ALCOHOL, ETHER & PHENOL

HYDROXY DERIVATIVES

Hydroxy derivatives
↓
Aliphatic hydroxy derivatives | Aromatic hydroxy derivatives

Aliphatic Hydroxy Derivatives

Hydroxy derivatives in which —OH is directly attached to sp^3 'C' (Alcoholic compounds).

Aromatic Hydroxy Derivatives

Hydroxy derivatives in which —OH is directly attached to sp^2 'C' or benzene ring (Phenolic compounds).

Aliphatic hydroxy derivatives :

(a) Classification according to number of —OH groups :

(i) Monohydric [one –OH] ⟶ CH_3CH_2—OH

(ii) Dihydric [two –OH] ⟶ $CH_2(OH)-CH_2(OH)$

(iii) Trihydric [three –OH] ⟶ $CH_2(OH)-CH(OH)-CH_2(OH)$

(iv) Polyhydric [n –OH] ⟶ $CH_2(OH)-CH(OH)-CH(OH)-CH(OH)-CH(OH)-CH_2(OH)$

(b) Classification according to nature of carbon :

(i) p or 1° – alcohol ⟶ CH_3CH_2-OH

(ii) s or 2° – alcohol ⟶ $(CH_3)_2CH-OH$

(iii) t or 3° – alcohol ⟶ $(CH_3)_3C-OH$

6.1 MONOHYDRIC ALCOHOL

6.1.1 General Methods of Preparation

(i) From alkanes (By oxidation):

$$(CH_3)_3\,C—H \xrightarrow[\Delta]{H^{\oplus}/KMnO_4} (CH_3)_3\,C—OH$$

(ii) From alkenes :

(a) By hydration :

$$CH_3—CH{=}CH_2 \xrightarrow[H_2O]{H^{\oplus}} CH_3-CH(OH)-CH_3$$

(b) By hydroboration oxidation :

$$CH_3—CH{=}CH_2 \xrightarrow[(2)\,H_2O_2/HO^{\ominus}]{(1)\,BH_3,THF} CH_3-CH_2-CH_2(OH) \quad (1°\text{ alcohol})$$

(c) By oxymercuration demercuration :

$$CH_3—CH{=}CH_2 \xrightarrow[(ii)\,NaBH_4]{(i)\,Hg(OAc)_2,H_2O} CH_3-CH(OH)-CH_3$$

(iii) From alkyl halides (By hydrolysis) :

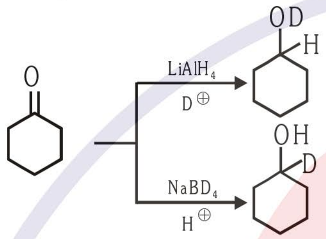
$$CH_3-CH_2-Cl \xrightarrow[\text{or Moist } Ag_2O]{\text{Aq. KOH}} CH_3CH_2-OH$$

(iv) From carbonyl compounds (By reduction) :

$$>C=O \xrightarrow{\text{Reducing agent}} >CH-OH$$

$$R-CHO \xrightarrow[H^{\oplus}]{LiAlH_4} R-CH_2-OH$$

$$R-\underset{\underset{O}{\|}}{C}-R \xrightarrow[H^{\oplus}]{NaBH_4} R-\underset{\underset{OH}{|}}{CH}-R$$



$$CH_3-CH=CH-CHO \xrightarrow[H^{\oplus}]{LiAlH_4} CH_3-CH=CH-CH_2-OH$$

Crotonaldehyde

(v) From ethers :

$$R-O-R \xrightarrow{dil.H_2SO_4} R-OH + R-OH$$

$$CH_3-O-CH_2CH_3 \xrightarrow{dil.H_2SO_4} CH_3-OH + CH_3CH_2-OH$$

(vi) From acid and derivatives (By reduction) :

$$R-COOH \xrightarrow[H^{\oplus}]{LiAlH_4} R-CH_2-OH + H_2O$$

$$R-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow[H^{\oplus}]{LiAlH_4} R-CH_2-OH + HCl$$

$$R-\underset{\underset{O}{\|}}{C}-OR \xrightarrow[H^{\oplus}]{LiAlH_4} R-CH_2-OH + R-OH$$

$$R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R \xrightarrow[H^{\oplus}]{LiAlH_4} R-CH_2-OH + R-CH_2-OH$$

Note : Amide on reduction gives amine not alcohol.

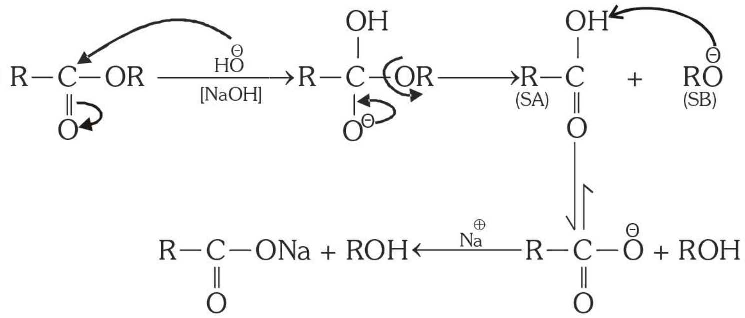
$$R-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow[H^{\oplus}]{LiAlH_4} R-CH_2-NH_2 + H_2O$$

(vii) From esters (By hydrolysis) :

(a) By alkaline hydrolysis :

$$R-\underset{\underset{O}{\|}}{C}-OR \xrightarrow{NaOH} R-\underset{\underset{O}{\|}}{C}-ONa + R-OH$$

Mechanism :



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5 \xrightarrow{NaOH} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-ONa + C_2H_5OH$$

Hydrolysis is Nucleophilic substitution reaction (NSR) and Order of reaction is 2. Alkaline hydrolysis is also called as saponification

$$Ph—COOC_2H_5 \xrightarrow{HO^{\ominus}} Ph—COO^{\ominus} + C_2H_5OH$$

(b) By acidic hydrolysis :

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR \underset{H_2O(excess)}{\overset{\overset{\oplus}{H}}{\rightleftharpoons}} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + R-OH$$

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{18}{O}C_2H_5 \overset{H_3\overset{\oplus}{O}}{\rightleftharpoons} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + C_2H_5\overset{18}{O}H$$

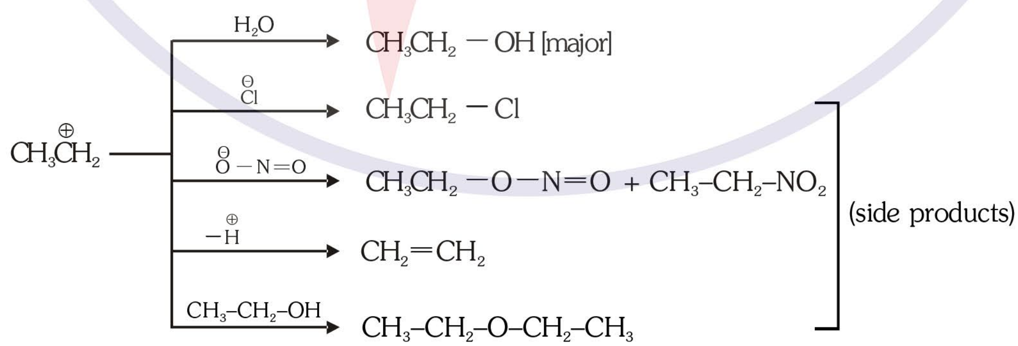
(viii) From p-amines :

$$R—NH_2 \xrightarrow[\text{or } HNO_2]{NaNO_2+HCl(aq.)} R—OH + N_2$$

$$CH_3CH_2—NH_2 \xrightarrow{HNO_2} CH_3CH_2—OH + N_2$$

Mechanism :

$$CH_3CH_2-NH_2 \xrightarrow{NaNO_2+HCl} \underset{\text{(Unstable)}}{CH_3CH_2-\overset{\oplus}{N_2}\overset{\ominus}{Cl}} \longrightarrow CH_3\overset{\oplus}{CH_2} + N_2 + \overset{\ominus}{Cl}$$



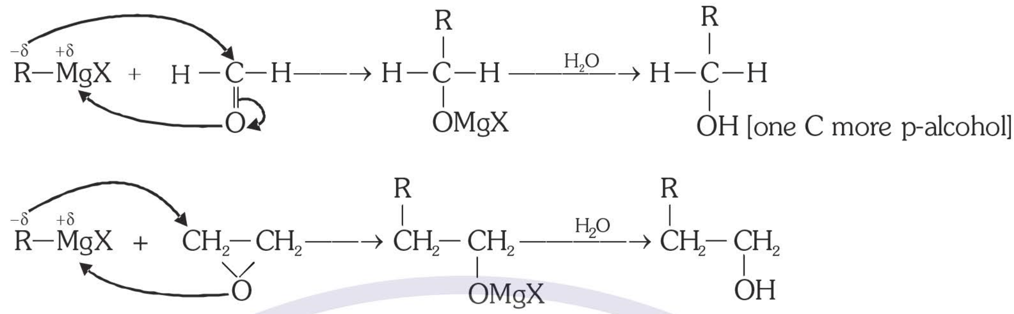
Intermediate is carbocation so rearrangement may be possible.

(ix) From Grignard reagent :

(a) p-alcohol :

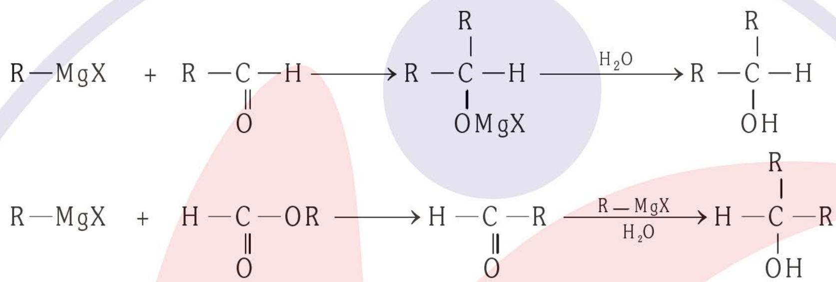
$$R{-}MgX + [O] \longrightarrow R{-}O{-}MgX \xrightarrow{H_2O} R{-}OH$$

[Same C-p-alcohol]

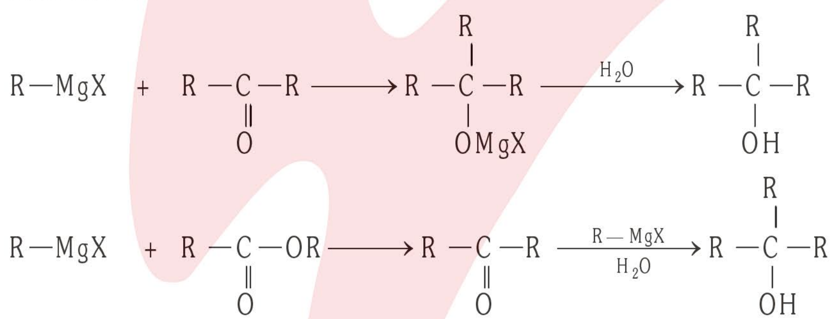


[two C more p-alcohol]

(b) s-alcohol :



(c) t-alcohol :



6.1.2 Physical properties :

(i) C_1 to C_{11} are colourless liquids and higher alcohols are solids.

(ii) Density of monohydric alcohol is less than H_2O.

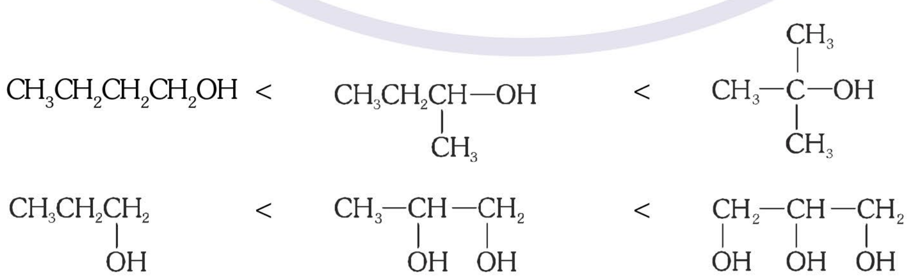
(iii) Density $\propto$ mol. wt. (for monohydric alcohol).

(iv) **Solubility :** C_1 to C_3 and t-butyl alcohol is completely soluble in H_2O due to H–bonding.

$$\text{solubility} \propto \frac{\text{No. of side chains}}{\text{molecular weight}}$$

Order of solubility :

$C_4H_9OH > C_5H_{11}OH > C_6H_{13}OH$



[Number of OH increases, H-bonding increases]

(v) **Boiling points :** $BP \propto \frac{\text{molecular weight}}{\text{No.of side chains}}$

Orber of BP : $C_4H_9OH < C_5H_{11}OH < C_6H_{13}OH$

$CH_3CH_2CH_2CH_2OH > CH_3CH_2CH(CH_3)-OH > (CH_3)_3C-OH$

$CH_3CH_2CH_2(OH) < CH_3-CH(OH)-CH_2(OH) < CH_2(OH)-CH(OH)-CH_2(OH)$

[Number of OH increases, H-bonding increases]

6.1.3 Chemical Properties

Monohydric alcohol shows following reactions

(A) Reaction involving cleavage of O ┼ H

(B) Reaction involving cleavage of C ┼ OH

(C) Reaction involving complete molecule of alcohol

(A) Reaction involving cleavage of O ┼ H : Reactivity order (Acidic nature) is

$CH_3-OH > CH_3CH_2-OH > (CH_3)_2CH-OH > (CH_3)_3C-OH$

(i) Acidic nature :

$H_2O > R-OH > CH\equiv CH > NH_3$ (Acidic strength)

Alcohols are less acidic than H_2O and neutral for litmus paper and give H_2 with active metals (Na, K)

$$R-OH + Na \longrightarrow R-ONa + \frac{1}{2}H_2$$

$$R-OH + K \longrightarrow R-OK + \frac{1}{2}H_2$$

(ii) Alkylation:

$$R-OH \xrightarrow{CH_2N_2/\Delta} R-O-CH_2-H$$

$$R-OH \xrightarrow{Na} R-ONa \xrightarrow{R-X} R-O-R$$

(Williamson synthesis)

(iii) Acylation :

$$R-OH + Cl-\underset{\underset{O}{\|}}{C}-R \longrightarrow R-O-\underset{\underset{O}{\|}}{C}-R$$

(Acylation)

$$R-OH + Cl-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow R-O-\underset{\underset{O}{\|}}{C}-CH_3$$

(Acetylation)

Salicylic acid

Acetoxy benzoic acid

Acetyl salicylic acid

Aspirin [Used as analgesic and antipyretic]

(iv) Benzoylation : (Schotten Baumann's Reaction) :

$$R-OH + Cl-\underset{\underset{O}{\|}}{C}-Ph \longrightarrow R-O-\underset{\underset{O}{\|}}{C}-Ph$$

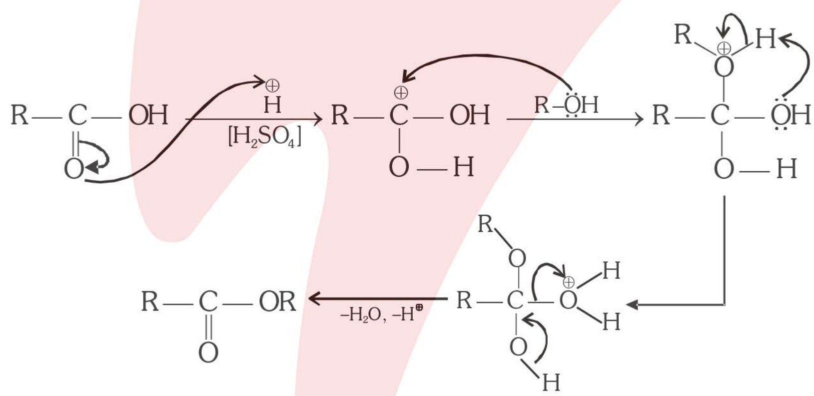
(Benzoylation)

(v) Esterification :

$$R-\underset{\underset{O}{\|}}{C}-OH + R-OH \xrightarrow[\Delta]{\text{conc. } H_2SO_4} R-\underset{\underset{O}{\|}}{C}-OR + H_2O$$

Conc. H_2SO_4 is used as catalyst and dehydrating agent.

Mechanism :



Ex. $CH_3-\underset{\underset{O}{\|}}{C}-\boxed{OH + H}-OC_2H_5 \xrightarrow[\Delta]{\text{conc. } H_2SO_4} CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5 + H_2O$

Ex. $Ph-\underset{\underset{O}{\|}}{C}-\boxed{OH + H}-\overset{18}{O}C_2H_5 \xrightarrow{\text{conc. } H_2SO_4} Ph-\underset{\underset{O}{\|}}{C}-\overset{18}{O}C_2H_5 + H_2O$

Dry HCl can also be used as dehydrating agent.

Ex. $CH_3-\underset{\underset{O}{\|}}{C}-\boxed{OH + H}-OC_2H_5 \xrightarrow[\Delta]{\text{dry HCl}} CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5 + H_2O$

(vi) Reaction with CH≡CH :

$$CH\equiv CH + 2CH_3—OH \xrightarrow[\Delta]{BF_3/HgO} CH_3CH\langle^{OCH_3}_{OCH_3}$$

Methylal

$$CH\equiv CH + 2CH_3CH_2—OH \xrightarrow[\Delta]{BF_3/HgO} CH_3CH\langle^{OC_2H_5}_{OC_2H_5}$$

Ethylal

(vii) Reaction with carbonyl compounds :

$$R—CHO + 2R—OH \xrightarrow{H^{\oplus}} R-CH\langle^{OR}_{OR}$$

Acetal

$$R-\underset{\underset{O}{\|}}{C}-R + 2R-OH \xrightarrow{H^{\oplus}} {}^{R}_{R}\rangle C\langle^{OR}_{OR}$$

Ketal

$$CH_3CHO + 2CH_3—OH \xrightarrow{H^{\oplus}} CH_3CH\langle^{OCH_3}_{OCH_3}$$

(viii) Reaction with Grignard reagent :

$$R—MgX + H—OR \longrightarrow R-H + Mg\langle^{X}_{OR}$$

(B) Reaction involving cleavage of C┼OH : Reactivity order or basic nature is

$$CH_3—OH < CH_3CH_2—OH < (CH_3)_2CH—OH < (CH_3)_3C—OH$$

(i) Reaction with halogen acid :

$$R—CH_2—OH + HCl \xrightarrow[\Delta]{ZnCl_2} R—CH_2—Cl + H_2O$$

Reactivity order of the acids is HI > HBr > HCl

(ii) Reaction with phosphorous halides :

$$3R—OH + PCl_3 \longrightarrow 3RCl + H_3PO_3$$

$$R—OH + PCl_5 \longrightarrow R—Cl + POCl_3 + HCl$$

(iii) Reaction with thionyl chloride ($SOCl_2$) :

$$R—OH + SOCl_2 \xrightarrow{Pyridine} R—Cl + \underset{(gas)}{SO_2\uparrow} + HCl$$

(iv) Reaction with NH_3 : Alumina (Al_2O_3) is used as dehydrating agent.

$$R\boxed{OH + H}NH_2 \xrightarrow[250^\circ C]{Al_2O_3} R—NH_2 + H_2O$$

(C) Reaction involving complete molecule of alcohol :

(i) Dehydration : Removal of H_2O

(a) Intermolecularly removal of H_2O [formation of ether]

(b) Intramolecularly removal of H_2O [formation of alkene]

$$C_2H_5{-}OH + \underset{\text{(conc.)}}{H_2SO_4} \xrightarrow{140^\circ C} C_2H_5{-}O{-}C_2H_5 \text{ (Williamson's continuous etherification)}$$

$$C_2H_5{-}OH + \underset{\text{(conc.)}}{H_2SO_4} \xrightarrow{170^\circ C} CH_2{=}CH_2 \text{ (Elimination)}$$

$$C_2H_5OH + \underset{\text{(Alumina)}}{Al_2O_3} \xrightarrow{250^\circ C} C_2H_5{-}O{-}C_2H_5$$

$$C_2H_5OH + \underset{\text{(Alumina)}}{Al_2O_3} \xrightarrow{350^\circ C} CH_2{=}CH_2$$

Ease of dehydration follows the order : **3° ROH > 2° ROH > 1° ROH**

(ii) Catalytic Dehydrogenation :

$$\underset{\text{(p- alcohol)}}{CH_3CH_2OH} \xrightarrow[300^\circ C]{Cu} \underset{\text{(Acetaldehyde)}}{CH_3CHO} + H_2$$

$$\underset{\text{(s- alcohol)}}{CH_3{-}\underset{\displaystyle OH}{\underset{|}{C}H}{-}CH_3} \xrightarrow[300^\circ C]{Cu} \underset{\text{(acetone)}}{CH_3{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}CH_3} + H_2$$

$$\underset{\text{(t–alcohol)}}{CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}OH} \xrightarrow[300^\circ C]{Cu} \underset{\text{(Iso - butylene)}}{CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2} + H_2O \text{ [dehydration]}$$

(iii) Oxidation :

$$\underset{\text{(p-alcohol)}}{R{-}CH_2{-}OH} \xrightarrow[H^{\oplus}/K_2Cr_2O_7]{H^{\oplus}/KMnO_4 \text{ or}} RCHO \xrightarrow[\text{Room temp.}]{[O]} \underset{\text{(same carbon acid)}}{RCOOH}$$

$$\underset{\text{(s-alcochol)}}{R{-}\underset{\displaystyle OH}{\underset{|}{C}H}{-}R'} \xrightarrow[H^{\oplus}/K_2Cr_2O_7]{H^{\oplus}/KMnO_4 \text{ or}} \underset{\text{(same carbon)}}{R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}R'}$$

$$R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}R' \xrightarrow[\text{Room temp.}]{H^{\oplus}/KMnO_4,\ [O]} \text{No reaction}$$

$$R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}R' \xrightarrow[\text{high temp.}]{H^{\oplus}/KMnO_4} \text{Acids (less carbon)}$$

$$\underset{\text{(t-alcohol)}}{R{-}\overset{\displaystyle R}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}{-}R} \xrightarrow[\text{Room temp.}]{[O]} \text{No reaction}$$

$$\underset{\text{(t-alcohol)}}{R{-}\overset{\displaystyle R}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}{-}R} \xrightarrow{\text{high temp.}} \text{Acids (less carbon)}$$

$$CH_3CH_2{-}\underset{\displaystyle OH}{\underset{|}{C}H}{-}CH_3 \xrightarrow[\text{high temp.}]{[O]} CH_3CH_2{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}CH_3 \xrightarrow{[O]} CH_3COOH + CH_3COOH$$

Carbonyl group goes with smaller alkyl group [Popoff's rule suggested for oxidation of unsymmetrical ketones]

(iv) Distinction between 1°, 2° and 3° alcohols :

(a) Lucas test : A mixture of HCl(conc.) and anhydrous $ZnCl_2$ is called Lucas reagent.

p-alcohol $\xrightarrow{ZnCl_2 + HCl}$ No turbidity at room temp. [On heating within 30 minutes.]

s-alcohol $\xrightarrow{ZnCl_2 + HCl}$ Turbidity appears within 5 minutes.

t-alcohol $\xrightarrow{ZnCl_2 + HCl}$ Turbidity appears within 2-3 sec.

(b) Victor - Meyer test :

p-alcohol $\longrightarrow$ Red colour

s-alcohol $\longrightarrow$ Blue colour

t-alcohol $\longrightarrow$ No colour

$R{-}CH_2{-}OH$ [1°]	$R_2CH{-}OH$ [2°]	$R_3C{-}OH$ [3°]
$\downarrow P + I_2$	$\downarrow P + I_2$	$\downarrow P + I_2$
$R{-}CH_2{-}I$	$R_2CH{-}I$	$R_3C{-}I$
$\downarrow AgNO_2$	$\downarrow AgNO_2$	$\downarrow AgNO_2$
$RCH_2{-}NO_2$	$R_2CH{-}NO_2$	$R_3C{-}NO_2$
$\downarrow HNO_2$	$\downarrow HNO_2$	$\downarrow HNO_2$
$R{-}C({=}N{-}OH){-}NO_2$	$R_2C(N{=}O){-}NO_2$	No reaction
Nitrolic acid (blue)	Pseudonitrol (blue)	Colourless
$\downarrow NaOH$	$\downarrow NaOH$	
Sodium nitrolate (Red)	No reaction (Remains blue)	

(C) Dichromate test :

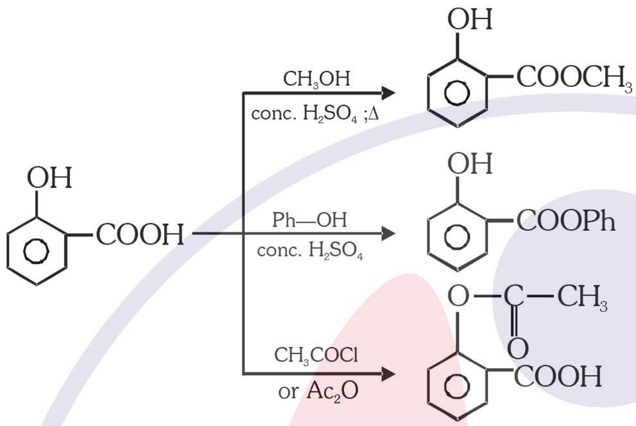
1° Alcohol $\xrightarrow[\text{orange }[Cr^{+6}]]{H^{\oplus}/K_2Cr_2O_7}$ Acid + Cr^{+3} [green]

2° Alcohol $\xrightarrow[\text{orange }[Cr^{+6}]]{H^{\oplus}/K_2Cr_2O_7}$ Ketone + Cr^{+3} [green]

3° Alcohol $\xrightarrow[\text{orange }[Cr^{+6}]]{H^{\oplus}/K_2Cr_2O_7}$ No oxidation, Remains orange

(v) Distinction between CH_3-OH and C_2H_5OH

	CH_3OH	CH_3CH_2OH
B.P.	65℃	78℃
I_2 + NaOH	No ppt	Yellow ppt of CHI_3
Cu/300℃	Smell of formalin [HCHO]	No smell
Salicylic acid	Smell like oil of wintergreen	No smell



Methyl salicylate (smell like oil of wintergreen)

Phenyl salicylate Salol (Antiseptic)

Aspirin (Analgesic & Antipyretic)

Important facts about alcohols

(i) Toxicity [ethyl alcohol < Iso propyl alcohol < methyl alcohol]

(ii) Absolute alcohol : Ethyl alcohol - 99.5%-100%

(iii) Power alcohol : Rectified spirit + C_6H_6 + Petrol for generation of power

(iv) Methylated spirit : Methanol + Pyridine + mineral naptha + rectified spirit.

(v) 70% CH_3OH is known as wood spirit.

(vi) 90% C_2H_5OH is known as Raw spirit.

(vii) C_2H_5OH is technically called WASH.

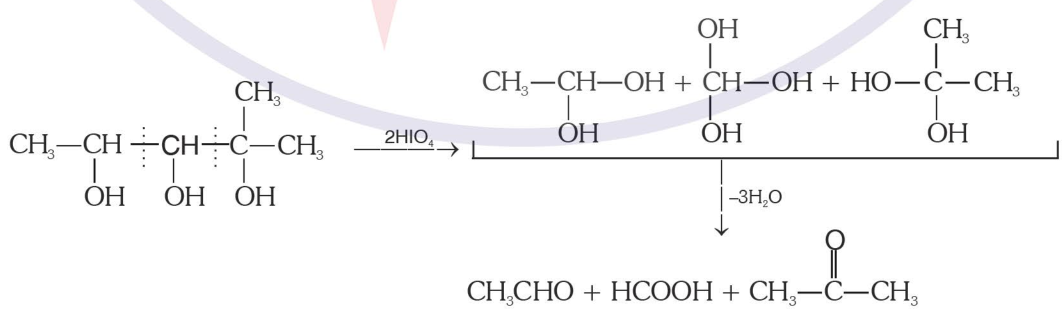
(viii) Rectified spirit contains 95.5% alcohol and 4.5% H_2O.

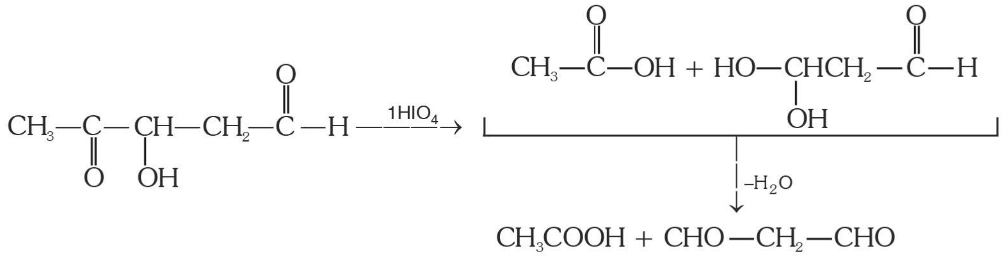
Condition for oxidation by HIO_4 or $(CH_3COO)_4Pb$

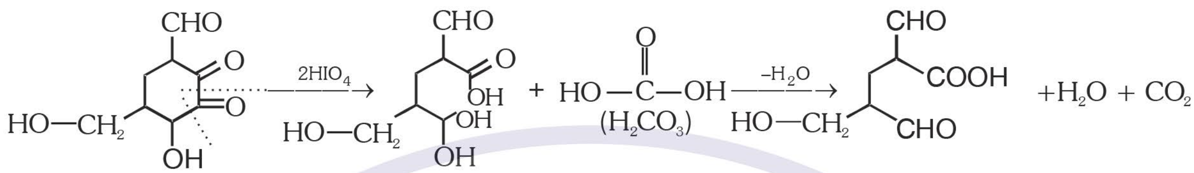
(i) At least 2 —OH or 2 >C=O or 1 —OH and 1 >C=O should be at vicinal carbons.

(ii) One HIO_4 breaks one C–C bond and adds one –OH to each carbon .

Ex.



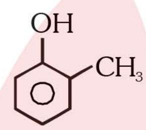
Ex. 

Ex. 

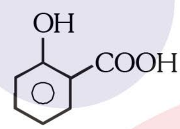
AROMATIC HYDROXY DERIVATIVES

Phenolic compounds : Compounds in which —OH group is directly attached to sp^2c [Benzene ring]

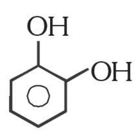
Phenol



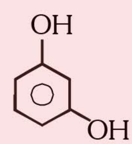
o-Cresol



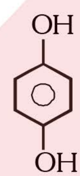
Salicylic acid



Catechol



Resorcinol



Quinol

All phenolic compounds give colour with neutral $FeCl_3$.

$$Ph\text{—}OH \xrightarrow{\text{neutral } FeCl_3} \text{Violet colour}$$

$$CH_3CH_2\text{—}OH \xrightarrow{\text{neutral } FeCl_3} \text{No colour}$$

.2 PHENOL (C_6H_5OH)

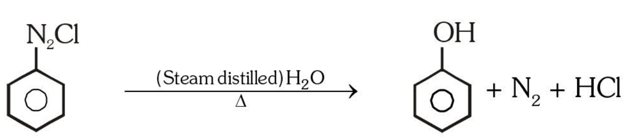
Phenol is also known as carbolic acid. In phenol —OH group is attached with sp^2 hybridised carbon.

.2.1 General Methods of Preparation

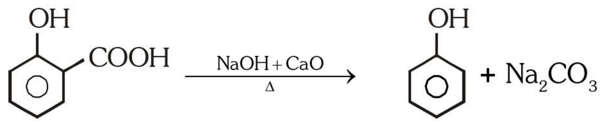
(1) From benzene sulphonic acid : When sodium salt of benzene sulphonic acid is fused with NaOH phenol is obtained.

$$C_6H_5SO_3Na \xrightarrow[(2)\ H^{\oplus}]{(1)\ NaOH, \Delta\ \&\ Pr.} C_6H_5OH + Na_2SO_3$$

(2) From benzene diazonium chloride : When benzene diazonium chloride solution is warmed with water, phenol is obtained with evolution of nitrogen.



(3) By distilling a phenolic acid with sodalime (decarboxylation):

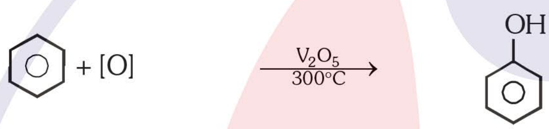


Salicylic acid

(4) From Grignard reagent : The Grignard reagent on reaction with oxygen and subsequent hydrolysis yields phenol.

$$C_6H_5MgBr \xrightarrow{[O]} C_6H_5OMgBr \xrightarrow{H_2O} C_6H_5OH + Mg\begin{matrix} Br \\ OH \end{matrix}$$

(5) From benzene :



(6) From chloro benzene :

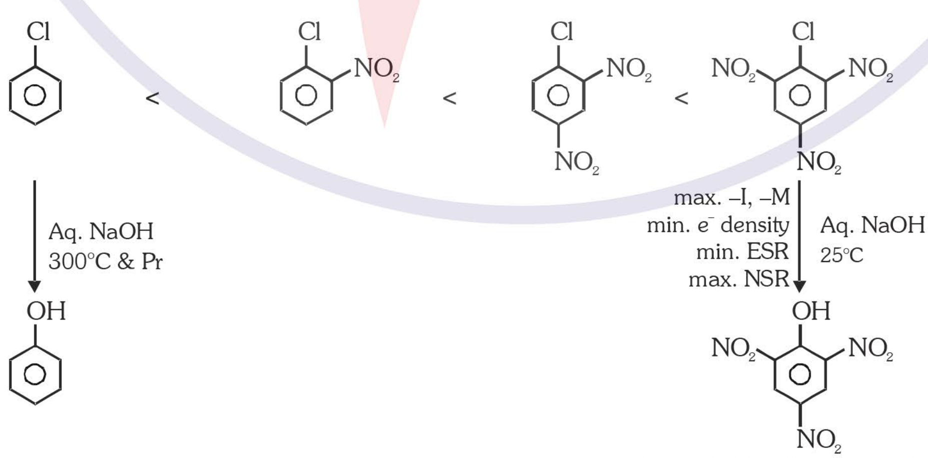
$$Ph{-}Cl \xrightarrow{\text{Aq. NaOH}} \text{No NSR at normal condition}$$

Stable by resonance

$$R{-}Cl \xrightarrow{\text{Aq. NaOH}} R{-}OH\ [NSR]$$

$$Ph{-}Cl \xrightarrow[(2)\,H^{\oplus}]{(1)\ \text{Aq. NaOH, } \Delta \,\&\, Pr} Ph{-}OH\ [\text{NSR at high temperature}]$$

Order for NSR :



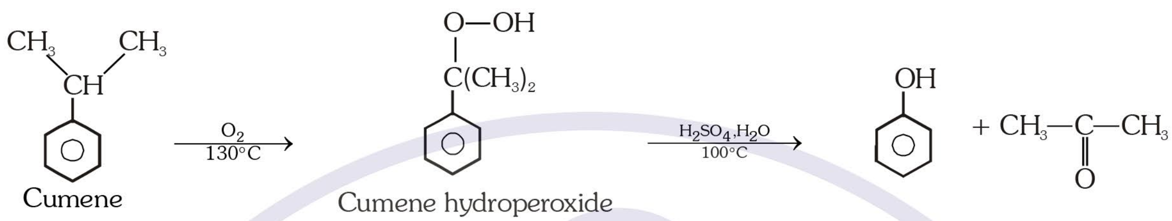
2, 4, 6–Trinitrophenol (Picric acid)

(7) Industrial preparation of phenol: Phenol can be prepared commercially by **:**

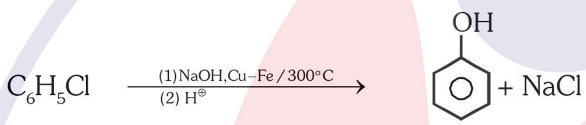
(a) Cumene

(b) Dow's process

(a) From cumene (Isopropyl benzene) : Cumene is oxidised with oxygen into cumene hydroperoxide in presence of a catalyst. This is decomposed by dil. H_2SO_4 into phenol and acetone.



(b) Dow process : This process involves alkaline hydrolysis of chloro benzene-(obtained by above process) followed by acidification.



6.2.2 Physical Properties

(i) Phenol is a colourless, crystalline solid.

(ii) It attains pink colour on exposure to air and light. (slow oxidation)

Phenoquinone(pink colour)

(iii) It is poisonous in nature but acts as antiseptic and disinfectant.

(iv) Phenol is slightly soluble in water, readily soluble in organic solvents.

(v) Solublity of phenol in water is much lower than alcohols because of larger hydrocarbon part in the molecule.

(vi) Due to intermolecular H-Bonding, phenol has relatively high boiling point than the corresponding hydrocarbons, aryl halides.

6.2.3 Chemical Properties

(A) Reactions due to –OH group :

(i) Acidic Nature : Phenol is a weak acid. The acidic nature of phenol is due to the formation of stable phenoxide ion in solution. The phenoxide ion is stable due to resonance. The negative charge is spread through out the benzene ring which is stabilising factor in the phenoxide ion. Electron withdrawing groups ($-NO_2$, –Cl) increase the acidity of phenol while electron releasing groups ($-CH_3$ etc.) decrease the acidity of phenol.

$$C_6H_5OH + H_2O \rightleftharpoons C_6H_5\overset{\ominus}{O} + H_3\overset{\oplus}{O}$$

Phenol is stronger acid than alcohols but weaker than the carboxylic acids and even carbonic acid.

(ii) Reaction with PCl_5 : Phenol reacts with PCl_5 to form chloro benzene. $POCl_3$ formed as biproduct reacts with phenol to form triphenyl phosphate.

$$C_6H_5OH + PCl_5 \xrightarrow{\Delta} C_6H_5Cl + POCl_3 + HCl$$

$$3C_6H_5OH + POCl_3 \longrightarrow (C_6H_5)_3PO_4 + 3HCl$$

(iii) Reaction with Zn dust: When phenol is distilled with zinc dust benzene is obtained.

$$C_6H_5OH + Zn \xrightarrow{\Delta} C_6H_6 + ZnO$$

(iv) Reaction with NH_3 : Phenol reacts with NH_3 in presence of anhydrous $ZnCl_2$ to form aniline.

$$C_6H_5OH + NH_3 \xrightarrow[300°C]{\text{Anhydrous } ZnCl_2 \text{ or } (NH_4)_2SO_3/NH_3 150°C} C_6H_5NH_2 + H_2O$$

(v) Reaction with $FeCl_3$: Phenol gives violet colouration with $FeCl_3$ solution (neutral) due to formation of a complex.

$$C_6H_5OH + FeCl_3 \longrightarrow \text{Violet colour}$$

This reaction is used to differentiate phenol from alcohols.

(vi) Acetylation : Phenol reacts with acid chlorides or acid anhydrides in alkali solution to form phenyl esters.

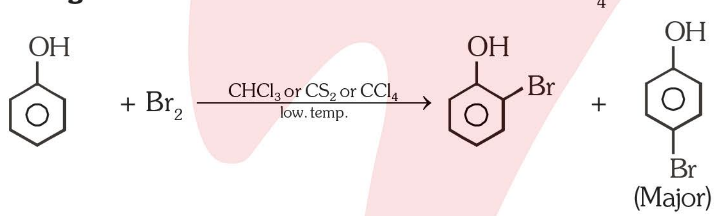
$$C_6H_5OH + ClCOCH_3 \xrightarrow[-HCl]{NaOH} C_6H_5O-\underset{\underset{O}{\|}}{C}-CH_3$$

(vii) Benzoylation (Schotten-Baumann reaction)

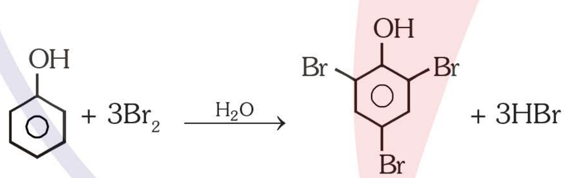
$$C_6H_5OH + Cl-\underset{\underset{O}{\|}}{C}-C_6H_5 \xrightarrow[-HCl]{NaOH} C_6H_5O-\underset{\underset{O}{\|}}{C}-C_6H_5$$

(B) Reaction of Benzene Ring : The —OH group is ortho and para directing. It activates the benzene ring.

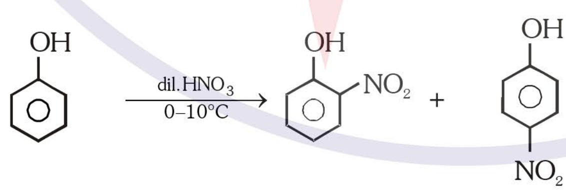
(i) Halogenation : Phenol reacts with bromine in CCl_4 to form mixture of o–and p–bromo phenol.



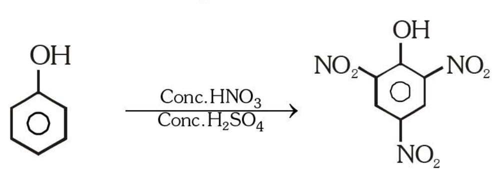
Phenol reacts with bromine water to form a white ppt. of 2,4,6-tribromo phenol. (Test for phenol)



(ii) Nitration : Phenol reacts with dil. HNO_3 at 0°–10°C to form o- and p- nitro phenols.

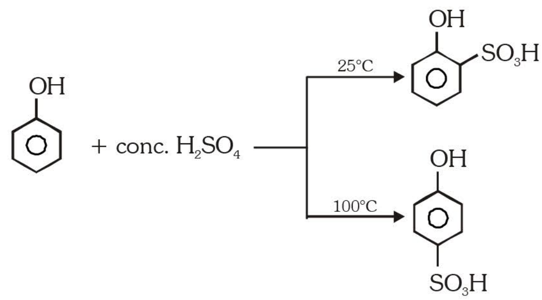


When phenol is treated with nitrating mixture than it forms 2,4,6- trinitro phenol (picric acid) but it is not good method to form picric acid because nitric acid oxidise phenol into p-Benzoquinone

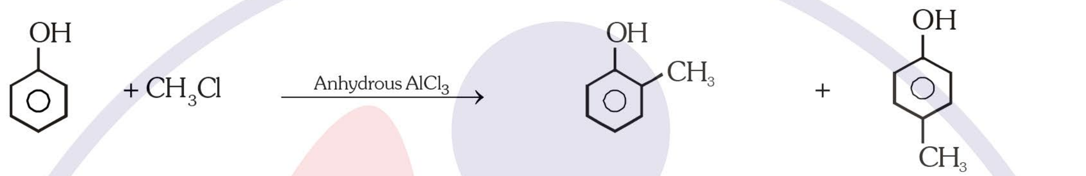


[2, 4, 6–Trinitrophenol (Picric acid)]

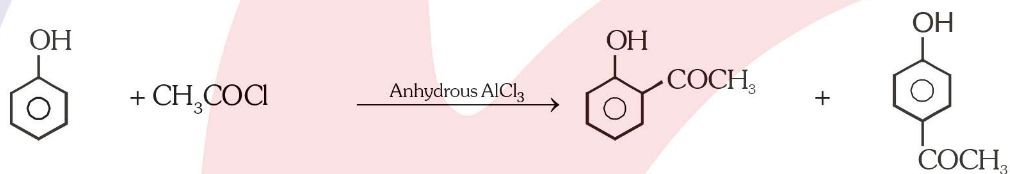
(iii) Sulphonation: Phenol reacts with fuming H_2SO_4 to form o–and p–hydroxy benzene sulphonic acid at different temperatures.



(iv) Friedel - Craft 's reaction:



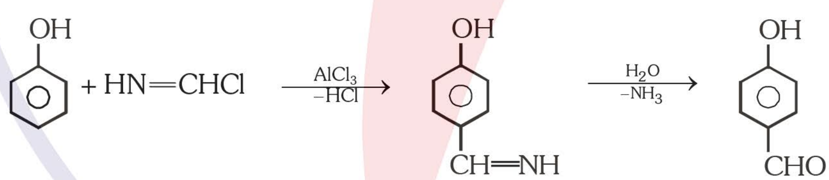
o – cresol p – cresol (Major)



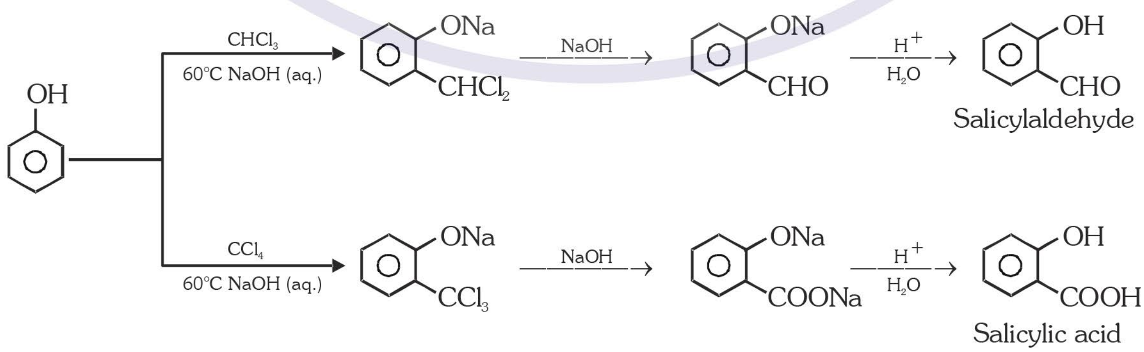
o – and p – hydroxy acetophenone

(v) Gattermann aldehyde synthesis : When phenol is treated with liquid HCN and HCl gas in presence of anhydrous $AlCl_3$ it yields mainly p- hydroxy benzaldehyde (formylation)

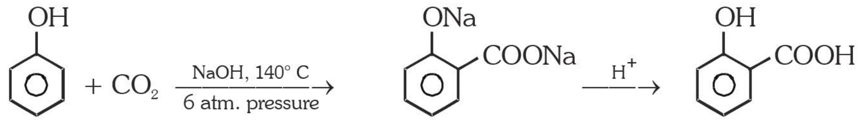
$$HCl + HCN \xrightarrow{AlCl_3} HN{=}CHCl$$



(vi) Reimer-Tiemann reaction : Phenol on refluxing with chloroform and NaOH (aqueous) followed by acid hydrolysis yields o–hydroxy benzaldehyde. When CCl_4 is used salicylic acid is formed.

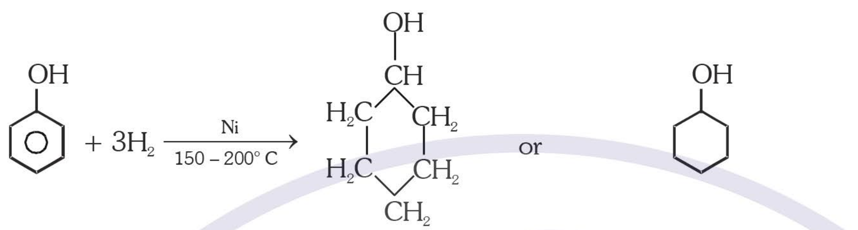


(vii) Kolbe's Schmidt reaction : It involves the reaction of C_6H_5OH with CO_2 and NaOH at 140^0 C followed by acidification to form salicylic acid.



Sodium salicylate   Salicylic acid

(viii) Hydrogenation: Phenol when hydrogenated in presence of Ni at 150-200^{0}C forms cyclohexanol.

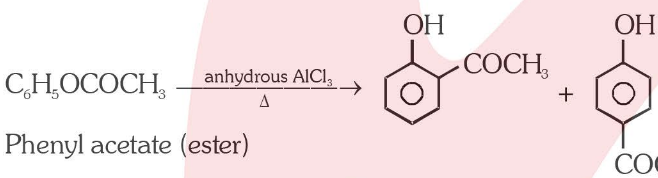


Cyclohexanol. ($C_6H_{11}OH$)   (used as a good solvent)

(ix) Fries rearrangement reaction:

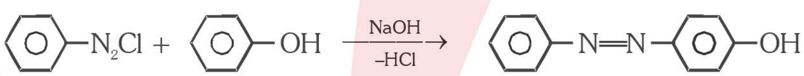
$$C_6H_5OH + CH_3COCl \xrightarrow{\text{Pyridine}} C_6H_5OCOCH_3$$

Phenyl Acetate



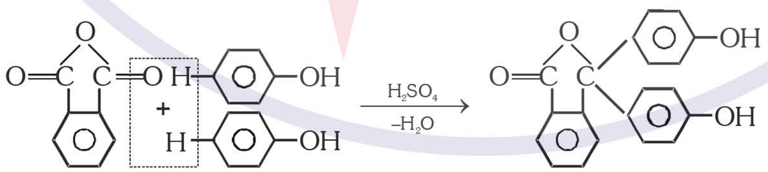
Phenyl acetate (ester)

(x) Coupling reactions: Phenol couples with benzene diazonium chloride in presence of an alkaline solution to form a dye (p- hydroxy azobenzene) orange dye.



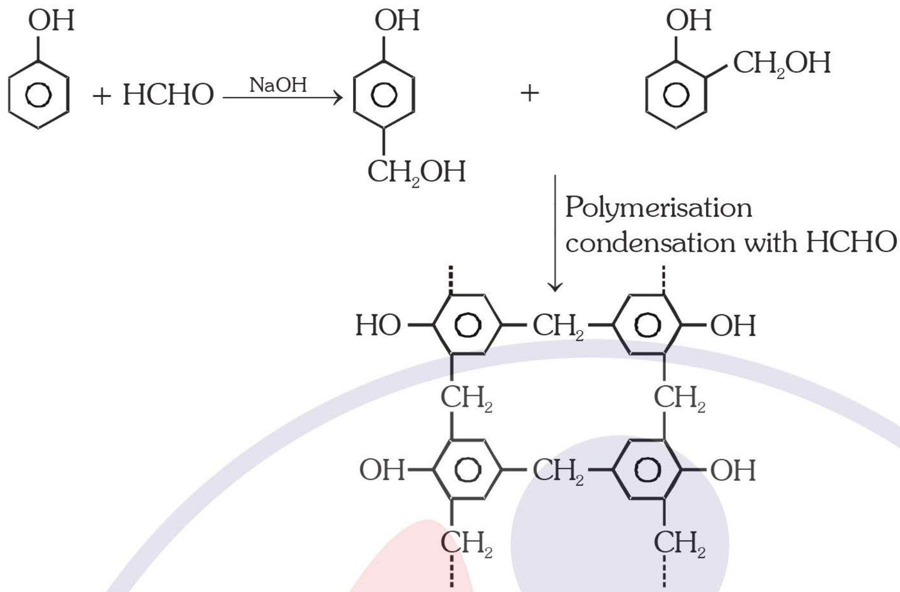
p–hydroxy azobenzene (Orange dye)

Phenol couples with phthalic anhydride in presence of conc. H_2SO_4 to form a dye (phenolphthalein) used as an indicator.



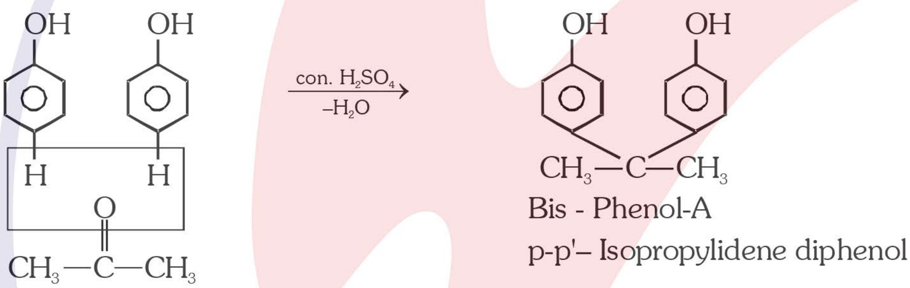
Phthalic anhydride Phenol (2 molecules) Phenolphthalein (Colourless in acidic medium and pink in alkaline medium)

(xi) Lederer Manasse (Condensation with formaldehyde) : Phenol condenses with HCHO (excess) in presence of NaOH or weak acid (H^+) to form a polymer known as bakelite (resin).

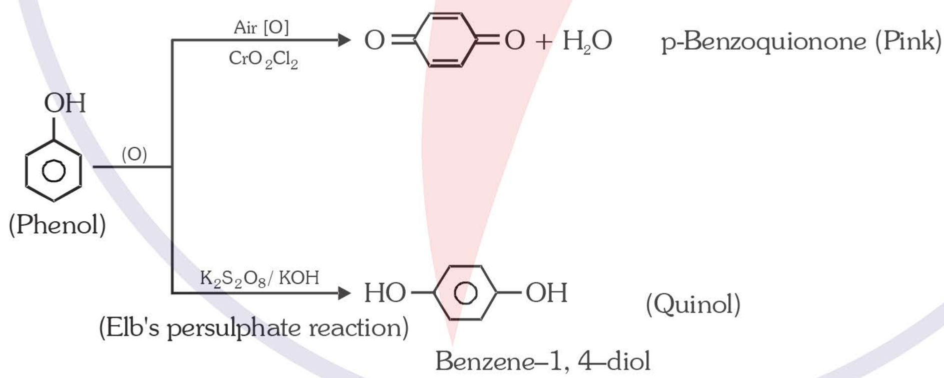


Polymer bakelite (Phenol formaldehyde resin)

(xii) Reaction with acetone: (Condensation with acetone)



(xiii) Oxidation:



Test of Phenol :

(1) Phenol turns blue litmus to red.

(2) Aqueous solution of phenol gives a violet colour with a drop of ferric chloride.

(3) Phenol gives Liebermann's nitroso test.

(4) Aqueous solution of phenol gives a white ppt. of 2,4,6-tribromophenol with bromine water.

(5) Phenol combines with phthalic anhydride in presence of conc. H_2SO_4 to form phenolphthalein which gives pink colour with alkali.

Differences between phenol and alcohol (C_2H_5OH) :

(1) Phenol is more acidic than aliphatic alcohol due to resonance in phenoxide ion.

(2) Phenol gives violet colour with $FeCl_3$ while aliphatic alcohol does not give.

(3) Phenol gives triphenyl phosphate with PCl_5 while aliphatic alcohol does not.

(4) Phenol on oxidation gives quinone while alcohol gives aldehyde or ketone and acids.

Uses of Phenol :

Phenol is used :

(1) As an antiseptic in soaps and lotions. "Dettol" (mixture of chloroxylenol and terpineol)

(2) In manufacture of azodyes, phenolphthalein, picric acid (explosive), cyclohexanol (Solvent for rubber), plastics (bakelite) etc.

(3) In manufacture of drugs like aspirin, salol, phenacetin etc.

(4) As preservative for ink.

6.3 ETHER

R—O—R (Dialkyl ether), alkoxy alkane. It's General formula is $C_nH_{2n+2}O$.

$CH_3—O—CH_2CH_3$ (Methoxy ethane) or Ethyl methyl ether

Ether is monoalkyl derivative of R–OH and dialkyl derivative of H_2O

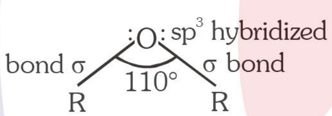
$$R—OH \xrightarrow[+R]{-H} R—O—R \xleftarrow[+2R]{-2H} H—O—H$$

Classification : They may be classified as :

(a) Simple or symmetrical ether. e.g. R–O–R

(b) Mixed or unsymmetrical ether e.g. R–O–R'

Structure :



The molecule of ether is bent due to presence of lone pair.
The bond angle is 110^0. It is greater than that of water (105^0) due to the repulsion between bulkier alkyl groups. Due to bent structure, it posses dipole moment and hence are polar molecules.

6.3.1 General Methods of Preparation

(a) From alkyl halides :

(i) By Williamson's synthesis :

$$R—X + NaO—R \longrightarrow R—O—R + NaX \text{ [S}_N2 \text{ Reaction]}$$

Ex. $CH_3—CH_2—Cl + CH_3—ONa \longrightarrow CH_3—CH_2O—CH_3 + NaCl$

Ex. $(CH_3)_3C—Cl + CH_3ONa \longrightarrow H_3C—C(=CH_2)—CH_3$ (Major)   3° RX fails to give ethers

Ex. $(CH_3)_3C—ONa + CH_3—CH_2—Cl \xrightarrow{\Delta} (CH_3)_3C—O—CH_2—CH_3$

Ex. $CH_2=CH—Cl + CH_3CH_2—ONa \longrightarrow$ No reaction

[Stable by Resonance]

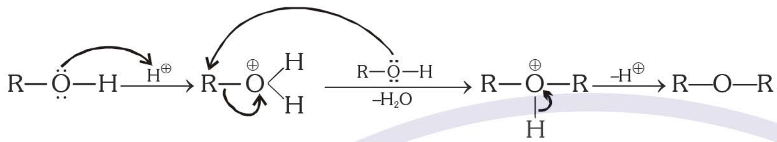
(ii) Reaction with Dry Ag_2O : $2RX + Ag_2O \xrightarrow{\Delta} R\text{—}O\text{—}R + 2AgX$

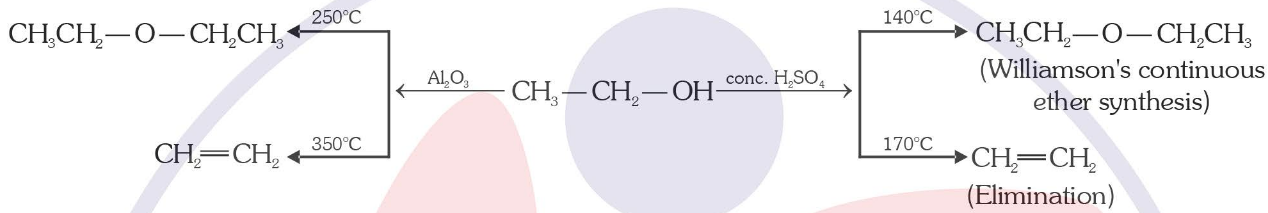
Ex. $2CH_3\text{—}CH_2\text{—}Cl + Ag_2O \xrightarrow{\Delta} CH_3CH_2OCH_2CH_3 + 2AgCl$

(b) From R–OH:

(i) By Bimolecular dehydration : $R\text{—}OH \xrightarrow[\Delta]{Con.\ H_2SO_4} R\text{—}O\text{—}R$

Mechanism :





(ii) Reaction with CH_2N_2 (diazomethane) :

$$R\text{—}OH + CH_2N_2 \xrightarrow[BF_3]{\Delta} R\text{—}O\text{—}CH_2\text{—}H + N_2$$

6.3.2 Physical Properties

(i) CH_3OCH_3 , $CH_3OCH_2CH_3$ are gases and higher ethers are volatile liquids.

(ii) Ether are less polar.

(iii) Ethers are less soluble in H_2O.

(iv) Ethers have less BP then corresponding alcohol.

6.3.3 Chemical properties

Ethers are less polar so less reactive and do not react with active metals [Na,K], cold dil. acid, oxidising and reducing agent. They do not have any active functional group.

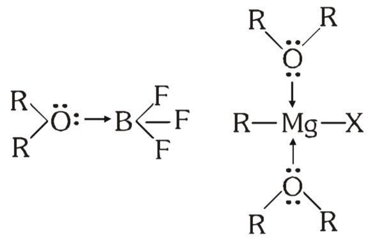
(1) Basic nature : Due to presence of ℓ.p on oxygen atom ether behave as lewis base

Ethers react with cold conc. acid and form oxonium salts.

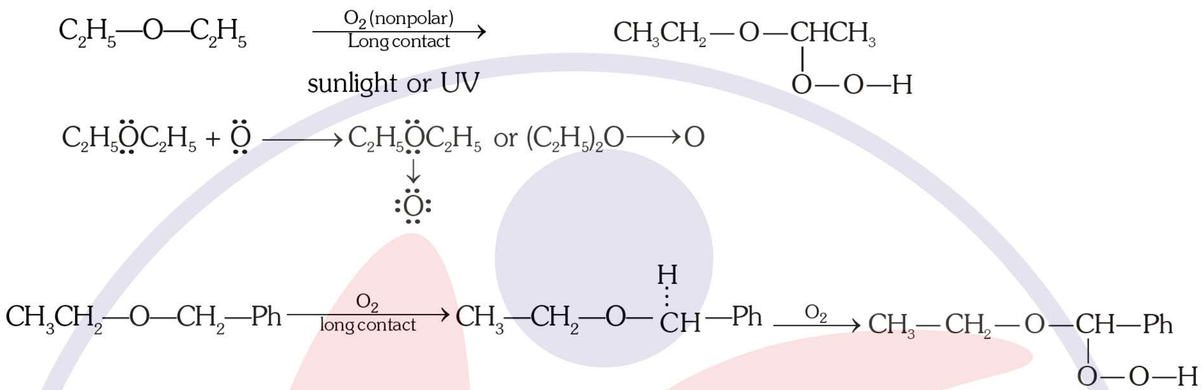
Ex. $C_2H_5\ddot{O}C_2H_5 \xrightarrow{cold\ ;\ conc.\ HCl} \left[C_2H_5\text{—}\overset{\oplus}{O}(H)\text{—}C_2H_5\right]Cl^{\ominus}$ (diethyl oxonium chloride)

Ex. $C_2H_5\text{—}\ddot{O}\text{—}C_2H_5 \xrightarrow[H_2SO_4]{cold\ ;\ conc.} \left[C_2H_5\text{—}\overset{\oplus}{O}(H)\text{—}C_2H_5\right]HSO_4^{\ominus}$ (diethyl oxonium hydrogen sulphate)

Ethers form dative bond with Lewis acids like BF_3, $AlCl_3$, RMgX etc.

Ex.  [Ether is used as a solvent] for Grignard reagent.

(2) Formation of peroxides : Ether add up atmospheric oxygen or ozonised oxygen. It is explained by Free radical mechanism as intermediate is free radical.



Peroxides are unstable and explosives.

(3) Reaction with PCl_5 : $ROR + PCl_5 \xrightarrow{\text{heat}} 2RCl + POCl_3$

(4) Reduction : $CH_3CH_2OCH_2CH_3 \xrightarrow[\text{heat}]{\text{Red P + HI}} 2CH_3CH_3$

(5) Reaction with HX : R–O–R' + HI $\longrightarrow$ R–OH + R'–I

Uses of ether :

(i) General anaesthetic agent.

(ii) Solvent for oil, fats, resins, Grignard reagent.

(iii) For providing inert & moist free medium to organic reaction e.g. Wurtz reactions.

(iv) In perfumery.

(v) Di-isopropyl ether $\longrightarrow$ In petrol as an antiknock compound.

(vi) Mixture of alcohol and ether is used as a substitute of petrol. Trade name **"Natalite"**