ALCOHOLS, ETHERS AND PHENOLS

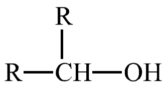
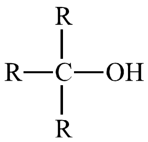
1. INTRODUCTION

The compounds in which hydroxyl group (–OH) is attached to a saturated carbon atom are called as **Alcohols**. The compounds in which a hydroxyl group is attached to an unsaturated carbon atom of a double bond are called as **Enols**. The saturated carbon may be that of an alkyl, alkenyl, alkynyl, cycloalkyl or benzyl group. However, if a hydroxyl group is attached to a benzene ring, the compounds are called as **Phenols**.

The alcohols are further classified as : **Monohydric** (containing one –OH group), **Dihydric** (containing two –OH groups) and **Trihydric** (containing three –OH groups).

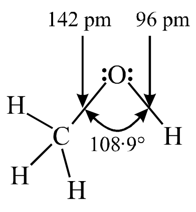
Alcohols find usage in industry as well as day to day life. For example, ordinary spirit used for polishing wooden furniture is chiefly ethanol. Sugar, cotton, paper are all made up of compounds containing –OH groups. Phenols are used in several important polymers such as *Bakelite* and in several drugs such as *Aspirin*. Ethers are commonly used as solvents and anaesthetics.

2. CLASSIFICATION

CH_3—OH	Methanol	
R—CH_2—OH	1° Alcohol	Primary
	2° Alcohol	Secondary
	3° Alcohol	Tertiary
R—O—R	Symmetrical Ether	
R—O—R'	Unsymmetrical Ether	

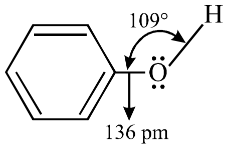
3. STRUCTURES OF FUNCTIONAL GROUPS

In alcohols, the oxygen of the –OH group is attached to carbon by a sigma (σ) bond formed by the overlap of a sp^3 hybridised orbital of carbon with a sp^3 hybridised orbital of oxygen. The following figure depicts structural aspects of methanol, phenol and methoxymethane.



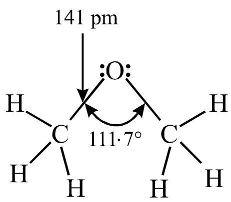
Methanol

Bond angle is slightly less due to LP-LP repulsion.



Phenol

Lone pair of oxygen is delocalised on ring due to which C—O bond length is less.



Methoxymethane

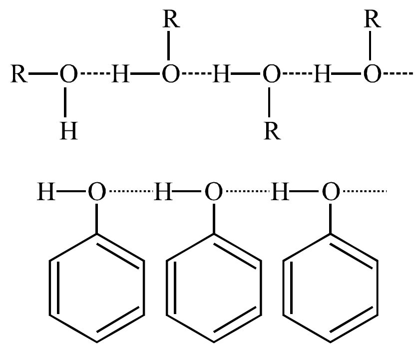
Bond angle in methoxymethane is more than tetrahedral angle due to repulsive interaction between the two bulky (R) groups. The C—O bond length is same as in alcohols.

4. PHYSICAL PROPERTIES

4.1 Boiling Point

The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). In alcohols, the boiling point decreases with increase in branching (decrease in Van der Waals forces due to decrease in surface area).

The –OH group in alcohols and phenols contains a hydrogen, bonded to an electronegative oxygen atom. Therefore, it is capable of forming intermolecular hydrogen bond, strength of which is even greater than amine.



It is due to the presence of strong intermolecular hydrogen bonding that alcohols and phenols have higher boiling points corresponding to other classes of compounds, namely, hydrocarbons, ethers and haloalkanes/haloarenes, amines of comparable molecular masses.

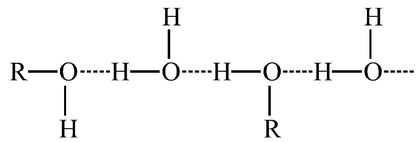
Their boiling points are lower than carboxylic acid which have even more strong H-bond. For isomeric alcohols boiling points decreases with increase in branching due to decrease in van der Waals forces with decrease in size. **The order of boiling point is 1° alcohol > 2° alcohol > 3° alcohol.**

In ethers, boiling point is very less, and comparable to those of alkane of comparable molecular mass due to less dipole moment and absence of H-bonding.

4.2 Solubility

The solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules. The solubility decreases with increase in the size of hydrophobic group (R). Higher alcohol are insoluble. Branching increases solubility, due to decrease in surface area of non-polar hydrocarbon part.

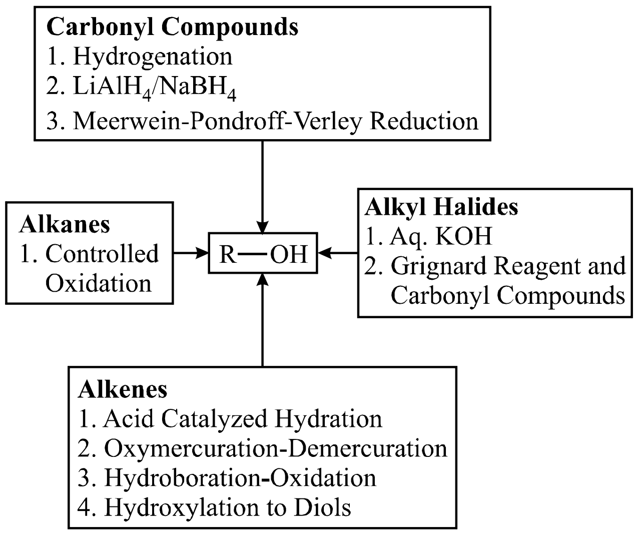
n-butyl alcohol < isobutyl alcohol < sec-butyl alcohol < tert-butyl alcohol



Lower ethers are water soluble but solubility is less than alcohol due to less H-bonding with water and low polarity.

Refer to Table 1, 2, 3 and 4 for reference to physical properties of alcohols, phenols and ethers.

5. PREPARATION OF ALCOHOLS



5.1 Alkane

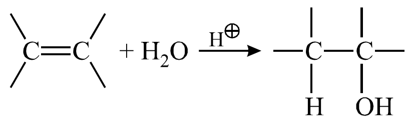
Controlled Oxidation

$$CH_4 + [O] \xrightarrow[\text{100 atm, 200°C}]{\text{Cu tube}} CH_3OH$$

5.2 Alkenes

5.2.1 Acid Catalyzed Hydration

Markovnikov addition with carbocation rearrangements.

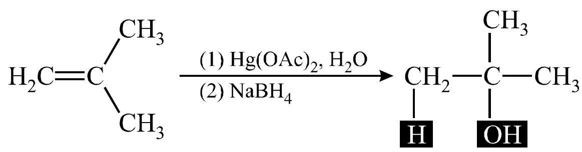


Markovnikov orientation

5.2.2 Oxymercuration-Demercuration

Markovnikov addition without carbocation rearrangements.

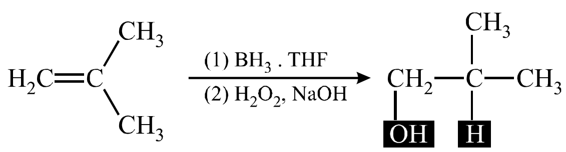
Example - 1



5.2.3 Hydroboration-Oxidation

Anti-Markovnikov addition.

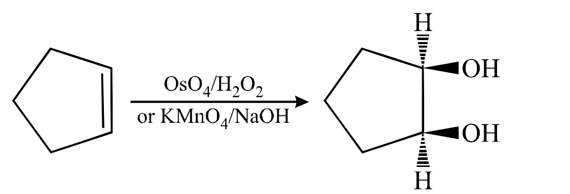
Example - 2



5.2.4 SYN Hydroxylation

Reagents : Cold dil. $KMnO_4$/NaOH or OsO_4/H_2O_2

Example - 3

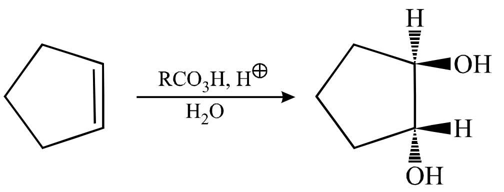


Cyclopentene   cis-Cyclopentane-1, 2-diol

5.2.5 ANTI Hydroxylation

Reagents : Peroxy Acids followed by Acidic Hydrolysis

Example - 4



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

5.3 Alkyl Halide

5.3.1 Second-order Substitution

Primary (and some Secondary) Halides

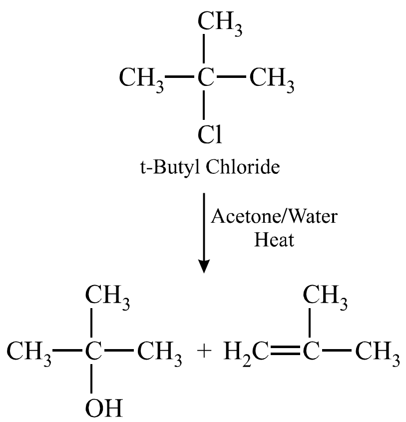
Example - 5

$$(CH_3)_2CHCH_2CH_2{-}Br \xrightarrow[H_2O]{KOH} (CH_3)_2CHCH_2CH_2{-}OH$$

5.3.2 First-order Substitution

Tertiary (and some Secondary) Halides

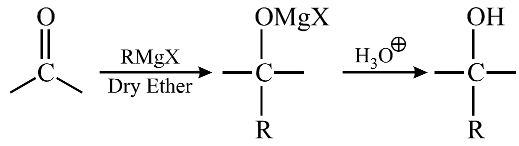
Example - 6



t-Butyl Chloride → t-Butyl Alcohol + Isobutylene

5.3.3 Grignard Reagent/Organolithium Reagent

Nucleophilic addition to the carbonyl group



(a) Addition to Formaldehyde - *1° Alcohol*

Example - 7

$$CH_3CH_2MgBr + H_2C{=}O$$

Ethyl Magnesium Bromide

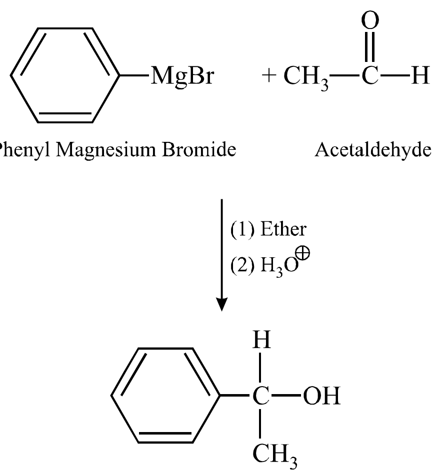
$$\downarrow \text{(1) Ether; (2) } H_3O^{\oplus}$$

$$CH_3CH_2{-}CH_2{-}OH$$

Propan-1-ol

(b) Addition to an Aldehyde - *2° Alcohol*

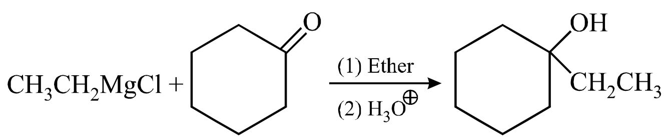
Example - 8



Phenyl Magnesium Bromide + Acetaldehyde → 1-Phenylethanol

(c) Addition to a Ketone - *3° Alcohol*

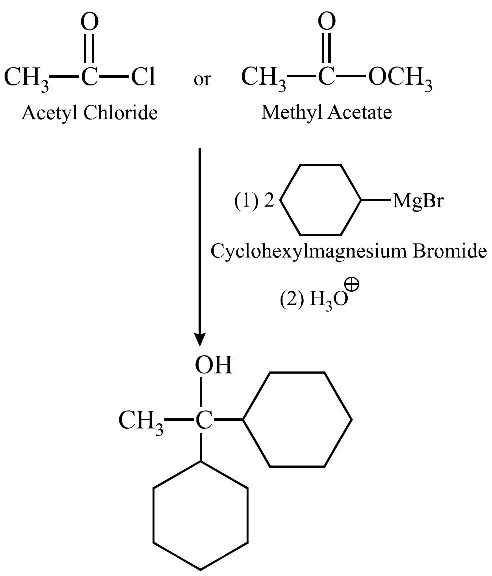
Example - 9



Cyclohexanone → 1-Ethylcyclohexanol

(d) Addition to an Acid Halide or an Ester - *3° Alcohol*

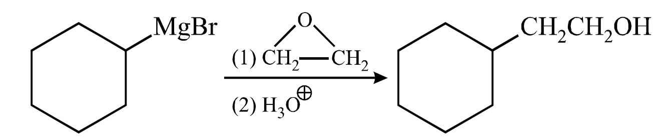
Example - 10



1, 1-Dicyclohexylethanol

(e) Addition to Ethylene Oxide - *1° Alcohol* (with two carbon atoms added)

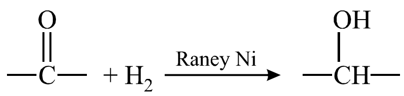
Example - 11



Cyclohexyl Magnesium Bromide   2-Cyclohexylethanol

5.4 Carbonyl Compounds

5.4.1 Catalytic Hydrogenation

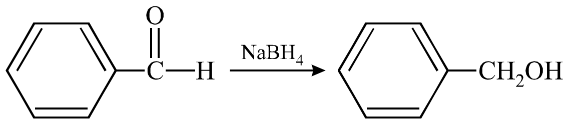


This method is usually not as selective or as effective as the use of hydride reagents.

5.4.2 Reduction with Metal Hydrides

1. Reduction of an aldehyde gives a primary alcohol

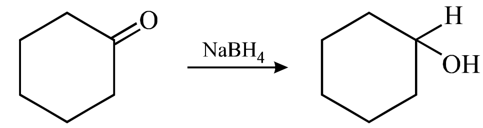
Example - 12



Benzaldehyde   Benzyl Alcohol

2. Reduction of a ketone gives a secondary alcohol

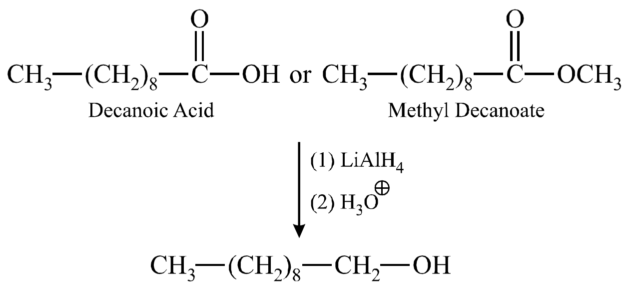
Example - 13



Cyclohexanone   Cyclohexanol

3. Reduction of an acid or ester gives a primary alcohol

Example - 14

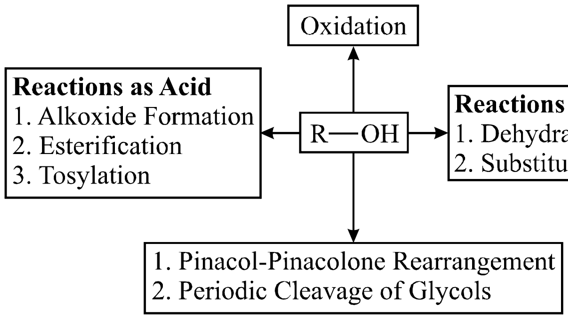


Decan-1-ol

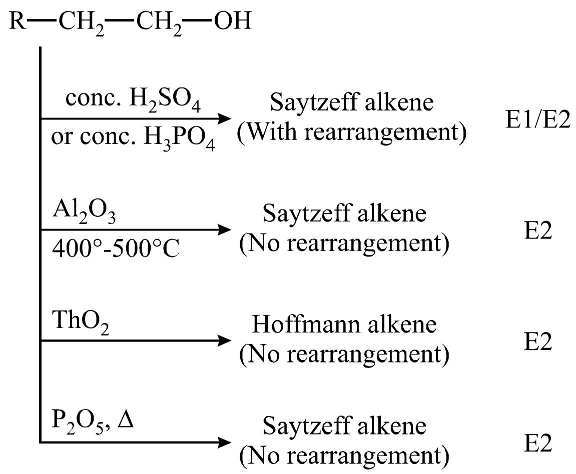
Reactions of $LiAlH_4$ and $NaBH_4$

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

6. REACTIONS OF ALCOHOLS

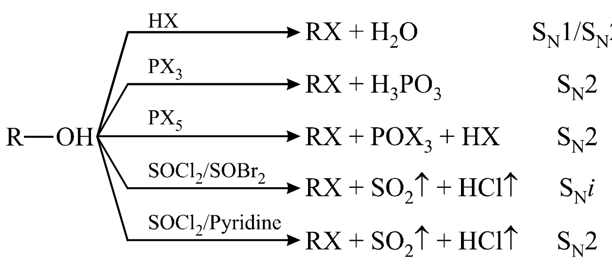


6.1 Dehydration



Note... Reactions with Al_2O_3, ThO_2 and P_2O_5 occur in gaseous phase.

6.2 Substitution



Note... Reaction of alcohol with $SOCl_2$ in the presence of Pyridine is known as **Darzen's Process**.

6.3 Esterification

$$RO\text{—}\boxed{H + HO}\text{—}\overset{O}{\overset{\|}{C}}\text{—}R' \longrightarrow RO\text{—}\overset{O}{\overset{\|}{C}}\text{—}R' + H_2O$$

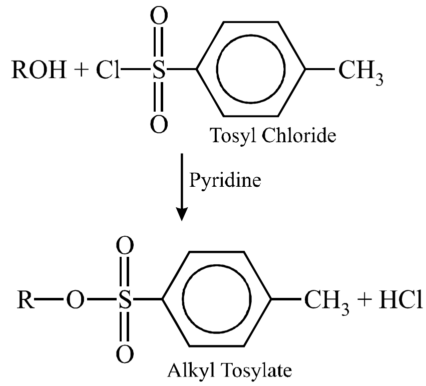
Fruity Smell

Esterification is catalyzed by an acid or base.

6.4 Tosylation

Tosylation is used to convert poor leaving group OH into good leaving group OTs.

Example - 15

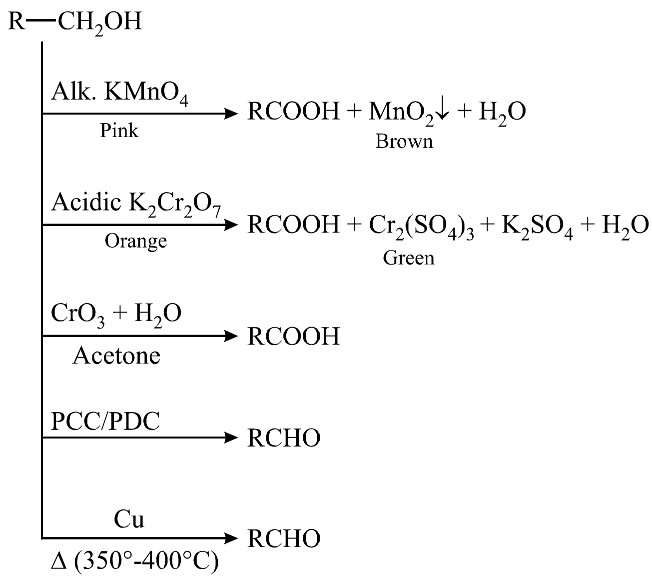


Example - 16

$$\underset{\text{Isopropyl Alcohol}}{(CH_3)_2CH\text{—}OH} \xrightarrow{\text{TsCl/Pyridine}} \underset{\text{Isopropyl Tosylatc}}{(CH_3)_2CH\text{—}OTs}$$

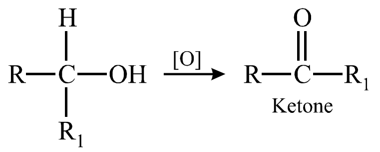
6.5 Oxidation

(a) Primary Alcohols



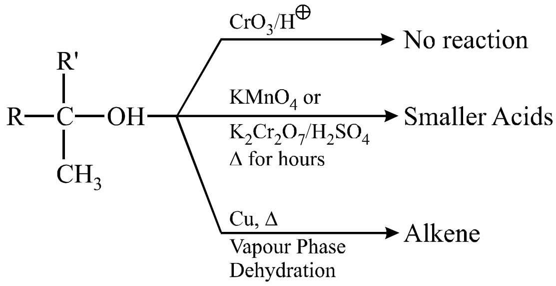
> **Note...** **Oxidation of Alcohols : Points to Remember**
>
> 1. Jones Reagent – CrO_3 + H_2O/Acetone
> 2. PCC – Pyridinium Chlorochromate
> 3. PDC – Pyridinium Dichromate
> 4. CrO_3/Pyridine in CH_2Cl_2–Collins Reagent.
> 5. Cr (VI) oxidizes primary alcohol to aldehyde in anhydrous/ non-aqueous state and to carboxylic acid otherwise.

(b) Secondary Alcohols



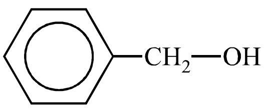
Secondary alcohol in the presence of any oxidising agent is oxidised to ketone.

(c) Tertiary Alcohols



MnO_2 is an oxidising agent which oxidises only allylic, benzylic & propargylic alcohols.

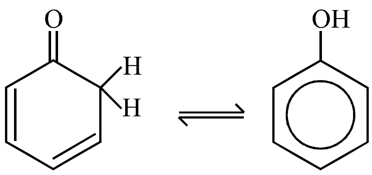
R—CH=CH—CH_2—OH Allylic Alcohol



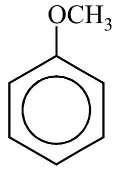
Benzylic Alcohol

R—C≡C—C—OH Propargylic Alcohol

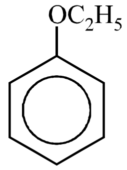
7. PHENOL



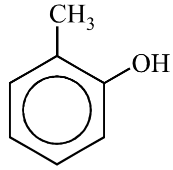
Common Phenols and Aromatic Ethers



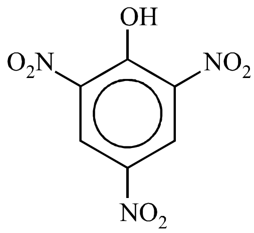
Anisole



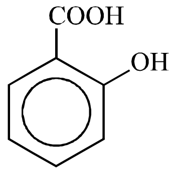
Phenetole



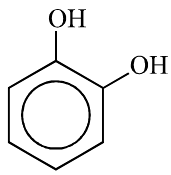
o-Cresol



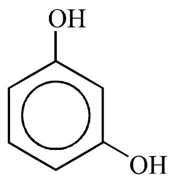
Picric Acid



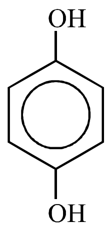
Salicylic Acid



Catechol

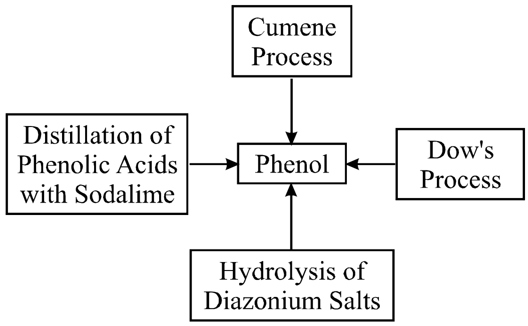


Resocinol



Hydroquinone

8. PREPARATION OF PHENOLS

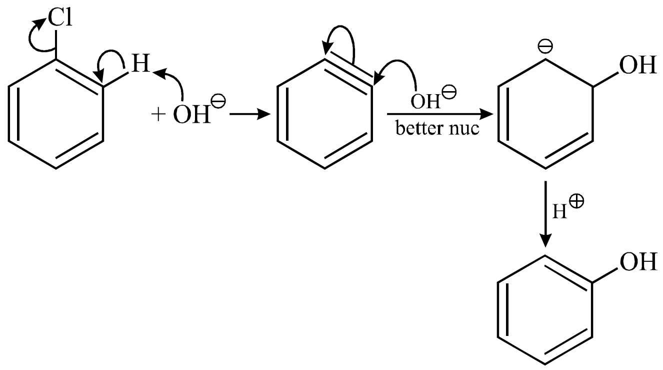


8.1 Dow's Process

This is industrial method for preparation of phenol. It occurs through Benzyne Mechanism.

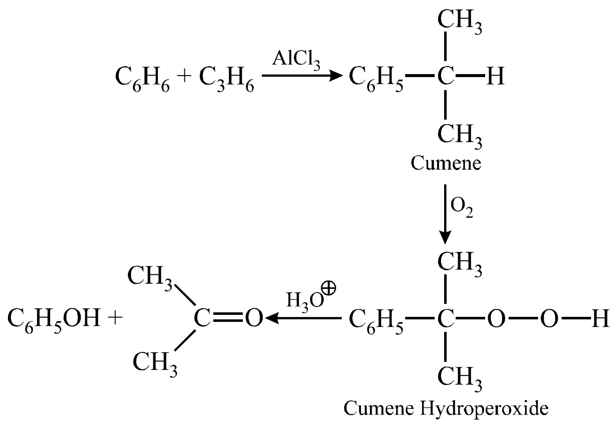
Example - 17

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



8.2 Cumene Process

Example - 18

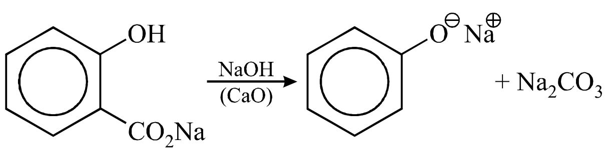


8.3 Hydrolysis of Diazonium Salts

$$ArN_2^{\oplus}HSO_4^{\ominus} + H_2O \longrightarrow ArOH + N_2 + H_2SO_4$$

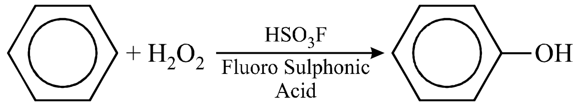
8.4 Distillation of Phenolic Acids with Sodalime

Example - 19



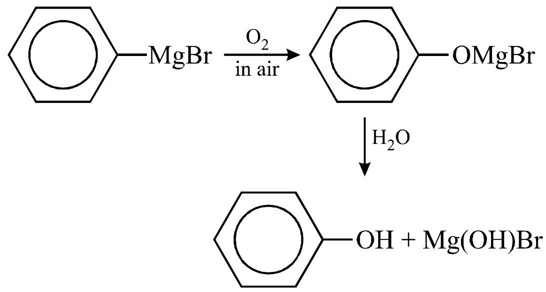
8.5 Benzene

Example - 20



8.6 Grignard Reagent

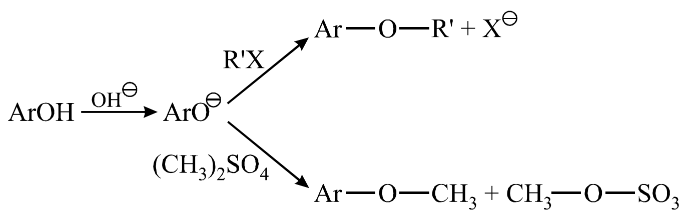
Example - 21



9. REACTIONS OF PHENOLS

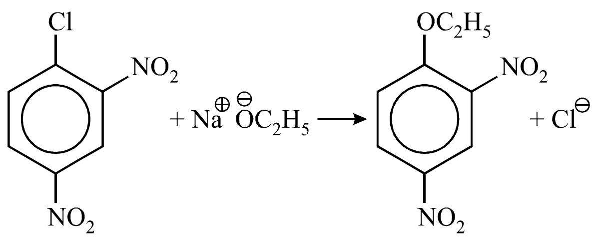
9.1 Formation of Ethers

(a) Williamson Synthesis



(b) Nucleophilic Aromatic Substitution

Example - 22



9.2 Formation of Esters

Example - 23

$$(CH_3CO)_2O + C_6H_5OH + NaOH$$
$$\downarrow$$
$$CH_3COOC_6H_5 + CH_3COO^{\ominus}Na^{\oplus} + H_2O$$

Phenyl Acetate

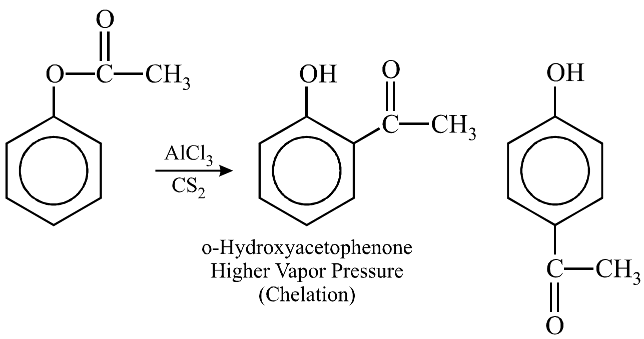
Example - 24

$$C_6H_5COCl + C_6H_5OH + NaOH$$
$$\downarrow$$
$$C_6H_5COOC_6H_5 + NaCl + H_2O$$

Phenyl Benzoate

9.3 Fries Rearrangement

Example - 25



o-Hydroxyacetophenone
Higher Vapor Pressure
(Chelation)

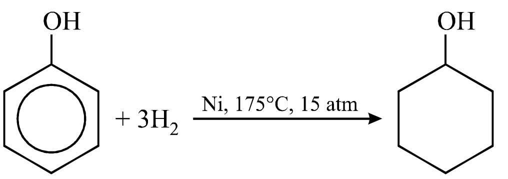
p-Hydroxyacetophenone

> **Note...** **Kinetic Control versus Thermodynamic Control**
>
> 1. Para isomer is the major product at 25°C. It has lower ΔH and is formed more rapidly (rate controlled product).
> 2. Ortho isomer is the chief product at 165°C (equilibrium controlled product).

9.4 Reactions of Benzene Ring

9.4.1 Hydrogenation

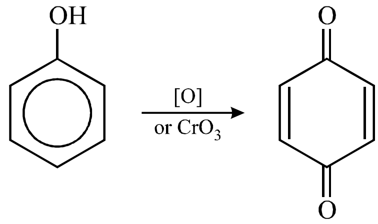
Example - 26



Cyclohexanol

9.4.2 Oxidation to Quinones

Example - 27

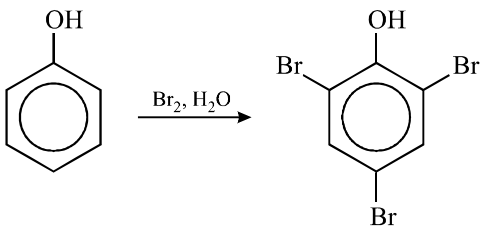


Quinone

9.4.3 Electrophilic Substitution

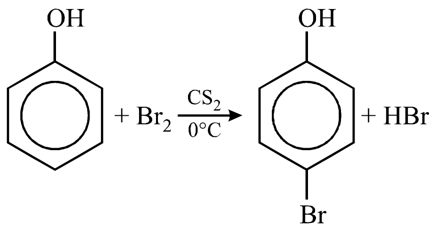
(a) Halogenation

Example - 28



2, 4, 6 - Tribromophenol

Example - 29

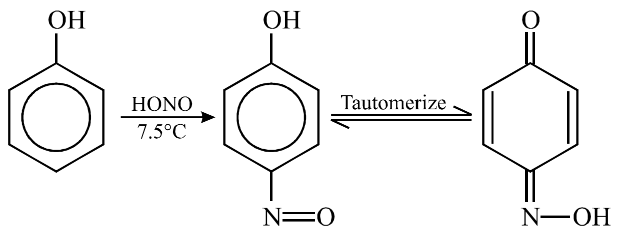


p-Bromophenol
(major)

> **Note...** Monobromination is achieved with non-polar solvents such as CS_2 to decrease the electrophilicity of Br_2 and also to minimize phenol ionization. In polar solvents such as water, phenol ionizes to phenoxide ion which is strongly activated and therefore, bromination takes place at all the activated positions.

(b) Nitrosation

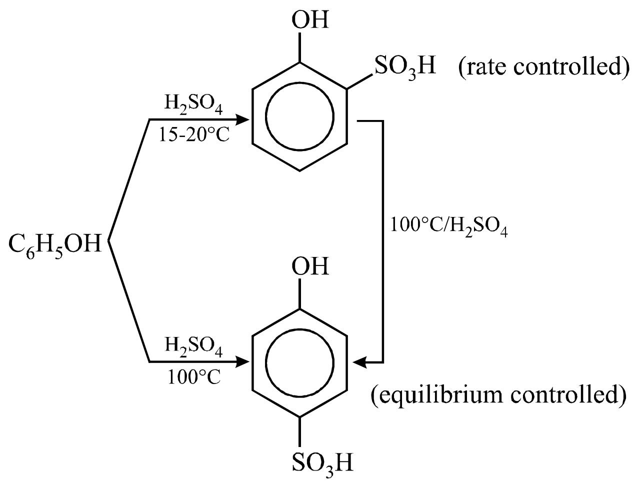
Example - 30



Quinone-Monoxime

(c) Sulphonation

Example - 31



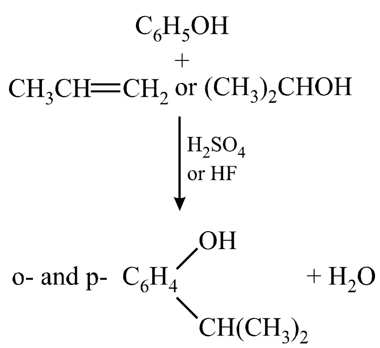
(d) Diazonium Salt Coupling - Azophenols

$$ArN_2^{\oplus} + C_6H_5G \longrightarrow p\text{-}G—C_6H_4—N{=}N—Ar$$

G is an electron releasing groups such as –OH, –OR, $–NR_2$, –NHR, $–NH_2$.

(e) Ring Alkylation

Example - 32



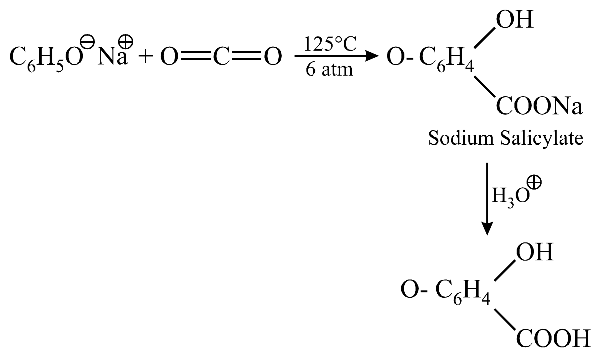
RX and $AlCl_3$ give poor yields because $AlCl_3$ co-ordinates with lone pair of oxygen.

(f) Ring Acylation

This is achieved using Fries Rearrangement.

(g) Kolbe's Synthesis

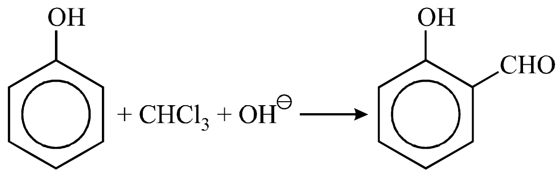
Example - 33



Salicylic Acid

(h) Riemer-Tiemann Synthesis of Phenolic Aldehydes

Example - 34

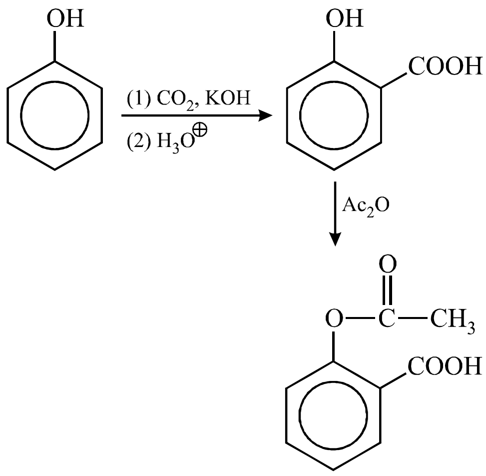


Salicylaldehyde

This reaction involves formation of carbene, CCl_2.

(i) Formation of Aspirin

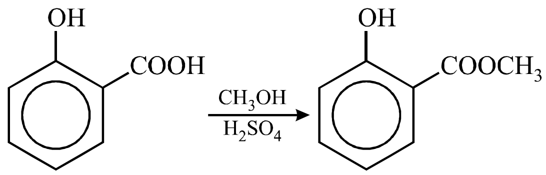
Example - 35



Acetylsalicylic Acid
(Aspirin)

(j) Formation of Oil of Wintergreen

Example - 36



Methyl Salicylate
(Oil of Wintergreen)

10. ETHERS

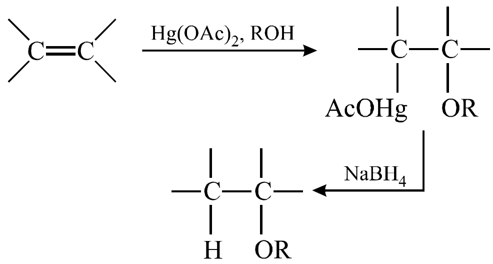
10.1 Williamson Ether Synthesis

$$R{-}\ddot{\underset{..}{O}}{:}^{\ominus} + R'{-}X \longrightarrow R{-}\ddot{\underset{..}{O}}{-}R' + \ddot{X}^{\ominus}$$

Note... **Substrate and Leaving Group in Williamson Synthesis**

1. Leaving group X = Cl, Br, I, OTs, etc.
2. Substrate - Alkyl group R′ must be primary.

10.2 Alkoxymercuration-Demercuration



This reaction follows Markovnikov orientation.

10.3 Bimolecular Dehydration of Alcohols

This reaction is an industrial method for synthesis of ethers.

$$\underset{1°}{2R{-}OH} \overset{H^{\oplus}}{\rightleftharpoons} R{-}O{-}R + H_2O$$

11. REACTIONS OF ETHERS

11.1 Cleavage by HBr and HI

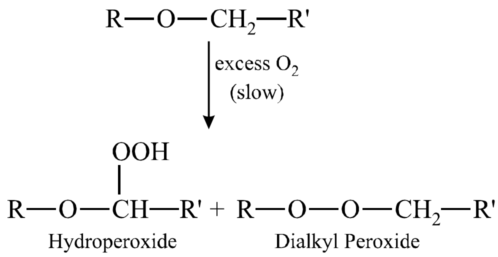
$$R{-}O{-}R' \xrightarrow[(X = Br,\ I)]{\text{excess HX}} R{-}X + R'{-}X$$

$$\underset{\text{Ar = Aromatic Ring}}{Ar{-}O{-}R} \xrightarrow[(X = Br,\ I)]{\text{Excess HX}} Ar{-}OH + R{-}X$$

Example - 37

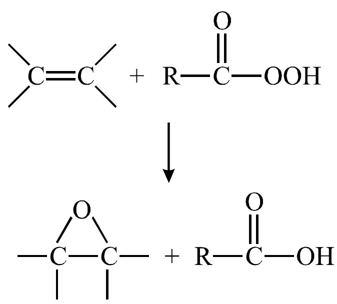
$$\underset{\text{Ethyl Methyl Ether}}{CH_3CH_2{-}O{-}CH_3} \xrightarrow{\text{Excess HI}} \underset{\text{Ethyl Iodide}}{CH_3CH_2I} + \underset{\text{Methyl Iodide}}{CH_3I}$$

11.2 Autoxidation

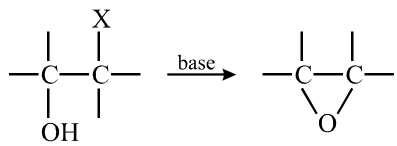


12. PREPARATION OF EPOXIDES

12.1 Peroxy Acid Epoxidation

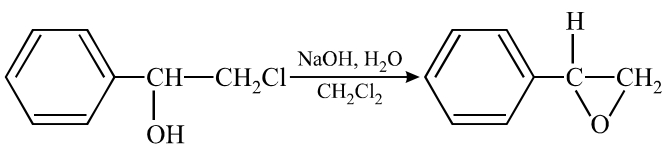


12.2 Base-promoted cyclization of halohydrins



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

Example - 38

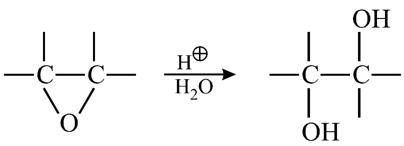


2-Chloro-1-Phenylethanol 2-Phenyloxirane

13. REACTIONS OF EPOXIDES

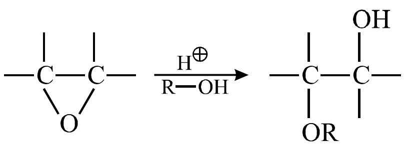
13.1 Acid-catalyzed Opening

(a) In water



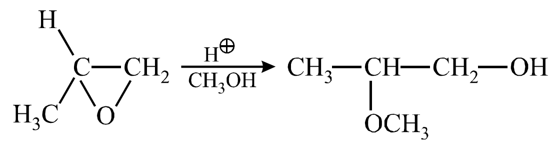
Anti stereochemistry is followed.

(b) In alcohols



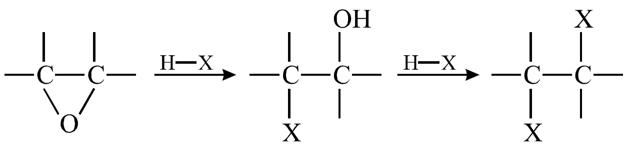
The alkoxy group bonds to the more highly substituted carbon.

Example - 39



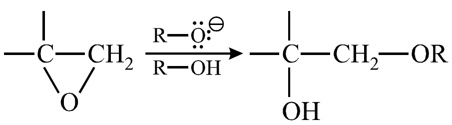
Methyl Oxirane (Propylene Oxide) — 2-Methoxy-propan-1-ol

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



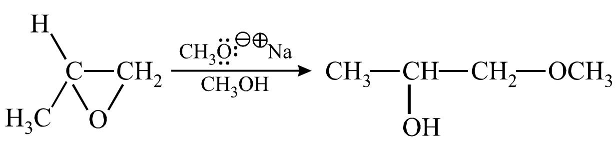
13.2 Base-catalyzed Opening

(a) With Alkoxides



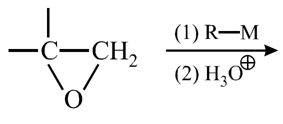
The alkoxy group bonds to the less highly substituted carbon.

Example - 40



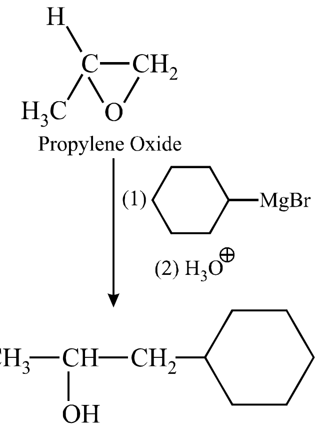
Propylene Oxide — 1-Methoxy-2-Propanol

(b) With Organometallics



M = Li or MgX — R bonds to the less substituted carbon

Example - 41



1-Cyclohexyl-2-Propanol

Note... **Opening of Epoxide Ring**

1. In acid catalyzed opening, nucleophile attacks on that epoxide carbon from which more stable carbocation can be made.
2. In base catalyzed opening, nucleophile attacks on the less hindered carbon.

14. ACIDIC STRENGTH

(i) Alcohols are weaker acids than thiols even though oxygen is more electronegative than sulphur. Conjugate base of alcohol i.e. RO^- is more basic than RS^- as in RO^- negative charge is placed on smaller oxygen atom so it will have more charge density. But in RS^- negative charge is dispersed on bigger sulphur so it is a poor base and its conjugate acid will be more acidic. Order of acidic strength of some of the compound are given as :

$$RSO_3H > RCOOH > Phenol > H_2O > ROH >$$

$$HC \equiv CH > NH_3 > CH_2 = CH_2 > CH_3 - CH_3$$

(ii) All alcohols (except CH_3OH) are weaker acids than H_2O due to +I effect of alkyl group. CH_3OH is slightly stronger than H_2O. Phenols are stronger than alcohol due to electron withdrawing benzene ring & resonance stabilized phenoxide ion. Alkoxide ions, the conjugate base of alcohol have no resonance so they are less stable and more basic. Phenol is weaker than carboxylic acid which have strong electron withdrawing carbonyl group and more stable resonating structures.

15. TESTS FOR ALCOHOLS, PHENOLS & ETHERS

15.1 Analysis of Alcohols – Characterization

(a) Alcohols dissolve in cold concentrated sulfuric acid. This property they share with alkenes, amines, practically all compounds containing oxygen, and easily sulfonated compounds. (Alcohols, like other oxygen-containing compounds, form oxonium salts which dissolve in the highly polar sulfuric acid.)

(b) Alcohols are not oxidized by cold dilute, neutral permanganate (although primary and secondary alcohols are oxidized by permanganate under more vigorous conditons.) However, as we have seen, alcohols often contain impurities that are oxidized under these conditions, and so the permanganate test must be interpreted with caution.

(c) Alcohols do not decolorize bromine in carbon tetrachloride. This property serves to distinguish them from alkenes and alkynes.

Alcohols are further distinguished from alkenes and alkynes and from nearly every other kind of compound by their oxidation by chromic anhydride (CrO_3) in aqueous sulfuric acids. Within two seconds, the clear orange solution turns blue-green and becomes opaque.

$$\underset{1° \text{ or } 2°}{ROH} + \underset{\text{Clear}}{HCrO_4} \longrightarrow \text{Opaque, blue-green}$$

Tertiary alcohols do not give this test. Aldehydes do, but are easily differentiated in other ways.

(d) Reactions of alcohols with sodium metal with the evolution of hydrogen gas is of some use in characterization. A wet compound of any kind, of course, will do the same thing, until the water is used up.

(e) The presence of the –OH group in a molecule is often indicated by the formation of an ester upon treatment with an acid chloride or anhydride. Some esters are sweet-smelling; others are solids and sharp melting points, and can be derivatives in identifications. If the molecular formulas of starting material and product are determined, it is possible to calculate how many –OH groups are present.

(f) Whether an alcohol is primary, secondary or tertiary is shown by the **Lucas test**, which is based upon the difference in reactivity of the three classes toward hydrogen halides. Alcohols (of not more than six carbons) are soluble in the Lucas reagent, a mixture of concentrated hydrochloric acid and zinc chloride. The corresponding alkyl chlorides are insoluble. Formation of a chloride from an alcohol is indicated by the cloudiness that appears when the chloride separates from the solution. Hence, the time required for cloudiness to appear is a measure of the reactivity of the alcohol.

A tertiary alcohol reacts immediately with the Lucas reagent, and a secondary alcohol reacts within five minutes. A primary alcohol does not react appreciably at room temperature. Benzyl alcohol and allyl alcohol react as rapidly as teritary alcohols with the Lucas reagent. Allyl chloride, however, is soluble in the reagent.

(g) Whether or not an alcohol contains one particular structural unit is shown by the **iodoform test**. The alcohol is treated with iodine and sodium hydroxide (sodium hypoiodite, NaOI). An alcohol of the structure yields a yellow precipitate of iodoform (CHI_3 m.p. 119°).

$$R—CH(OH)—CH_3 \qquad R = H/R/Ar$$

Positive Iodoform Test	Negative Iodoform Test
$CH_3—CH(OH)—H$	Any other primary alcohol
$CH_3—CH(OH)—CH_3$	$CH_3—CH(OH)—CH_3$
$CH_3—CH(OH)—CH_2CH_2CH_3$	$CH_3CH_2—CH(OH)—CH_2CH_3$
$C_6H_5—CH(OH)—CH_3$	$C_6H_5—CH_2—CH_2OH$

The reaction involves oxidation, halogenation and cleavage.

$$R—CH(OH)—CH_3 + NaOI \longrightarrow R—C(=O)—CH_3 + NaI + H_2O$$

$$R—C(=O)—CH_3 + 3NaOI \longrightarrow R—C(=O)—CI_3 + 3NaOH$$

$$R—C(=O)—CI_3 + NaOH \longrightarrow RCOO^{\ominus}Na^{\oplus} + \underset{\text{Yellow Precipitate}}{CHI_3}$$

As would be expected from the equations, a compound of structure also gives a positive test.

$$R—C(=O)—CH_3 \qquad R = H/Alkyl/Aryl$$

In certain special cases this reaction is used not as a test, but to synthesize the carboxylic acid, RCOOH. Here, hypobromite or the cheaper hypochlorite would probably be used.

15.2 Analysis of Glycols, Periodic Acid Oxidation

Upon treatment with periodic acid, HIO_4, compounds containing two or more –OH or C=O groups attached to adjacent carbon atoms undergo oxidation with cleavage of carbon-carbon bonds.

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

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

15.3 Miscellaneous Tests

(a) **Ceric Ammonium Nitrate Test -** Alcohols give red colour with this reagent.

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

(b) **Potassium Dichromate Test -** Alcohols turn orange dichromate to green. Tertiary Alcohol do not give this test.

(c) **Ester Test -** Alcohol gives fruity smell of ester with carboxylic acid.

(d) Methanol forms oil of winter green with salicylic acid.

15.4 Victor Meyer's Test

1° Alcohol	2° Alcohol	3° Alcohol
RCH_2OH	R_2CHOH	R_3C-OH
$\downarrow P + I_2$	$\downarrow P + I_2$	$\downarrow P + I_2$
RCH_2I	R_2CH-I	R_3C-I
$\downarrow AgNO_2$	$\downarrow AgNO_2$	$\downarrow AgNO_2$
RCH_2-NO_2	R_2CH-NO_2	R_3C-NO_2
$\downarrow$ HONO	$\downarrow$ HONO	$\downarrow$ HONO
$R-C(=N-OH)-NO_2$ Nitrolic acid	$R_2C(N=O)-NO_2$ Pseudonitrol	No Reaction
$\downarrow$ NaOH	$\downarrow$ NaOH	$\downarrow$ NaOH
Blood Red Colour	Blue Colour	Colourless

15.5 Differentiation Tests

15.5.1 Alcohols and Phenols

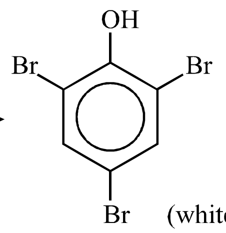
1. **Litmus Test :** Phenol turns blue litmus red but not alcohols.
2. **$FeCl_3$:** Phenol $\xrightarrow{\text{Neutral } FeCl_3}$ Blue-Violet
3. **Coupling reaction :**

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

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

4. **Bromine Water Test :**

Phenol + Br_2 $\xrightarrow{H_2O}$



(white ppt.)

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

15.5.2 Alcohols and Ethers

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

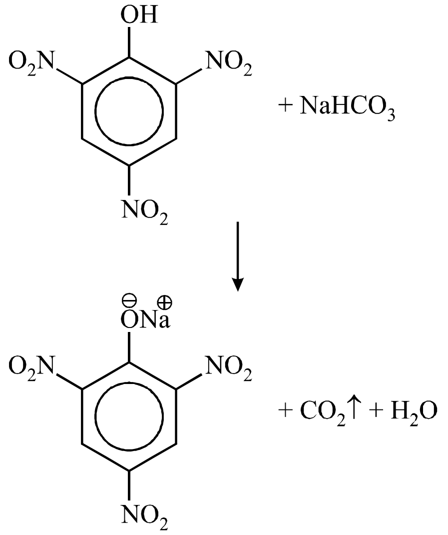
(b) Alcohols give fumes of HCl with PCl_5 but not ethers.

15.5.3 Sodium Bicarbonate Test

Phenol, ROH and H_2O do not displace CO_2 from carbonate & bicarbonates but RCOOH & RSO_3H gives brisk effervescence of CO_2 which proves that RCOOH & RSO_3H are stronger acids H_2CO_3 but phenol is weaker acid than H_2CO_3. Nitrophenols also give effervescence of CO_2 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.

$$RCOOH + NaHCO_3 \longrightarrow RCO\overset{\ominus}{O}\overset{\oplus}{Na} + CO_2\uparrow + H_2O$$

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



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.

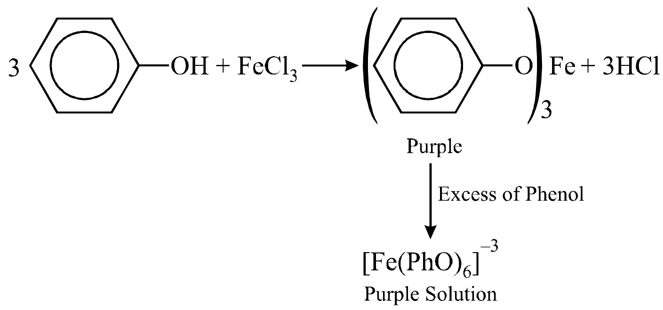


Table 1 : Physical Properties of Selected Alcohols

IUPAC Name	Common Name	Formula	MP(°C)	BP(°C)	Density
methanol	methyl alcohol	CH_3OH	– 97	65	0.79
ethanol	ethyl alcohol	CH_3CH_2OH	– 114	78	0.79
1-propanol	n-propyl alcohol	$CH_3CH_2CH_2OH$	– 126	97	0.80
2-propanol	isopropyl alcohol	$(CH_3)_2CHOH$	– 89	82	0.79
1-butanol	n-butyl alcohol	$CH_3(CH_2)_3OH$	– 90	118	0.81
2-butanol	sec-butyl alcohol	$CH_3CH(OH)CH_2CH_3$	– 114	100	0.81
2-methyl-1-propanol	isobutyl alcohol	$(CH_3)_2CHCH_2OH$	– 108	108	0.80
2-methyl-2-propanol	t-butyl alcohol	$(CH_3)_3COH$	25	83	0.79
1-pentanol	n-pentyl alcohol	$CH_3(CH_2)_4OH$	– 79	138	0.82
3-methyl-1-butanol	isopentyl alcohol	$(CH_3)_2CHCH_2CH_2OH$	– 117	132	0.81
2, 2-dimethyl -1-propanol	neopentyl alcohol	$(CH_3)_3CCH_2OH$	52	113	0.81
cyclopentanol	cyclopentyl alcohol	cyclo-C_5H_9OH	– 19	141	0.95
1-hexanol	n-hexanol	$CH_3(CH_2)_5OH$	– 52	156	0.82
cyclohexanol	cyclohexyl alcohol	cyclo-$C_6H_{11}OH$	25	162	0.96
1-heptanol	n-heptyl alcohol	$CH_3(CH_2)_6OH$	– 34	176	0.82
1-octanol	n-octyl alcohol	$CH_3(CH_2)_7OH$	– 16	194	0.83
1-nonanol	n-nonyl alcohol	$CH_3(CH_2)_8OH$	– 6	214	0.83
1-decanol	n-decyl alcohol	$CH_3(CH_2)_9OH$	6	233	0.83
2-propen-1-ol	allyl alcohol	$H_2C{=}CH{-}CH_2OH$	– 129	97	0.86
phenylmethanol	benzyl alcohol	$Ph{-}CH_2OH$	– 15	205	1.05
diphenylmethanol	diphenylcarbinol	Ph_2CHOH	69	298	
triphenylmethahnol	triphenylcarbinol	Ph_3COH	162	380	1.20
1, 2-ethanediol	ethylene glycol	$HOCH_2CH_2OH$	– 13	198	1.12
1, 2-propanediol	propylene glycol	$CH_3CH(OH)CH_2OH$	– 59	188	1.04
1, 2, 3-propanetriol	glycerol	$HOCH_2CH(OH)CH_2OH$	18	290	1.26

Table 2 : Physical Properties of Some Representative Ethers

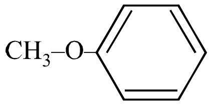
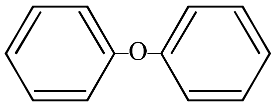
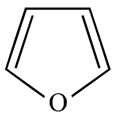
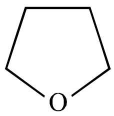
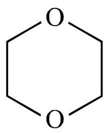
Name	Structure	MP(°C)	BP(°C)	Density (g/mL)
dimethyl ether	CH_3–O–CH_3	– 140	– 25	0.66
ethyl methyl ether	CH_3CH_2–O–CH_3		8	0.72
diethyl ether	CH_3CH_2–O–CH_2CH_3	– 116	35	0.71
di-n-propyl ether	$CH_3CH_2CH_2$–O–$CH_2CH_2CH_3$	– 122	91	0.74
diisopropyl ether	$(CH_3)_2CH$–O–$CH(CH_3)_2$	– 86	68	0.74
1, 2-dimethoxyethane (DME)	CH_3–O–CH_2CH_2–O–CH_3	– 58	83	0.86
methyl phenyl ether (anisole)		– 37	154	0.99
diphenyl ether		27	259	1.07
furan		–86	32	0.94
tetrahydrofuran (THF)		–108	65	0.89
1, 4-dioxane		11	101	1.03

Table 3 : Comparison of the Boiling Points of Ethers, Alkanes and Alcohols of Similar Molecular Weights

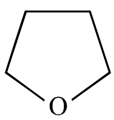
Compound	Formula	MW	BP(°C)	Dipole Moment (D)
water	H_2O	18	100	1.9
ethanol	CH_3CH_2–OH	46	78	1.7
dimethyl ether	CH_3–O–CH_3	46	– 25	1.3
propane	$CH_3CH_2CH_3$	44	– 42	0.1
n-butanol	$CH_3CH_2CH_2CH_2$–OH	74	118	1.7
tetrahydrofuran		72	65	1.63
diethyl ether	CH_3CH_2–O–CH_2CH_3	74	35	1.2
pentane	$CH_3CH_2CH_2CH_2CH_3$	72	36	0.1

Table 4 : Solubility of Alcohols in Water (at 25°C)

Alcohol	Solubility in Water
methyl	miscible
ethyl	miscible
n-propyl	miscible
t-butyl	miscible
isobutyl	10.0%
n-butyl	9.1%
n-pentyl	2.7%
cyclohexyl	3.6%
n-hexyl	0.6%
phenol	9.3%
hexane-1, 6-diol	miscible

Table 5 : Acid-Dissociation Constants of Representative Alcohols

Alcohol	Structure	K_a	pK_a
methanol	CH_3–OH	3.2×10^{-16}	15.5
ethanol	CH_3CH_2–OH	1.3×10^{-16}	15.9
2-chloroethanol	Cl–CH_2CH_2–OH	5.0×10^{-15}	14.3
isopropyl alcohol	$(CH_3)_2$CH–OH	3.2×10^{-17}	16.5
t-butyl alcohol	$(CH_3)_3$C–OH	1.0×10^{-18}	18.0
cyclohexanol	C_6H_{11}–OH	1.0×10^{-18}	18.0
phenol	C_6H_5–OH	1.0×10^{-10}	10.0
Comparison with other Acids			
water	H_2O	1.8×10^{-16}	15.7
acetic acid	CH_3COOH	1.6×10^{-5}	4.8
hydrochloric acid	HCl	$1.6 \times 10^{+2}$	– 2.2