Revision Notes

Class – 12 Chemistry

Chapter 11 – Alcohols, phenols and Ethers

1. Introduction

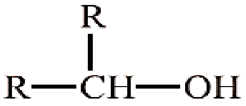
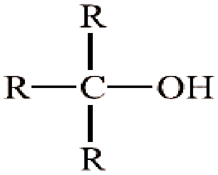
Alcohols are compounds that have a hydroxyl group $(-OH)$ attached to a saturated carbon atom. Enols are compounds that have a hydroxyl group attached to an unsaturated carbon atom of a double bond. The saturated carbon can be alkyl, alkenyl, alkynyl, cycloalkyl, or benzyl. If, on the other hand, a hydroxyl group is attached to a benzene ring. Phenols are the name given to these compounds.

The alcohols are further classified as monohydric (containing one $-OH$ group), dihydric (containing two $-OH$ groups), and trihydric (containing three $-OH$ groups) (containing three $-OH$ groups).

Alcohol is used in both industry and everyday life. Chiefly ethanol, for example, is a common spirit used to polish wooden furniture. Sugar, cotton, and paper are all composed of compounds that contain groups. Phenols are found in a variety of important polymers, including Bakelite, as well as pharmaceuticals such as Aspirin. Ethers are commonly used as anaesthetics and solvents.

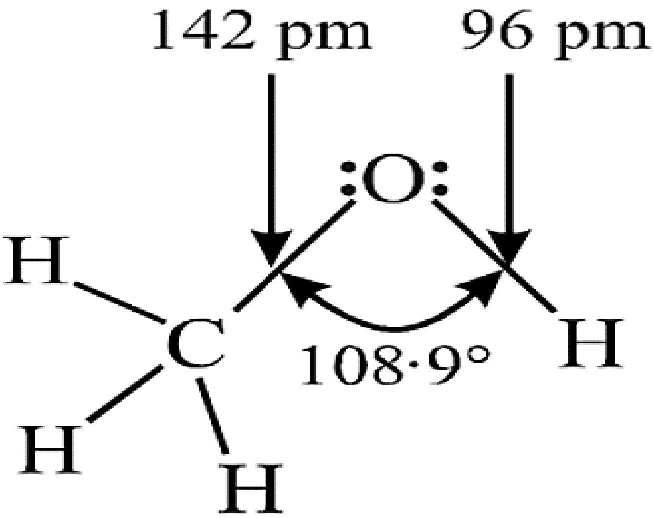
In alcohols, the oxygen of the group is attached to carbon by a sigma (bond formed by the overlap of a sp hybridised forbital of carbon with a sp hybridised orbital of oxygen. The following figure depicts structural aspects of methanol, phenol and methoxymethane.

2. Classification

$CH_3—OH$	Methanol	
$R—CH_2—OH$	1° Alcohol	Primary
 $R—CH(R)—OH$	2° Alcohol	Secondary
 $R—C(R)(R)—OH$	3° Alcohol	Tertiary
$R—O—R$	Symmetrical Ether	
$R—O—R'$	Unsymmetrical Ether	

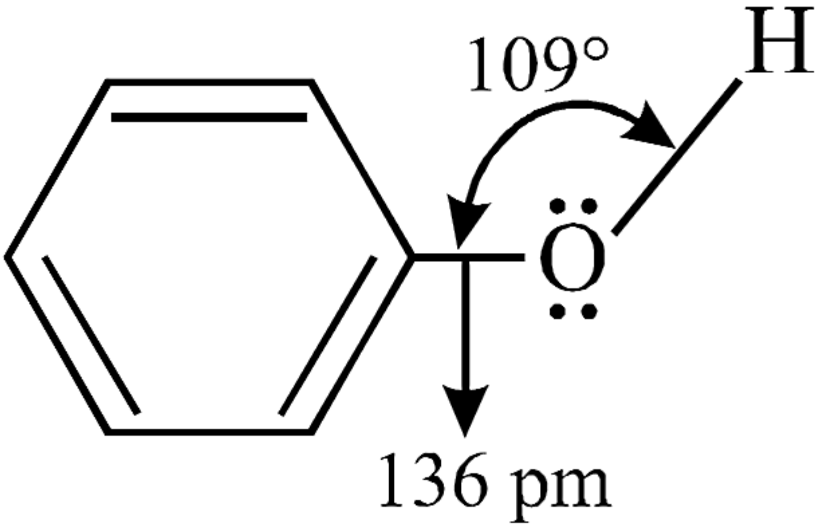
3. Structure of functional groups

In the structure of alcohols, the oxygen of hydroxyl group is connected to carbon through a sigma bond which is formed by the overlapping of sp^3 hybridised orbital of C with a sp^3 hybridised orbital of oxygen. The structural aspects of phenol, methanol and methoxymethane are depicted by the following figure.



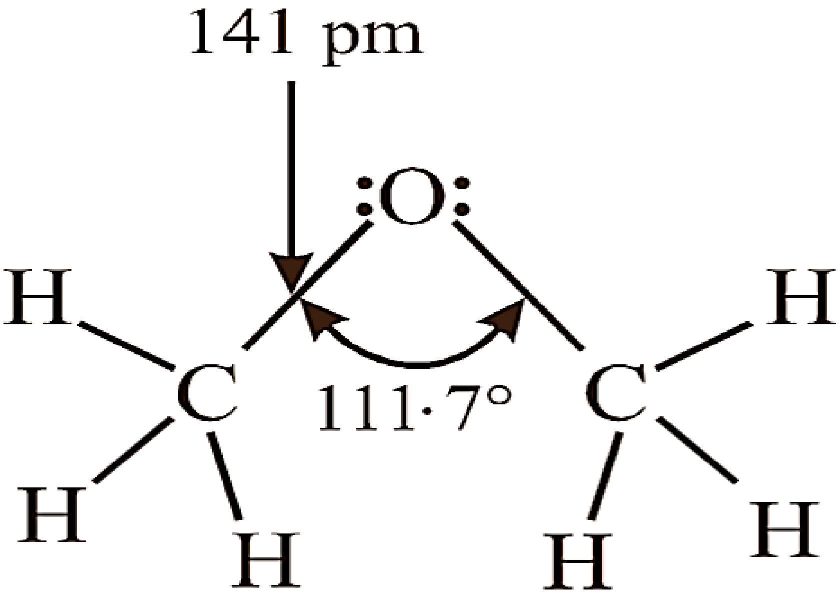
Methanol

Due to lone pair-lone pair repulsion, bond angle is slightly less.



Phenol

Since a pair of oxygen is delocalised on the ring, the length of the $C - O$ bond is reduced.



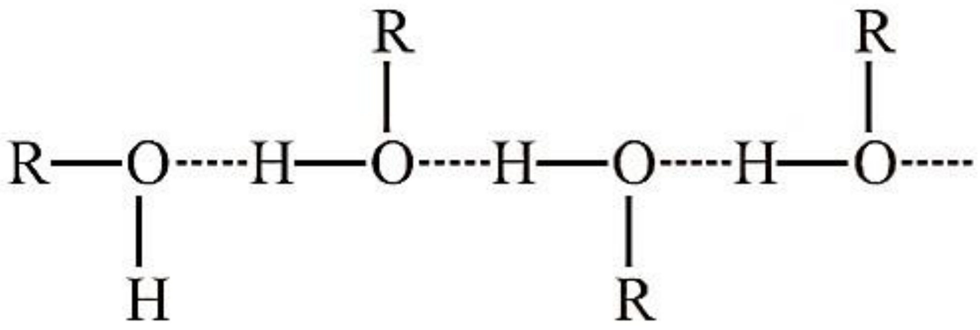
Methoxymethane

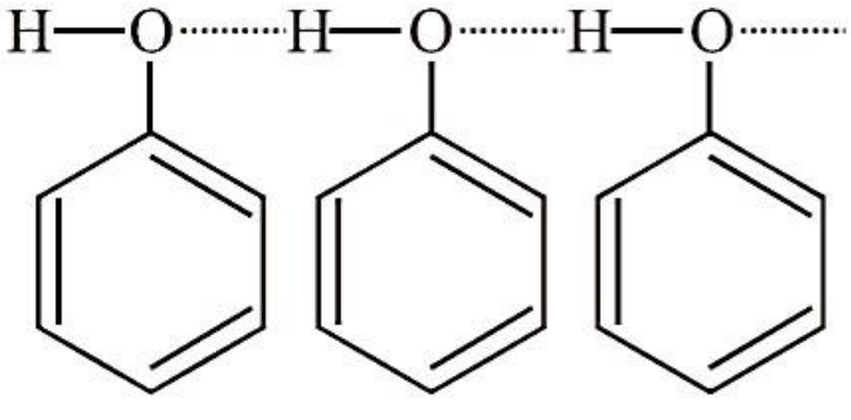
Due to the general repulsive interaction between the two bulky (R) groups, the bond angle in methoxymethane is greater than the tetrahedral angle. The length of the C - O bond is the same as in alcohols.

4. Physical Properties

4.1 Boiling point

The boiling points of alcohols and phenols rise as the number of carbon atoms increases (increase in van der Waals forces). The boiling point of alcohols decreases as branching increases (decrease in Van der Waals forces due to decrease in surface area). In alcohols and phenols, the -OH group contains a hydrogen atom that is bonded to a electronegative oxygen atom. As a result, it is capable of forming intermolecular hydrogen bonds with greater strength than amine.





Alcohols and phenols have higher boiling points than other classes of compounds, such as hydrocarbons, ethers, and haloalkanes/haloarenes, amines with comparable molecular masses, due to the presence of strong intermolecular hydrogen bonding.

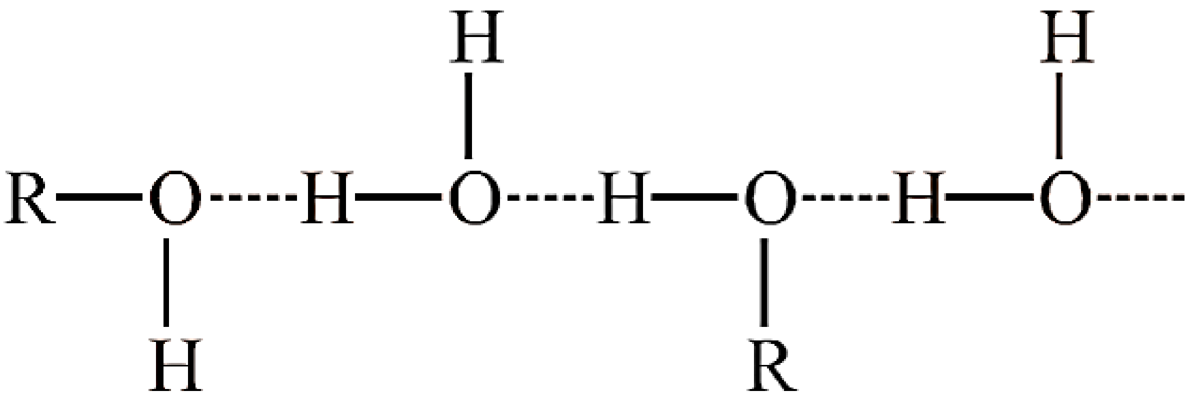
Their boiling points are lower than those of carboxylic acid, which has a stronger hydrogen bond. Boiling points for isomeric alcohols decrease as branching increases due to a decrease in van der Waals forces as size decreases. **The boiling point sequence is primary alcohol > secondary alcohol > tertiary alcohol.**

Due to lower dipole moment and the absence of H-bonding, the boiling point of ethers is very low and comparable to that of alkanes of comparable molecular mass.

4.2 Solubility

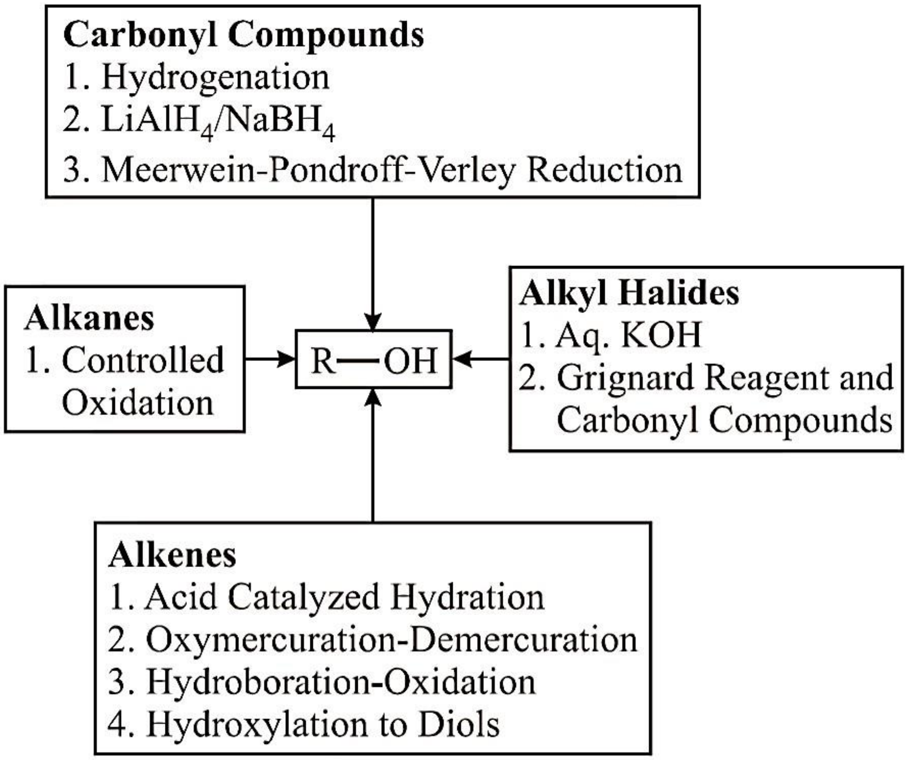
Alcohols and phenols are soluble in water due to their ability to form hydrogen bonds with water molecules. Solubility decreases as the size of the hydrophobic group increases (R). Higher concentrations of alcohol are insoluble. Because of the decrease in surface area of the non-polar hydrocarbon part, branching increases solubility.

n-butylalcohol < isobutylalcohol < sec-butylalcohol < tert-butylalcohol



Lower ethers are water soluble, but their solubility is lower than that of alcohol due to less H-bonding with water and being less polar.

5. Preparation of alcohols



5.1 Alkane

Controlled oxidation

CH_4 + O[100 atm] 200°C

Cu tubeCH_3OH

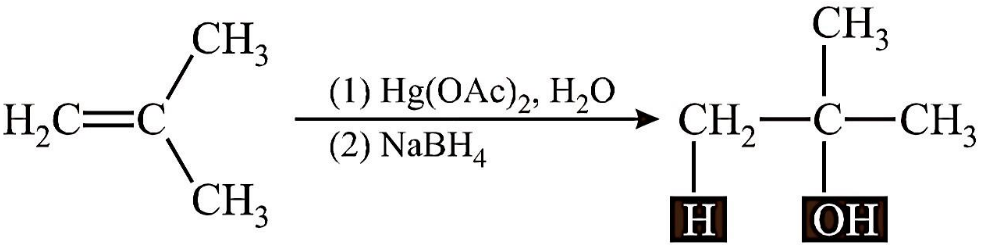
5.2 Alkenes

5.2.1 Acid Catalyzed Hydration

Markovnikov addition with carbocation rearrangements.

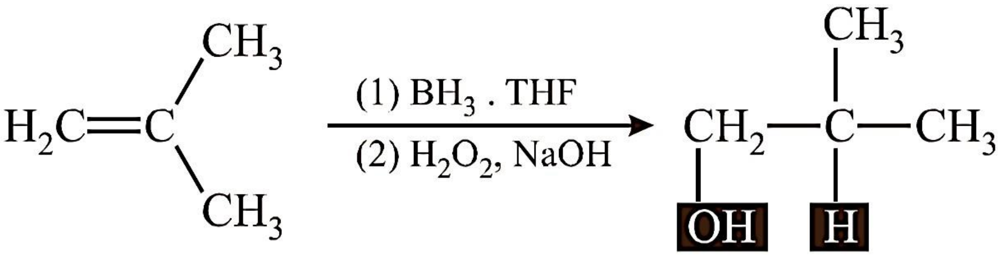
5.2.2 Oxymercuration-Demercuration

Markovnikov addition without carbocation rearrangements.
Example - 1



5.2.3 Hydroboration-Oxidation Anti-Markovnikov addition.

Example-2

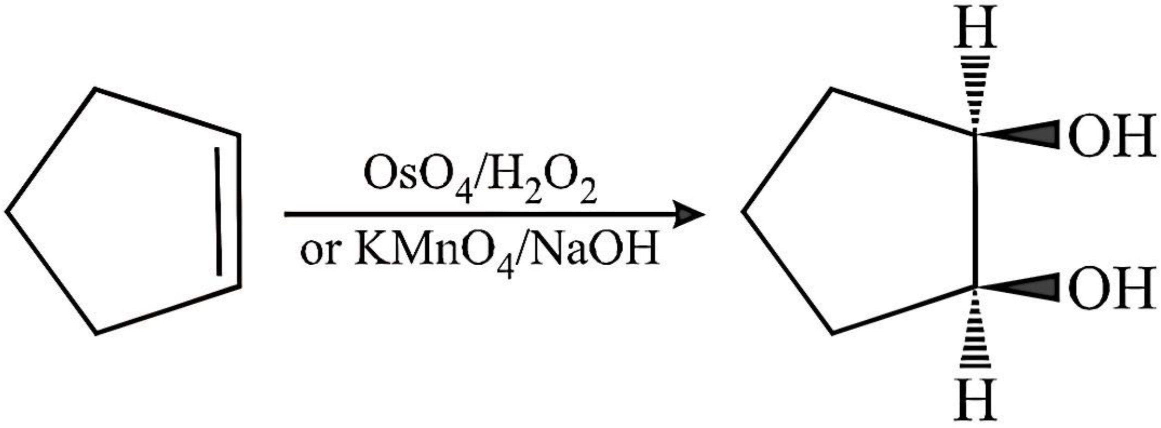


5.2.4 SYN Hydroxylation

Reagents: Cold dil.

$KMnO_4$ / NaOH or OsO_4 / H_2O_2

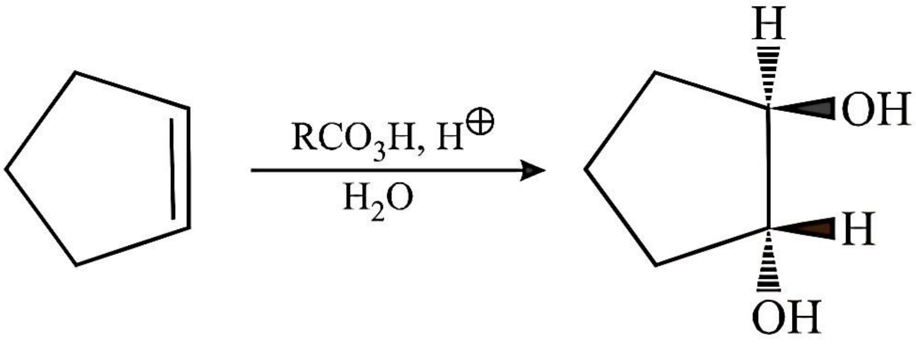
Example-3



5.2.5 ANTI Hydroxylation

Reagents: Peroxy acids followed by acidic hydrolysis

Example-4



Cyclopentene

trans-Cyclopentane-1, 2-diol
(+ Enantiomer)

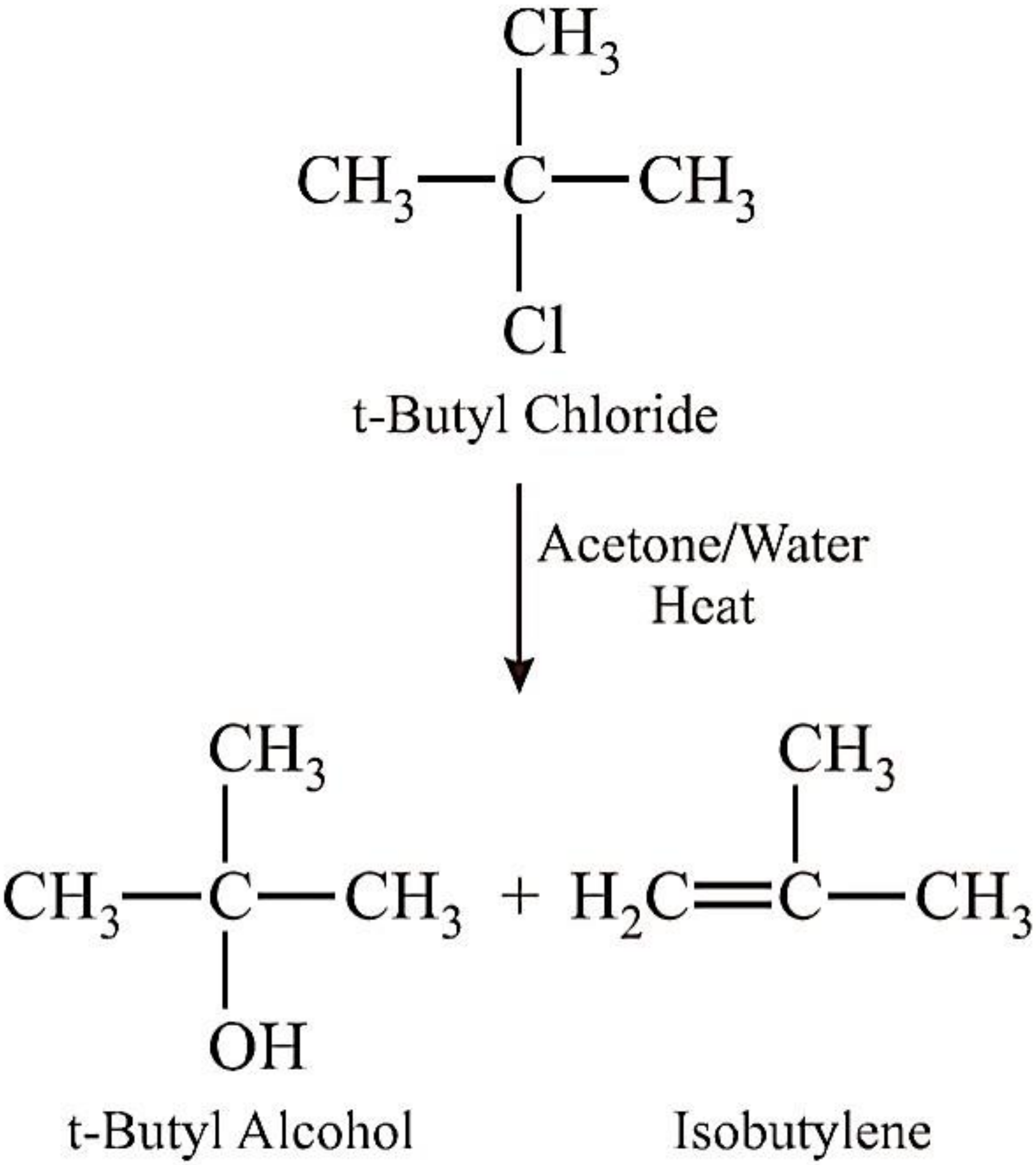
5.3 Allkyl Halide

5.3.1 Second order Substitution

Primary and some Secondary Halides

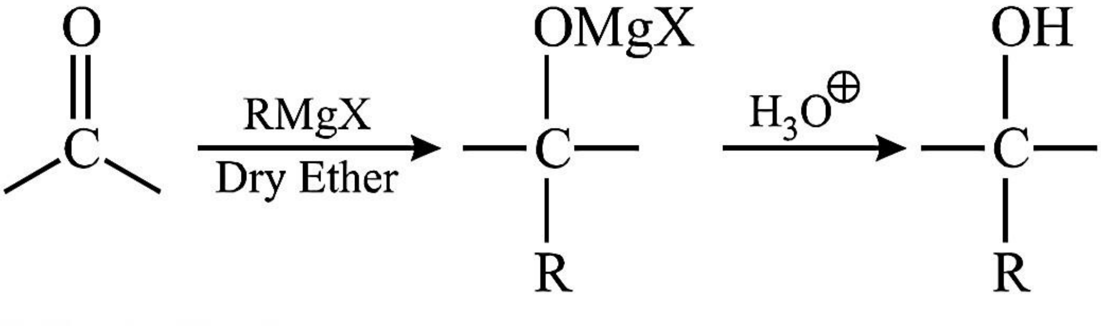
$$(CH_3)_2\,CHCH_2CH_2-Br \xrightarrow[H_2O]{KOH} (CH_3)_2\,CHCH_2CH_2-OH$$

Example -6

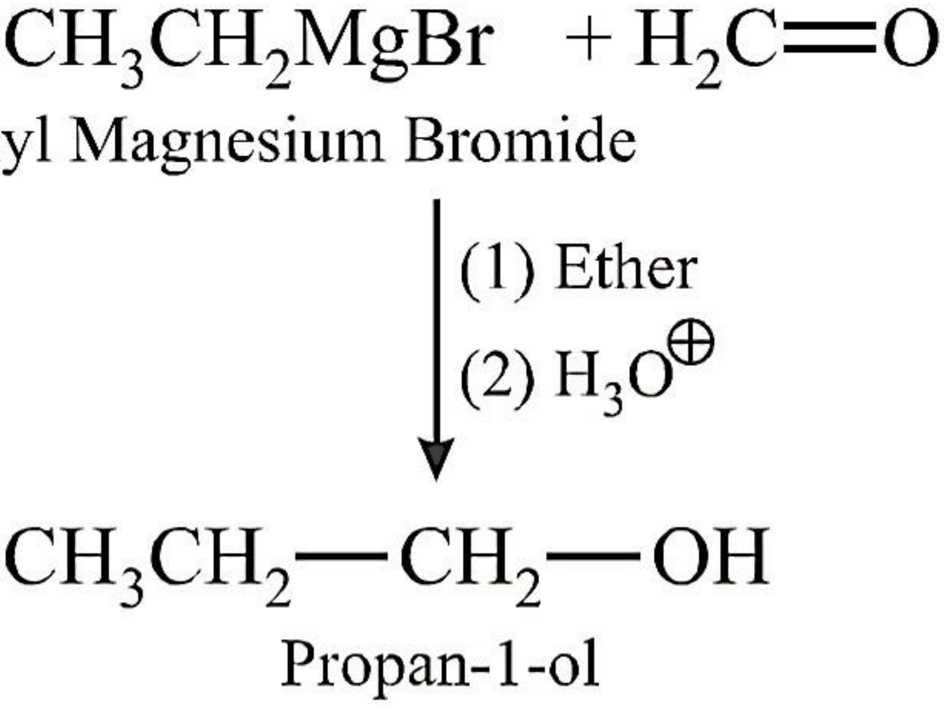


5.3.2 Grignard Reagent/ Organolithium Reagent

Nucleophilic addition to the carbonyl group

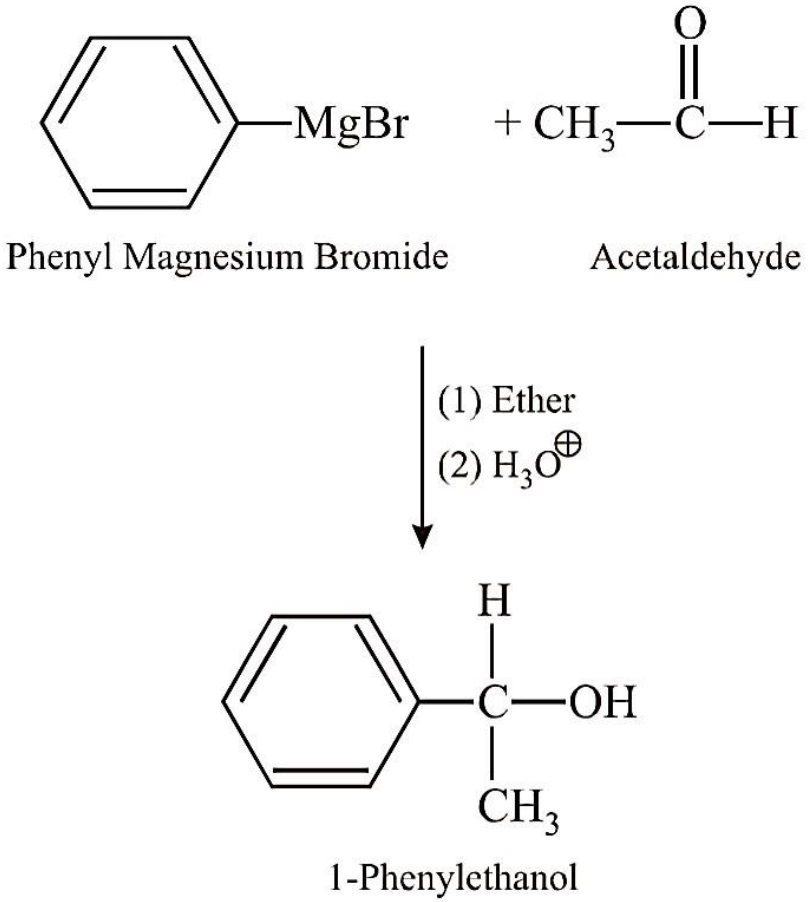


(a) Addition to Formaldehyde-primary alcohol
Example-7



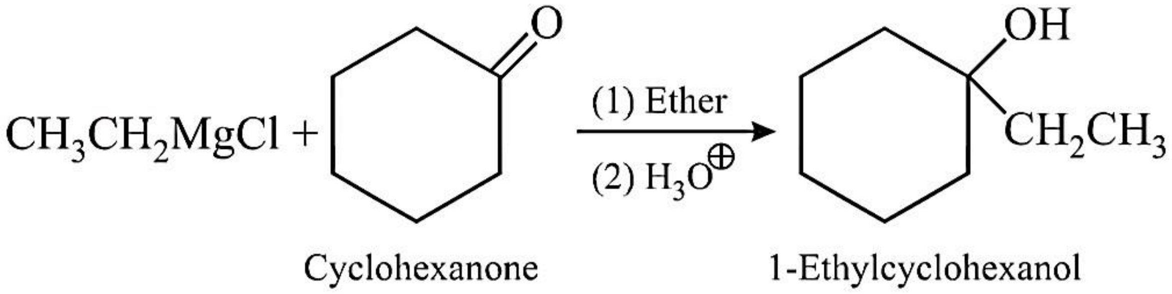
(b) Addition to aldehyde-seconary alcohol

Example-8



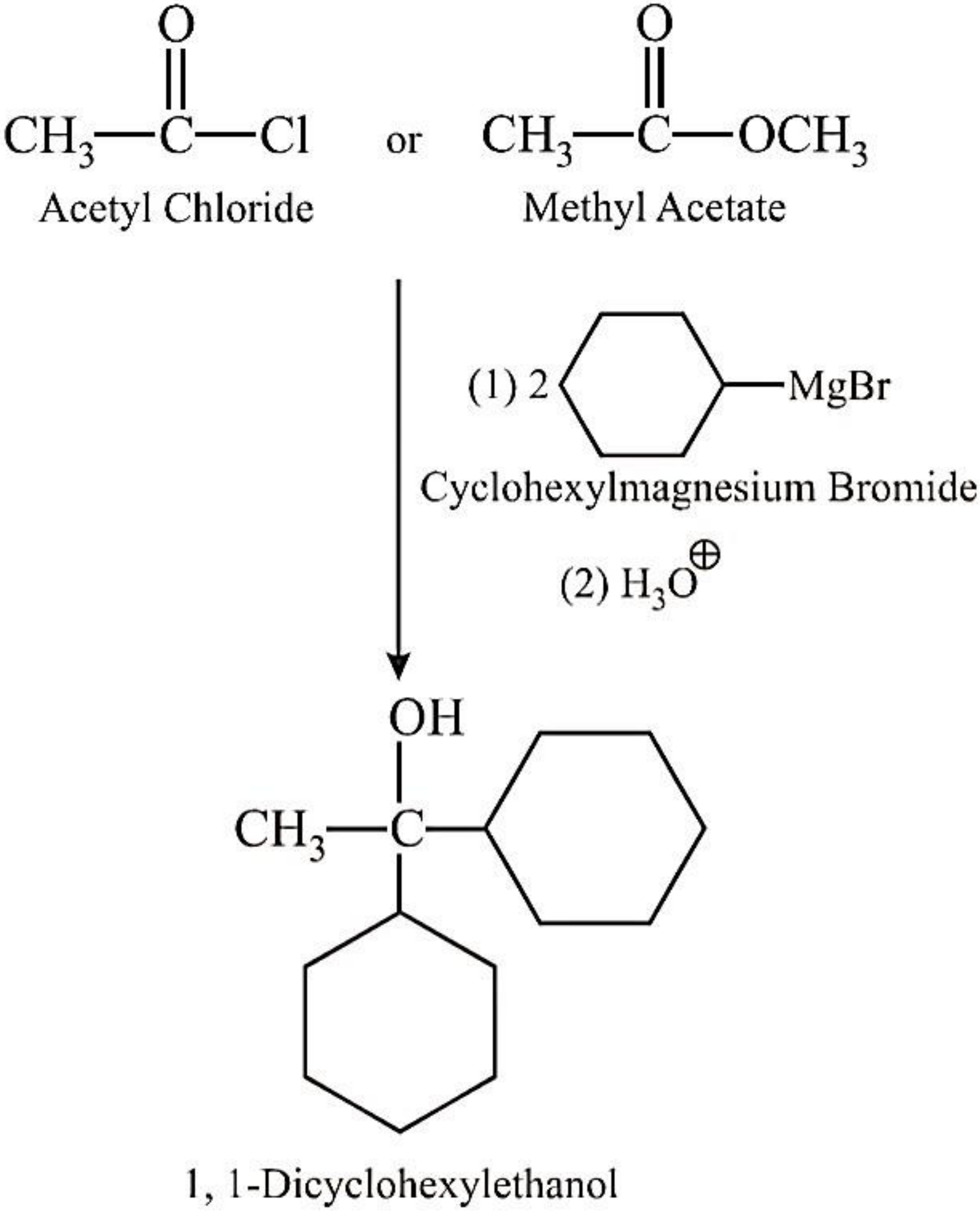
(c) Addition to a ketone-tertiary alcohol

Example-9



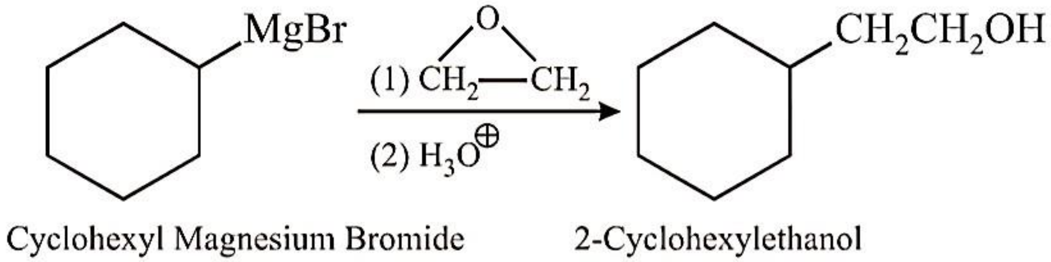
(d) Addition to an acid-halide or an Ester-tertiary alcohol

Example-10



(e) Addition to Ethylene oxide-primary alcohol (with two carbon atoms added)

Example-11



5.4 Carbonyl Compounds

5.4.1 Catalytic Hydrogenation

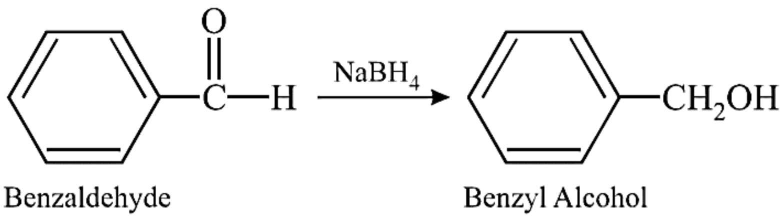
$$-\overset{\overset{O}{\|}}{C}- + H_2 \xrightarrow{\text{Raney Ni}} -\overset{\overset{OH}{|}}{CH}-$$

This method is usually not known as effective or selective as the use of hydride reagents.

5.4.2 Reduction with Metal hydrides

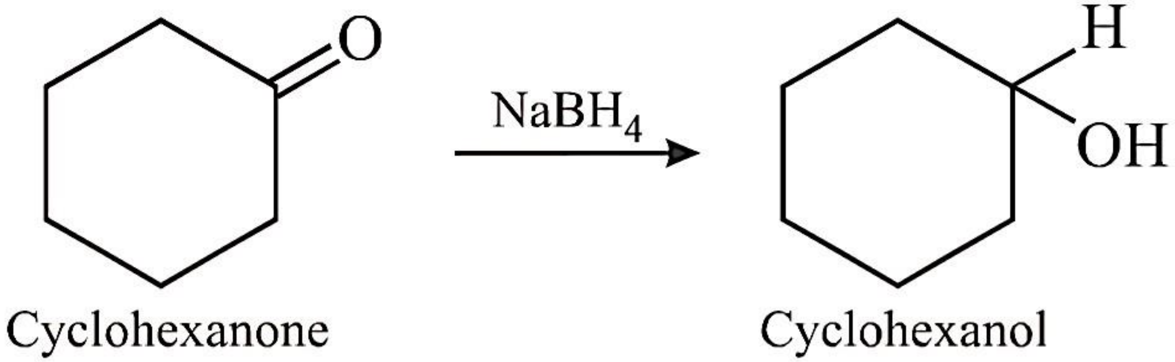
1. Primary alcohol is produced on reduction of an aldehyde.

Example:



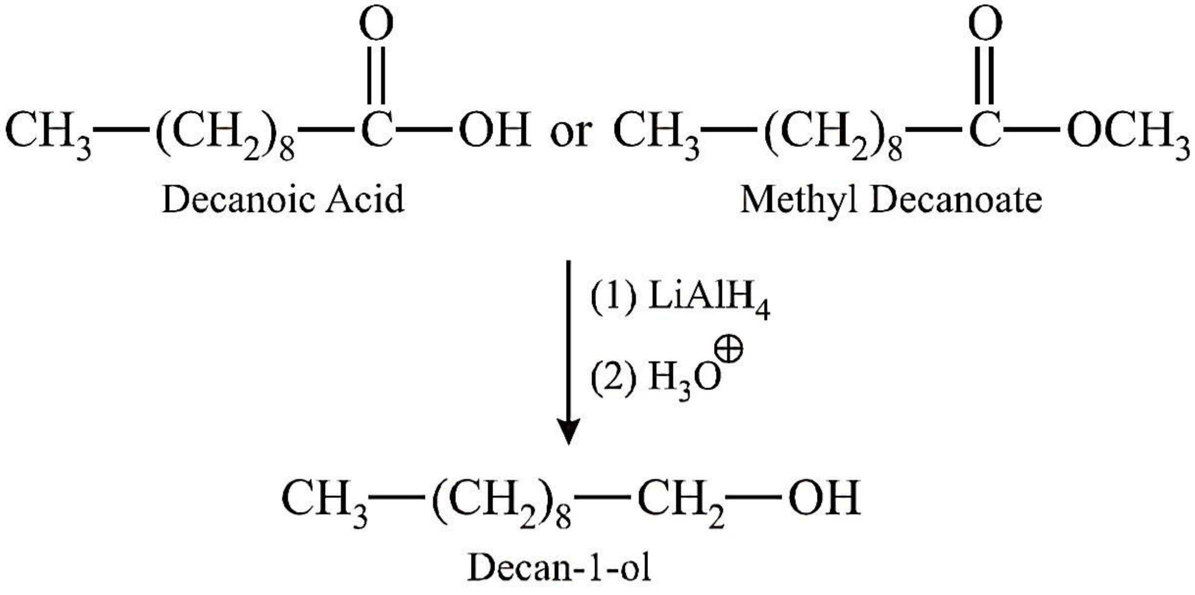
2. Secondary alcohol is produced on reduction of a ketone.

Example:

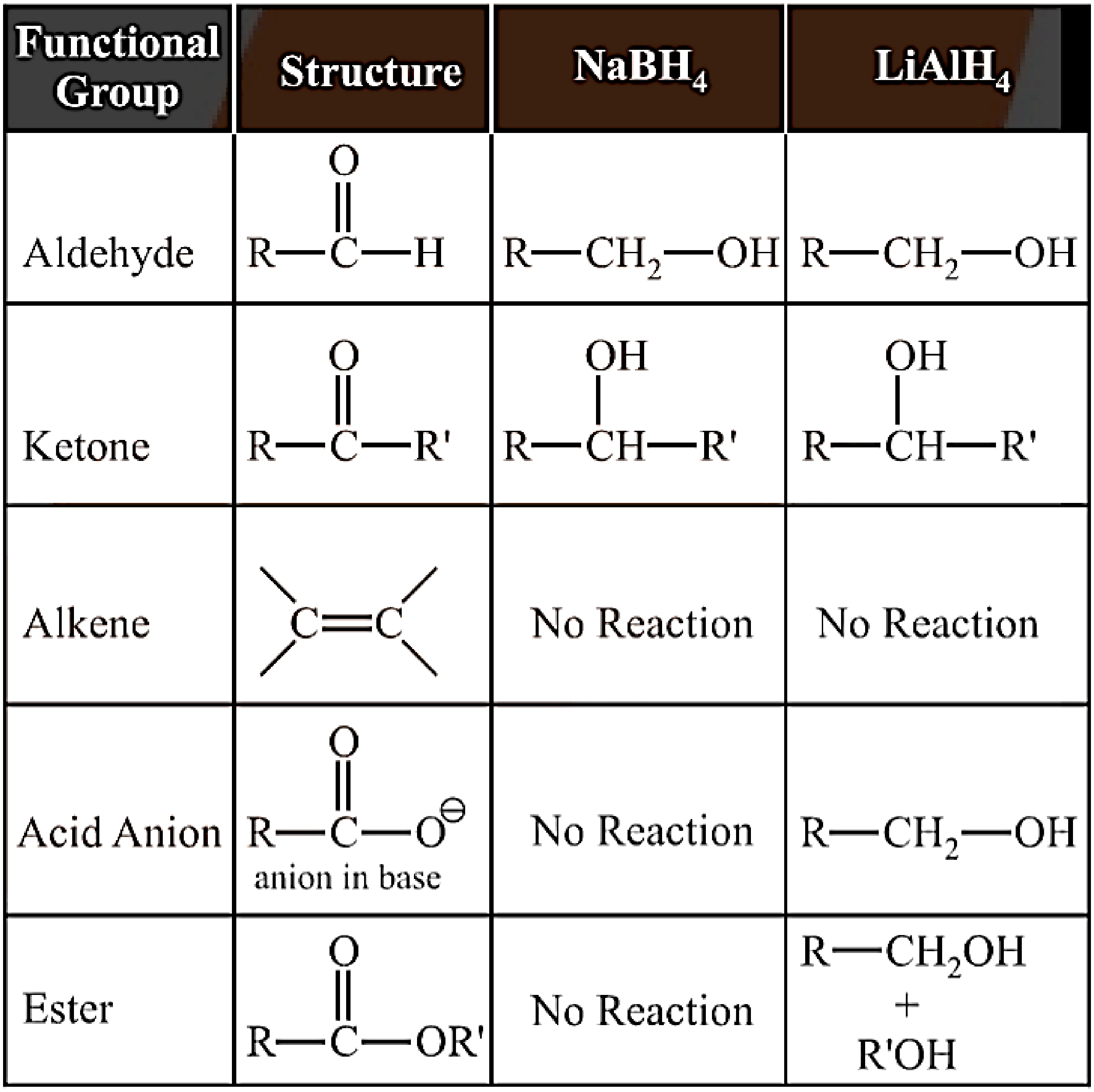


3. Tertiary alcohol is produced on reduction of an acid or ester.

Example:

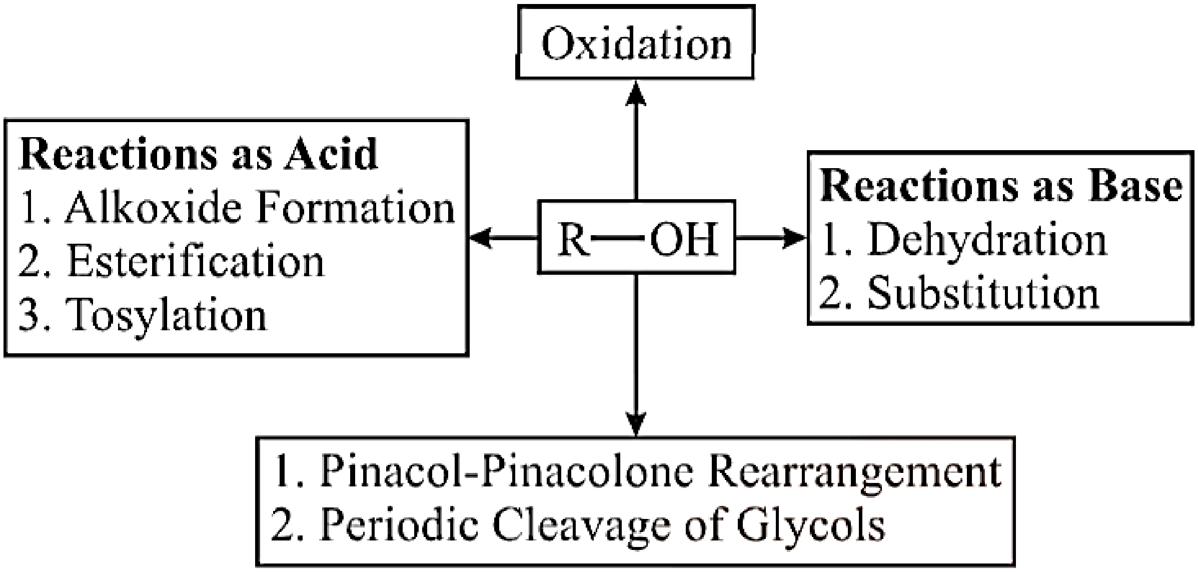


Reduction of $LiAlH_4$ **and** $NaBH_4$

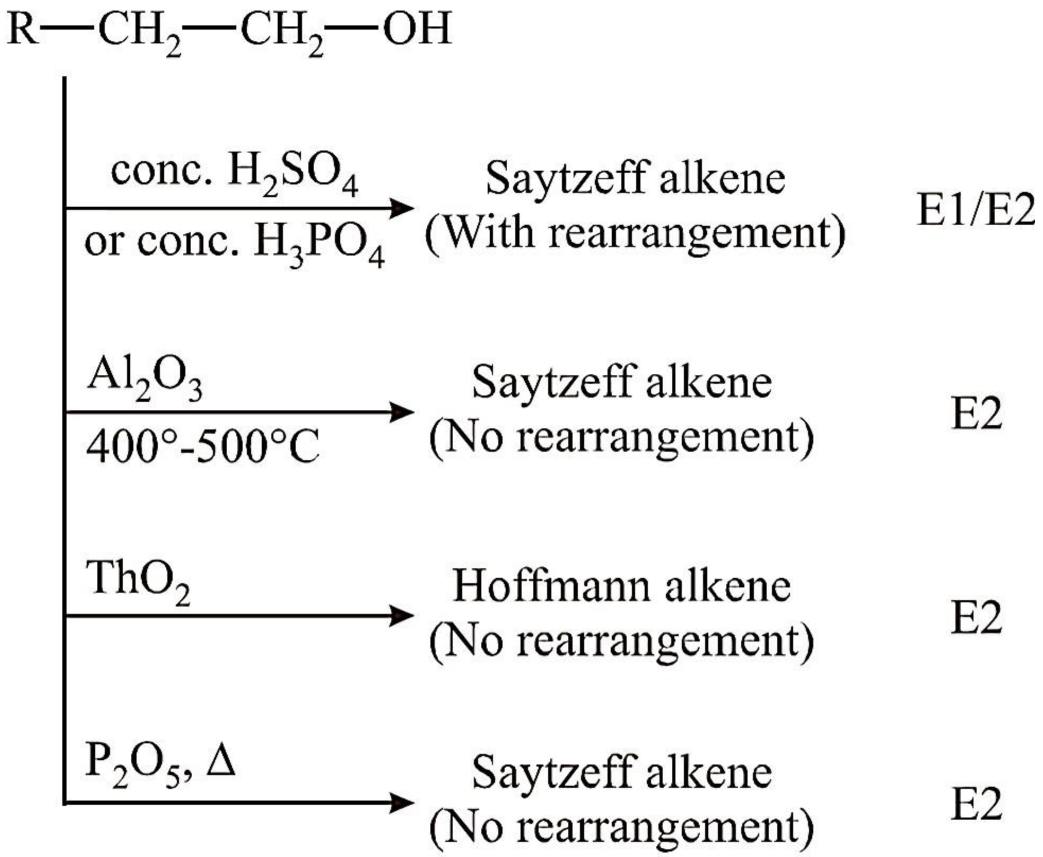


Functional Group	Structure	$NaBH_4$	$LiAlH_4$
Aldehyde	$R-\overset{\overset{O}{\|}}{C}-H$	$R-CH_2-OH$	$R-CH_2-OH$
Ketone	$R-\overset{\overset{O}{\|}}{C}-R'$	$R-\overset{\overset{OH}{\|}}{CH}-R'$	$R-\overset{\overset{OH}{\|}}{CH}-R'$
Alkene	$>C=C<$	No Reaction	No Reaction
Acid Anion	$R-\overset{\overset{O}{\|}}{C}-O^{\ominus}$ anion in base	No Reaction	$R-CH_2-OH$
Ester	$R-\overset{\overset{O}{\|}}{C}-OR'$	No Reaction	$R-CH_2OH$ + $R'OH$

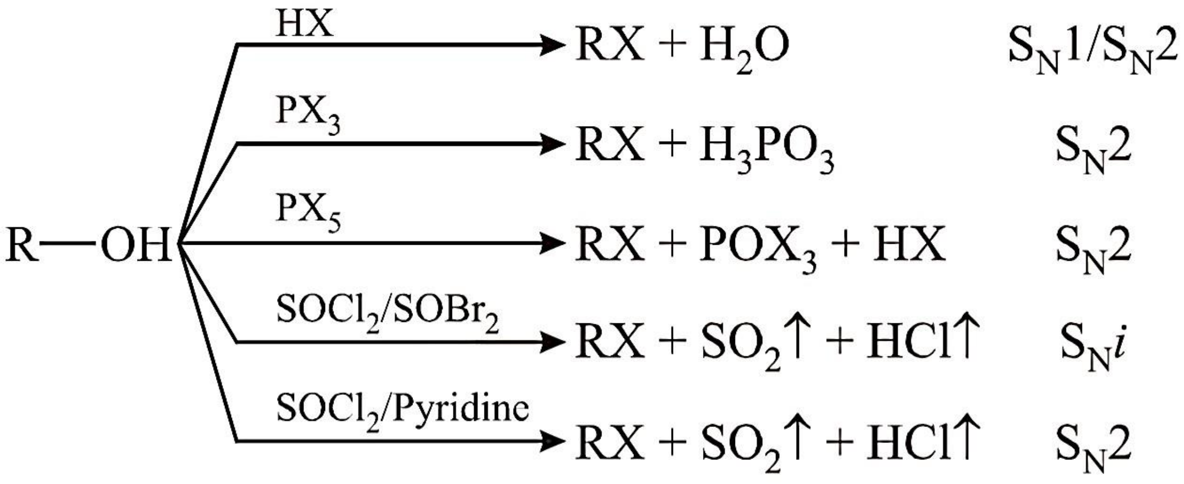
6. Reaction of alcohols



6.1 Dehydration

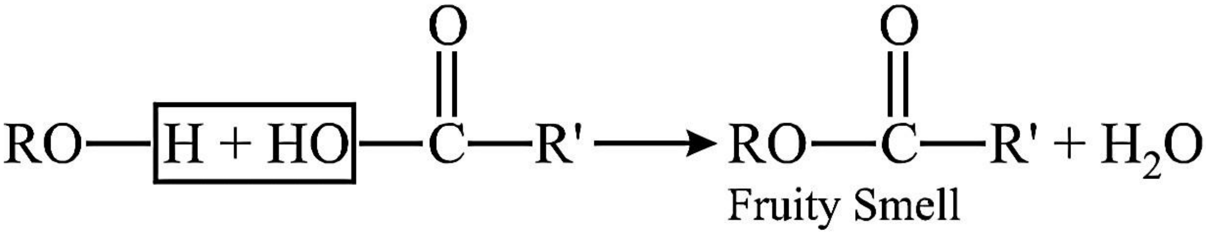


6.2 Substitution



6.3 Esterification

It is catalyzed by an acid or a base.

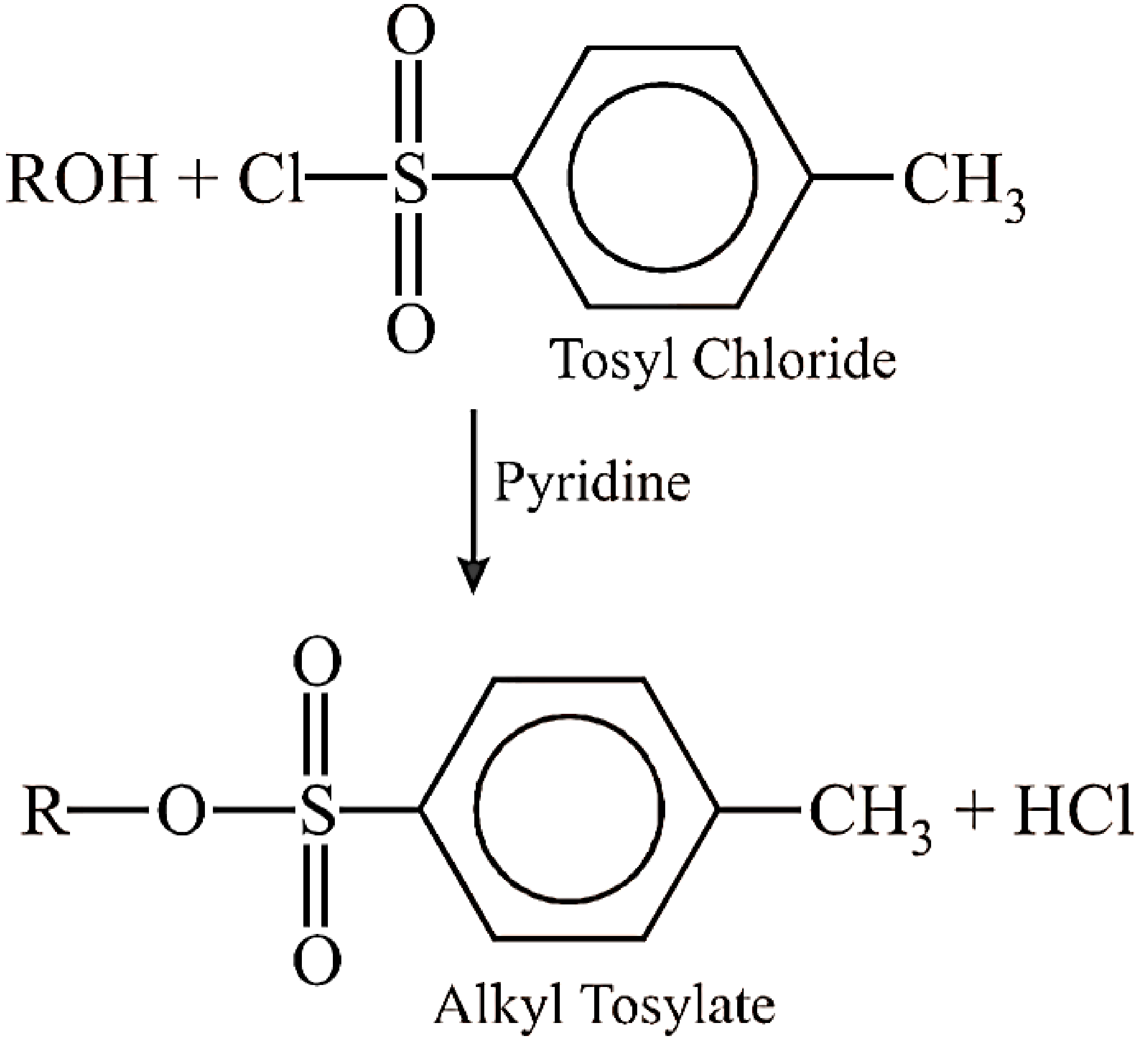


$$RO-\boxed{H + HO}-\overset{\overset{\displaystyle O}{\|}}{C}-R' \longrightarrow \underset{\text{Fruity Smell}}{RO-\overset{\overset{\displaystyle O}{\|}}{C}-R'} + H_2O$$

6.4 Tosylation

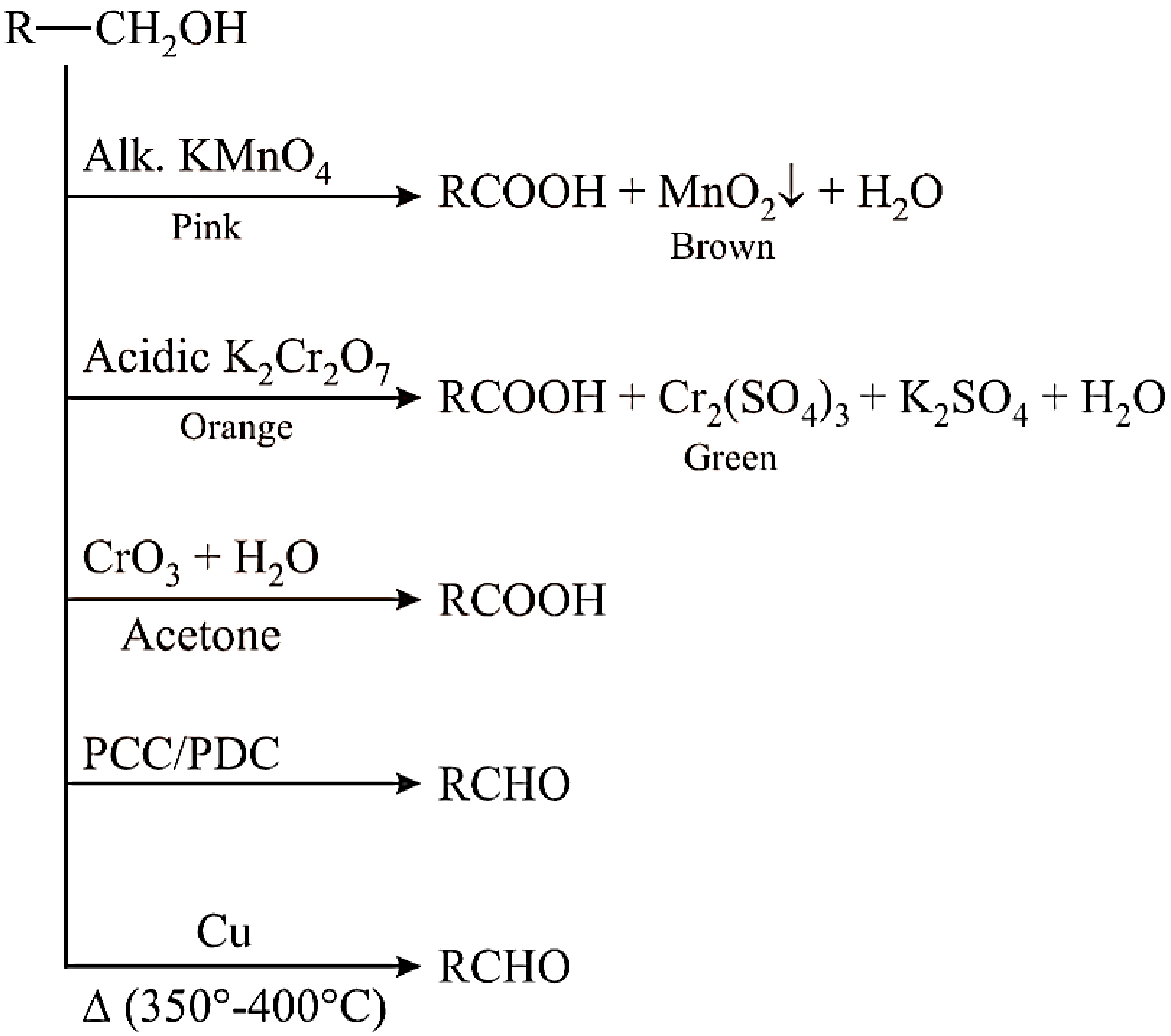
It is used to convert poor leaving group OH to good leaving group OTs.

Example:



6.5 Oxidation

(a) Primary Alcohols



$$R{-}CH_2OH \xrightarrow[\text{Pink}]{\text{Alk. }KMnO_4} RCOOH + \underset{\text{Brown}}{MnO_2\downarrow} + H_2O$$

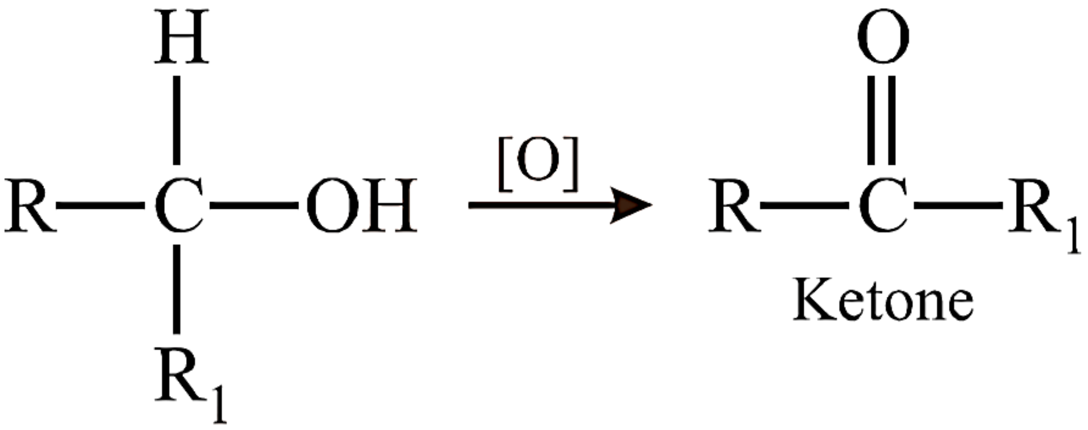
$$R{-}CH_2OH \xrightarrow[\text{Orange}]{\text{Acidic }K_2Cr_2O_7} RCOOH + \underset{\text{Green}}{Cr_2(SO_4)_3} + K_2SO_4 + H_2O$$

$$R{-}CH_2OH \xrightarrow[\text{Acetone}]{CrO_3 + H_2O} RCOOH$$

$$R{-}CH_2OH \xrightarrow{\text{PCC/PDC}} RCHO$$

$$R{-}CH_2OH \xrightarrow[\Delta\ (350°\text{-}400°C)]{Cu} RCHO$$

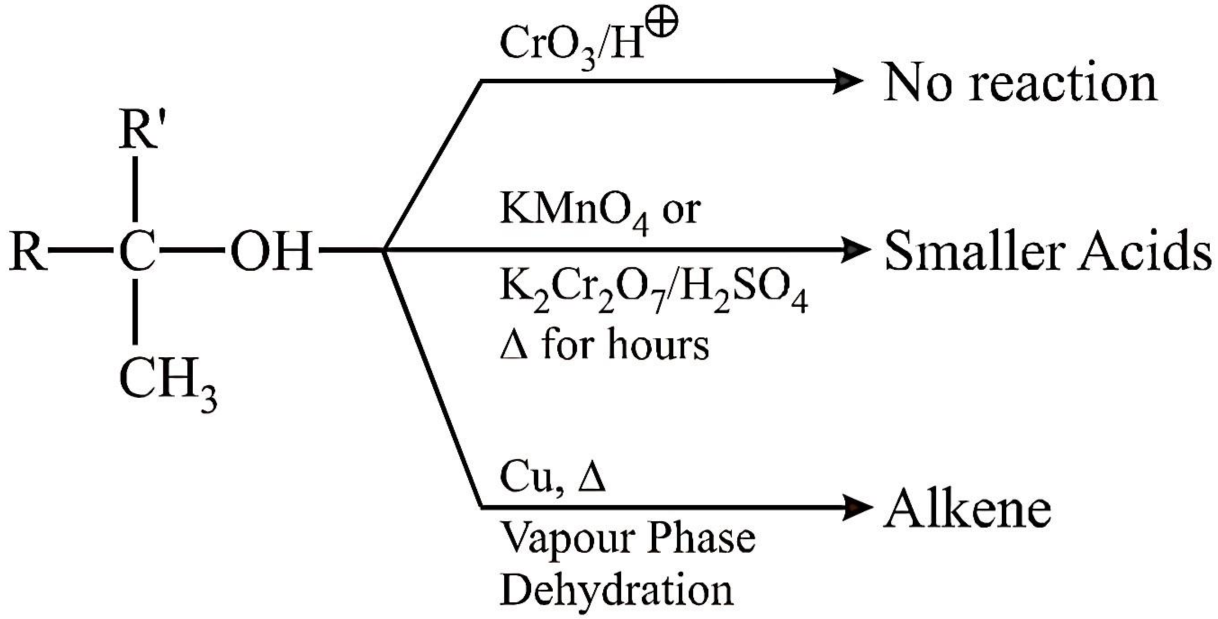
(b) Secondary alcohols



$$R{-}\underset{R_1}{\overset{H}{C}}{-}OH \xrightarrow{[O]} \underset{\text{Ketone}}{R{-}\overset{O}{\overset{\|}{C}}{-}R_1}$$

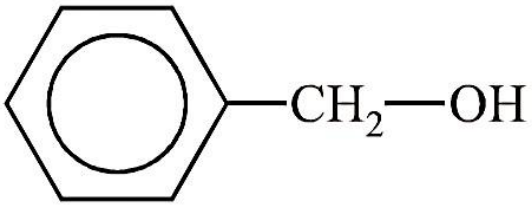
In the presence of any oxidizing agent, secondary alcohol is oxidized to alcohol.

(c) Tertiary alcohols



MnO_2 is an oxidizing agent which is used to oxidise only benzylic, allylic and propargylic alcohols.

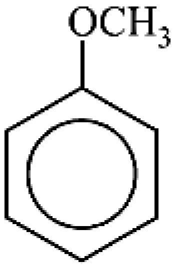
$R-CH=CH-CH_2-OH$ Allylic Alcohol



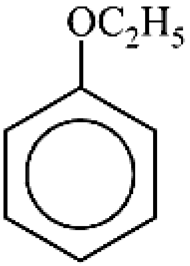
Benzylic Alcohol

$R-C\equiv C-C-OH$ Propargylic Alcohol

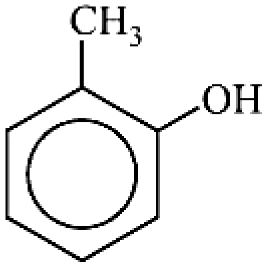
Common Phenols and Aromatic Ethers



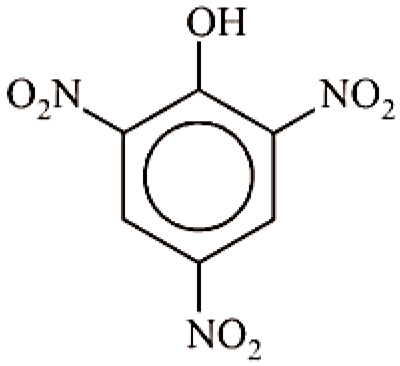
Anisole



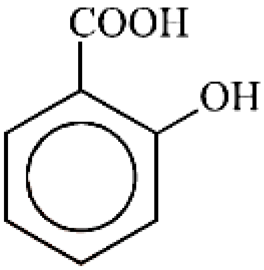
Phenetole



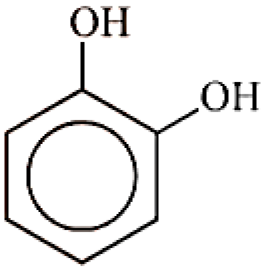
o-Cresol



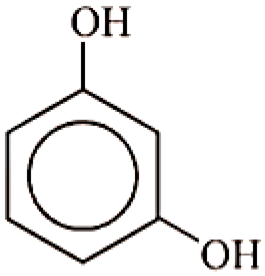
Picric Acid



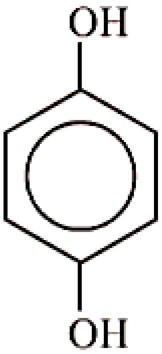
Salicylic Acid



Catechol

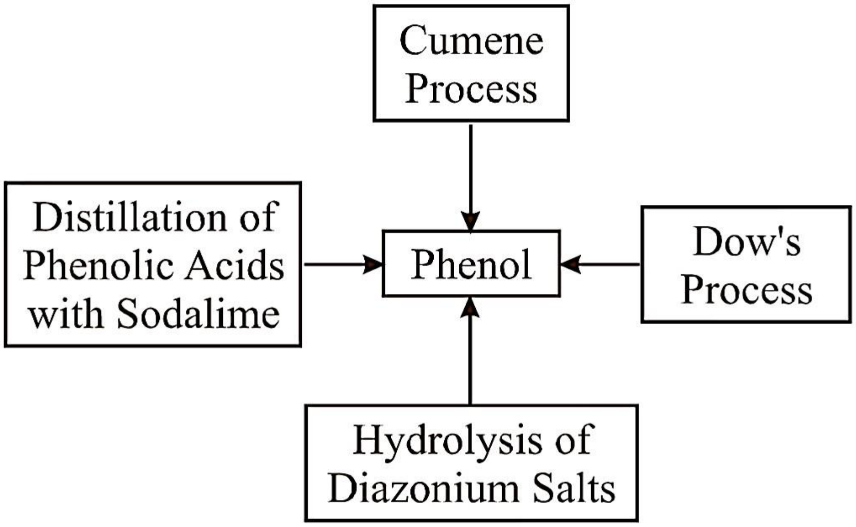


Resocinol



Hydroquinone

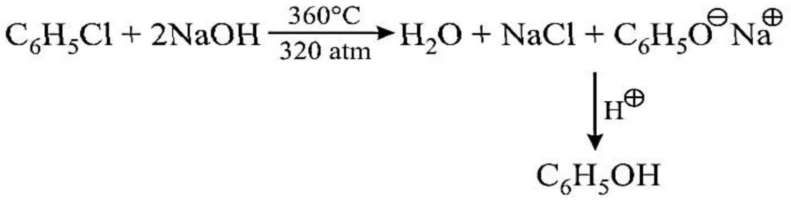
7. Preparation of Phenols



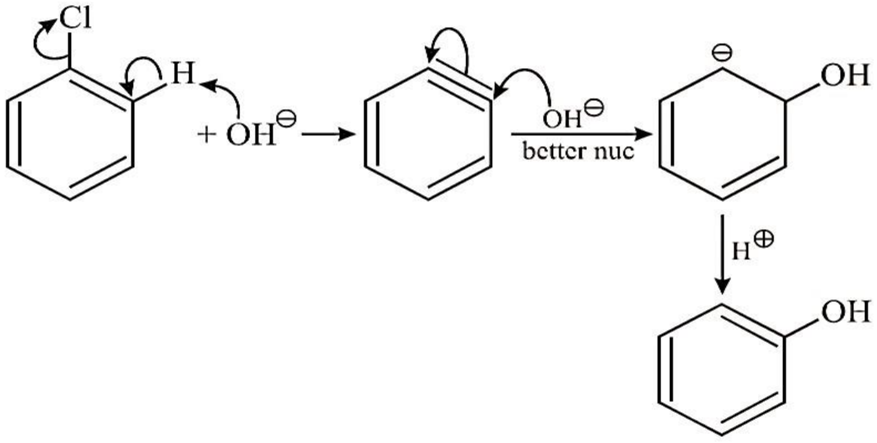
7.1 Dow’s Process

It is an industrial method which is used for the preparation of phenol. It takes place through benzene mechanism.

Example:

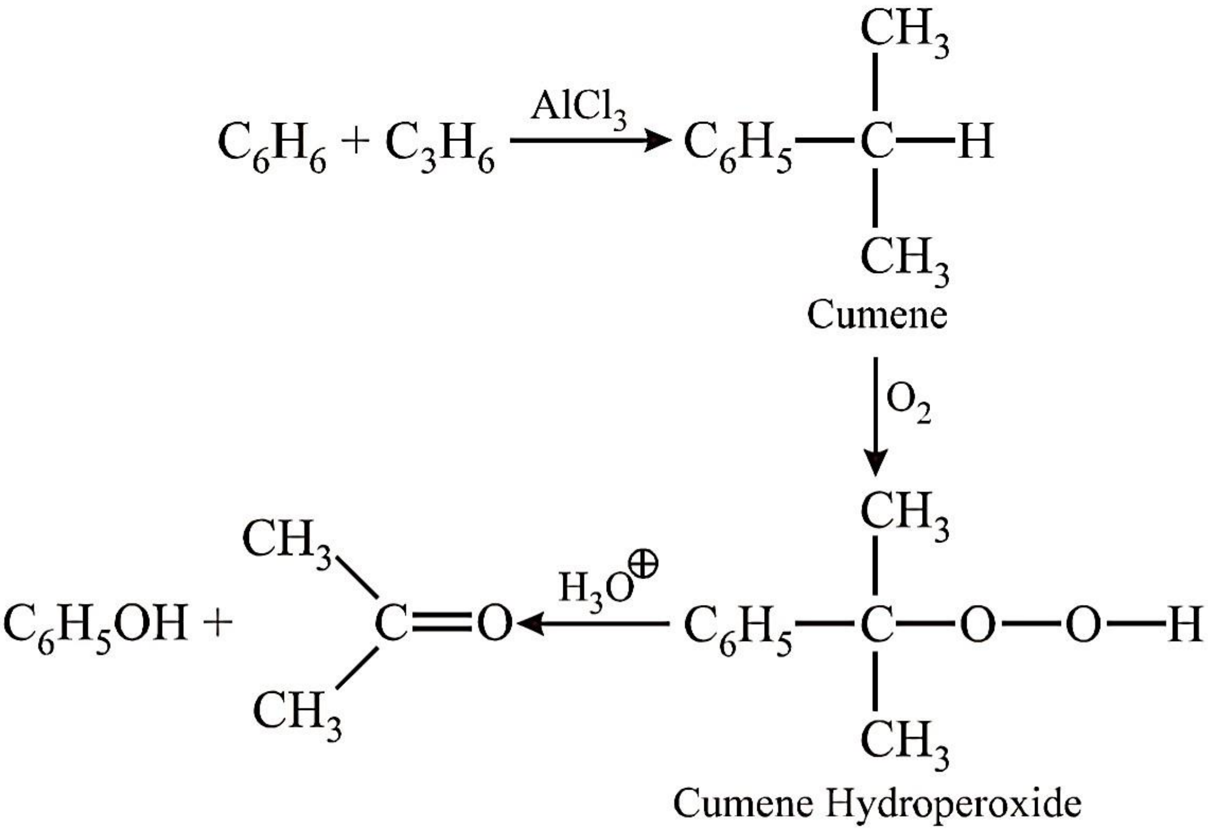


$$C_6H_5Cl + 2NaOH \xrightarrow[320\ atm]{360°C} H_2O + NaCl + C_6H_5O^{\ominus}Na^{\oplus} \xrightarrow{H^{\oplus}} C_6H_5OH$$



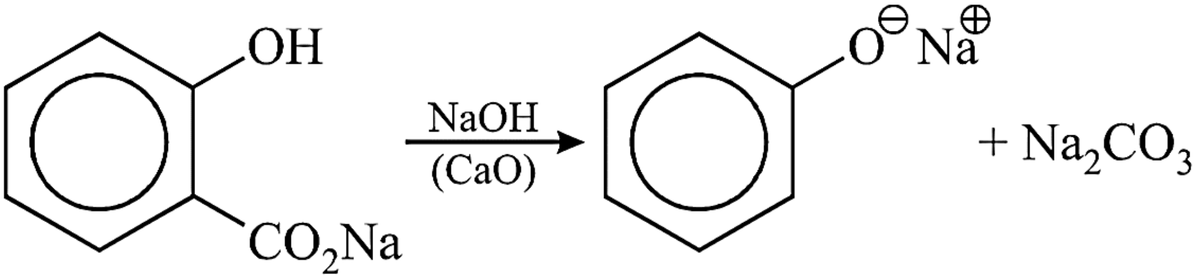
7.2 Cumene Process

Example:



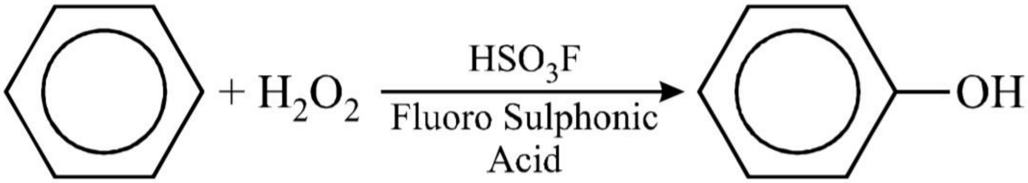
7.3 Distillation of phenolic acids with soda lime

Example:



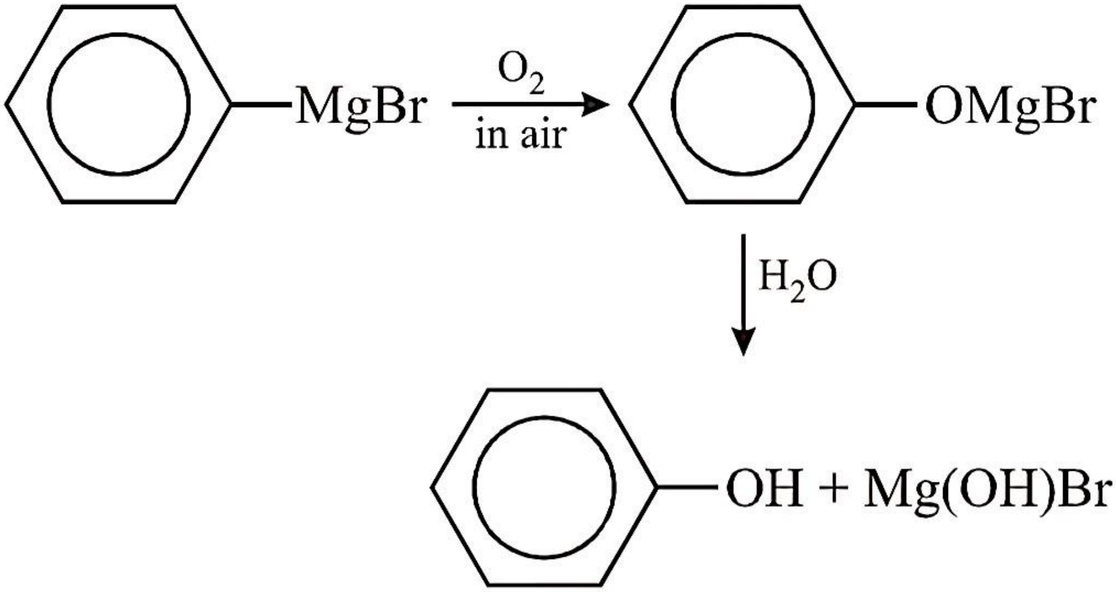
7.4 Benzene

Example:



7.5 Grignard reagent

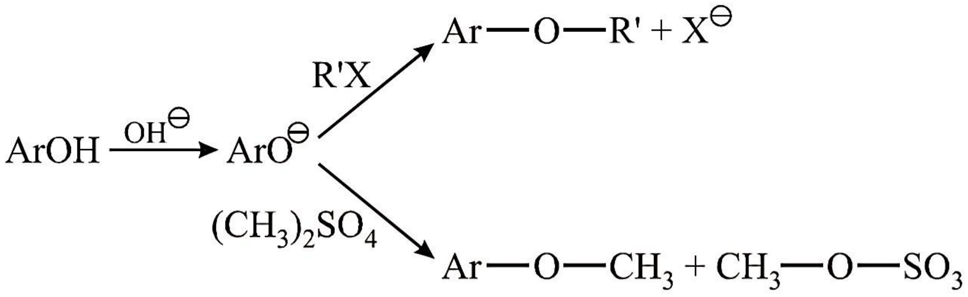
Example:



8. Reaction of phenols

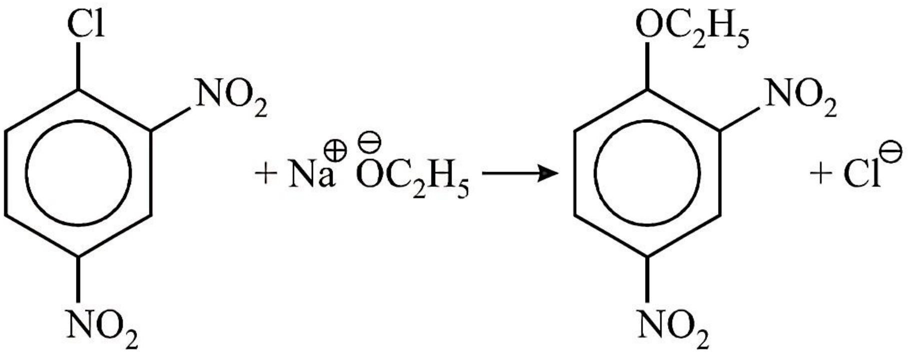
8.1 Formation of ethers

(a) Williamson synthesis



(b) Nucleophilic Aromatic substitution

Example:



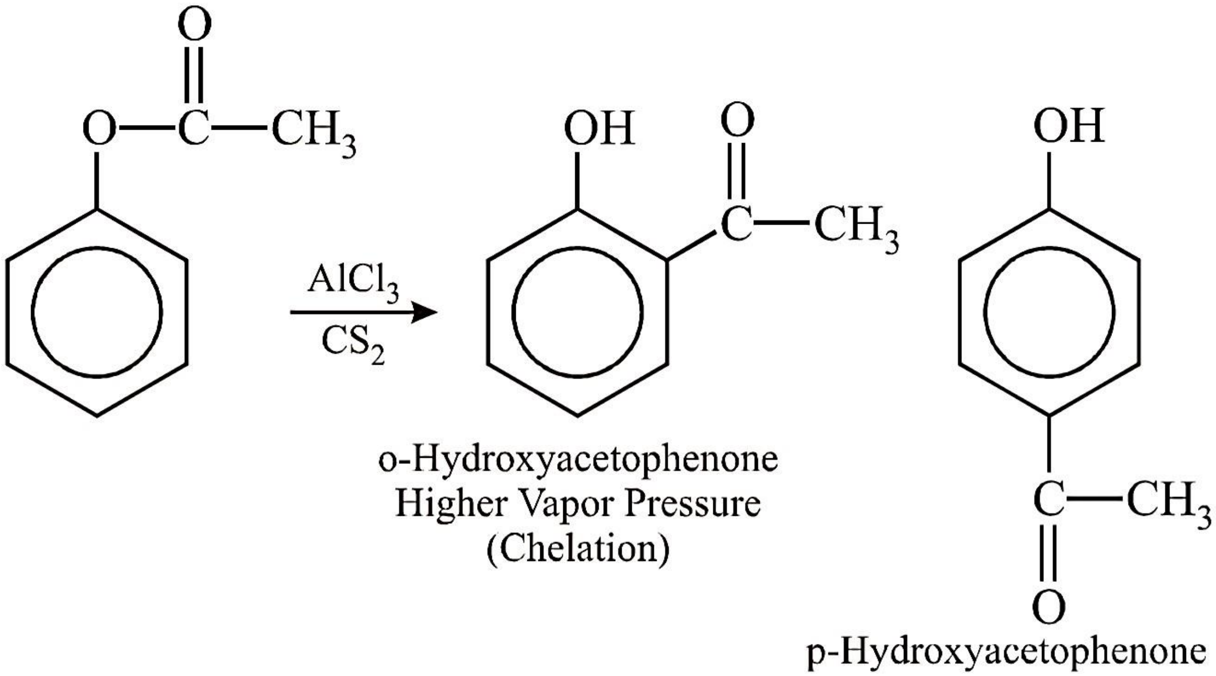
8.2 Formation of Esters

Example:

$$(CH_3CO)_2O + C_6H_5OH + NaOH \longrightarrow \underset{\text{Phenyl Acetate}}{CH_3COOC_6H_5} + CH_3COO^{\ominus}Na^{\oplus} + H_2O$$

8.3 Fries Rearrangement

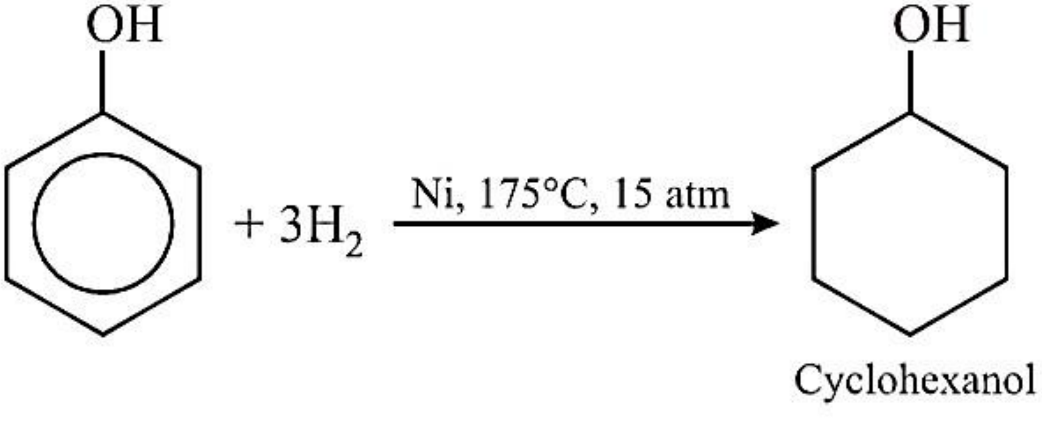
Example:



8.4 Reactions of Benzene Ring

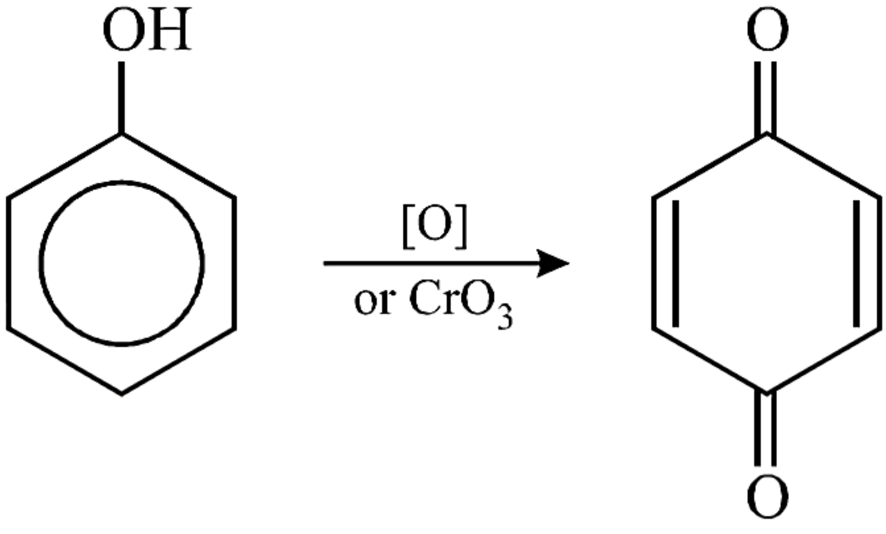
8.4.1 Hydrogenation

Example:



8.4.2 Oxidation to quinones

Example:

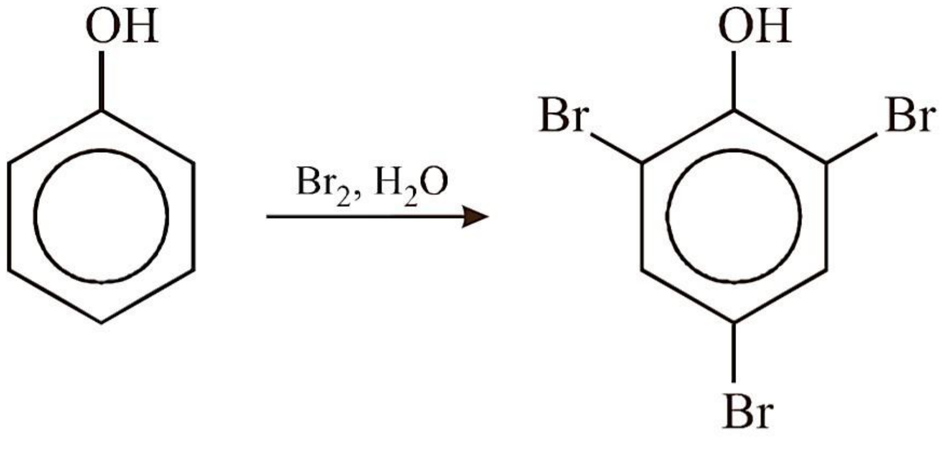


Quinone

8.4.3 Electrophilic substitution

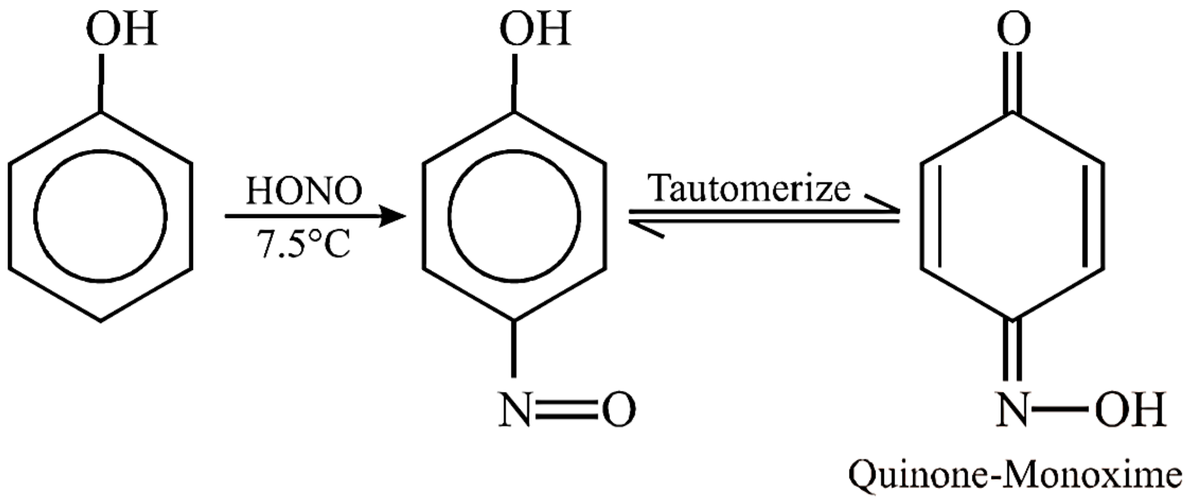
(a) Halogenation

Example:

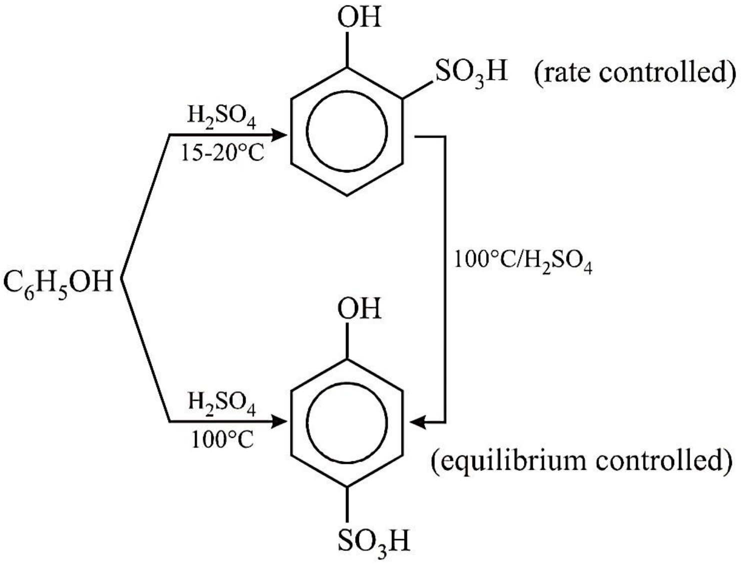


2, 4, 6 - Tribromophenol

(b) Nitration



(c) Sulphonation



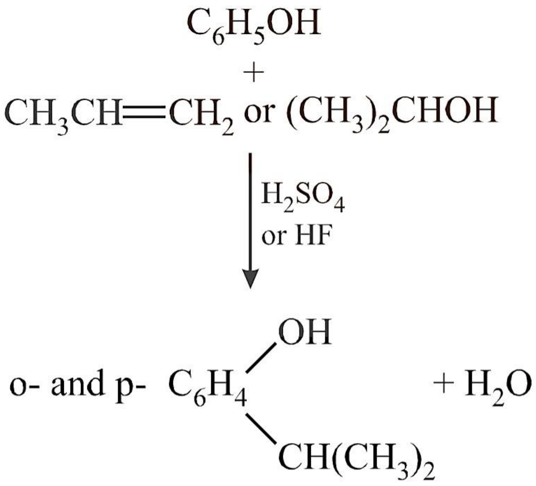
(d) Diazonium Salt Coupling-Azophenols

$$ArN_2^{\oplus} + C_6H_5G \rightarrow p - G - C_6H_5 - N = N\text{ - }Ar$$

Here, G is an electron releasing groups such as -OH, -OR.

(e) Ring Alkylation

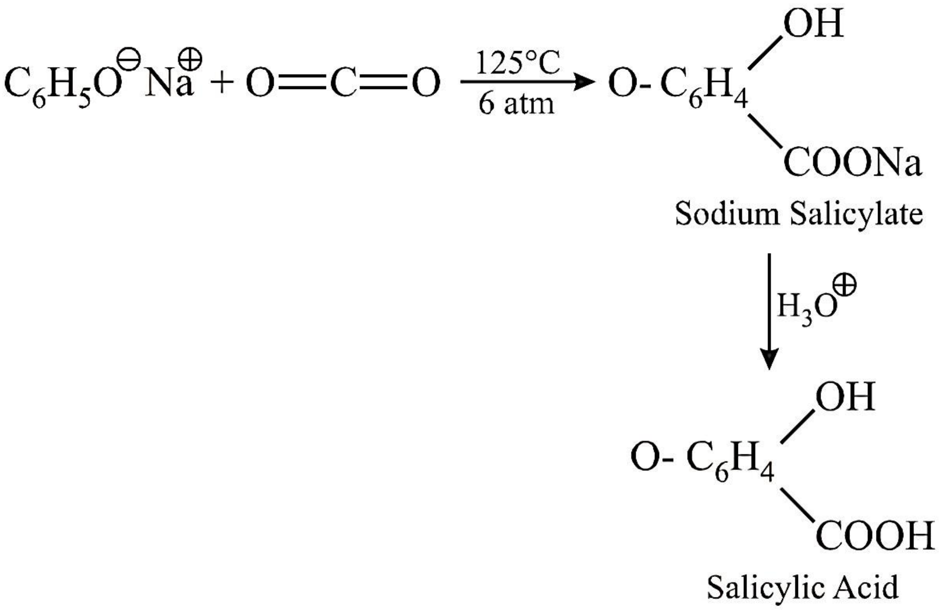
Example:



RX and $AlCl_3$ give poor yields as aluminum chloride coordinates with lone pair of oxygen.

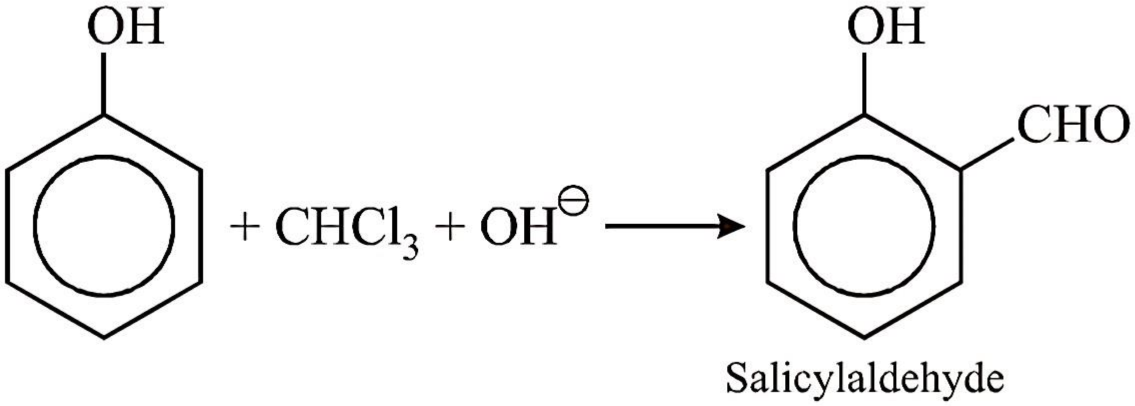
(f) Kolbe's Synthesis

Example:



(g) Reimer-Tiemann Synthesis of phenolic Aldehydes

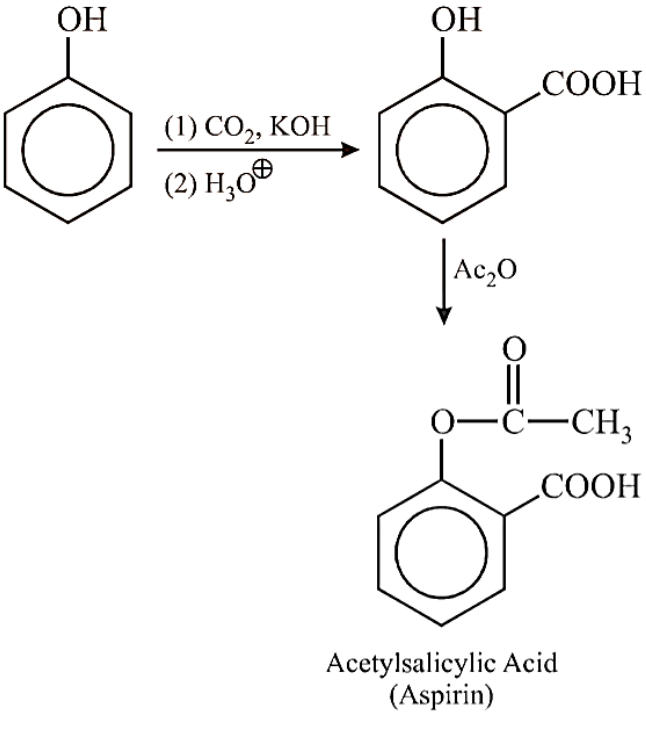
Example:



This reaction involves the formation of CCl_2 .

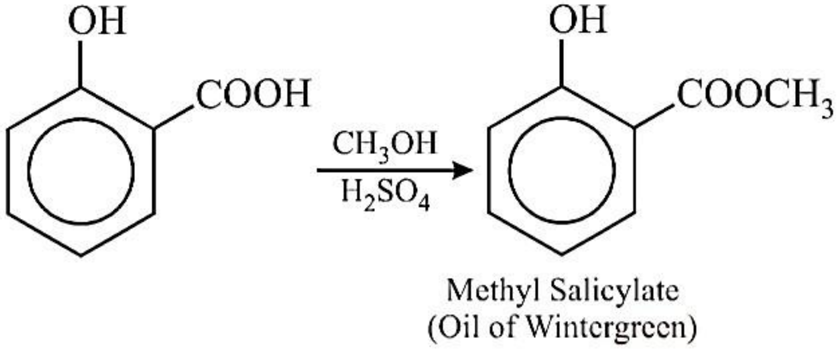
(i) Formation of Aspirin

Example:



(j) Formation of oil of wintergreen

Example:



Methyl Salicylate
(Oil of Wintergreen)

9. Ethers

9.1 Williamson Ether Synthesis

$R-O^{-}+R'-X\rightarrow R-O-R'+X^{-}$

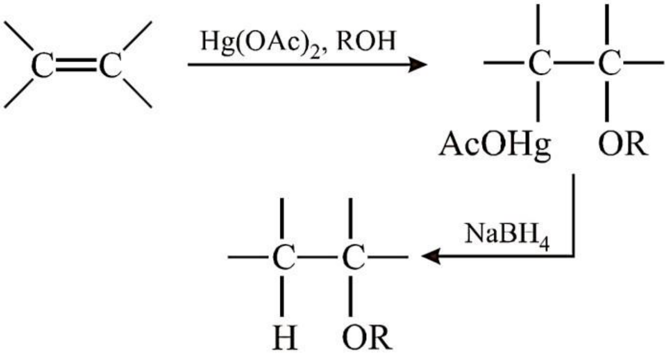
Note:

Substrate and leaving Group in Williamson synthesis

1. Leaving group, that, is, $X=\mathrm{Cl, Br, I, OTs\ etc.}$

2. Substrate-Alkyl group R’ should be primary.

9.2 Alkoxymercuration-Demercuration



This type of reaction follows Markovnikov orientation.

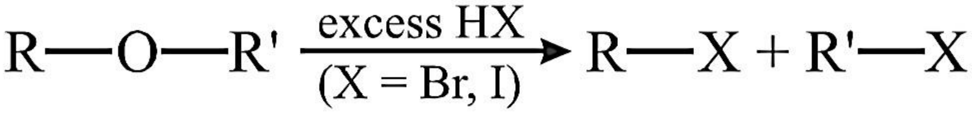
9.3 Bimolecular Dehydration of Alcohols

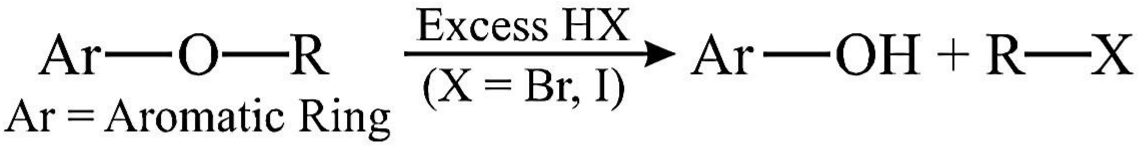
This is an industrial method which is used for the synthesis of ethers.

$$2R \xrightarrow[1^{\circ}]{H^{\oplus}} OH\;R-O-R+H_2O$$

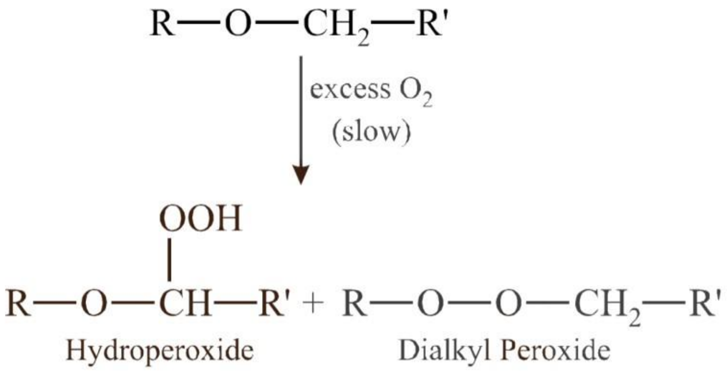
10. Reactions of ethers

10.1 Cleavage by HBr and HI



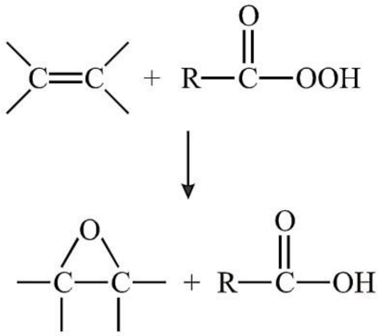


10.2 Autoxidation

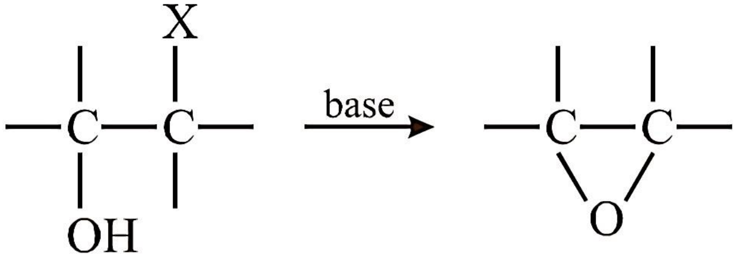


11. Preparation of epoxide

11.1 Peroxy Acid Epoxidation

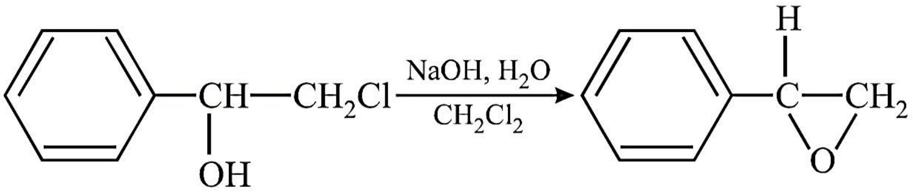


11.2 Base-promoted cyclization of halohydrins



X = Cl, Br, I, OTs, etc.

Example

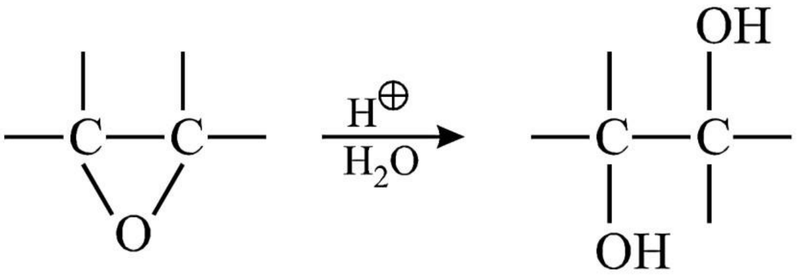


2-Chloro-1-Phenylethanol 2-Phenyloxirane

12. Reactions of Epoxides

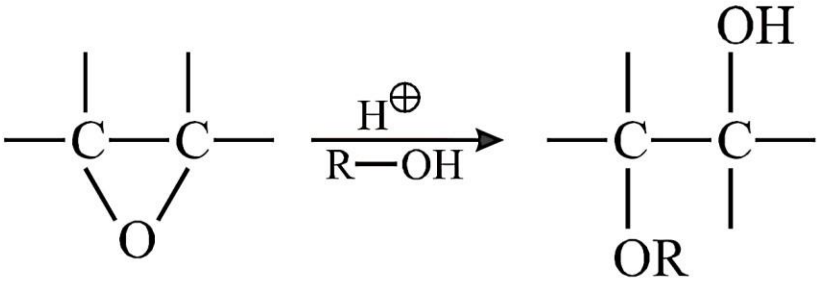
12.1 Acid-catalyzed opening

(a) In water



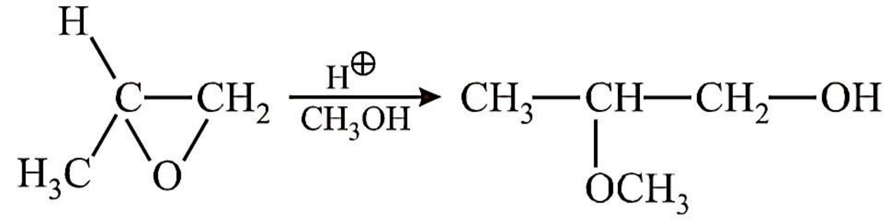
Anti-stereochemistry is followed here.

(b) In alcohols



Here, the alkoxy group is bonded to the more highly substituted carbon.

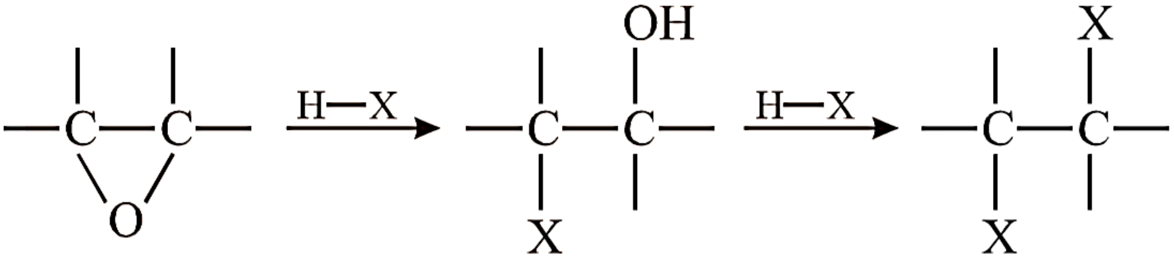
Example:



Methyl Oxirane (Propylene Oxide)

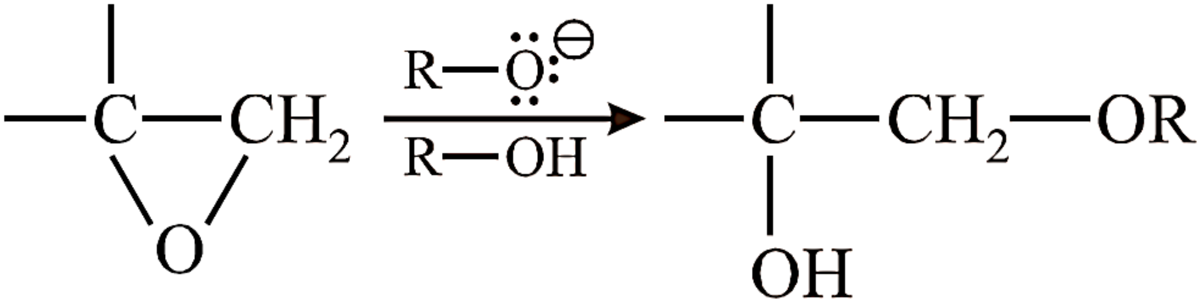
2-Methoxy-propan-1-ol

(c) Hydrohalic Acids (X = Cl, Br, I)



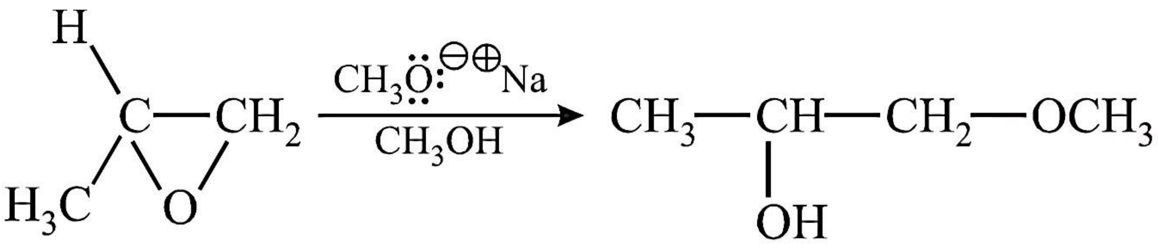
12.2 Base-Catalyzed opening

(a) With Alkoxides



The alkoxy group is bonded to less highly substituted carbon.

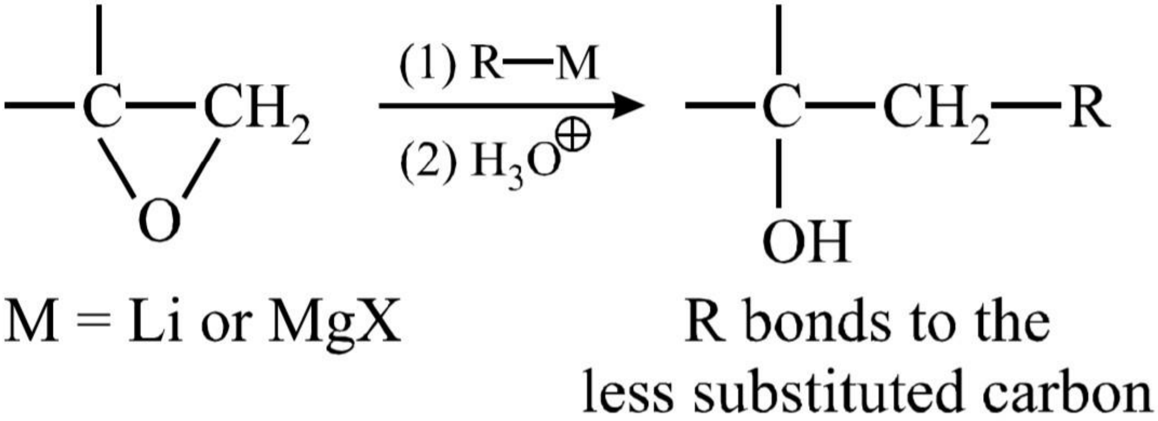
Example:



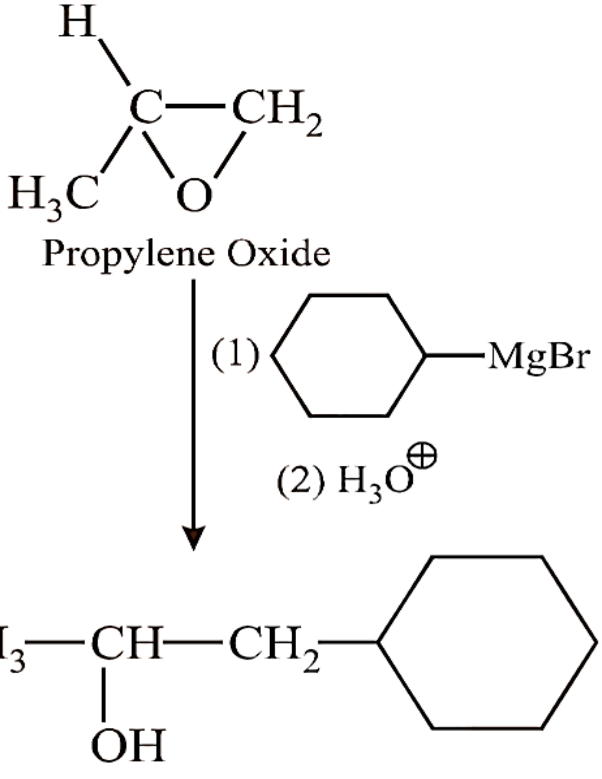
Propylene Oxide

1-Methoxy-2-Propanol

(b) With Organometallics



Example:



Note:

Opening of Epoxide Ring

1. In acid catalyzed opening, a nucleophile attacks the epoxide carbon, allowing a more stable carbocation to be formed.

2. Nucleophile attacks on the less hindered carbon in base catalyzed opening.

13. ACIDIC STRENGTH

(i) Despite the fact that oxygen is more electronegative than sulfur, alcohols are weaker acids than thiols. RO^-, the conjugate base of alcohol, is more basic than RS^- because the negative charge in RO^- is placed on smaller oxygen atoms, resulting in higher charge density. However, because the RS^- negative charge is dispersed on larger sulphur, it is a poor base and its conjugate acid is more acidic.

(ii) Due to the +I effect of the alkyl group, all alcohols (except CH_3OH) are weaker than H_2O . CH_3OH is slightly more powerful than H_2O. Because of the electron withdrawing benzene ring and the resonance stabilized phenolic ion, phenols are stronger than alcohol. Because alkoxide ions, the conjugate base of alcohol, lack resonance, they are less stable and more basic. Phenol is less stable than carboxylic acid, which has a strong electron-drawing carbonyl group and more stable, resonating structures.

14. Test for Alcohols, phenols and ethers

14.1 Analysis of Alcohols-Characterization

(a) Cold concentrated sulfuric acid dissolves alcohols. This property is shared by alkenes, amines, almost all oxygen-containing compounds, and easily sulfonated compounds. (Alcohol, like other oxygen-containing compounds, produces oxonium salts that dissolve in the highly polar sulfuric acid.)

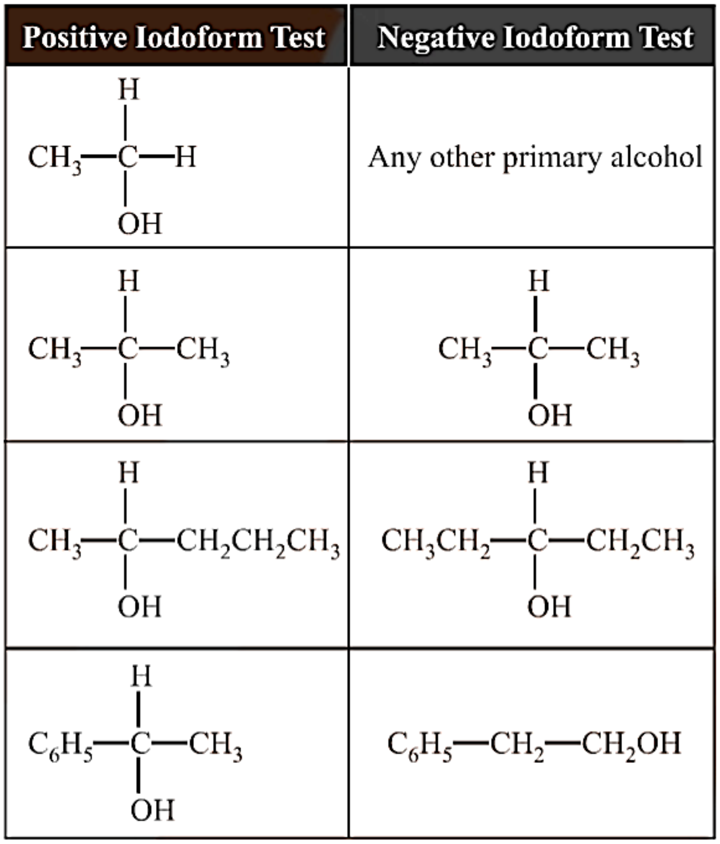
(b) Cold dilute, neutral permanganate does not oxidize alcohols (although primary and secondary alcohols are oxidized by permanganate under more vigorous conditions). However, as we've seen, alcohols frequently contain impurities that oxidize under these conditions, so the permanganate test should be used with caution.

(c) Alcohols have no effect on the color of bromine in carbon tetrachloride. This characteristic distinguishes them from alkenes and alkynes.

(d) The evolution of hydrogen gas from alcohol reactions with sodium metal is useful in characterization.

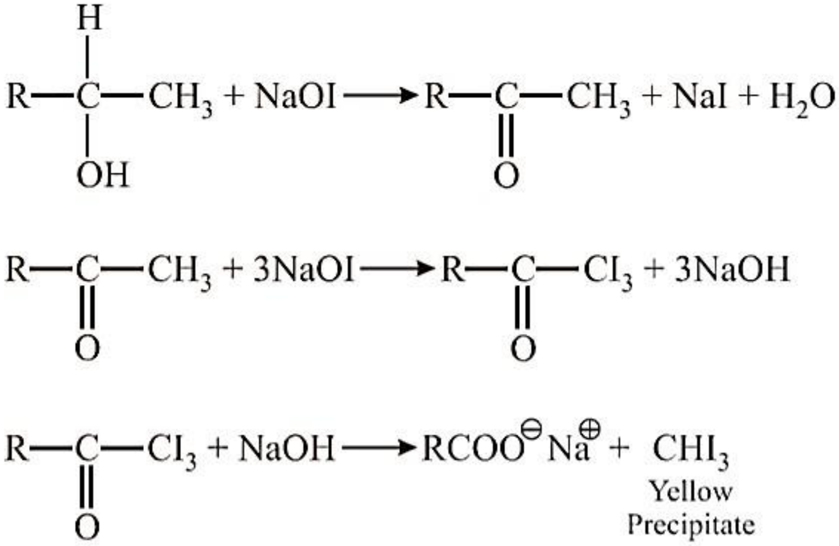
(e) The formation of an ester upon treatment with an acid chloride or anhydride often indicates the presence of a hydroxide group in a molecule. Some esters have a pleasant odor; others have high melting points and can be used to make identifications.

(f) The Lucas test, which is based on the difference in reactivity of the three classes towards hydrogen halides, determines whether an alcohol is primary, secondary, or tertiary. Alcohols with fewer than six carbons are soluble in the Lucas reagent, which is a solution of concentrated hydrochloric acid and zinc chloride. The cloudiness that appears when the chloride separates from the solution indicates the formation of a chloride from an alcohol. As a result, the time required for cloudiness to appear is a measure of the alcohol's reactivity. The Lucas reagent reacts immediately with tertiary alcohol. Within five minutes, a secondary alcohol reacts. At room temperature, a primary alcohol does not react significantly. Benzyl alcohol and alllyl alcohol react with the Lucas reagent as quickly as tertiary alcohols. Allyl chlorides, on the other hand, is soluble in the reagent.



Positive Iodoform Test	Negative Iodoform Test
$CH_3-\underset{OH}{\overset{H}{C}}-H$	Any other primary alcohol
$CH_3-\underset{OH}{\overset{H}{C}}-CH_3$	$CH_3-\underset{OH}{\overset{H}{C}}-CH_3$
$CH_3-\underset{OH}{\overset{H}{C}}-CH_2CH_2CH_3$	$CH_3CH_2-\underset{OH}{\overset{H}{C}}-CH_2CH_3$
$C_6H_5-\underset{OH}{\overset{H}{C}}-CH_3$	$C_6H_5-CH_2-CH_2OH$

Oxidation, halogenation, and cleavage are all involved in the reaction.



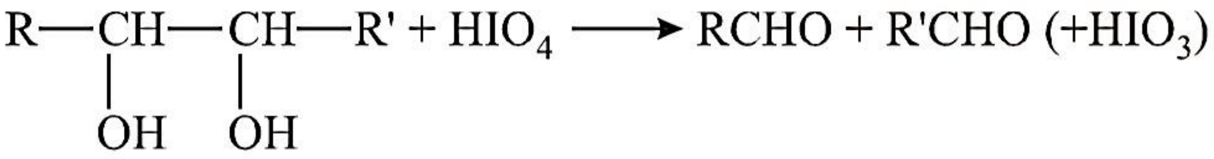
$$R-\underset{OH}{\overset{H}{C}}-CH_3 + NaOI \longrightarrow R-\underset{O}{\overset{}{\underset{\|}{C}}}-CH_3 + NaI + H_2O$$

$$R-\underset{O}{\underset{\|}{C}}-CH_3 + 3NaOI \longrightarrow R-\underset{O}{\underset{\|}{C}}-CI_3 + 3NaOH$$

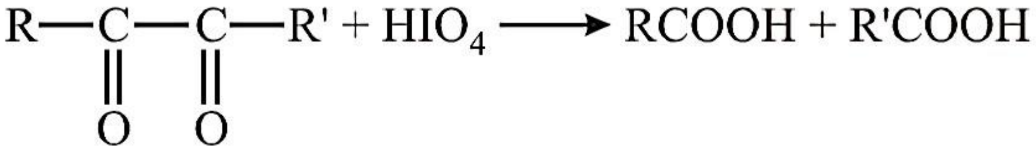
$$R-\underset{O}{\underset{\|}{C}}-CI_3 + NaOH \longrightarrow RCOO^{\ominus}Na^{\oplus} + \underset{\text{Yellow Precipitate}}{CHI_3}$$

14.2 Analysis of Glycols, Periodic Acid Oxidation

HIO_4 compounds with two or more-OH or C=O groups attached to adjacent carbon atoms undergo oxidation with cleavage of carbon-carbon bonds when exposed to periodic acid.



$$R-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-R' + HIO_4 \longrightarrow RCHO + R'CHO\ (+HIO_3)$$



$$R-\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-R' + HIO_4 \longrightarrow RCOOH + R'COOH$$

14.3 Miscellaneous Tests

(a) Ceric Ammonium Nitrate Test-

With this reagent, alcohols produce a red color.

$$Ce(NH_4)_2(NO_3)_6 \ + \ RCH_2OH \rightarrow Ce(NH_4)_2(NO_3)_5 + RCOOH + HNO_3$$

(b) Potassium Dichromate Test –

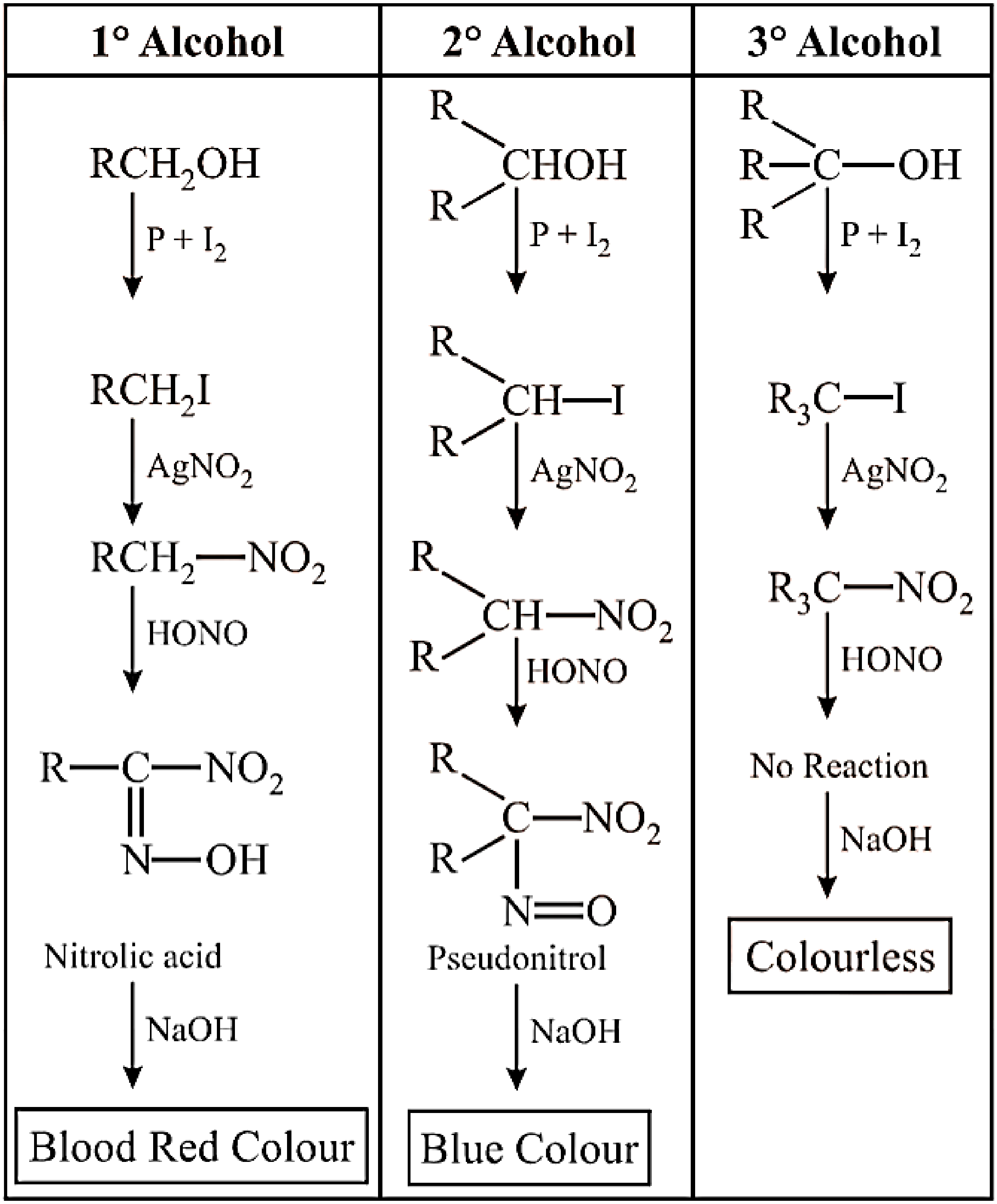
Alcohols change the color of orange dichromate to green. Tertiary alcohols fail this test.

(c) Ester test:

Alcohol produces a fruity aroma of ester with carboxylic acid.

(d) Methanol reacts with salicylic acid to produce winter green oil.

14.4 Victor Meyer's Test



14.5 Differentiation Test

14.5.1 Alcohols and Phenols

1. Litmus Test: Phenol turns blue litmus red but not alcohol.

2. Ferric chloride:

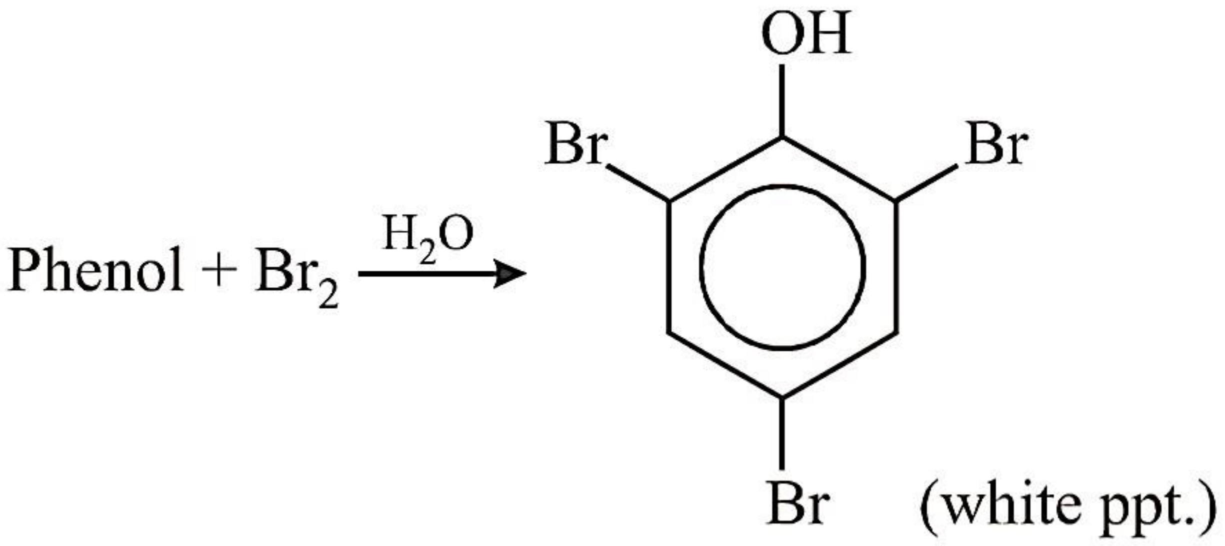
$FeCl_3$: Phenol $\overset{\text{Neutral } FeCl_3}{\text{�}}$ Blue-Violet

3. Coupling reaction:

Phenol + Diazonium Salt $\xrightarrow[\text{medium}]{\text{weakly basic}}$ Yellow or

Diazonium Salt + Alcohol $\xrightarrow[\text{medium}]{\text{weakly basic}}$ No Reaction

4. Bromine water test:



$$\text{Alcohol} + Br_2 \xrightarrow{H_2O} \text{No Reaction}$$

14.5.2 Alcohols and Ethers

(a) Alcohols react with Na to give H_2, but not ethers.

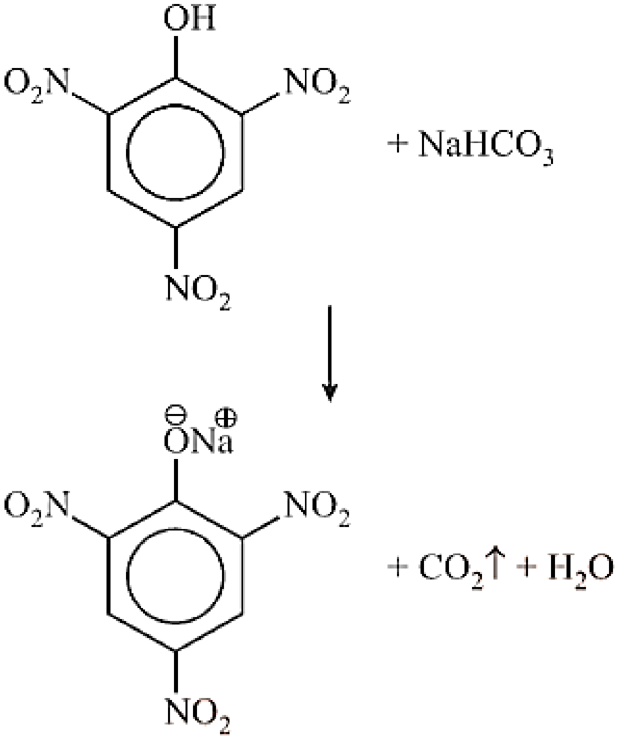
(b) Alcohol gives fumes of HCl with PCl_5 but not ethers.

15.5.3 Sodium Bicarbonate Test

Phenol, ROH and H_2O do not displace CO_2 from carbonate & bicarbonates but $RCOOH$ & $SO H$ gives brisk effervescence of CO_2 which proves that $RCOOH$ & $RS OH$ are stronger acids $H CO$ but phenol is weaker acid than H_2CO_3. Nitrophenols also give effervescence ofCO with Na_2CO_3. Trinitrophenol (Picric Acid) is highly acidic due to strong electron withdrawing effect of three groups its acidic strength is comparable to that of carboxylic acids. Its anion is highly resonance stabilised.

$$RCOOH + NaHCO_3 = RCOON^{\ominus\oplus} + CO_2\uparrow + H_2O$$

$$Ph - OH + NaHCO_3 = \text{No Reaction}$$



15.5.4 $FeCl_3$ Test:

Phenol gives characteristic purple colour with $FeCl_3$ but alcohols do not react with $FeCl_3$. Carboxylic acids also form buff coloured precipitate with $FeCl_3$. Only acetic acid forms red coloured precipitate with $FeCl_3$, so it can be used as a test for acetate salts.