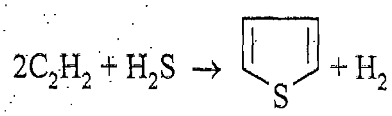


The numbering in thiophene ring system can be given as follows :

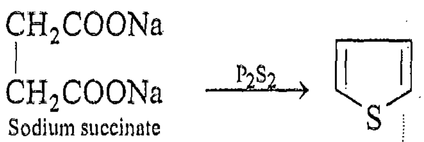


Synthesis of Thiophene

1. It is prepared commercially by passing a mixture of acetylene and hydrogen sulphide through a tube containing alumina at 400°C.



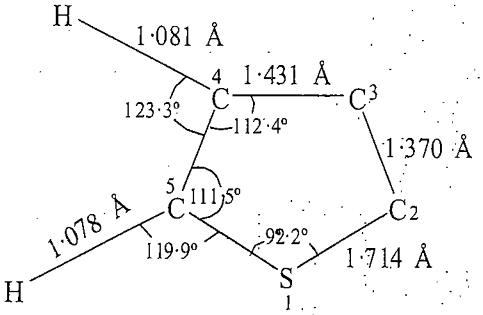
2. It can be synthesized by heating sodium succinate with phosphorus trisulphide leading to cyclization.



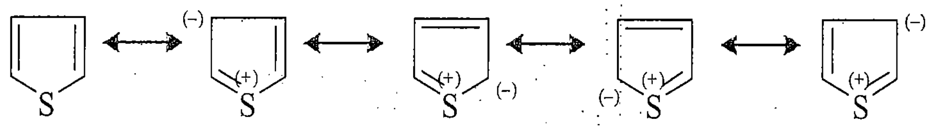
Physical Properties

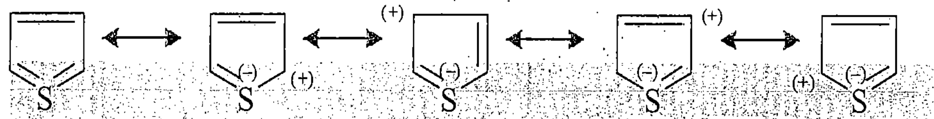
- It is Thiophene is a colourless liquid,
- b.p. 84·1°C and f.p. –38·3°C, which has an odour very similar to that of benzene.
- It is slightly denser than water, with which it is immiscible with most organic solvents.

Structure of Thiophene :



Thiophene has more number of resonating structuress than furan since sulphur atom has vacant d-orbtial. Sulphur can donate the lone pair of electrons as well as accept electrons using empty d orbital. By donating electrons it attains aromaticity ((4n + 2) π-electron system). Two sets of resonating structures [(i) and (ii)] are possible (i) is attained by donating electrons whereas (ii) is attained by accepting electrons.

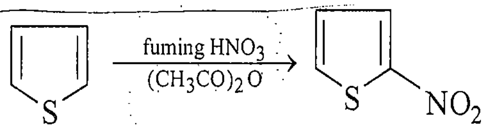
(i)


(ii)


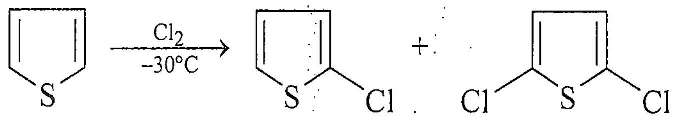
The estimating of ring current shows that thiophene is more aromatic than furan.

Chemical Properties

1. Thiophene can be nitrated by fuming nitric acid in acetic anhydride.

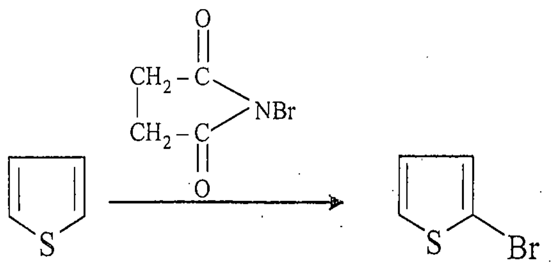


2. Thiophene gets chlorinated at 2 as well as 2 and 5 positions (mixture of products) when chlorination is carried out at –30°C.



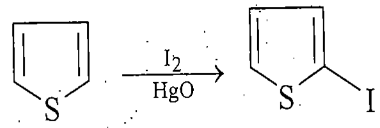
2-chlorothiophene 2, 5-dichlorothiophene

Thiophene gets bromianted at 2-position when treated with N-bromosuccinimide.

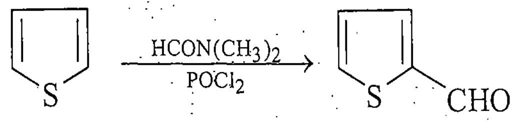


2-bromothiophene

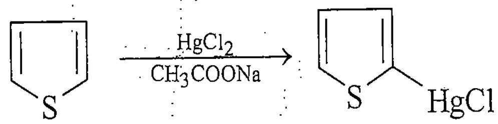
Iodination at 2-position of thiphene is carried out by treating with iodine in presence of yellow mercuric oxide.



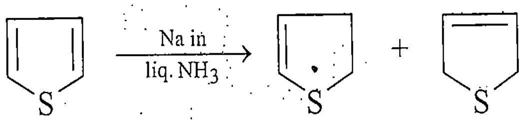
3. Thiophene can be formylated at 2-position using dimethylformamide and phosphorus oxychloride.



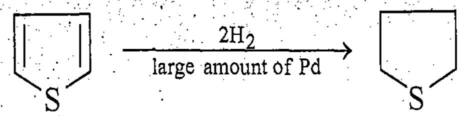
4. Thiophene on treatment with mercuric chloride in the presence of small amount of sodium acetate produces 2-mercuri-chloride as the main product.



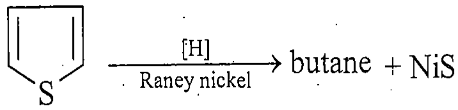
5. Thiophene on reduction with sodium in liquid ammonia gives a mixture of 2, 3-dihydrothiophene (2-thiolen) and 2, 5-dihydrothiophene (3-thiolen).



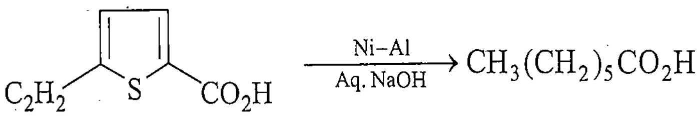
6. Catalytic reduction of thiophene with large amount of palladium yields 2, 3, 4, 5-tetrahydrothiophene.



7. Catalytic reduction of thiophene with Raney nickel gives n-butane as a result of ring cleavage.

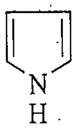


8. Desulphurisation of thiophene derivatives can be brought about by Raney nickel and aliphatic mono or dicarboxylic acids are formed. For example n-heptanoic acid can be prepared from 5-ethylthiophene-2- carboxylic acid.

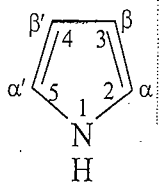


PYRROLE

Pyrrole is a five membered heterocyclic compound with nitrogen as hetero atom. The structure of pyrrole is as follows :

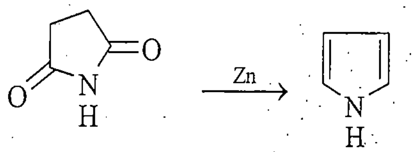


The numbering in pyrrole system can be given as follows.

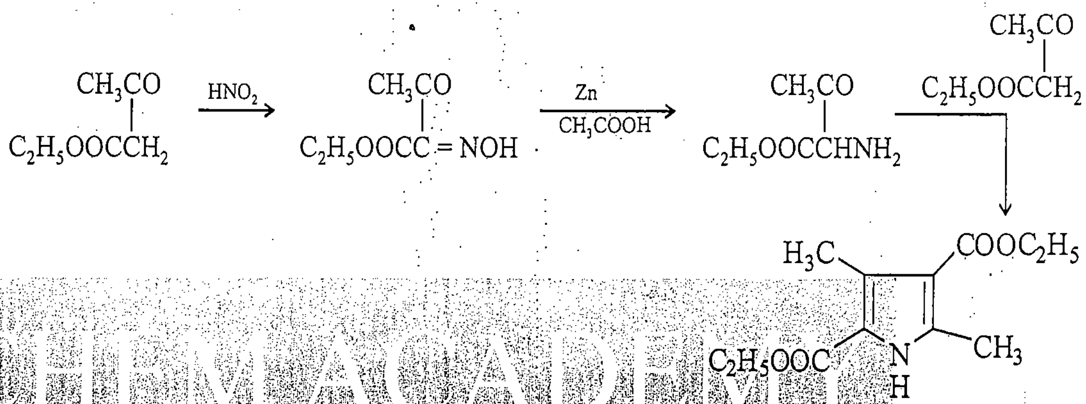


Synthesis of Pyrrole

1. Pyrrole is also formed when succinimide is distilled with zinc dust.



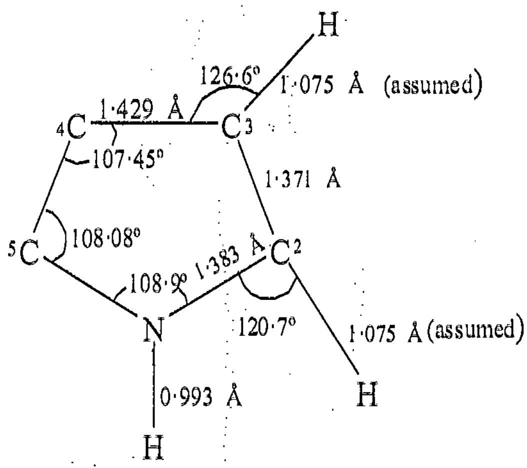
2. Knorr pyrrole synthesis is carried out by the condensation between an α-aminoketone and a β-diketone or β-ketoester.



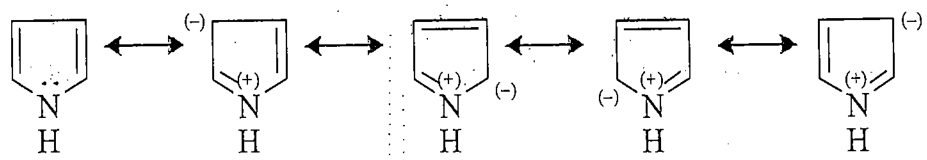
Physical Properties

- Pyrrole is a colouless liquid ,
- b.p. 129°C at 760 mm, f.p. –24°C, with an odour resembling that of chloroform.
- It runs brown on standing in air and is misicible with most organic solvents.
- It is somewhat soluble (6%) in water and dissolves 3% of its weight of water at 25°C.
- Pyrrole is both a very weak acid (pK_a 17·5) and a very weak base (pK_a – 3·8).

Structure of Pyrrole

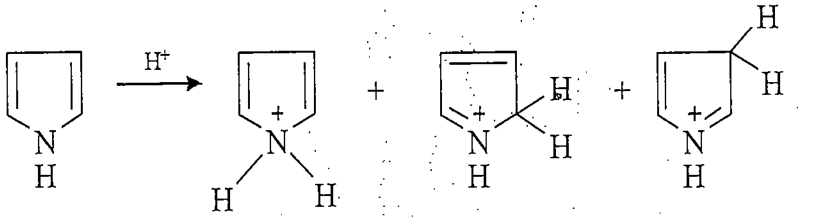


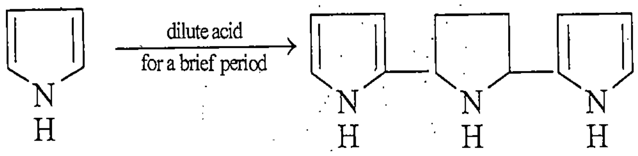
Pyrrole is a resonance hybrid of the following canonical forms. It is less aromatic than thiophene and more aromatic than furan. Order of aromaticity is thiophene > pyrrole > furan.



Basicity of Pyrrole

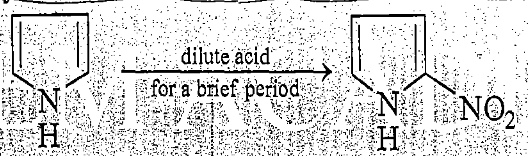
Pyrrole is slightly basic since the lone pair of electrons is not availabe on nitrogen as these are involved in the formation of a $(4n + 2)$ π-electron, and not available for protonation. However, in acid solution protonation occurs more at carbon. In concentrated solution pyrrole polymerises to form pyrrole-red. One contact with dilute acid for a brief period, pyrrole forms the trimer.



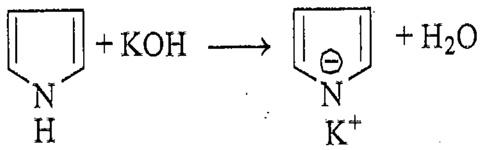


Chemical Properties

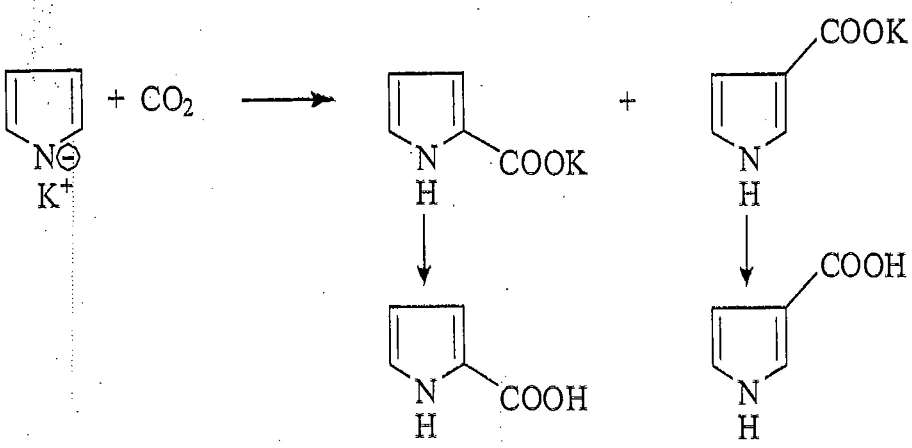
1. Pyrrole gives 2-nitropyrrole when nitrated with nitric acid in acetic anhydride at low temperatures.



2. The imino-hydrogen of pyrrole is replaceable by potassium, alkyl or acyl groups. When pyrrole is heated with solid potassium hydroxide, potassiopyrrole salt is formed.

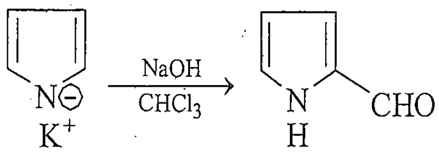


The potassiopyrrole salt reacts with CO_2 (Kolbe Schmitt reaction). It gives a mixture of 2- and 3-pyrrole carboxylic acids.



2-pyrrolecarboxylic acid   3-pyrrolecarboxylic acid

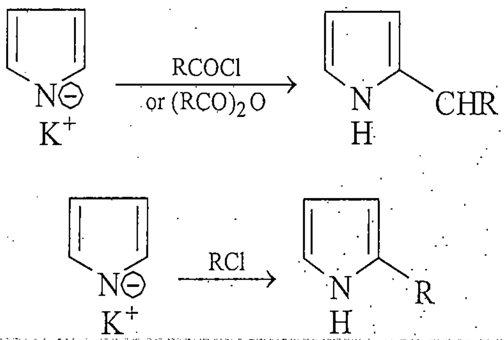
The poassiopyrroel reacts with chloroform (Reimer-Tiemann reaction) to give pyrrole-2-aldehyde.



However in addition to 2-aldehyde a little amount of 3-chloropyridine is also formed.

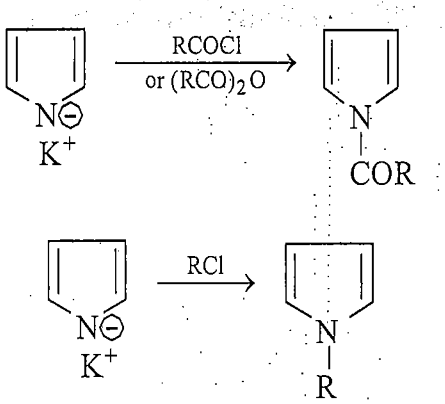
3. The potassiopyrrole reacts with acyl chlorides, acid anhydrides and alkyl halides to form N-derivatives at high temperatures.

At High Temperature

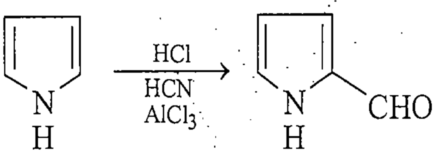


However, initially N-derivatives are formed and they undergo Hoffmann-Martius rearrangement to give 2-derivatives.

At Low Temperature

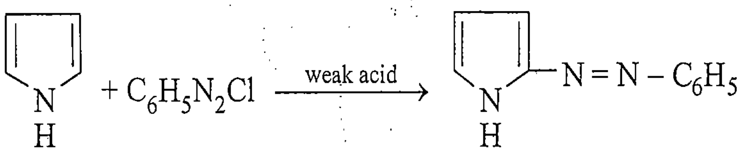


4. Pyrrole undergoes the "**Gattermann reaction**" to form 2-aldehyde.

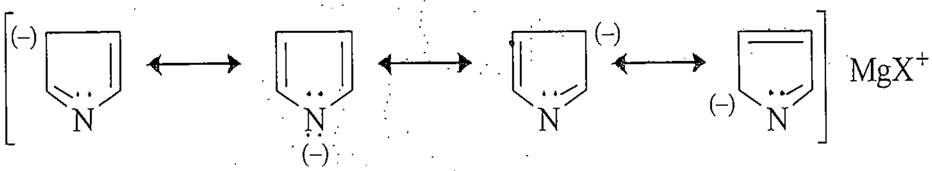


5. In weakly acidic solution, pyrole couples with diazonium salts in the 2-positions.

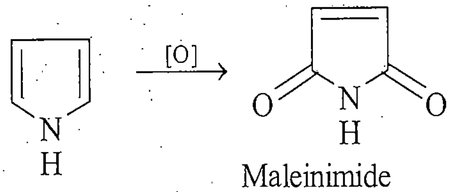
Coupling Reactions



6. Pyrrole forms pyrrolylmagnesium bromide when treated with methylmagnesium bromide which reacts with series of alkyl halides to give both 2- and 3-alkylpyrroles. This is due to the following resonating structures of pyrrole ring.

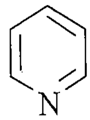


7. Pyrrole is oxidized by chromium trioxide in acetic acid to maleinimide.


Maleinimide

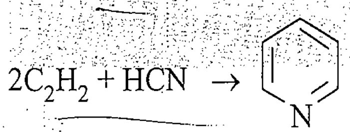
PYRIDINE

Pyridine is a six membered heterocyclic compound with nitrogen as the heteroatom. The structure of pyridine is as follows.

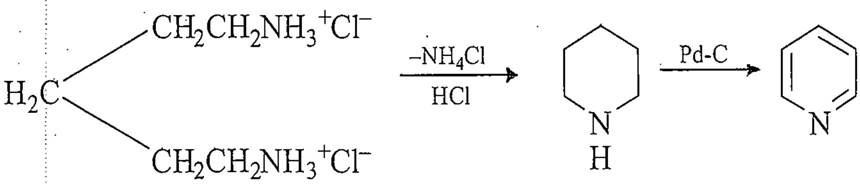


Synthesis of Pyridine

1. It is synthesised by passing a mixture of acetylene and hydrogen cyanide through a red-hot tube.



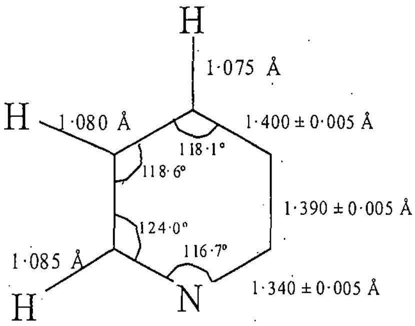
2. It is also synthesised by heating the hydrochloride of pentamethylenediamine and oxidizing the product, piperidine, with concentrated sulphuric acid at 300°C or by catalytic dehydrogenation usign Pd and charcoal.



Physical Properties

- Pyridine is a very hygroscopic colouless liquid.
- f.p. –42°C, b.p. 115°C, with a characteristic and somewhat unpleasent smell .
- It is miscible with most organic solvents and with water.
- Drying is best effected with potassium hydroxide or barium oxide, as pyridine reacts with sodium.
- Pyridine is very powerful solvent for many types of organic compounds, and it often dissolves salts to give conducting solutions.

Structure



The structure of pyridine is a hybrid of the following canonical forms. The lone pair of electrons are not involved in resonance.

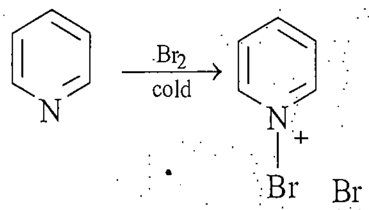
From the above structure, it is clear that the position 3 and 5 are the sites for electrophilic attack and position 2, 4 and 6 are the site for nucleophilic attack. Ring is highy deactivated by the electron withdrawing nature of nitrogen. Hence nitration and sulphonation are difficult. Presence of +I group accelerates the electrophilic substitutions. If the +I group is present in the 3-position the substitution takes place at 2- or 6-position. If the +I group is present in the 2- or 4-position, the substitution takes place at 3- or 5-position.

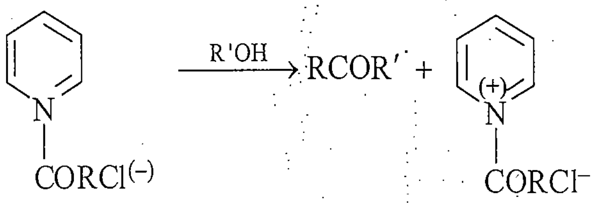
Chemical Properties

1. Pyridine is used in many reactions where it is desired to carry out dehydrogenation e.g. removal of HBr from bromosuccinic ester.

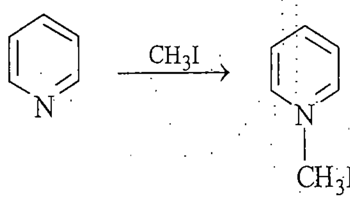
$$\begin{array}{l} CH_2COOC_2H_5 \\ | \\ CHBrCOOC_2H_5 \end{array} \xrightarrow[KOH]{Pyridine} \begin{array}{l} CHCOOH \\ \| \\ CHCOOH \end{array}$$

2. Pyridine reacts with halogen inthe cold to form 1-halogenopyridinium halides.





3. Pyridine form quaternary salts when heated with alkykl halides.

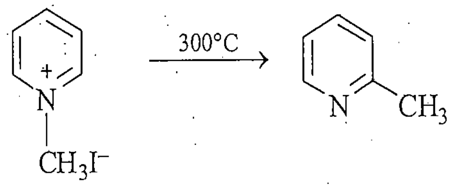


Pyridine methiodine

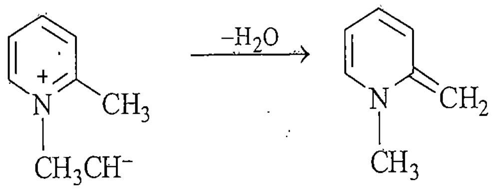
or

1-methylpyridinium iodide

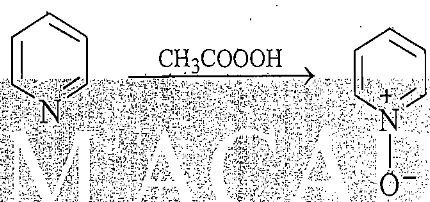
These quaternary halides of pyridine undergo **"Hofmann-Martius rearrangement"** to give 2- and 4-methylpyridine.



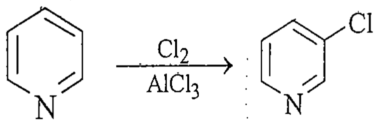
The quaternary hydroxides of pyridine on heating give anhydro-bases with the removal of a moleculeof water. However, this is possible only when suitable alkyl groups is in the 2- or 4-position.



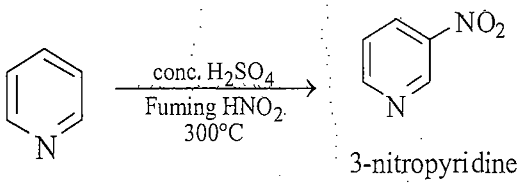
4. Pyridine is oxidised by peracids to pyridine oxide.



5. Pyridine does not undergo Friedel-Crafts reaction since it is having a complex forming tendency.
6. Chlorination of pyridine in the presence of aluminium chloride gives 3-chloropyridine.

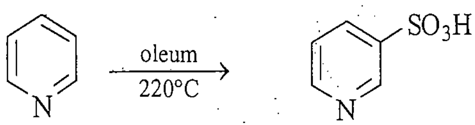


7. Pyridine is nitrated to 3-nitropyridine by heating with concentrated sulphuric acid and fuming nitric acid at 300°C.



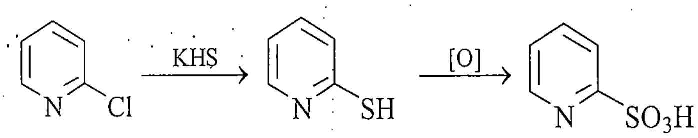
3-nitropyridine

8. Pyridine is sulphonated at 3 position when heated with 20% oleum with little mercuric sulphate at 220°C.

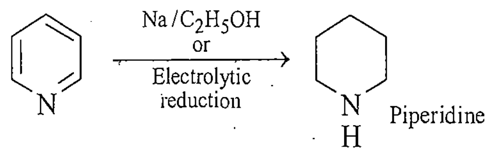


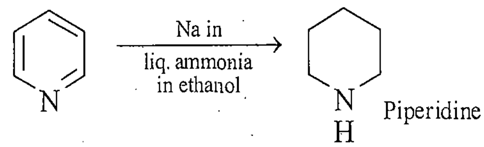
pyridine-3-sulfonic acid

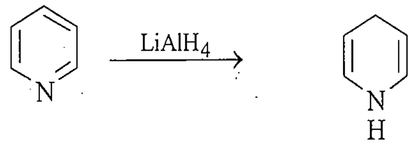
9. 2- and 4-pyridinesulphonic acid are obtained by oxidising corresponding thiols which are produced by the action of KHS on chloropyridine.



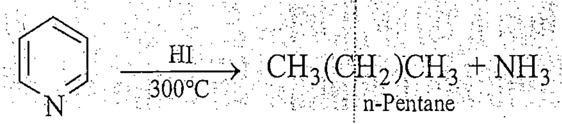
10. Pyridine on reudction gives different products depending on the methods.





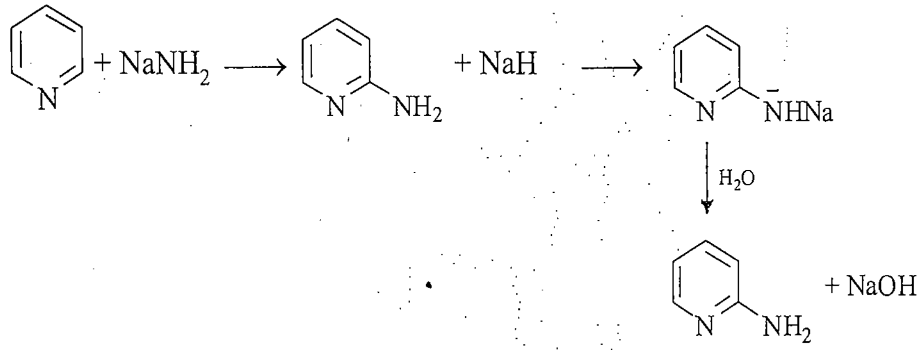


1,4-dihydropyridine

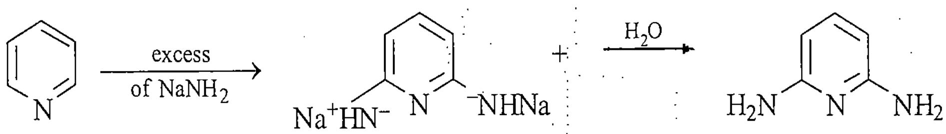


11. Pyridine also undergoes nuceophilic reactions. With sodamide on heating, pyridine gives 2-aminopyridine. (This reaction is called **Chichibabin reaction**).

If sodamide is excess 2, 6-diaminopyridine is the product.



2-aminopyridine



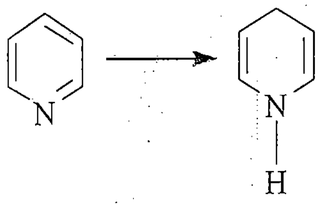
2, 6-Diaminopyridine

EXERCISE - I

Single Answer Correct Type

1. The nitrogen atom in pyridine is

(a) sp^2 hybridized (b) sp^3 hybridized (c) sp hybridized (d) cannot be predicted

2. 

The above reaction is brought about by

(a) Na/liq. NH_3 (b) Na/C_2H_5OH (c) $LiAlH_4$ (d) HI/Δ

3. Pyridine is less basic than aliphatic amine because the lone pair of electrons on N-atom in pyridine resides in

(a) sp^2 hybrid orbital (b) sp hybrid orbital (c) sp^3 hybrid orbital (d) sp^2 d hybrid orbital

4. The order of aromaticity of furan, thiophene and pyrrole is as

(a) thiophene > furan > pyrrole (b) furan > pyrrole > thiophene

(c) thiophene > pyrrole > furan (d) pyrrole > thiophene > furan

5. Pyrrole reacts with chloroform in presence of base to give pyrrole-2-carboxyaldehyde. This reaction is an example of

(a) Reimer-Tiemann reaction (b) Gomberg reaction

(c) Houben-Hoesch reaction (d) Cannizzaro reaction

6. Nicotinic acid reacts with soda lime to give

(a) pyrrole (b) piperidine (c) pyrrolidine (d) pyridine

7. Pyridine reacts with a mixture of KNO_3 and H_2SO_4 at 300°C to give

(a) 1-nitropyridine (b) 2-nitropyridine (c) 3-nitropyridine (d) 4-nitropyridine

8. Which of the following reagents will react with pyrrole to form 2-formalpyrrole?

(a) HCOOH (b) $CHCl_3/KOH$ (c) H_2O_2 (d) $(CH_3CO)_2O/SnCl_4$

9. Quinoline undergoes nucleophilic substitution on heating with $NaNH_2$ to give

(a) 2-aminoquinoline (b) 4-aminoquinoline (c) 3-aminoquinoline (d) 8-aminoquinoline

10. Which of the following reagents will react with furan to form 2-furansulphonic acid?

(a) Dilute H_2SO_4 at 200°C (b) SO_2 at 100°C

(c) Dilute H_2SO_4 at 100°C (d) SO_3 in pyridine at 100°C

11. Pyridine undergoes nucleophilic substitution with $NaNH_2$ at 100°C to give

(a) 3-aminopyridine (b) 2-aminopyridine

(c) 3, 5-diaminopyridine (d) 2, 5-diaminopyridine

12. Reaction of furfural with NaOH gives

(a) Furoin (b) Furoic acid

Gnn12900

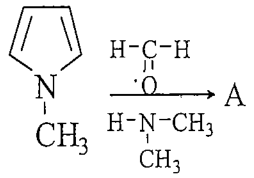
(c) Furfuryl alcohol and sodium salt of furane-2-carboxylic acid

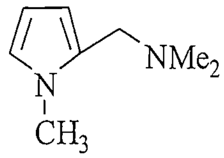
(d) No reaction

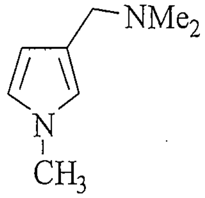
13. Position which are inactive towards electrophilic attack on pyridine

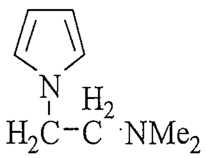
(a) Only 2nd (b) Only 3rd (c) 3rd and 4th (d) 2nd and 4th

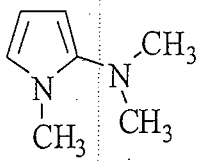
14. Major product formed in the given reaction is



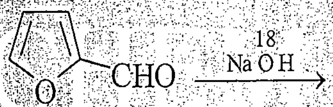
(a) 

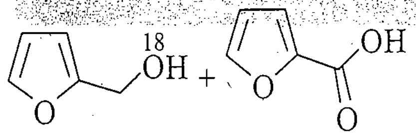
(b) 

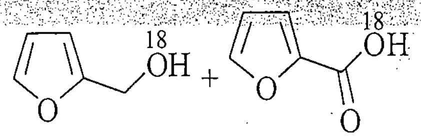
(c) 

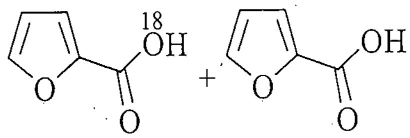
(d) 

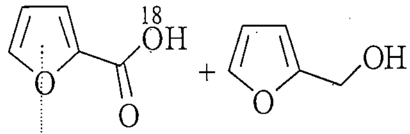
15. Major product formed



(a) 

(b) 

(c) 

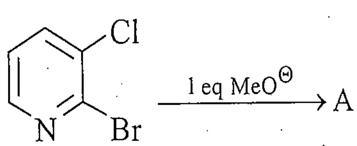
(d) 

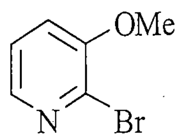
16. Correct order of aromaticity character of given heterocyclic

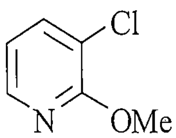
(I) Pyridine (II) Pyrrole (III) Thiophene (IV) Furan

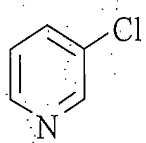
(a) I > II > IV > III (b) I > III > IV > II (c) I > III > II > IV (d) III > II > IV > I

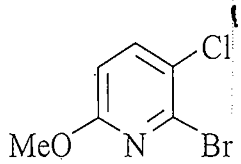
17. Major product formed in the given reaction is



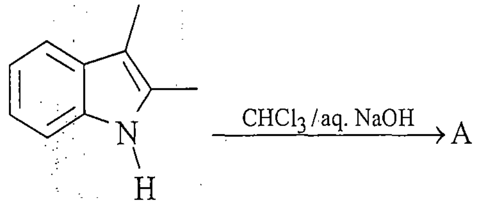
(a) 

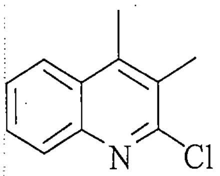
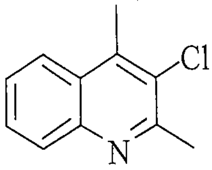
(b) 

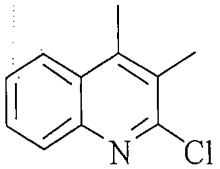
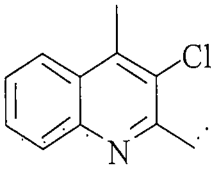
(c) 

(d) 

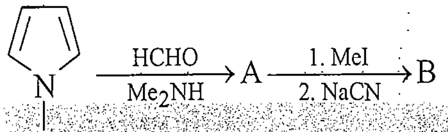
18. In the following reaction, the intermediate and the major product A are

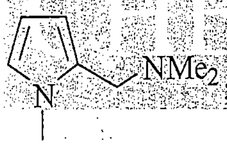
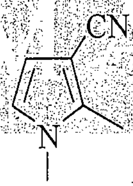
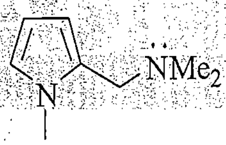
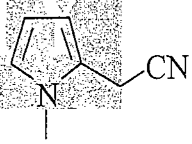


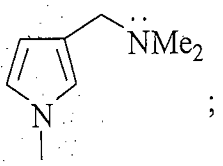
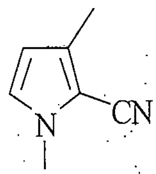
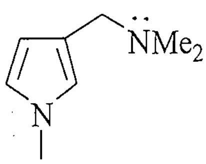
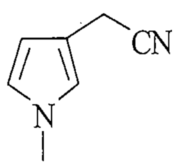
(a) :CHCl and  (b) :CHCl and 

(c) :CCl_2 and  (d) :CCl_2 and 

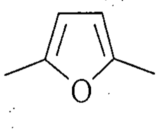
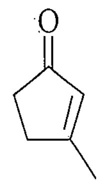
19. The major product A and B in the following reaction sequence are

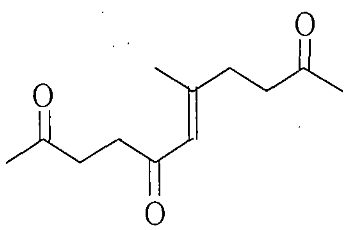
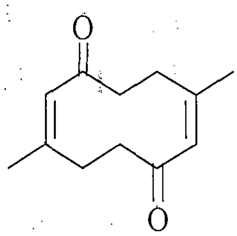


(a) A =  ; B =  (b) A =  ; B = 

(c) A =  ; B =  (d) A =  ; B = 

20. The major product formed in the reaction of 2,5-hexanedione with P_2O_5 is

(a)  (b) 

(c)  (d) 

EXERCISE - II

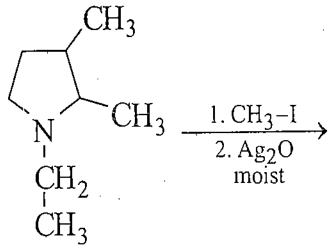
One or More Than One Correct

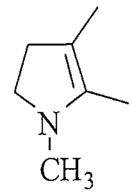
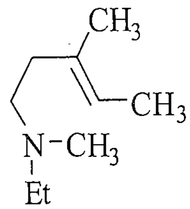
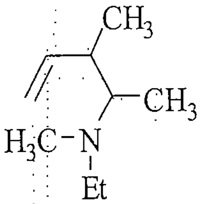
1. The correct order relative reactivity towar eletrophilic aromatic substitution —

(a) Pyrrole > Thiophene > Benzene (b) Benzene > Pyrrole > thiophene

(c) Pyrrole > Furan > thiophene > Benzene (d) Furan > Pyrrole > thiophene > Benzene

2. Possible alkene formed in given reaction is

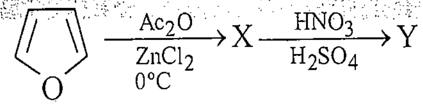


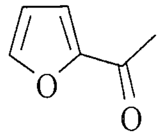
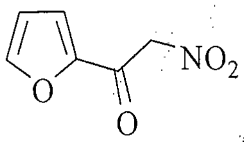
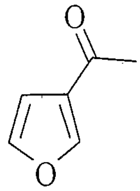
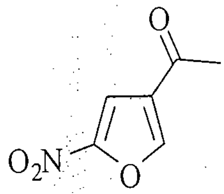
(a)  (b)  (c)  (d) $CH_2 = CH_2$

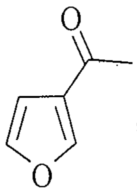
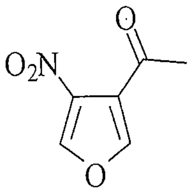
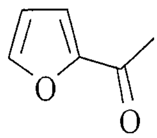
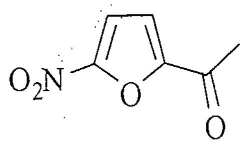
EXERCISE - III

Previous Year Questions

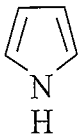
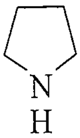
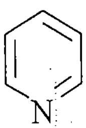
1. The major product X and Y in the following reaction sequence are



(a) X =  ; Y =  (b) X =  ; Y = 

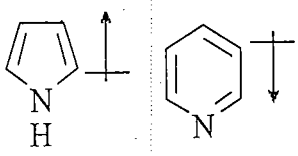
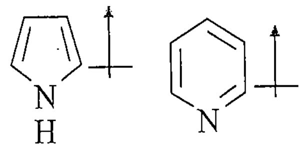
(c) X =  ; Y =  (d) X =  ; Y = 

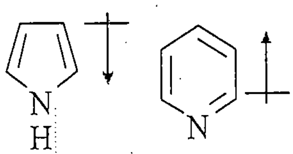
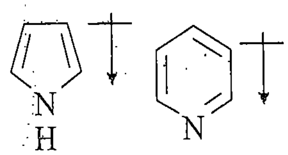
2. The correct order of the pKa values for the conjugate acids of heterocyclie compounds given below is

(I)  (II)  (III)  (IV) 

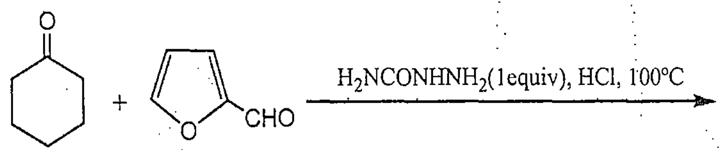
(a) II > III > I > IV (b) IV > II > III > I (c) III > II ≥ IV > I (d) III > IV > II > I

3. The correct orientation of dipoles in pyrrole and pyridine is

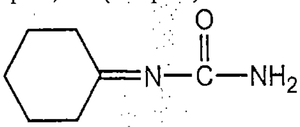
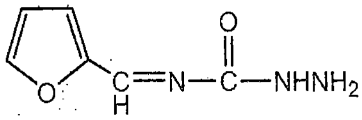
(a)  (b) 

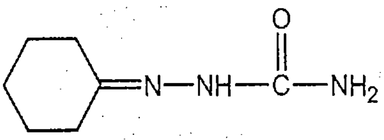
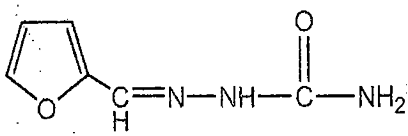
(c)  (d) 

4. The major product in the following reaction is

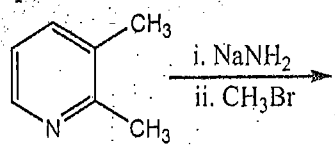


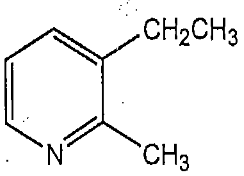
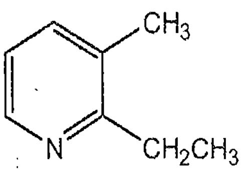
(1 equiv) (1 equiv)

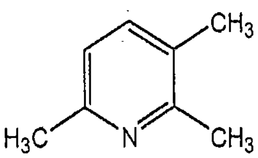
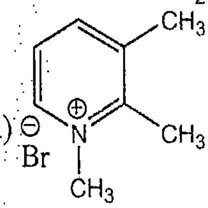
(a)  (b) 

(c)  (d) 

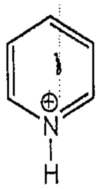
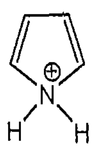
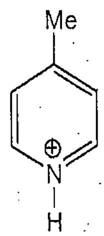
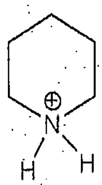
5. Among the following the major product obtained in the reaction below is:



(a)  (b) 

(c)  (d) 

6. The correct order of acidity among

    ; is

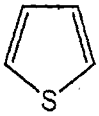
(i) (ii) (iii) (iv)

(a) (i) < (ii) < (iii) < (iv) (b) (iv) < (i) < (iii) < (ii)

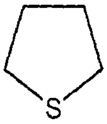
(c) (ii) < (i) < (iii) < (iv) (d) (ii) < (iv) < (i) < (iii)

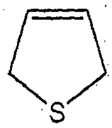
7. The compound (X) in the reaction sequence

$$\begin{matrix} CH_2COONa \\ | \\ CH_2COONa \end{matrix} \xrightarrow[\text{heat}]{P_2S_3} (X) \xrightarrow{\text{Raney Ni}} CH_3CH_2CH_2CH_3$$

(a) 

(b) $\begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix}$

(c) 

(d) 

ANSWER KEY

EXERCISE - I

1. a	2. a	3.a	4. c	5. a	6. d	7. c
8. b	9. a	10. d	11. b	12. c	13. d	14. a
15. d	16. c	17. b	18. d	19. b	20. a	

EXERCISE - II

1. a,c	2. b,c,d

EXERCISE - III

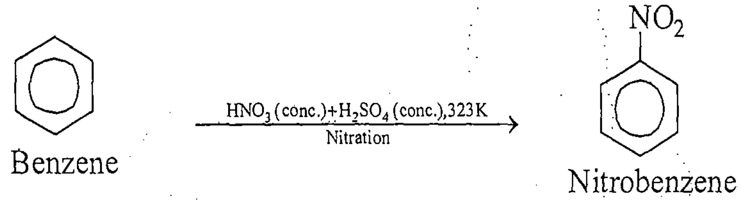
1. d	2. c	3. a	4. c	5. d	6. b	7. a

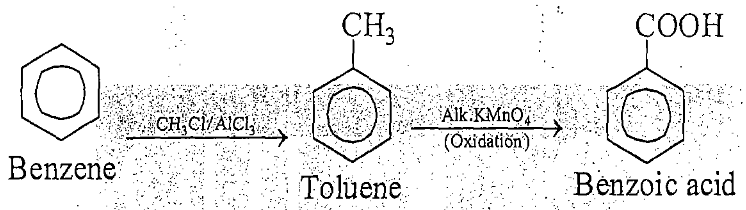
CHAPTER

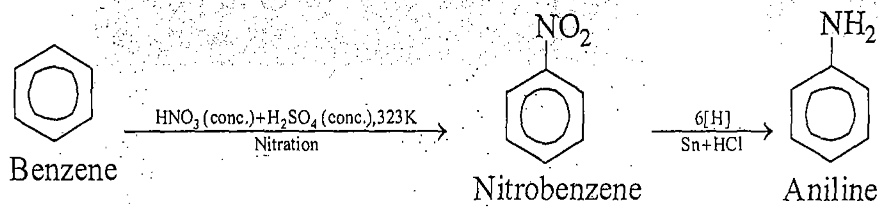
10

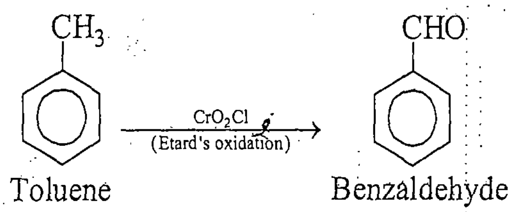
Qualitative Organic Analysis

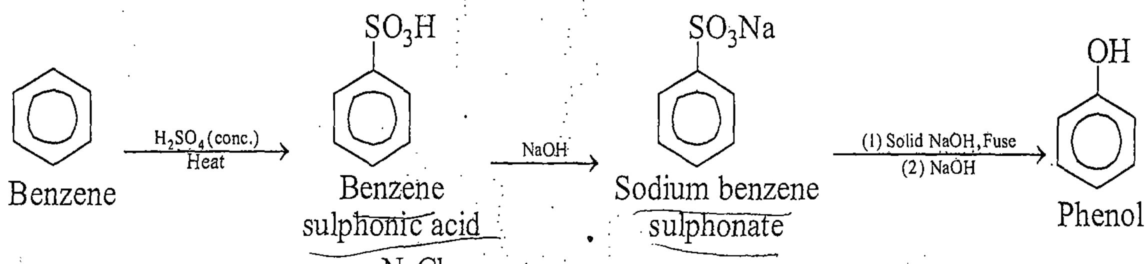
FUNCTIONAL GROUP INTERCONVERSIONS

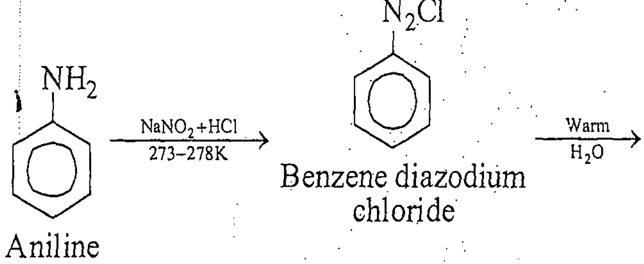
1. 

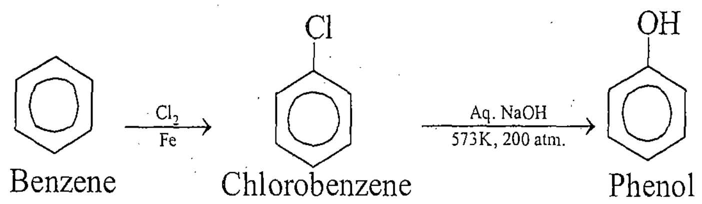
2. 

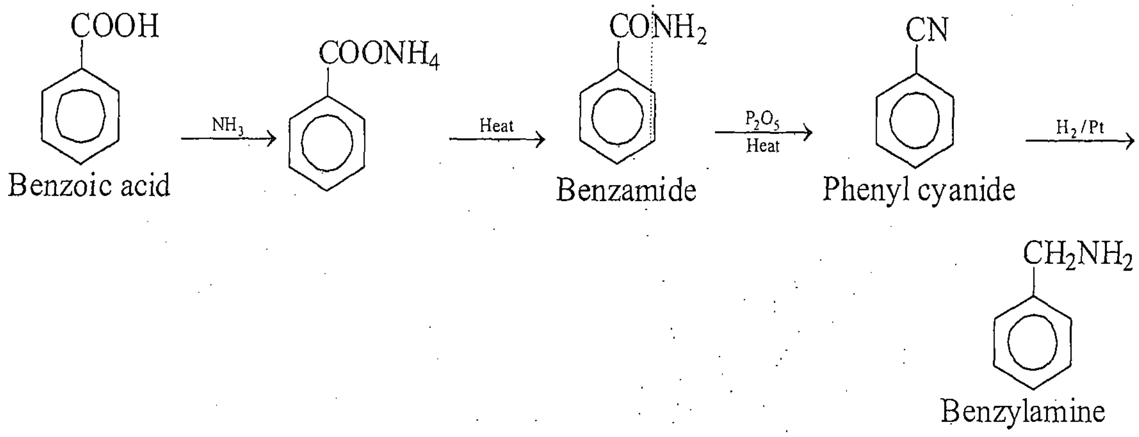
3. 

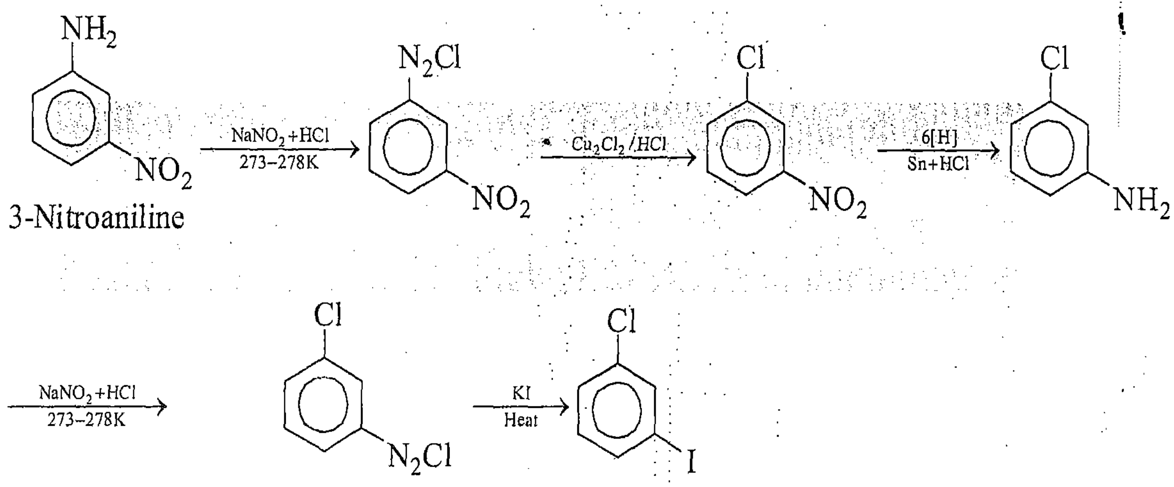
4. 

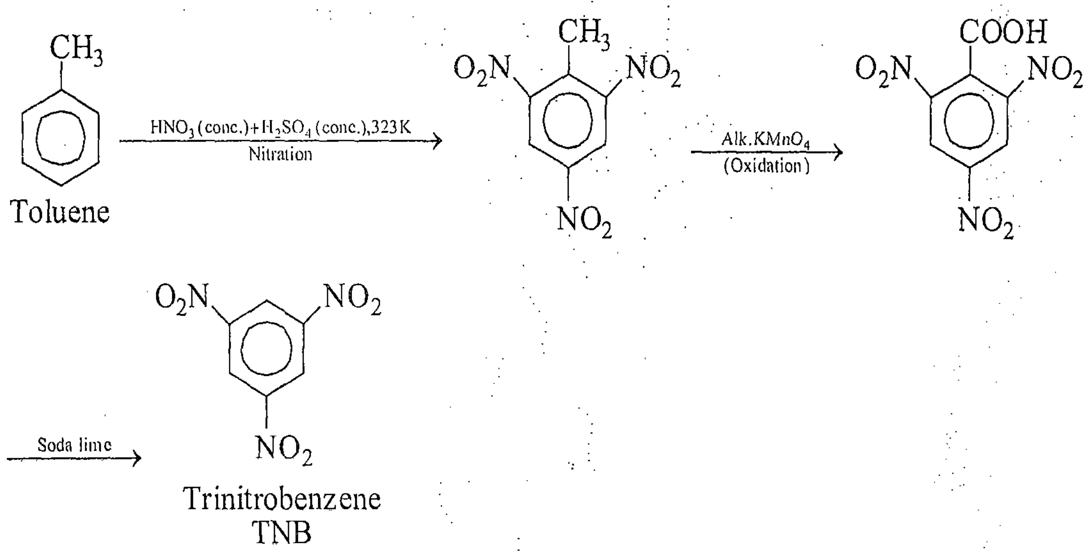
5. 

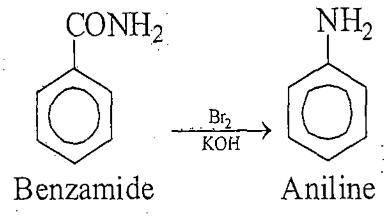
6. 

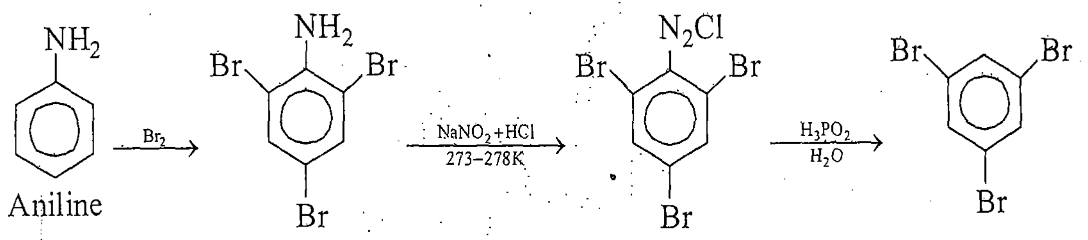
7. 
Cl
OH
Cl_2
Fe
Aq. NaOH
573K, 200 atm.
Benzene
Chlorobenzene
Phenol

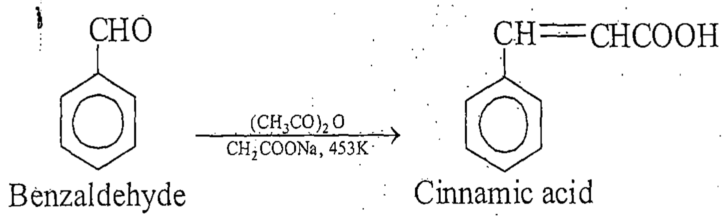
8. 
COOH
$COONH_4$
$CONH_2$
CN
NH_3
Heat
P_2O_5
Heat
H_2/Pt
Benzoic acid
Benzamide
Phenyl cyanide
CH_2NH_2
Benzylamine

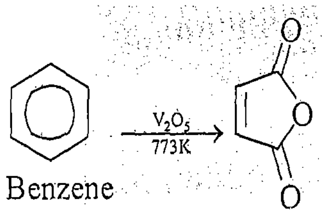
9. 
NH_2
NO_2
3-Nitroaniline
$NaNO_2$+HCl
273–278K
N_2Cl
Cu_2Cl_2/HCl
Cl
6[H]
Sn+HCl
$NaNO_2$+HCl
273–278K
KI
Heat
I

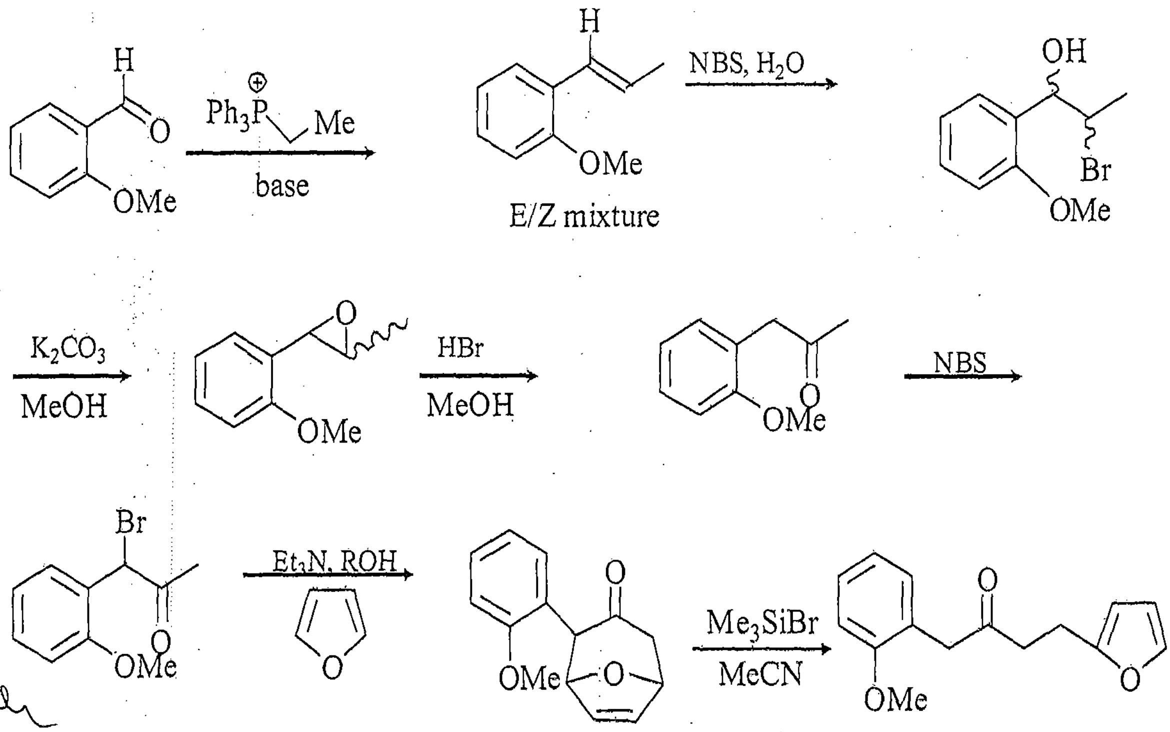
10. 
CH_3
Toluene
HNO_3(conc.)+H_2SO_4(conc.),323K
Nitration
O_2N
NO_2
Alk.$KMnO_4$
(Oxidation)
COOH
Soda lime
Trinitrobenzene
TNB

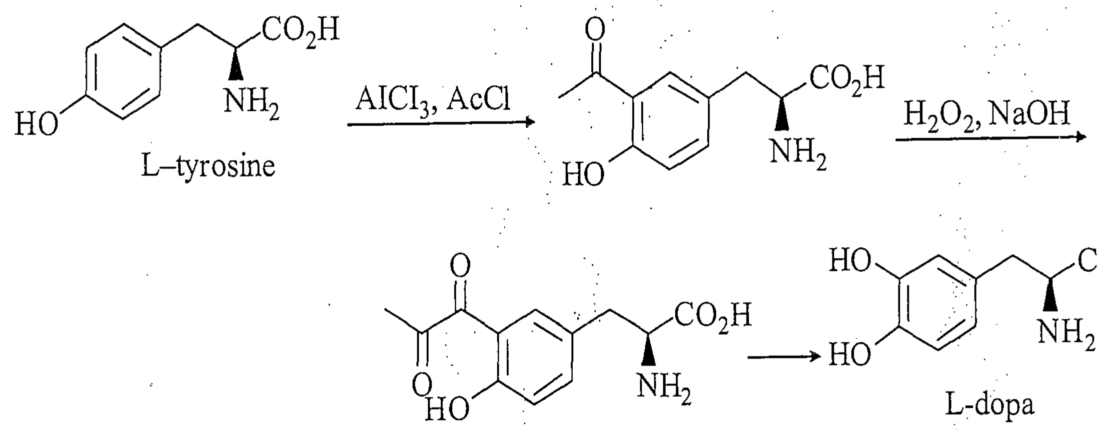
11. 
CONH$_2$
NH$_2$
Br_2
KOH
Benzamide
Aniline

12. 
NH$_2$
Aniline
Br_2
NH$_2$
Br
Br
Br
$NaNO_2$+HCl
273–278K
N_2Cl
Br
Br
Br
H_3PO_2
H_2O
Br
Br
Br

13. 
CHO
Benzaldehyde
$(CH_3CO)_2O$
CH_3COONa, 453K
CH=CHCOOH
Cinnamic acid

14. 
Benzene
V_2O_5
773K
O
O
O

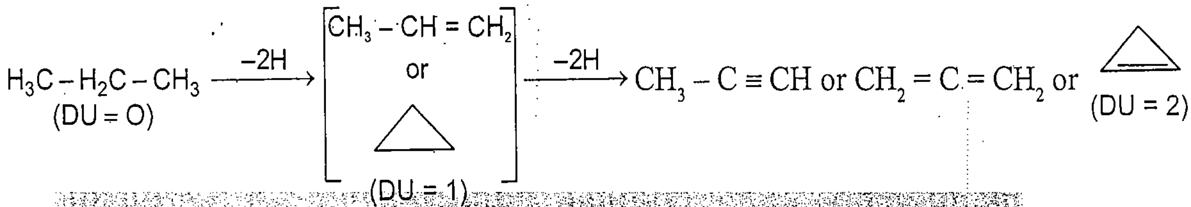
15. 
H
O
OMe
$Ph_3\overset{\oplus}{P}$ Me
base
H
OMe
E/Z mixture
NBS, H_2O
OH
Br
OMe
K_2CO_3
MeOH
O
OMe
HBr
MeOH
O
OMe
NBS
Br
O
OMe
Et_3N, ROH
O
O
OMe
O
Me_3SiBr
MeCN
O
OMe
O

16. 

STRUCTURAL IDENTIFICATION BY CHEMICAL REACTION AND TESTS

1. Calculation of Degree of Unsaturation (DU):-

It is the hydrogen deficiency index (HDI) or Double Bond Equivalence (DBE)



That means Deficieny of 2H is equivalent to 1 DU

(i) 1DU = Presence of 1 Double Bond or Presence of 1 Ring closure

(ii) 2DU = Presence of 2 Double bond or 1 Triple bond or two ring closure or 1 double bond + 1 ring closure.

G.F.	D.U.
(i) C_xH_y	$(x+1)-\left(\frac{y}{2}\right)$
(ii) $C_xH_yO_z$	$(x+1)-\left(\frac{y+0}{2}\right)$
(iii) $C_xH_yX_s$	$(x+1)-\left(\frac{y+s}{2}\right)$
(iv) $C_xH_yN_w$	$(x+1)-\left(\frac{y-w}{2}\right)$
(v) $C_xH_yO_zX_sN_w$	$(x+1)-\left(\frac{y+s-w}{2}\right)$

If N, O are simultaneous include only N,

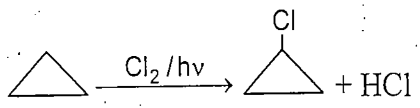
2. Monochlorination:-

When an alkane or a cycloalkane is treated with halogen (Cl_2, Br_2, F_2, I_2), a photochemical reaction takes

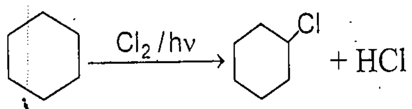
place and a C – H bond cleaves and a C – Cl bond is formed. So, one H-atom is substituted by one halogen atom. This is known as monohalogenation reaction.

Ex.1 $CH_4 \xrightarrow{Cl_2/h\nu} CH_3Cl + HCl$

Ex.2 $CH_3-CH_3 \xrightarrow{Cl_2/\text{Sunlight}} CH_3-CH_2Cl + HCl$

Ex.3 

Ex.4 $CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH_3 \xrightarrow{Cl_2/h\nu} CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH_2Cl + HCl$

Ex.5 

Application : If a molecule has more than one type of H-atom, then on monochlorination, it forms a mixture of monochloroisomers. All these isomers are position isomers.

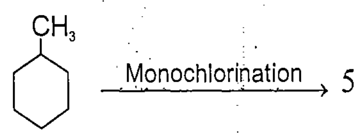
Conclusion : Hence, it can be concluded that the total number of position isomers (structural) of monochloro compounds is equal to the number of different types of H-atoms present in the reactant. The different type of H-atoms are also known as non-identical Hydrogens or non-equivalent Hydrogens or chemically different Hydrogens.

Ex.6 $CH_3-CH_2-CH_3 \xrightarrow{\text{Monochlorination}} 2$ (structural)

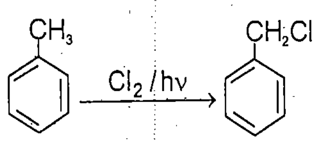
Ex.7 $CH_3-CH_2-CH_2-CH_3 \xrightarrow{\text{Monochlorination}} 2$ (structural)

Ex.8 $CH_3-CH_2-CH_2-CH_2-CH_3 \xrightarrow{\text{Monochlorination}} 3$ (structural)

Ex.9 $CH_3-\overset{\overset{\large CH_3}{|}}{C}H-CH_2-CH_3 \xrightarrow{\text{Monochlorination}} 4$ (structural)

Ex.10  (structural)

Remark : In aromatic hydrocarbons, the hydrogen atoms of the side-chain are chlorinated but H-atoms of benzene ring are stable. In pure benzene, no monochlorination occurs.

Ex.11 

3. **Catalytic Hydrogenation** of $C=C$; $C\equiv C$

(i) Alkenes, Alkynes, polyenes or polyynes can be hydrogenated by using catalysts Ni/Pt/Pd at room temperature.

(ii) All $C-C$ π bonds ($C=C$, $C\equiv C$) are hydrogenated. The reaction can't be stopped at any intermediate stage.

(iii) Aromatic π bonds which are stable at room temperature but can be hydrogenated at high temperature.

(iv) It can be concluded that the hydrogenation product of an alkene or alkyne or any unsaturated compound is always a saturated compound.

(v) The number of moles of H_2 consumed by 1 mole of compound is equal to the number of π bonds presents.

(vi) All positional isomers of alkenes or alkynes (due to multiple bond) always give same product on hydrogenation.

(vii) During catalytic hydrogenation no rearrangement in carbon skeleton takes place.

General reaction :

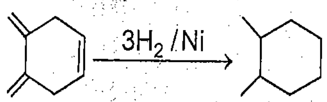
$$R-CH=CH-R+H_2 \xrightarrow{Ni} R-CH_2-CH_2-R$$

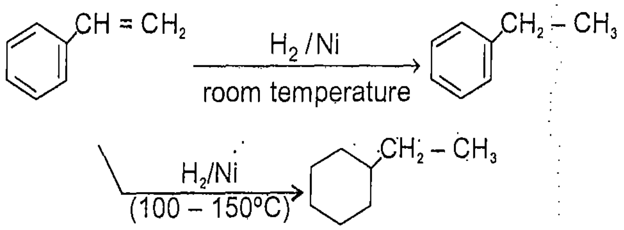
$$R-C\equiv C-R+2H_2 \xrightarrow{Ni/Pt/Pd} R-CH_2-CH_2-R$$

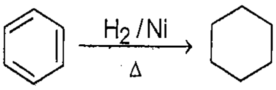
$$\downarrow Ni/Pt/Pd$$

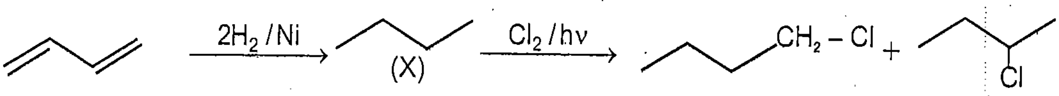
$$\underset{\text{(Not isolated)}}{R-CH=CH-R} \xrightarrow{H_2} R-CH_2-CH_2-R$$

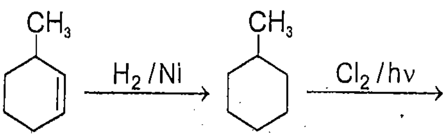
$$CH_2=CH-CH_2-CH_3 \xrightarrow{H_2/Ni} CH_3-CH_2-CH_2-CH_3$$

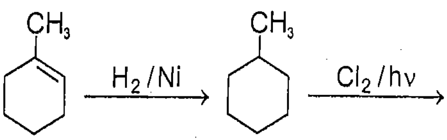




 [Reaction cannot be stopped at any intermediate stage]

Ex.12 

Ex.13  5 Monochloro product (structural)

Ex.14  5 Monochloro product (structural)

4. Ozonolysis:

(i) It tells about position of unsaturation.

(ii) Alkene and polyalkene on ozonolysis undergo oxidative cleavage.

(iii) (a) The reagent of reductive ozonolysis is

(i) O_3 (ozone) (ii) Zn and H_2O or Zn and CH_3COOH or $(CH_3)_2S$

(b) The reagent of oxidative ozonolysis is O_3 and H_2O_2.

(iv) The products are carbonyl compounds (aldehydes or ketones). This type of ozonolysis is known as reductive ozonolysis.

(v) Ozonolysis does not interfere with other functional groups.

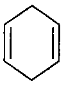
General Reaction :

$$R-CH=CH-R \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} R-CH=O+O=CH-R+ZnO+H_2O$$

Ex.15 $CH_2=CH_2 \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} CH_2=O+CH_2=O$

Ex.16 $CH_3-CH_2-CH=CH_2 \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} CH_3-CH_2-CH=O+O=CH_2$

Ex.17 $CH_2=CH-CH_2-CH=CH-CH_3 \xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3} CH_2=O+O=CH-CH_2-CH=O+O=CH-CH_3$

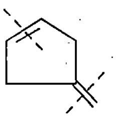
Ex.18  $\xrightarrow[(2)\ Zn/H_2O]{(1)\ O_3}$ $OHC-CH_2-CHO$ (Propandial)

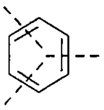
Applications:

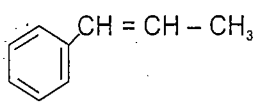
→ The process is used to determine the position of C = C in a molecule.

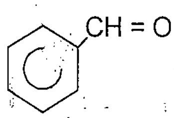
→ If the products are rejoined, the position of C = C can be determined in the reactant molecule. All C = C (except aromatic ones) undergo oxidative cleavage under normal conditions.

→ At higher temperature, the aromatic double bonds can also undergo ozonolysis.

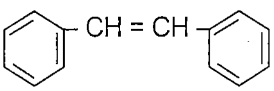
Ex.19  $\xrightarrow[Zn]{O_3}$ $O=CH-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-HC=O+O=CH_2$

Ex.20  $\xrightarrow[Zn]{O_3(\Delta)}$ $3\ O=\overset{H}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}=O$ (Ethanedial)

Ex.21 

$\xrightarrow[O_3\ /\ Zn]{\text{low temperature}}$ 

$+O=CH-CH_3$

Ex.22 

$\xrightarrow[Zn/H_2O]{O_3}$ $C_6H_5-CH=O$

PRACTICAL ORGANIC CHEMITRY

Introduction

The main objective of an organic chemist is the determination of the structure of a new organic compound which has been obtained in pure state either from a natural source or synthesised in the laboratory.

- In order to establish the correct structure of an organic compound, it is necessary to detect element and functional group present in the organic compound.

Detection of elements (Qualitative Analysis) :-

- Most of the organic compounds contain 2 to 5 different elements
- The principal elements present are carbon, hydrogen and oxygen.
- Less commonly present elements are nitrogen, sulphur and halogens.
- In few organic compounds , phosphorus and metal may also be present
- The order of abundance of these elements in organic compounds is given below:-

Carbon	$\longrightarrow$	Always present
Hydrogen	$\longrightarrow$	Nearly always present
Oxygen	$\longrightarrow$	Generally present
Nitrogen, halogen, sulphur	$\longrightarrow$	Less commonly present
Phosphorus and metal	$\longrightarrow$	Rarely present

- Detection of nitrogen, sulphur and halogens are tested in an organic compounds by lassaigne's test.
- The organic compound (N,S or halogen) is fused with sodium metal as to convert these elements in ionisable inorganic substance i.e. nitrogen into sodium cyanide, sulphur into sodium sulphide and halogens into sodium halides.
- These cyanide, sulphide or halide ions can be confirmed in the aqueous solution by usual test. The aqueous solution (fused sodium extract) is called lassaigne's filterate.

Identification of Elements in Organic Compounds

Element	Test / Reaction	Remark
1. Nitrogen	Lassaigne's test $Na + C + N \rightarrow NaCN$ $FeSO_4 + 6NaCN \rightarrow Na_4[Fe(CN)_6] + Na_2SO_4$ $3Na_4[Fe(CN)_6] + 4FeCl_3 \rightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl$	The appearance of green or prussian blue colour confirms the persence of nitrogen.
2. Sulphur	(a) Oxidation test $3KNO_3 \rightarrow 3KNO_2 + 3[O]$ $Na_2CO_3 + S + 3[O] \rightarrow Na_2SO_4 + CO_2$ $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4 \downarrow + 2NaCl(aq)$ (b) Lassaigne's test $2Na + S \rightarrow Na_2S$ $Na_2S + Na_2[Fe(CN)_5NO] \rightarrow Na_4[Fe(CN)_5NO.S]$	Formation of a white ppt. indicates presence of sulphur Appearance of purple colouration confirms the presence of sulphur
3. Halogens	Lassaigne's test $X + Na \rightarrow NaX$ $NaX + AgNO_3 \rightarrow NaNO_3 + AgX\downarrow$	A white ppt. soluble in NH_4OH solution indicates chlorine. A dull yellow ppt. partly soluble in NH_4OH solution indicates bromine. A yellow ppt. completely insoluble in NH_4OH solution indicates iodine
4. Phosphorus	$\underbrace{P + 3H}_{\text{from organic compound}} + \underbrace{4O}_{\text{from } HNO_3} \xrightarrow{HNO_3} H_3PO_4$ $H_3PO_4 + \text{Magnesia mixture} \rightarrow MgP_2O_7 + H_2O$ $2MgNH_4PO_4 \rightarrow Mg_2P_2O_7\downarrow + 2NH_3 + H_2O$	A white ppt. of magnesium pyrophosphate indicates phosphorus
5. Nitrogen and Sulphur	Lassaigne's test $Na + C + N + S \rightarrow NaSCN \xrightarrow{FeCl_3} Fe(SCN)_3$	Blood red colouration confirms presence of both nitrogen & sulphur

Identification of Functional Groups by Laboratory Tests

Functional Groups	Reagent	Observation	Reaction	Remarks
C – C	conc. H_2SO_4 conc. NaOH $KMnO_4$ $LiAlH_4$	NR NR NR NR	————	Inert paraffins
C = C / C ≡ C	[Bayer's reagent] alk. dil. cold $KMNO_4$	Pink colour Disappears	$CH_2=CH_2+H_2O+O \xrightarrow{\text{alk.}KMnO_4} \underset{OH}{CH_2}-\underset{OH}{CH_2}$	Hydroxylation
	Br_2 / H_2O	Red colour decolourises	$Br_2+CH_2=CH_2 \longrightarrow$ white ppt	Bromination
C = C	O_3(ozone)	>C = O Compounds	$H_2C=CH_2+O_3 \xrightarrow{Zn/H_2O} 2HCHO$	Ozonolysis
C ≡ C	O_3	Acid formed.	$R-C\equiv C-R' \xrightarrow{O_3} RCOOH + R'COOH$	Ozonolysis
R – C ≡ CH	(a) Cuprous chloride + NH_4OH	Red ppt.	$R-C\equiv CH + CuCl \xrightarrow{NH_4OH} R-C\equiv C\,Cu\downarrow$ (red)	
	(b) $AgNO_3 + NH_4OH$	White ppt.	$R-C\equiv CH + Ag^+ \longrightarrow R-C\equiv C\,Ag\downarrow$ (white)	
(R – OH)	Na	Bubbles of H_2 come out	$2ROH + Na \rightarrow 2RONa + H_2\uparrow$	Presence of active 'H'
ROH 3° 2° 1°	Lucas Reagent [Conc. HCl + anhyd. $ZnCl_2$]	(3)° Cloudiness appears immidiately (2°) Cloudiness appears within 5 min. (1°) Cloudiness appear after 30 min.	$R-OH + HCl \xrightarrow{\text{anhydrous } ZnCl_2} \underset{\text{cloudiness}}{R-Cl} + H_2O$	Lucas Test I. ter.alcohol II. sec. alcohol III. pri.alcohol

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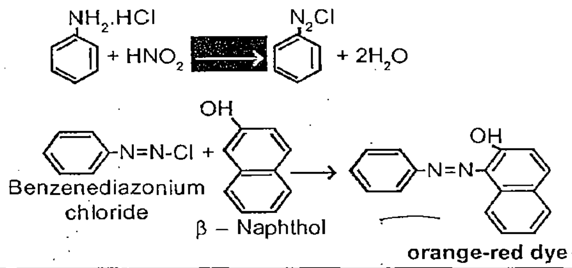
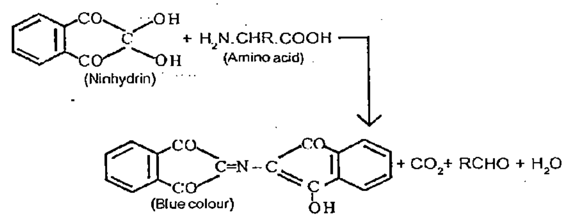
Functional Groups	Reagent	Observation	Reaction	Remarks
Ar – OH Enols	$FeCl_3$ (Neutral)	Coloured ppt. (violet, blue, green buff)	$6C_6H_5OH + FeCl_3 \longrightarrow [Fe(PhO)_6]^{-3}$	Test of enols / phenols
$>C=O$	2, 4-Dinitrophenyl hydrazine (2, 4-DNP) solution	Yellow orange ppt.	$>C=O + H_2N{-}NH{-}C_6H_3(NO_2)_2$ $>C=N{-}NH{-}C_6H_3(NO_2)_2 \downarrow$ (yellow orange ppt.)	DNP-test
R – CHO	Fehling solution A & B	Red ppt.	$RCHO + Cu^{+2} \rightarrow RCOOH + Cu_2O\downarrow + 2H_2O$ Fehling sol^n. Red	Fehling's test
	Tollen's reagent	Black ppt. or silver mirror	$RCHO + Ag^+ \rightarrow RCOOH + 2Ag$ (Silver mirror)	Tollen's test
	Schift's Reagent *	Pink colour resume		
$R-COCH_3$ or $ArCOCH_3$ or CH_3CHO	I_2 / NaOH	Yellow ppt of CHI_3 (iodoform)	$R-\overset{O}{\overset{\Vert}{C}}-CH_3 \xrightarrow{I_2/NaOH} R-\overset{O}{\overset{\Vert}{C}}-ONa + \underset{(Iodoform)}{CHI_3}$	Iodoform reaction
$R-\overset{O}{\overset{\Vert}{C}}-OH$	Blue litmus	Litmus change to red.		Litmus test.
	Conc. $NaHCO_3$ solution	Effervescence evolve.	$R-COOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2\uparrow$	Sodium bicarbonate test
Ester	NaOH, phenophthalein.	Pink colour ↓ disappear on heating.	R COOR' + NaOH + Phenophthalein (pink) $\downarrow \Delta$ R COOH + R' OH (Colourless solution)	
Amides	Conc. NaOH, Δ	Smell of NH_3	$RCONH_2 + NaOH \xrightarrow{\Delta} RCOONa + NH_3\uparrow$	

★ Schiff's reagent : p-Rosiniline hydrochloride saturated with SO_2 so it is colourless. The pink colour is resumed by RCHO.

Functional Groups	Reagent	Observation	Reaction	Remarks
Nitro Compounds (RCH_2NO_2) or $ArNO_2$	Mulliken's test	black ppt	$Ar{-}NO_2$ ($R{-}NO_2$) $\xrightarrow[(1)]{Zn\,/\,NH_4Cl,\ \Delta}$ ArNHOH $\xrightarrow{\text{Tollen Toller ent AgNC AgNC,OH}}$ Ag↓	
Amines (pri.) RNH_2	$CHCl_3$, KOH	Nauseating odour (Offensive smell) (Carbylamine)	$R\,NH_2 + CHCl_3 + 3KOH \rightarrow RNC + 3KCl + 3H_2O$	Carbylamine Reaction
	HNO_2 ($NaNO_2$ + HCl)	Effervescence of N_2	$R\,NH_2 + HONO \rightarrow ROH + N_2 + H_2O$	
Ar. amines. $ArNH_2$	HNO_2 ($NaNO_2$ + HCl) + β-Naphthol	Orange red dye is formed	$NaNO_2 + HCl \rightarrow NaCl + HNO_2$ 	Dye test
R_2NH Sec. Amines	(i) $NaNO_2 + H_2SO_4$ (ii) Phenol	red colouration Liebermann test Reddish violet colour.		
Carbohydrate	Molisch's reagent (10% β-naphthol in alcohol).	Violet colour		
Amino acids	Ninhydrin reagent (0.2 % sol.^{n})	Blue colour		Ninhydrin test

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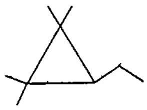
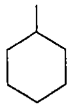
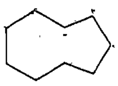
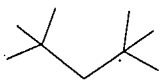
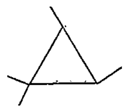
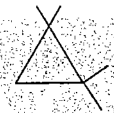
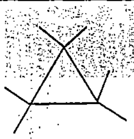
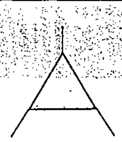
SOLVED PROBLEMS

1. Identify X, Y & Z with the help of following reactions.

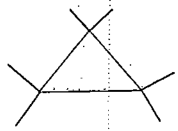
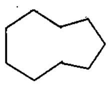
(X) (C_9H_{18}) (Saturated Hydrocarbon) $\xrightarrow{Cl_2\,/\,h\upsilon}$ Single monochloro structural product

(Y) (C_8H_{18}) $\xrightarrow{Cl_2\,/\,h\upsilon}$ Single monochloro structural product

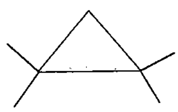
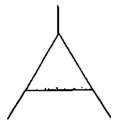
(Z) (C_7H_{14}) (Saturated Hydrocarbon) $\xrightarrow{Cl_2\,/\,h\upsilon}$ Two monochloro structural products

	X	Y	Z
A		$(CH_3)_3C-C(CH_3)_3$	
B			
C			
D		$(CH_3)_3C-C(CH_3)_3$	

Ans. C, D.

Sol. X =  or 

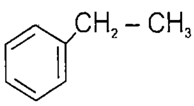
$$Y = CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$$

Z = , 

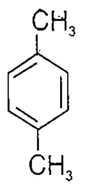
2. $X(C_8H_{10})$ (Aromatic) $\xrightarrow{Cl_2\,/hv}$ Two monochloro (structural)

$Y(C_8H_{10})$ (Aromatic) $\xrightarrow{Cl_2\,/hv}$ One monochloro (structural)

Ans. DU = 4

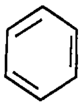
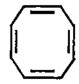
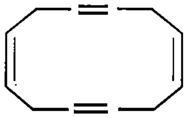
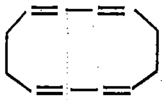


(X)

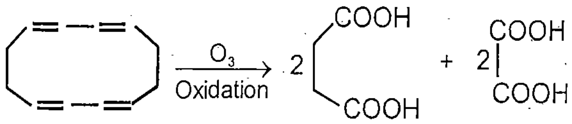


(Y)

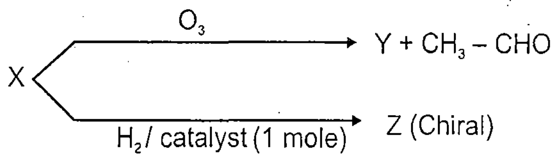
3. An organic hydrocarbon on oxidative ozonolysis produces oxalic acid and butanedioic acid. Its structure is

(A)  (B)  (C)  (D) 

Ans. (D)

Sol. 

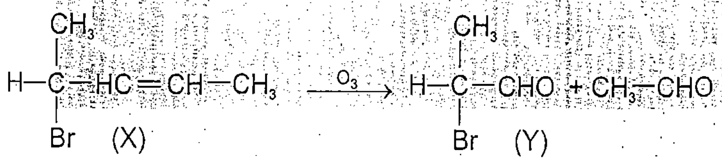
4. An optically active acyclic compounds X (molecular formula C_5H_9Br) give following reactions

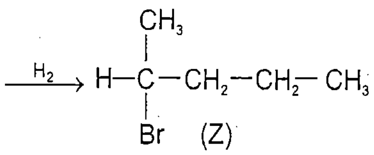


The **incorrect** statements about 'X' are:

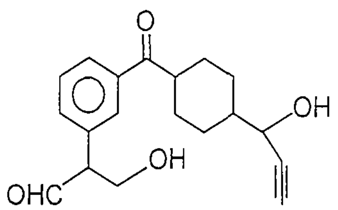
(A) It has two stereoisomers
(B) It gives an achiral product (Y) on ozonolysis
(C) It has two asymmetric carbon atoms
(D) It has four stereoisomers and all are optically active

Ans. (A,B,C)

Sol. 

(X) 

5. A set of reagents (1 to 8) are successively reacted with the following compound



1. $NaHCO_3$
2. 2, 4, DNP
3. Na metal
4. $AgNO_3 + NH_4OH$
5. Fehling's solution
6. $Cu_2Cl_2 + NH_4OH$ (with alcohols)
7. Br_2 / H_2O
8. $NaNO_2 + HCl$

The reagents which give positive test with the given compound are :

(A) 1, 2, 3, 4, 5 (B) 3, 4, 5, 6, 8 (C) 1, 2, 3, 4, 8

(D) All reagents except 1 and 8

Ans. (D)

Sol. There is no COOH group or NH_2 group.

$\therefore$ Regents 1 and 8 will fail to give test.

6. Compounds I and II can be distinguished by using reagent.

(I)	(II)
4-Amino-2-methylbut-3-en-2-ol	4–Amino–2,2-dimethylbut- 3-yn-1-ol.

(A) $NaNO_2$ / HCl

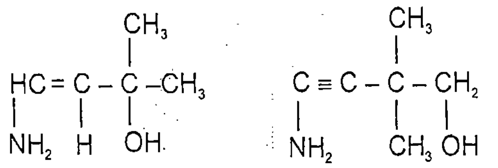
(B) Br_2 / H_2O

(C*) HCl / $ZnCl_2$ (anhydrous)

(D) Cu_2Cl_2 / NH_4OH

Ans. (C)

Sol.



(I) (II)

(I) gives immediately turbidity by Lucas reagent and (II) does not give turbidity appriciably.

Fehling's test → Alliphatic aldehydes are oxidised to corresponding acids with Fehling's Benedict sol. Cu(II) converted to Cu2O

Cu2O red ppt →

Cu+ → d10 → p–s charge Transfer spectra

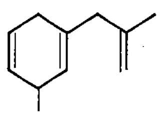
But I think, p–s, lies in UV region if lower donor like O2– are used; check once..

Aldehydes gives Schiff's reagent test & restores the magenta colour of Schiff's reagent. This is not given by ketones

EXERCISE - I

Single Answer Correct Type

1. Quinine is the most important alkaloid obtained from cinchona bark. It's molecular formula is $C_{20}H_{24}N_2O_2$. It may contain
(a) 5 double bond & 6 ring (b) 6 double bond & 4 ring
(c) 6 double bond & 3 ring (d) 7 double bond & 5 ring

2.  $\xrightarrow{H_2/Ni}$ Q
(P)
Which of the following is the correct statement about P & Q.
(a) Product will be 1-methyl-3-(2-methylpropyl)cyclohexane.
(b) Product will be 3-methyl-1-(2-methylpropyl)cyclohexane.
(c) DU of reactant P is 3.
(d) DU of product Q is zero.

imp
3. An alkane E is produced by hydrogenation of only one alkyne D. Identify D.

$D(C_6H_{10}) \xrightarrow{H_2/Ni} E(C_6H_{14})$
only one alkyne only one alkane (only one alkyne)

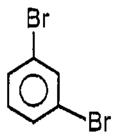
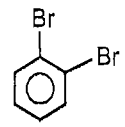
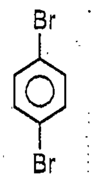
(a) $HC\equiv C-CH_2-CH_2-CH_3$ (b) $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-C\equiv C-H$
(c) $CH_3-\underset{CH_3}{CH}-C\equiv C-CH_3$ (d) $CH_3-CH_2-C\equiv C-CH_2-CH_3$

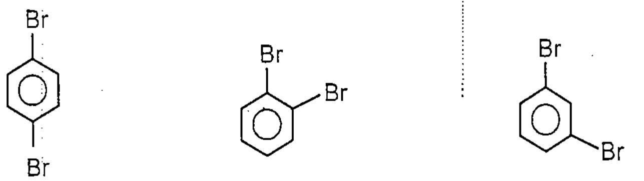
4. $C_5H_{10} \xrightarrow{H_2/Ni} (X) \xrightarrow{Cl_2/h\nu}$ 3 monochloro structural isomers
for compound C_5H_{10} how many pairs of geometrical isomers are possible
(a) 1 pair (b) 2 pair (c) 3 pair (d) No pair

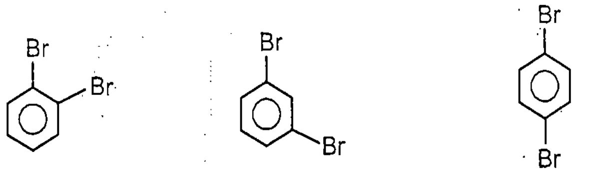
5. How many alkynes will produce 3-Chloro-3-ethylpentane in the following sequence of reactions :
Alkynes $\xrightarrow{\text{Catalytic hydrogenation}}$ $\xrightarrow{\text{Photochemical Chlorination}}$ 3-chloro-3-ethylpentane
(a) 1 (b) 2 (c) 3 (d) 4

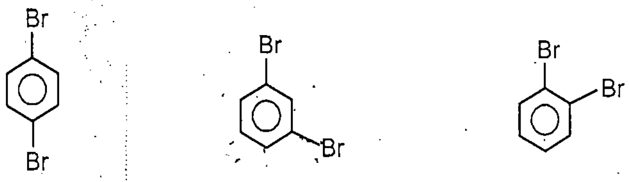
6. Three aromatic isomers X, Y, Z have molecular formula $C_6H_4Br_2$. On mononitration 'X' gives one, 'Y' gives two and 'Z' gives three isomeric products of molecular formula $C_6H_3Br_2NO_2$. Identify X, Y and Z.

X **Y** **X**

(a)   

(b) 

(c) 

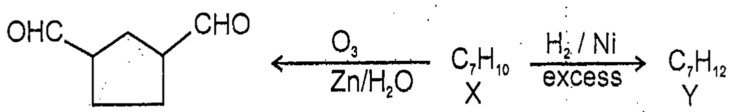
(d) 

7. An organic compound $X(C_5H_{10})$ on ozonolysis gives Y & Z. The product mixture Y and Z on reaction with NH_2-OH gives four oximes. The structure of X is

(a) $CH_3-C(=CH_2)-CH_2CH_3$ (b) $CH_3-CH=CH-CH_2-CH_3$

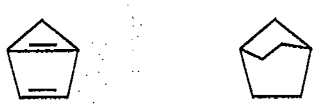
(c) $(CH_3)_2C=CH-CH_3$ (d) $H_3C-CH(CH_3)-CH=CH_2$

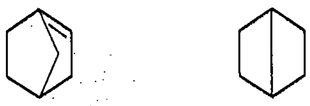
8. For the following reactions sequence



The structure consistent with X and Y are :

X **Y** **X** **Y**

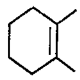
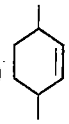
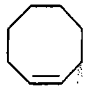
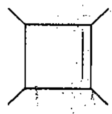
(a)  (b) 

(c)  (d) 

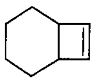
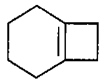
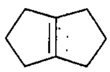
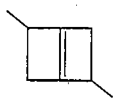
9. The chemical reactions of an unsaturated compound 'M' are given below. Determine the possible structural formula of 'M'

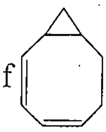
(M) C_8H_{14} $\xrightarrow{O_3}$ $C_8H_{14}O_2$(N)

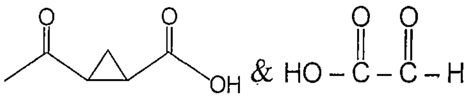
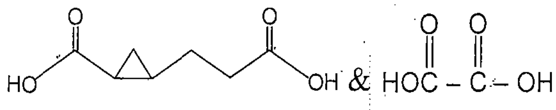
(M) C_8H_{14} $\xrightarrow{H_2/Ni}$ C_8H_{16}(O) $\xrightarrow{Cl_2/h\upsilon}$ $C_8H_{15}Cl$(P) (only one monochloro product)

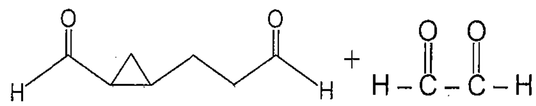
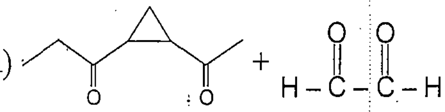
(a)  (b)  (c)  (d) 

10. Compound A(C_8H_{12}) does not show stereoisomerism. It adds only one mole of H_2. On ozonolysis it gives a symmetrical diketone B($C_8H_{12}O_2$). Identify A.

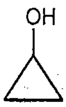
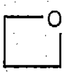
(a)  (b)  (c)  (d) 

11. What are the reductive ozonolysis products of 

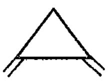
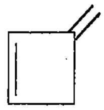
(a)  (b) 

(c)  (d) 

12. Compound 'A' (C_3H_6O), decolourizes Br_2 water. It liberates colourless, odourless gas on addition of sodium metal. On ozonolysis, it gives B and compound 'C' ($C_2H_4O_2$). Identify 'A'.

(a)  (b) $CH_2=CH-CH_2OH$ (c)  (d) CH_3-CH_2-CHO

13. A compound P(C_5H_6) gives Baeyers test positive and on hydrogenation from a hydrocarbon B(C_5H_{10}) which gives only one monochloro product. The compound "P" is.

(a)  (b)  (c)  (d) $CH\equiv C-CH_2-CH=CH_2$

14. Compound A (C_3H_5N) gives precipitate with Tollen's reagent and H_2 gas is also evolved on addition of Li metal. Compound A can be :

(a) $CH_3-CH_2-C\equiv N$ (b) $H-C\equiv C-NH-CH_3$

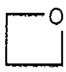
(c) $CH_3-CH_2-N \equiv C$ (d) $CH_2=C=N-CH_3$

15. Compound 'A' ($C_{16}H_{16}$) on ozonolysis gives only one product 'B', (C_8H_8O). 'B' gives positive Iodoform test and forms sodium benzoate as one of the product. Identify the structure of 'A.

(a) $Ph-CH_2-CH=CH-CH_2-Ph$ (b) $CH_3-C(CH_3)=C(Ph)-Ph$

(c) $Ph-C(CH_3)=C(CH_3)-Ph$ (d) $Ph-CH=C(CH_3)-CH_2-Ph$

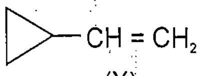
16. Compound X(C_3H_6O) gives negative tests with the following reagents. (a) Br_2 (b) 2, 4-Dinitrophenylhydrazine (c) Na metal. It gives two monochloro structural isomers. Identify 'X'.

(a) $CH_2=CH-O-CH_3$ (b) CH_3-CH_2-CHO (c)  (d) 

EXERCISE - II

One or More Than One Correct Answer Type

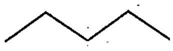
1. Select the correct statement(s) about the following reaction

 $\xrightarrow{H_2/Ni}$ (Y) $\xrightarrow{Cl_2/h\nu}$ Monochloro products

(X)

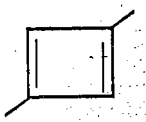
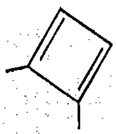
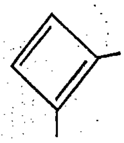
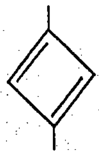
(a) The reactant (X) has four positional isomers (including 'X' itself)
(b) The hydrogenated product Y has three positional isomers
(c) Four monochloro products are fomed which are all positional isomers
(d) Only one monochloro positional isomer shows geometrical isomerism

2. The correct statement(s) about the products of the following reaction is / are

 $\xrightarrow{Cl_2/h\nu}$ monochloro products.

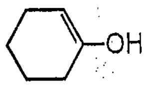
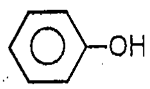
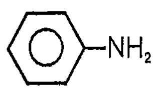
(a) Three structural isomers are formed
(b) All the formed structural isomers are optically active
(c) Total number of isomers formed are four
(d) Total optically active isomers are two

3. An organic compound with molecular formula C_6H_8, on reductive ozonolysis gives 2 moles of 2-oxopropanal. The structure of the compound will be :

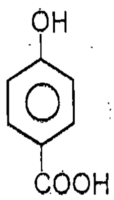
(a)  (b)  (c)  (d) 

4. Which statement(s) is/are correct.
(a) DU tells about H-defficiency from any molecule in the form of multiple bond or ring.
(b) Hydrogenation tells about carbon skeleton.
(c) Monohalogenation tells about type of chemically different H.
(d) Ozonolysis tells about position of double or trible bond in molecule.

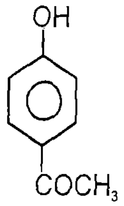
5. Which will give colour with $FeCl_3$?

(a) 
(b) $CH_3-\overset{OH}{\overset{|}{C}}=CH-\overset{O}{\overset{||}{C}}-OC_2H_5$
(c) 
(d) 

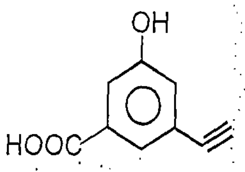
6. Which will perform iodoform reaction with I_2/OH^- ?
(a) $CH_3COCH_2CH_3$ (b) CH_3CONH_2 (c) $C_6H_5COCH_3$ (d) CH_3CHO

7. Correct statement about  is

(a) It gives coloured solution with neutral $FeCl_3$ solution
(b) It liberates one mole H_2 gas with Na metal
(c) It gives CO_2 gas with $NaHCO_3$.
(d) It forms sweet smelling compound with alcohols.

8. Correct statement about  is

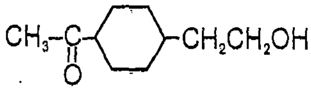
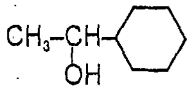
(a) It gives coloured solution with neutral $FeCl_3$ solution
(b) It liberates half mole H_2 gas with Na metal
(c) It gives +ve Iodoform test.
(d) It forms sweet smelling compound with alcohols.

9. Correct statment about  is

Tollen test

(a) librate $\frac{3}{2}$ mole of H_2 on treatment with Na.
(b) + test with $FeCl_3$
(c) + test with $NaHCO_3$ (d) + test with tollen's reagent

10. Which of the following will give positive iodoform test.

(a) $CH_3-\underset{\substack{\|\\ O}}{C}-OH$ (b) $Ph-\underset{\substack{\|\\ O}}{C}-CH_3$ (c)  (d) 

ANSWER KEY

EXERCISE - I

1. b	2. a	3. b	4. a	5.a	6. b	7. b
8. d	9. c	10. c	11. c	12. b	13. c	14. b
15. c	16. d					

EXERCISE - II

1. a,c,d	2. a,c,d	3. a,c,d	4. a,b,c,d	5.a,b,c	6. a,c,d	7. a,b,c,d
8. a,b,c	9. a,b,c,d	10. b,c,d				

CHAPTER

11

SPECTROSCOPY

EXERCISE - I

Single Correct Type

Infrared Spectroscopy

1. Hooke's law relates the restoring force, f to the displacement q as
   (a) $f = -Kq$ (b) $f = Kq$ (c) $f = Kq^2$ (d) $f = -Kq^2$
2. The intensity of an absorption band is always proportional to the
   (a) Atomic population (b) Molecular population of the initial state
   (c) Molecular population of the final state (d) Temperature
3. The vibrational stretching frequency of diatomic molecule depends on
   (a) Force constant (b) Masses of two atoms
   (c) Both a and b (d) None
4. Force constant is expressed in
   (a) Dynes cm^{-1} (b) dyne $Å^{-1}$ (c) Nm^{-1} (d) All
5. For HCl, $\mu = 1.63 \times 10^{-27}$ kg, the observed frequency $\bar{\nu} = 2890\ cm^{-1}$ or $\nu = 8.67 \times 10^{13}$ Hz. The force constant K is
   (a) 4.83 m dyn $Å^{-1}$ (b) 8.43 dynes cm^{-1} (c) 483 μm^{-1} (d) Both a and c
6. q for NO, CO, HCl is 0.048 Å, 0.05 Å, 0.10 Å. Thus q is
   (a) Larger when the force constant is smaller (b) Smaller when the force constant is smaller
   (c) Larger when the force constant is larger (d) None
7. Since the nuclei in a polyatomic molecule do not always vibrate in a simple harmonic manner, there arises
   (a) Harmonicity (b) Anharmonicity in molecular vibrations
   (c) Fundamental frequencies (d) All
8. The frequency of vibration of H_2 is 4159 cm^{-1} and dissociation energy is 4.5 eV. Assuming that it vibrates as a SHO, its vibrational quantum number corresponding to dissociation energy, D is
   (a) 8 (b) 10 (c) 7 (d) 6

9. The vibrations, without a centre of symmetry are, active in
(a) Infrared but inactive in Raman (b) Raman but inactive in IR
(c) Raman and IR (d) None

10. The frequency of vibration of a bond is a function of :
(a) Force constant of the bond (b) Masses of the atoms involved in bonding
(c) Both a and b (d) Bond order

11. The order of decreasing vibrational frequency for C – Cl, C – Br, C – C, C – O and C – H is
(a) C – H, C – C, C – O, C – Cl, C – Br (b) C – Cl, C – Br, C – C, C – H, C – O
(c) C – O, C – H, C – Br, C – Cl, C – C (d) C – Br, C – Cl, C – C, C – O, C – H

12. The increasing order of stretching frequencies for $C \equiv C$; $C = C$ and $C - C$ is
(a) $C-C > C=C > C \equiv C$ (b) $C \equiv C > C=C > C-C$
(c) $C-C > C=C < C \equiv C$ (d) $C=C < C-C > C \equiv C$

13. Ethanol and glycol in CCl_4 exhibit broad O – H str. near 3350 cm^{-1} in IR spectra.On dilution with CCl_4, the spectrum of glycols does not change but that of ethanol exhibits a sharp band at 3600 cm^{-1} in addition to band at 3350 cm^{-1} because
(a) Intermolecular H-bonding is concentration dependent
(b) Intramolecular H-bonding is not affected on dilution
(c) Both a and b
(d) None

14. In the IR spectrum of aroyl chloride, a weak band near 1750 cm^{-1} results from
(a) inductive effect
(b) Fermi resonance between C = O band and first overtone
(c) conjugation effect (d) All

15. Compound, C_5H_{10} shows absorption at 1380 cm^{-1}. It is
(a) Pentene (b) Cyclopentane (c) Pentyne (d) All

16. Ketenes absorb in IR at a very high frequency (2150 cm^{-1}) because
(a) The inner C is sp-hybridised
(b) The more s character in a bond, the stronger it is
(c) Inner C is sp^2 hybridised (d) Both a and b

17. Ring strain in lactone (cyclic ester) or a lactam (cyclic amide)
(a) Increases carbonyl stretching frequency (b) Decreases carbonyl stretching frequency
(c) Increases C = C frequency (d) Decreases C = C frequency

18. In α-haloketones
(a) Two C = O stretching bands are observed
(b) One band has normal frequency

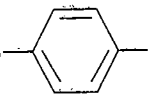
(c) Other band is at higher frequency due to eclipsed interaction between halogen atom and C = O group

(d) All statements are correct

19. A compound C_8H_6 decolorises Br_2 in CCl_4 and gives a white precipitate with Tollen's reagent. It has sharp band at 3300 cm^{-1} and weak bands at 3085, 2110 cm^{-1}. It is

(a) Phenyl acetylene (b) Phenyl propylene (c) Phenyl ethylene (d) Octene

20. A compound of molecular formula C_8H_8O has a strong infrared absorption band near 1690 cm^{-1}. The most likely structure for the compound is

(a) $C_6H_5CH_2CHO$ (b) $C_6H_5\ \underset{O}{CH-CH_2}$ (c) HO––CH = CH_2 (d) $C_6H_5COCH_3$

21. The wave number of IR absorption is .... the reduced mass.

(a) directly proportional to (b) inversely proportional to

(c) independent of (d) directly proportional to square of

22. The number of vibrational degrees of freedom in $C_6H_5CH_3$ will be

(a) 39 (b) 15 (c) 18 (d) 40

23. Which of the following molecules will not show infrared spectrum?

(a) H_2 (b) HCl (c) CH_4 (d) H_2O

24. The phosphorescence spectrum of the excited species is due to

(a) Singlet to triplet transitions (b) Triplet to singlet transitions

(c) Vibration modes (d) Electron spin transitions

25. Among the isomers of C_4H_6 given below, the compound which exhibits an absorption band at 3300 cm^{-1} in the IR spectrum, is

(a) 1,3-butadiene (b) 1-butyne (c) 2-butyne (d) cyclobutene

26. Monomeric saturated aliphatic carboxylic acids show carbonyl stretching frequency near 1760 cm^{-1} while saturated aliphatic ketones near 1720 cm^{-1} because

(a) Mesomeric (M) effect is dominant in acids over the inductive (I) effect

(b) I effect is dominant in carboxylic acids over the mesomeric effect

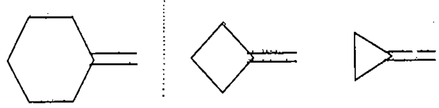
(c) I effect in ketones is dominant over the M effect.

(d) M effect in ketones is dominant

27. The exceptionally low carbonyl stretching frequency (1650 cm^{-1}) in 2, 4, 6-cycloheptatrienone is due to

(a) Conjugation effect (b) Steric effect (c) Field effect (d) Electronic effect

28. The correct order of IR stretching frequency of the C = C in the following olefins is



I II III

(a) I > II > III (b) II > III > I (c) III > II > I (d) III > I > II

(a)

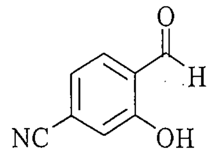
29. The bond that gives the most intense band in the infrared spectrum for its stretching vibration is

(a) C–H (b) N–H (c) O–H (d) S–H

30. The IR stretching frequencies (cm^{-1}) for the compound X are as follows:

3300-3500 (s, br); 3000 (m); 2225 (s); 1680 (s).

TMS precessional frequencies absorption op energy huge frequency



X

The correct assignment of the absorption bands is

(a) $\bar{\nu}_{(OH)} = 3300-3500;\ \bar{\nu}_{(CH)} = 3000;\ \bar{\nu}_{(CN)} = 2225;\ \bar{\nu}_{(CO)} = 1680$

(b) $\bar{\nu}_{(OH)} = 3000;\ \bar{\nu}_{(CH)} = 3300-3500;\ \bar{\nu}_{(CN)} = 2225;\ \bar{\nu}_{(CO)} = 1680$

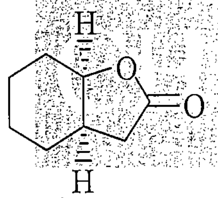
(c) $\bar{\nu}_{(OH)} = 3300-3500;\ \bar{\nu}_{(CH)} = 3000;\ \bar{\nu}_{(CN)} = 1680;\ \bar{\nu}_{(CO)} = 2225$

(d) $\bar{\nu}_{(OH)} = 3000;\ \bar{\nu}_{(CH)} = 3300-3500;\ \bar{\nu}_{(CN)} = 1680;\ \bar{\nu}_{(CO)} = 2225$

31. In the IR spectrum of p-nitrophenyl acetate, the carbonyl absorption band appears at

(a) 1670 cm^{-1} (b) 1700 cm^{-1} (c) 1730 cm^{-1} (d) 1760 cm^{-1}

32. In the IR spectrum, carbonyl absorption band for the following compound appear at

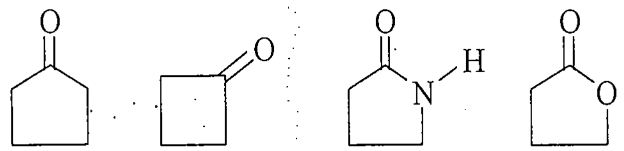


(a) 1810 cm^{-1} (b) 1770 cm^{-1} (c) 1730 cm^{-1} (d) 1690 cm^{-1}

33. The stark splitting for a given field is larger for a molcule AX as compared to BX. Which one of the following is true ? (μ is dipole moment)

(a) $\mu_{AX} = \mu_{BX}$ (b) $\mu_{AX} = 2\mu_{BX}$ (c) $\mu_{AX} > \mu_{BX}$ (d) $\mu_{AX} < \mu_{BX}$

34. Arrange in the decreasing order of carbonyl frequency



(I) (II) (III) (IV)

(a) IV > I > II > III (b) I > IV > III > II (c) IV > II I > III (d) II > IV > I > III

NMR Spectroscopy

35. The ^{1}H NMR spectrum of $CH_3OCHClCH_2Cl$ will exhibit

(a) A three proton doublet. One proton singlet and a two proton doublet

(b) A three proton singlet. One proton singlet and a two proton doublet

(c) A three proton singlet. One proton triplet and a two proton doublet

(d) A three proton triplet. One proton triplet and a two proton triplet

36. An organic compound with molecular formula $C_3H_6Cl_2$ exhibits only one signal in the ^1H NMR spectrum. The compound is

(a) 2, 2-dichloropropane (b) 1, 2-dichloropropane
(c) 1, 3-dichloropropane (d) 1, 1-dichloropropane

37. ^{1}H-NMR spectrum of compound with molecular formula $C_4H_9NO_2$ shows δ 5.30 (broad, 1H), 4.10 (q, 2H), 2.80 (d, 3H), 1.20 (t, 3H) ppm. The structure of the compound that is consistent with the above data is

(a) $CH_3NHCOOCH_2CH_3$ (b) $CH_3CH_2NHCOOCH_3$
(c) $CH_3OCH_2CONHCH_3$ (d) $CH_3CH_2OCH_2CONH_2$

38. Which of the following has three types of hydrogens in the following compounds

(a) $Br-CH=CH_2$ (b) $CH_3-CH_2-CH_3$
(c) $C_6H_5CH_3$ (d) $CH_3-CH_2-CH(CH_3)-NO_2$

39. Only one signal is present in the PMR spectra of

(a) C_3H_4, C_3H_6 (b) C_4H_6, C_5H_{12} (c) C_8H_{18}, C_2H_6O (d) All

40. How many Hertz does 1 ppm correspond to for an PMR spectrometer operating at a radiofrequency of 60 MHz and 100 MHz?

(a) 6 Hz, 10 Hz (b) 60 Hz, 100 Hz (c) 100 Hz, 60 Hz (d) None

41. Compound $C_4H_{10}O$ gave PMR spectrum consisting of two groups of lines (multiplets) with relative intensities in the ratio 3 : 2. Other compound of the same formula exhibited two lines with relative area of 9 : 1. Compounds are

(a) Diethyl ether (b) t-Butyl alcohol (c) Both a and b (d) None

42. Distance between the centres of the peaks of doublet is called

(a) Coupling constant (b) Spin constant (c) Spin-spin coupling (d) None

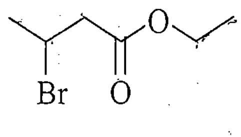
43. The PMR spectra of H_2, CH_4, C_2H_6 and C_6H_6 exhibit

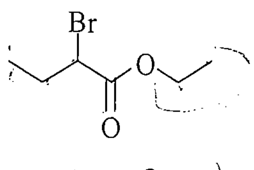
(a) Singlet (b) Doublet (c) Triplet (d) Quintet

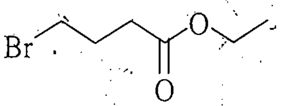
44. An organic compound having molecular formula $C_6H_{11}BrO_2$ exhibits the following peaks in 1H NMR spectrum.

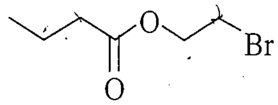
d 4.1 (2H, q, J = 7.5 Hz), 4.0 (2H, t, J = 7.5 Hz), 1.5-2.2 (2H, m), 1.25 (3H, t, J = 7.5 Hz)

The structure of the compound is

(a) 

(b) 

(c) 

(d) 

45. A proton H_b is coupled to four equivalent protons H_a. The multiplicity and the relative intensity of lines in the signal H_b is

(a) Doublet, 1 : 4 (b) Triplet 1 : 4 : 6
(c) Quintet, 1 : 4 : 6 : 4 : 1 (d) Quartet 1 : 4 : 6 : 4

46. The peaks expected in low-resolution NMR spectrum of vinyl chloride and ethyl cyclopropane are

(a) 3, 5 (b) 5, 3 (c) 6, 3 (d) 3, 6

47. The NMR frequency in MHz of bare H^1 in a magnetic field of intensity 1.4092 tesla is (given g_N = 5.585, $\mu_N = 5.05 \times 10^{-27}$ JT^{-1})

(a) 60 MHz (b) 120 MHz (c) 100 MHz (d) 15 MHz

48. At room temperature, the number of singlet resonances observed in the ^1H NMR spectrum of $Me_3CC(O)NMe_2$ (N, N-dimethyl pivalamide) is

(a) 3 (b) 4 (c) 5 (d) 2

49. Which of the following compounds is expected to show a sharp singlet for one of its proton at $\delta \geq$ 8 ppm in ^1H NMR spectrum, given that this signal remains unaffected on shaking the solution throughly with D_2O?

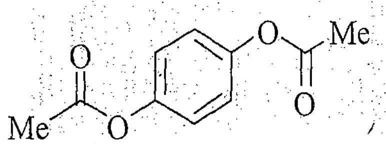
(a) CH_3CO_2H (b) $CH_3CONHC_6H_5$ (c) n-$C_6H_{13}C \equiv CH$ (d) n-$C_6H_{13}CHO$

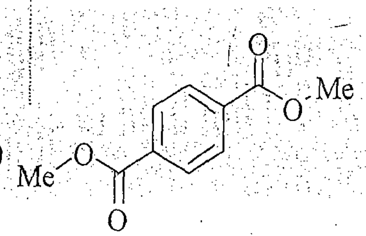
50. ^1H NMR spectrum of [18]-annulene shows

(a) only one peak at δ 7.2 (18H) (b) only one peak at δ 5.0 (18 H)

(c) two peaks at δ 9.0 (12 H) and δ – 3.0 (6H) (d) two peaks at δ 9.0 (6 H) and δ – 3.0 (12 H)

51. Compounds A and B exhibit, two singlets, each in their ^1H NMR spectra. The expected chemical shifts are

(A) 

(B) 

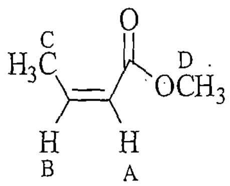
(a) 6.9 and 2.1 for A; 7.7 and 3.9 for B (b) 7.7 and 3.9 for A; 6.9 and 2.1 for B

(c) 6.9 and 3.9 for A; 7.7 and 2.1 for B (d) 7.7 and 2.1 for A; 6.9 and 3.9 for B

52. An organic compound (MF; $C_8H_{10}O$) exhibited the following ^1H NMR special data:
δ2.5 (3H, s), 3.8 (3H, s), 6.8 (2H, d, J 8 Hz), 7.2 (2H, d, J 8 Hz) ppm. The compound, among the choices, is

(a) 4-ethylphenol (b) 2-ethylphenol (c) 4-methylanisole (d) 4-methylbenzyl alcohol

53. Appropriate ^1H NMR chemical shifts (δ) for the protons A-D for the following compounds are



(a) A-6.8; B-5.7; C-3.9; D-2.1 ppm (b) A-6.8; B-5.7; C-2.1; D-3.9 ppm

(c) A-5.7; B-6.8; C-3.9; D-2.1 ppm (d) A-5.7; B-6.8; C-2.1; D-3.9 ppm

54. In 400 MHz ^1H NMR spectrum of organic compound exhibited a doublet, the two times of the doublet are at δ 2.35 and 2.38 ppm. The coupling constant (J) value is

(a) 3 Hz (b) 6 Hz (c) 9 Hz (d) 12 Hz

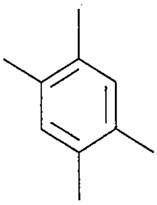
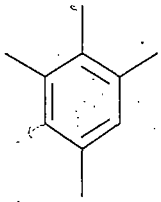
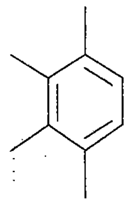
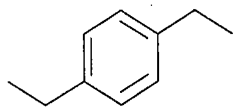
3J β<4<5<6<7

55. In NMR spectroscopy, the product of Nuclear 'g' factor (g_N), the nuclear magneton (β_N) and the magnetic field strength (B_0) gives the

(a) energy of transition from α to β state (b) chemical shift

(c) spin-spin coupling constant (d) magnetogyric ratio

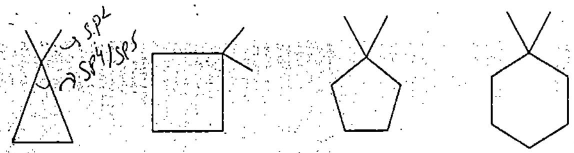
56. An organic compound having the molecular formulae $C_{10}H_{14}$ exhibited two singlets in the ^{1}H NMR spectrum and three signals in the ^{13}C NMR spectrum the compound is

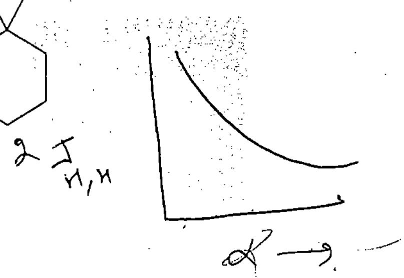
(a)  (b)  (c)  (d) 

57. The ^{1}H NMR spectrum of a dilute solution of a mixture of acetone and dichloromethane in $CDCl_3$ exhibits two singlets of 1 : 1 intensity. Molar ratio of acetone to dichloromethane in the solution is

(a) 3 : 1 (b) 1 : 3 (c) 1 : 1 (d) 1 : 1

58. The strength of coupling between geminal protons in the following molecules





(a) Decrease as size of ring increase

(b) Increase as the size of ring increase

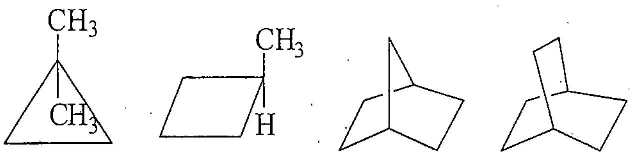
(c) Remains same

(d) No relation between the size of the ring & coupling

59. Value of gyramagnetic ratio of proton is

(a) 41.10 radian/Tesla (b) 42.57 MHz/Tesla (c) 26.75 radian/Tesla (d) 41.10 MHz/Tesla

60. No. of signals in ^{1}H NMR in the given molecules are



(a) 3, 4, 4, 3 respectively (b) 2, 6, 4, 2 respectively

(c) 2, 4, 6, 2 respectively (d) 2, 4, 2, 6 respectively

61. What will be the change in value of γ(gyromagnetic ratio) if we double the applied magnetic field

(a) It will remain same (b) It will get doubled

(c) It wil become half (d) It will become four times

62. Chemical shift value of proton attached to hetero atom depends upon

(A) Concentration (B) Temperature

(C) Solvent (D) External applied magnetic field

Which statement are correct

(a) Both (A) and (B) (b) (A), (B) and (C)

(c) (A), (B), (C) and (D) (d) (A), (C) and (D) only

63. A PMR spectrometer operates at 300 MHz. Find the value of magnetic field.
Given: $g_N = 5.585$ and $\beta_N = 5.05 \times 10^{-27}\ JT^{-1}$.

(a) 7.05 T (b) 6.38 T (c) 7.58 T (d) 5.93 T

64. H^1, C^{13}, F^{19}, P^{31} have nuclear spin equal to

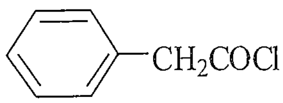
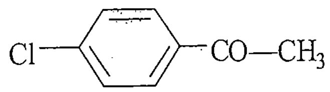
(a) 1/2 (b) 1 (c) 0 (d) 3/2

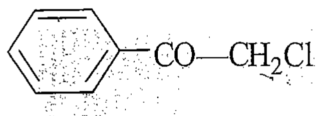
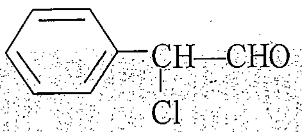
65. In p-xylene, the ratio of methyl protons to ring protons is 6 : 4 while for mesitylene, it is

(a) 6 : 4 (b) 3 : 2 (c) 9 : 3 (d) 6 : 3

Also check

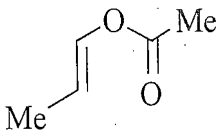
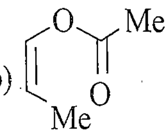
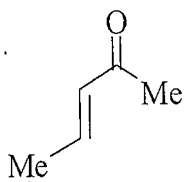
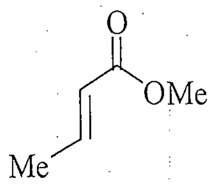
66. A compound of molecular formula C_8H_7ClO shows a romient band in its IR spectrum at 1690 cm^{-1}. ^1H NMR spectrum revealed only two major typ;es of protons in the ratio of 5 : 2. Which one of the following structures best fits the above data?

(a)  (b) 

(c)  (d) 

very nice ques.

67. An organic compound Q exhibited the following spectral data.
IR: 1760 cm^{-1}
^{1}HNMR: δ(ppm): 7.2 (1H, d, J = 16.0 Hz), 5.1 (1H, m), 2.1 (3H, s), 1.8 (3H, d, J = 7.0 Hz) ^{13}CNMR: δ(ppm): 170 (carbonyl carbon).
Compound Q is

(a)  (b)  (c)  (d) 

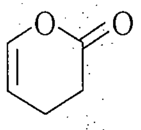
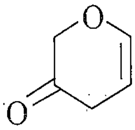
68. The NMR spectrum of a compound with molecular formulae $C_5H_6O_2$ is shown below. IR spectrum shows medium intensity band at 3270 and 2180 cm^{-1}. Draw structure of compound.

δ 1.3 (^{3}H, t)

δ 2.8 (^{1}H, s)

δ 4.3 (^{2}H, q)

(a) $CH_3—CH_2—\overset{\overset{\large O}{\|}}{C}—O—C\equiv C—H$ (b) $CH_3—CH_2—O—\overset{\overset{\large O}{\|}}{C}—C\equiv C—H$

(c) 　　(d) 

Ultraviolet Spectroscopy

69. Compare solvent shift on the $n \rightarrow \pi^*$ transition of acetone

(a) $H_2O = CH_3OH = C_2H_5OH = CHCl_3 = C_6H_{14}$

(b) $H_2O > CH_3OH > C_2H_5OH > CHCl_3 > C_6H_{14}$

(c) $H_2O < CH_3OH < C_2H_5OH < CHCl_3 < C_6H_{14}$

(d) $H_2O > CH_3OH < C_2H_5OH < CHCl_3 < C_6H_{14}$

70. Correct order of λ_{max} for $n \rightarrow \sigma^*$ transition is

(a) $R–OH > R–NH_2 > R–SH$　(b) $R–OH < R–NH_2 < R–SH$

(c) $R–OH > R–SH > R–NH_2$　(d) $R–OH < R–SH < R–NH_2$

71. Correct order of λ_{max} for $n \rightarrow \pi^*$ transition is

(a) $R-C\equiv N < R–NO_2 < R-N=N-R$　(b) $R-C\equiv N = R–NO_2 = R-N=N-R$

(c) $R-C\equiv N > R–NO_2 > R-N=N-R$　(d) $R-C\equiv N > R–NO_2 < R-N=N-R$

72. Correct order of λ_{max} for $\pi \rightarrow \pi^*$ transition is

(a) $R-C\equiv C-R > R_2C=CR_2 > R-CHO$　(b) $R-C\equiv C-R < R_2C=CR_2 < R-CHO$

(c) $R-C\equiv C-R = R_2C=CR_2 = R-CHO$　(d) $R-C\equiv C-R < R_2C=CR_2 > R-CHO$

73. Correct order of λ_{max} for $n \rightarrow \pi^*$ transition is

(a) RCOOH > RCOOR′ > $RCONH_2$　(b) RCOOH = RCOOR′ = $RCONH_2$

(c) RCOOH = RCOOR′ < $RCONH_2$　(d) RCOOH = RCOOR′ > $RCONH_2$

74. Compare λ_{max} for $n \rightarrow \pi^*$ transition is

(1) $CH_3-\overset{\overset{O}{\|}}{C}-H$ (2) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ (3) $CH_3-\overset{\overset{O}{\|}}{C}-Cl$ (4) $CH_3-\overset{\overset{O}{\|}}{C}-NH_2$ (5) $CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5$

(a) 1 > 2 > 3 > 4 > 5　(b) 1 < 2 < 3 < 4 < 5　(c) 1 > 2 < 3 > 4 < 5　(d) 1 > 2 > 3 < 4 > 5

75. The ultraviolet spectrum of benzonitrile shows a primary absorption band at 224 nm and a secondary band at 271 nm.

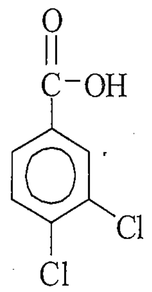
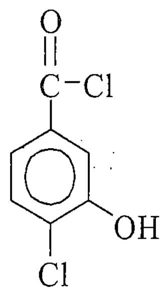
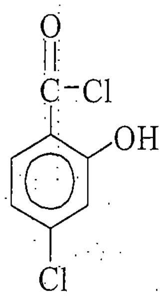
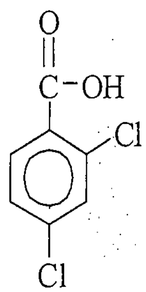
(i) If a solution of benzonitrile in water, with a concentration of 1×10^{-4} molar, is examined at a wavelength of 224 nm, the absorbance is determined to be 1.30. The cell length is 1 cm. What is the molar absorptivity of this absorption band?

(a) 2.3×10^4　(b) 3.3×10^4　(c) 1.3×10^4　(d) 4.3×10^4

(ii) If the same solution is examined at 271 nm, what will be the absorbance reading ($\varepsilon = 1000$)? What will be the intensity ratio, I_0/I? Respectively

(a) 0.1, 1.26　(b) 0.2, 2.26　(c) 0.3, 3.26　(d) 0.4, 4.26

76. The structural formula that are consistent with the following observations.
An acid, $C_7H_4O_2Cl_2$, shows a UV maximum at 242 nm.

(a) 
(b) 
(c) 
(d) 

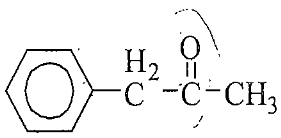
77. Match the following

	Column I		Column II
(1)	Cyclopentene	(P)	$n \rightarrow \sigma^*$
(2)	Dimethyl ether	(Q)	$\sigma \rightarrow \sigma^*$
(3)	Methyl vinyl ether	(R)	$n \rightarrow \pi^*$
(4)	Triethylamine	(S)	$\pi \rightarrow \pi^*$
(5)	Cyclohexane	(T)	$n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$
(6)	Acetaldehyde		

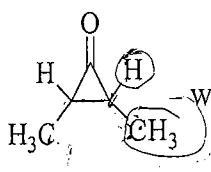
(a) 1-P, 2-S, 3-T, 4-S, 5-Q, 6-T
(b) 1-S, 2-P, 3-T, 4-P, 5-Q, 6-T
(c) 1-S, 2-P, 3-Q, 4-T, 5-Q, 6-P
(d) 1-T, 2-P, 3-S, 4-P, 5-Q, 6-T

EXERCISE - II

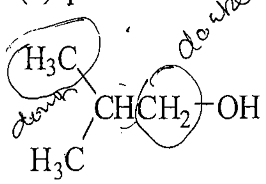
One or More Than One Correct Type

1.  will show

(a) tautomerism
(b) 3 signals
(c) IR frequency around 1715 cm^{-1}
(d) Nucleophilic substitution reaction

2.  will show

(a) quartet
(b) 1 doublet
(c) triplet
(d) 2 doublets

3.  will show

(a) triplet
(b) septet
(c) doublet
(d) singlet

4. Two doublets are shown by

(a) $CH_3-COOCH_2CH(CH_3)_2$

(b) $CH_3-O-\overset{\overset{\large O}{||}}{C}-CH_2-CH(CH_3)_2$

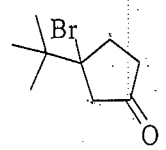
(c) $H-O-\overset{\overset{\large O}{||}}{C}-CH_2-CH\langle^{CHF_2}_{CHF_2}$

(d) $CH_3-CH_2-CH_3$

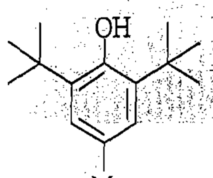
EXERCISE - III

Numerical Answer Type

1. Total number of ^1H NMR signals in the given compounds is



2. Total number of ^1H NMR peaks in the given compound $Cl_2HC-CH(OCH_2CH_3)_2$ is_____.
3. Total number of ^1H NMR peaks in the given compound is:



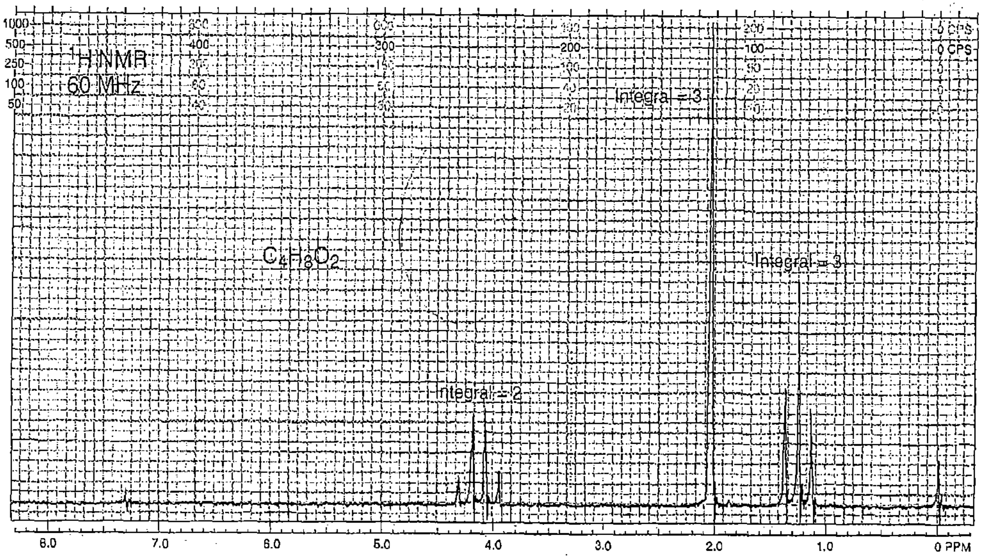
Creating of deshielded e⁻

4. Total number of deshielded protons ~~electrons~~ in the [18] annulene is_____. 12
5. δ_H(OH) value (in ppm) for different compounds A, B and C is 2.0, 5.0 and 11.0. The most acidic compound among A, B and C is that which has δ value is_______.
6. Total number of ^1H NMR signals in the diammonium EDTA is _______.
7. Total number of ^1H Signals in the zwitterion form of glycine is_____.
8. The compound shows a proton-NMR peak at 240 Hz down field from the TMS peak in a spectrometer operating at 60 MHz. What are the value of the chemical shift δ in the ppm relative to TMS?.
9. A proton has resonance 90 Hz downfield from TMS when the field strength is 1.41 Tesla (14,100 Gauss) and the osciollator frequency is 60 MHz.

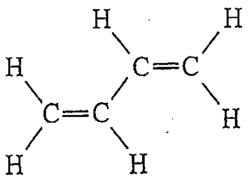
   (a) What will be its shift in Hertz if the field strength is increased to 2.82 Tesla and the oscillator frequency to 120 MHz?

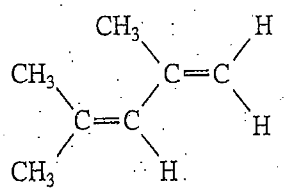
   (b) What will be its chemical shift in parts per million (δ)?

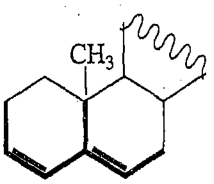
10. The following compound, with the formula $C_4H_8O_2$, is an ester. Give its structure and assign the chemical shift values.

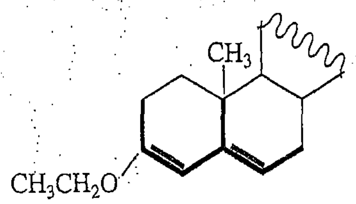


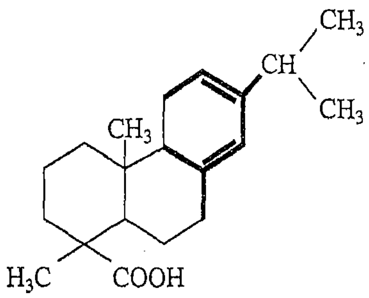
11. Calculate λ_{max} for the following

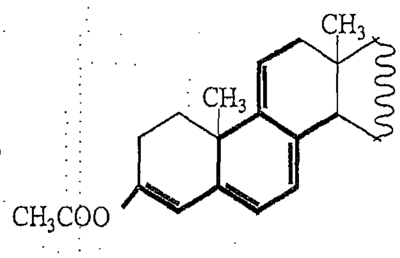
(a) 

(b) 

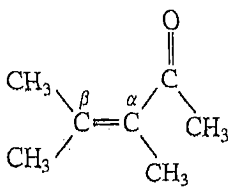
(c) 

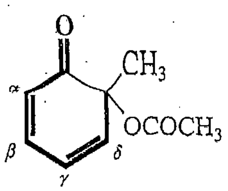
(d) 

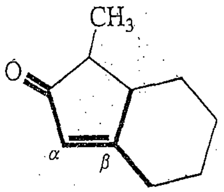
(e) 

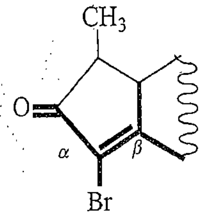
(f) 

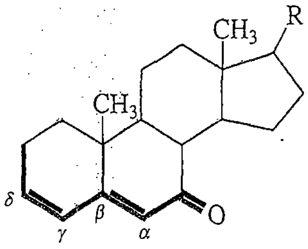
12. Calculate λ_{max} for the following

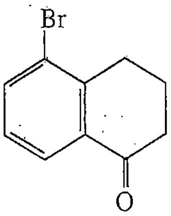
(a) 

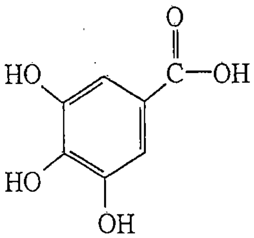
(b) 

(c) 

(d) 

(e) 

(f) 

(g) 

ANSWER KEY

EXERCISE - I

1. A	2. B	3. C	4. D	5. D	6. A	7. B
8. A	9. C	10. C	11. A	12. B	13. C	14. B
15. D	16. D	17. A	18. D	19. A	20. D	21. B
22. A	23. A	24. B	25. B	26. B	27. A	28. C
29. C	30. A	31. D	32. B	33. C	34. D	35. C
36. A	37. A	38. A	39. D	40. B	41. C	42. A
43. A	44. C	45. C	46. A	47. A	48. A	49. D
50. C	51. A	52. C	53.C	54. D	55. A	56. A
57. B	58. B	59. B	60. B	61. A	62. B	63. A
64. A	65. C	66. C	67. A	68. B	69. C	70. B
71. A	72. B	73. C	74. A	75. (i) C (ii) A	76. D	77. B

EXERCISE - II

1. A,B,C	2. A,B	3. C,D	4. A,B,C

EXERCISE - III

1. 4	2. 11	3. 4	4. 12	5. 11	6. 3	7. 2
8. 4						

9. (a) 180 Hz (b) 1.50 ppm

10. Ethyl acetate (ethyl ethanote)

11. (a) 214 nm (b) 229 nm (c) 234 nm (d) 240 nm (e) 278 nm (f) 353 nm

12. (a) 249 nm (b) 302 nm (c) 231 nm (d) 256 nm (e) 280 nm (f) 251 nm (g) 269 nm