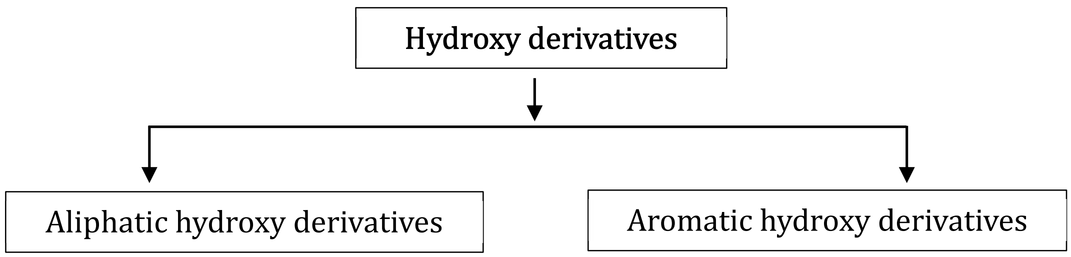
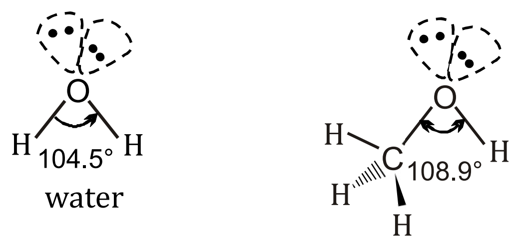
ALCOHOLS, PHENOLS AND ETHERS

INTRODUCTION OF ALCOHOL, PREPARATION AND PROPERTIES

ALCOHOL, PHENOL& ETHER



Alcohols feature oxygen atoms with sp^3 hybridization, but there's a notable difference in bond angles: the C – O – H angle in methanol (108.9°) is notably greater than the H – O – H angle in water (104.5°). This discrepancy arises from the relatively larger size of the methyl group compared to a hydrogen atom. The bulkier methyl group offsets the bond angle compression that results from the nonbonding electron pairs of oxygen. While the O – H bond lengths are similar in both water and methanol (0.96 Å), the C – O bond is notably longer (1.4 Å), which reflects the greater covalent radius of carbon compared to hydrogen.



Methyl alcohol

(I) **Aliphatic Hydroxy Derivatives**

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

(II) **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 CH_2 (each with OH: $\overset{|}{OH}$ OH)

(iii) Trihydric [three –OH] ⟶ $CH_2—CH—CH_2$ (each carbon with OH: OH OH OH)

(iv) Polyhydric [n –OH] ⟶ $CH_2—CH$ ------------- CH_2 (each carbon with OH: OH OH OH)

(b) **Classification according to nature of carbon**

(i) p or 1° – alcohol ⟶ $CH_3CH_2 – OH$

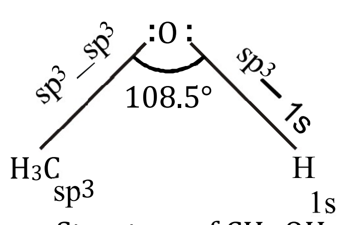
(ii) s or 2° – alcohol ⟶ $(CH_3)_2CH – OH$

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

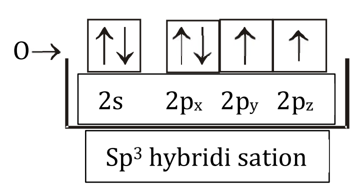
ALCOHOLS

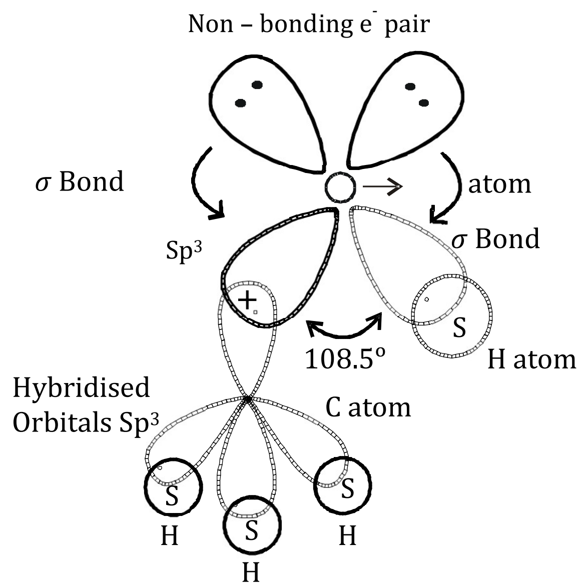
Structure of alcohol

Alcohols exhibit a bent molecular structure. The carbon atom bonded to the oxygen atom in the -OH group is sp^3 hybridized, and the central oxygen atom is also in an sp^3 hybridization state. The bond angle is approximately 108.50 degrees. In the process of sp^3 hybridization, the oxygen atom's $2s^2$, $2px^2$, $2py^1$, and $2pz^1$ orbitals combine to form sp^3 hybrid orbitals.



Structure of CH_3 OH





Out of these four orbitals, two contain one electron each, while the other two contain two electrons each. The orbitals with two electrons do not actively participate in bonding. The remaining two half-filled orbitals form sigma (σ) bonds with the s-orbitals of hydrogen atoms and the hybridized orbital of carbon atoms (O-C). Due to the influence of the lone pair, the bond angle of the tetrahedral oxygen atom is slightly less than the usual tetrahedral structure, measuring 109.028 degrees.

MONOHYDRIC ALCOHOL

GENERAL METHODS OF PREPARATION

(a) From alkanes (By oxidation)

$$(CH_3)_3C—H \xrightarrow[\Delta]{H^+/KMnO_4} (CH_3)_3C — OH$$

(b) From alkenes

(i) By hydration

$$CH_3 — CH = CH_2 \xrightarrow[H_2O]{H^+} CH_3\text{-}\underset{\displaystyle O}{\underset{|}{CH}} – CH_3$$

(ii) By hydroboration oxidation

$$CH_3— CH = CH_2 \xrightarrow[H_2O_2/HO]{BH_3} CH_3\text{-} CH_2 – \underset{\displaystyle OH}{\underset{|}{CH_2}}$$ (1° alcohol)

(iii) By oxymercuration demarcation

$$CH_3—CHCH_2 \xrightarrow[\text{(ii) } NaBH_4HO^-]{\text{(i) } Hg(OAc)_2, H_2O} CH_3—\underset{\substack{|\\OH}}{CH}—CH$$

(c) From alkyl halides (By hydrolysis)

$$CH_3—CH_2—Cl \xrightarrow[\text{or Moist A } g_2O]{\text{Aq. KOH}} CH_3CH_2—OH$$

(d) From carbonyl compounds (By reduction)

$$> CO \xrightarrow{\text{Reducing agent}} > CH—OH$$

- Reducing agents may be, $LiAlH_4/H^{\oplus}$, $NaBH_4/H^{\oplus}$

Na + EtOH [Bouveault-blanc Reduction]

NaH [Darzen reduction]

Ni / H_2

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

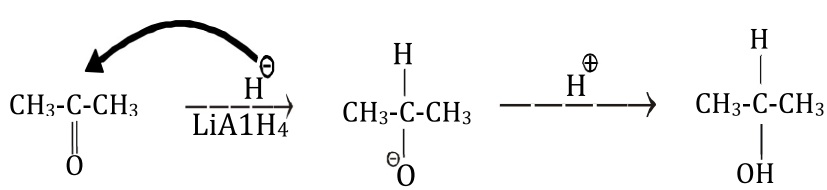
$$R—\underset{\substack{\|\\O}}{C}—R \xrightarrow[H^-]{NaBH_4}$$

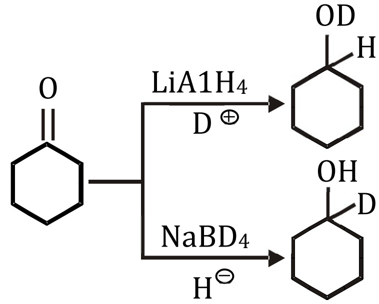
$$R – \underset{OH}{CH} – R$$

$$CH_3—\underset{\substack{\|\\O}}{C}—CH_3$$

$$\xrightarrow[H^+]{LiA1H_4} ?$$

MECHANISM





$CH_3—CHCH—CHO \xrightarrow[H^{\oplus}]{LiA1H_4} CH_3—CHCH—CH_2—OH$

Crotonaldehyde

$Ph—CH = CH—CHO \xrightarrow[H^{\oplus}/OH^{\ominus}]{LiA1H_4} Ph—CH_2—CH_2—CH_2—OH$

Cinnamaldehyde

(e) **From ethers**

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

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

(f) **From acid and derivatives (By reduction)**

$R— COOH \xrightarrow[H^{\oplus}]{LiA1H_4} R— CH_2— OH + H_2O$

$R—\overset{O}{\overset{\|}{C}}—Cl \xrightarrow[H^{\oplus}]{LiA1\ \ _4} R— CH_2— OH + HCl$

$R—\overset{O}{\overset{\|}{C}}—OR \xrightarrow[H^{\oplus}]{LiA1H_4} R — CH_2— OH + R— OH$

$R—\overset{O}{\overset{\|}{C}}—O—\overset{O}{\overset{\|}{C}}—OR \xrightarrow[H^{\oplus}]{LiA1H_4} R— CH_2— OH + R — CH_2— OH$

$R—\overset{O}{\overset{\|}{C}}—NY_2 \xrightarrow[H^{\oplus}]{LiA1H_4} R — CH_2— NH_2 + H_2O$

(g) **From esters (By hydrolysis)**

(i) **By alkaline hydrolysis**

$R—\overset{O}{\overset{\|}{C}}—OR \xrightarrow{NaOH} R—\overset{O}{\overset{\|}{C}}— ONa + R— OH$

(ii) By acidic hydrolysis

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

$$CH_3-\underset{\underset{O}{||}}{C}-\overset{18}{O}C_2H_5 \overset{H_3O^{\oplus}}{\rightleftharpoons} CH_3-\underset{\underset{O}{||}}{C}-OH + C_2H_5\overset{18}{O}H$$

This reaction is reversible reaction and it's order is 1 and it is also called Pseudo-Unimolecular reaction.

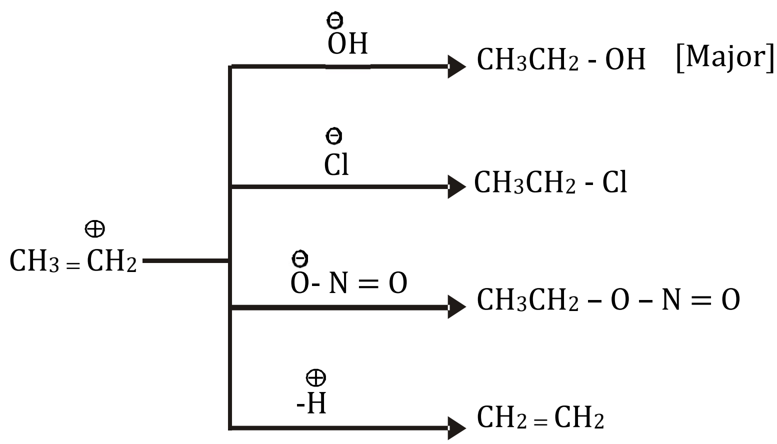
(h) From p-amines

$$R-NH_2 \xrightarrow[\text{or } HNO_2]{NaNO_2+HCl} R-OH + N_2 + H_2O$$

$$CH_3CH_2-NH_2 \xrightarrow{HNO_2} CH_3CH_2-OH + N_2 + H_2O$$

MECHANISM

$$CH_3CH_2-NH_2 \xrightarrow{NaNO_2+HCl} \underset{\text{Unstable}}{CH_3CH_2-\overset{\oplus}{N_2}\overset{\ominus}{Cl}} \longrightarrow CH_3\overset{\oplus}{C}H_2 + N_2 + \overset{\ominus}{Cl}$$



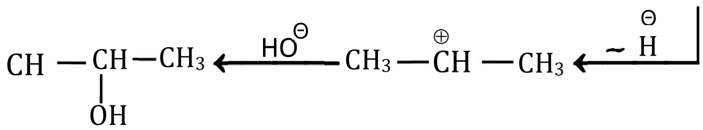
Inter mediate is carbocation so rearrangement may be possible.

Ex. $CH_3CH_2CH_2-NH_2 \xrightarrow{NaNO_2 + HCl} ?$

Sol. Mechanism

$$CH_3CH_2CH_2- \xrightarrow{NaNO_2+HCl} CH_3CH_2CH_2-\overset{\oplus}{N_2}\ \overset{\ominus}{Cl}$$

$$CH_3CH_2\overset{\oplus}{C}H_2 \longrightarrow$$

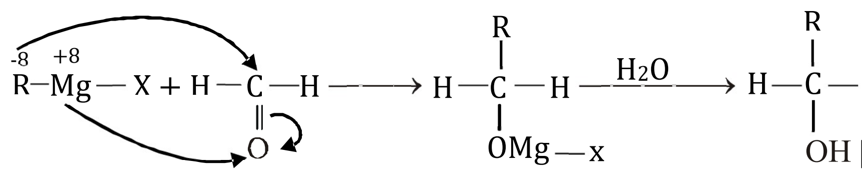


Exception: $CH_3 - NH_2 \xrightarrow{HNO_2} CH_3 - O - CH_3$

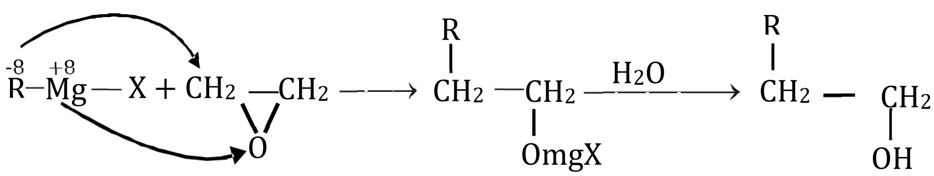
From Grignard reagent

(i) **p-alcohol**

$R—Mg—X + [O] \longrightarrow R — O — MgX \xrightarrow{H_2O} R—OH$ [Same C-p-alcohol]

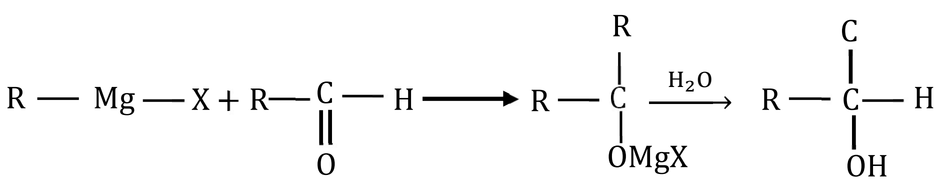


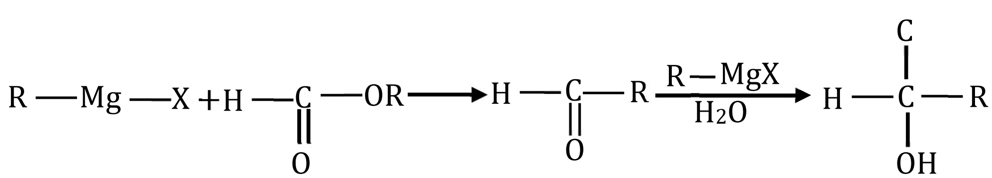
[one C more p-alcohol]



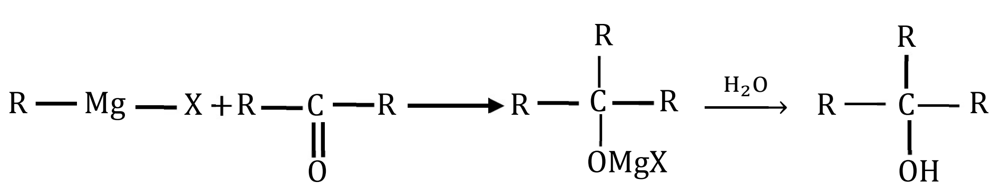
Two C more p-alcohol

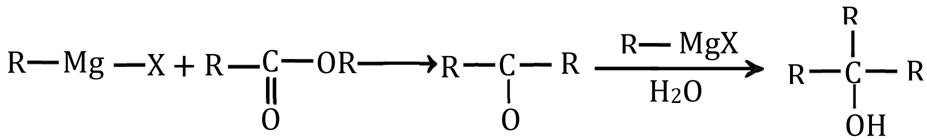
(ii) **s-alcohol**





(iii) **t-alcohol**





PHYSICAL PROPERTIES OF ALCOHOL

(i) C_1 to C_{11} represent clear, colorless liquids, while higher alcohols are in solid form.

(ii) The density of monohydric alcohols is lower than that of water (H_2O).

(iii) Density is directly proportional to the molecular weight for monohydric alcohols.

(iv) Solubility

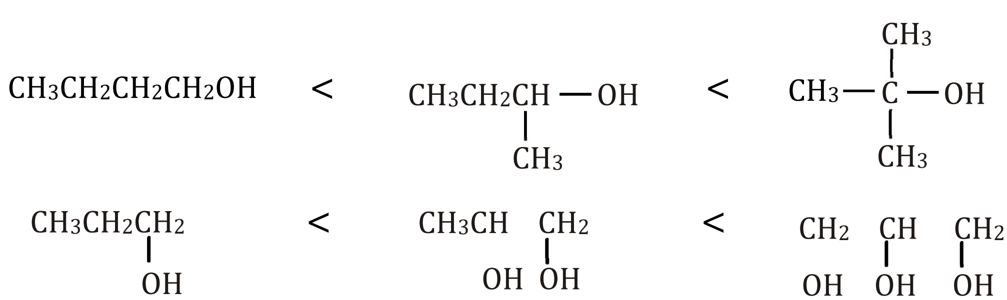
- The initial three members can fully dissolve in water, whereas the higher members are nearly insoluble in water but can dissolve in organic solvents such as benzene and ether.
- The solubility of lower alcohols arises from the formation of hydrogen bonds between the polar O–H groups of alcohol molecules and water.
- As the molecular mass increases, the solubility of alcohols in water diminishes.
- Among isomeric alcohols, solubility decreases as the degree of branching in the chain increases.

C_1 to C_3 and t-butyl alcohol is completely soluble in H_2O due to H–bonding.

$$\text{solubility} \propto \text{No. of side chains} \propto \frac{1}{\text{Molecular weight}}$$

Order of solubility

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

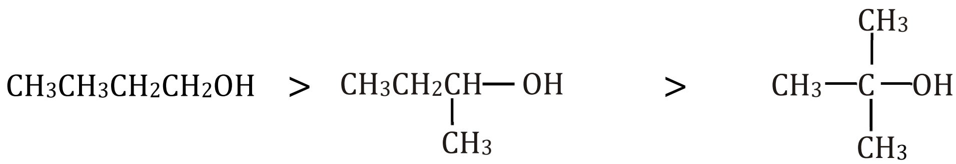


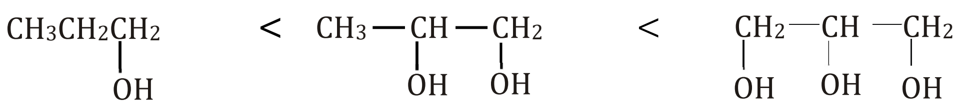
[Number of —OH increases, H-bonding increases]

(v) **Boiling points:** B.P. $\propto$ molecular weight

If molecular wt. is same then B.P. $\propto \frac{1}{\text{branching}}$

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





[Number of OH increases, H-bonding increases]

CHEMICAL PROPERTIES OF ALCOHOL

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**

$H_2O > R—OH > CHCH > NH_3$ (Acidic strength)

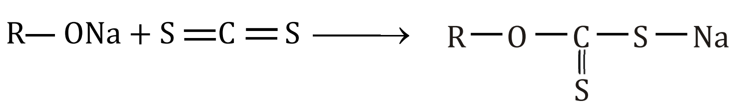
Alcohols are less acidic than H_2O and neutral for litmus paper and gives H_2 with active metals (Na, K)

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

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

(ii) **Reaction with CS_2**

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



Sodium alkyl xanthate (Used as floating agent)

(iii) **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)

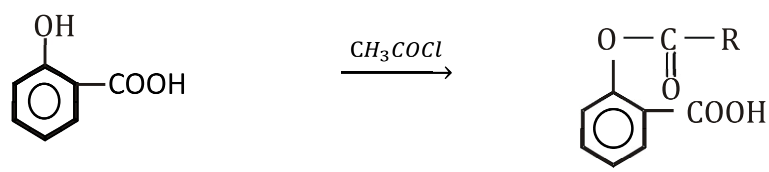
(iv) **Acylation**

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

(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]

(v) **Benzoylation: (Schotten Baumann's Reaction)**

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

(Benzoylation)

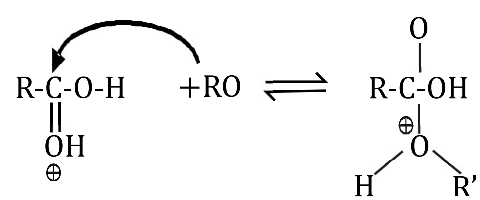
(vi) **Esterification:** Conc. H_2SO_4 is used as catalyst and dehydrating agent.

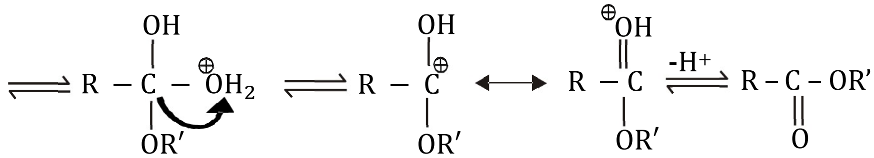
$$R-\underset{\underset{O}{\|}}{C}-OH + R-OH \xrightarrow{Conc.\ H_2SO_4} R-\underset{\underset{O}{\|}}{C}-OR + H_2O$$

MECHANISM

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$

$$R-\underset{\underset{O}{\|}}{C}-\ddot{O}-H + H^+ \rightleftharpoons R-\underset{\underset{OH}{\|}}{C}-O-H$$



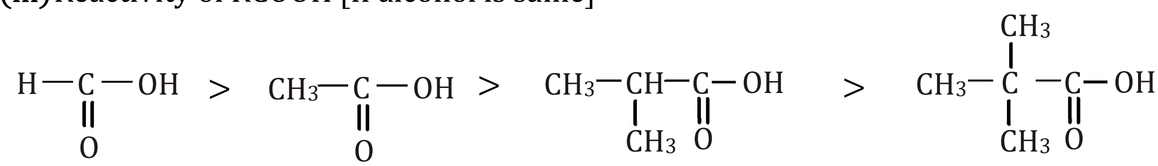


Note: This is a laboratory method to prepare ester.

(i) Reactivity for esterification $\propto \frac{1}{\text{Steric hinderence}}$

(ii) Reactivity of R – OH [If acid is same]: $CH_3-OH > 1° > 2° > 3°$ alcohol

(iii) Reactivity of RCOOH [If alcohol is same]



(vii) Reaction with CHCH

$$CHCH + 2CH_3{-}OH \xrightarrow[\Delta]{BF_3/HgO} CH_3CH(OCH_3)_2$$

Methylal

$$CHCH + 2CH_3CH_2{-}OH \xrightarrow[\Delta]{BF_3/HgO} CH_3CH(OC_2H_5)_2$$

Ethylal

(viii) Reaction with carbonyl compounds

$$R{-}CHO + 2R{-}OH \xrightarrow{H^+} R{-}CH(OR)_2$$

Acetal

$$R{-}\underset{\underset{O}{\|}}{C}{-}R + 2R{-}OH \xrightarrow{H^+} R_2C(OR)_2$$

Ketal

$$CH_3CHO + 2CH_3{-}OH \xrightarrow{H^+} CH_3CH(OCH_3)_2$$

Methylal

(ix) Reaction with Grignard reagent

$$R{-}Mg{-}X + H{-}OR \xrightarrow{H^+} R{-}H + Mg\begin{smallmatrix}X\\OR\end{smallmatrix}$$

(x) **Reaction with Ketene:** Ketene is used as acetylating agent.

$$CH_2=C=O + R\text{—}OH \longrightarrow CH_2=C(OR)\text{—}OH + CH_3\text{—}C(OR)=O$$

$$CH_2CO + C_2H_5\text{—}OH \longrightarrow CH_2=C(OC_2H_5)\text{—}OH + CH_3\text{—}C(OC_2H_5)=O$$

Ethyl acetate

(xi) **Reaction with isocyanic acid:** Ethyl urethane is used in preparation of urea

$$NHC\,O + H\text{—}OC_2H_5 \longrightarrow NH=C(OC_2H_5)\text{—}OH + NH_2=C(OC_2H_5)\text{—}O$$

Ethyl urethane

(xii) **Reaction with oxirane**

$$R\text{—}OH + \underset{\diagdown O \diagup}{CH_2\text{—}CH_2} \xrightarrow{H^+} CH_2(OR)\text{—}CH_2(OH)$$

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

$$CH_3\text{—}OH < CH_3CH_2\text{—}OH < (CH_3)_2CH\text{—}OH < (CH_3)_3C\text{—}OH$$

(i) **Reaction with halogen acid**

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

$$R_2CH\text{—}OH + HCl \xrightarrow[\Delta]{ZnCl_2} R_2CH\text{—}Cl + H_2O$$

2^0 alcohols

Reactivity of the acids is HI > HBr > HCI > HF

(ii) **Reaction with inorganic acids**

$$R\text{—}OH + H\text{—}O\text{—}N(\rightarrow O)=O \longrightarrow R\text{—}O\text{—}N(\rightarrow O)=O + H_2O$$

Nitric acid Alkyl nitrate

$$R\text{—}OH + HHSO_4 \longrightarrow R\text{—}HSO_4 + H_2O$$

Alkyl hydrogen sulphate

(iii) **Reaction with phosphorous halides**

$$3R{-}OH + PCl_3 \longrightarrow 3RCl + H_3PO_3$$

$$R{-}OH + PCl_5 \longrightarrow R{-}Cl + POCl_3 + HCl$$

(iv) **Reaction with thionyl chloride ($SOCl_2$)**

$$R{-}OH + SOCl_2 \xrightarrow[\text{Pyridine}]{} R{-}Cl + \underset{\text{(gas)}}{SO_2\uparrow} + HCl$$

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

$$R{-}OH + HNH_2 \xrightarrow[250^\circ C]{Al_2O_3} R{-}NH_2 + H_2O$$

(vi) **Reaction with halogens:** Oxidation and chlorination takes place simultaneously.

$$CH_3CH_2OH + Cl_2(dry) \longrightarrow CH_3CHO + 2HCl \text{ (Oxidation)}$$

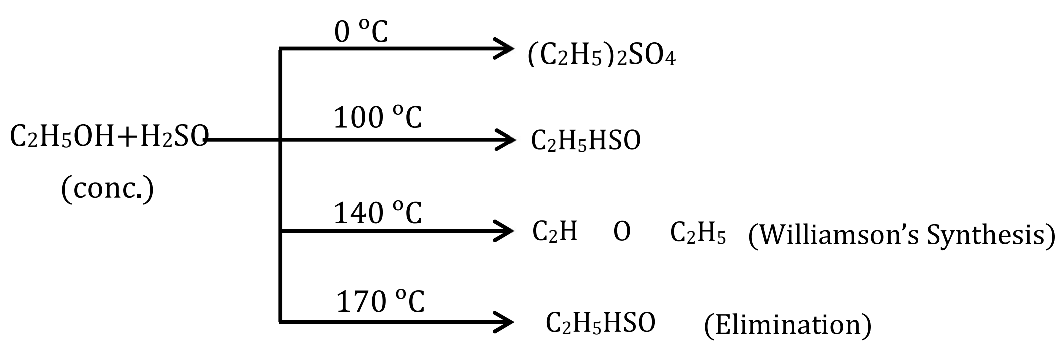
$$CH_3CHO + 3Cl_2 \longrightarrow \underset{\text{chloral}}{CCl_3CHO} + 3HCl \text{ (chlorination)}$$

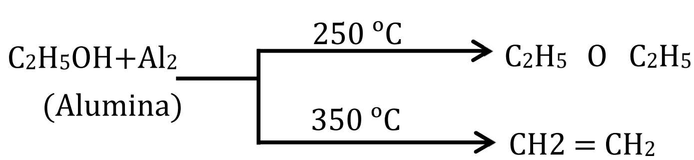
(C) **Reaction involving complete molecule of alcohol**

(i) **Dehydration:** Removal of H_2O by two type.

(a) Intermolecularly removal of H_2O [form ether]

(b) Intramolecularly removal of H_2O [form alkene]



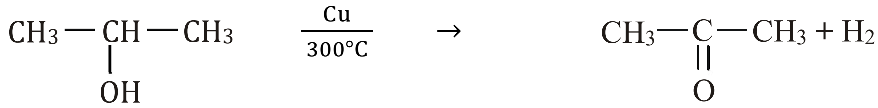


Ease of dehydration follow the order: 3° ROH > 2° ROH > 1° ROH > CH_3OH

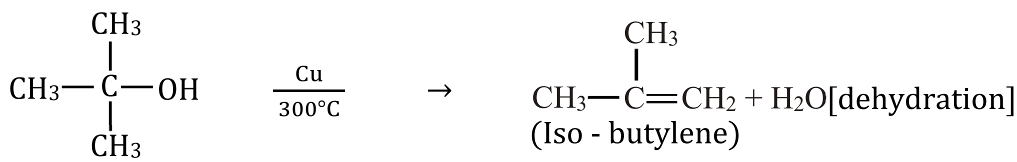
(ii) Catalytic Dehydrogenation: This reaction is useful in distinction of 1°, 2° and 3° alcohols.

$CH_3CH_2OH \xrightarrow[300°C]{Cu} CH_3CHO + H_2$

(p- alcohol) (Acetaldehyde)

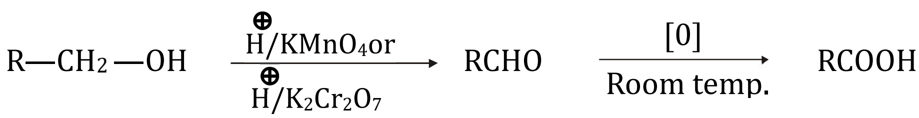


(s- alcohol) (acetone)

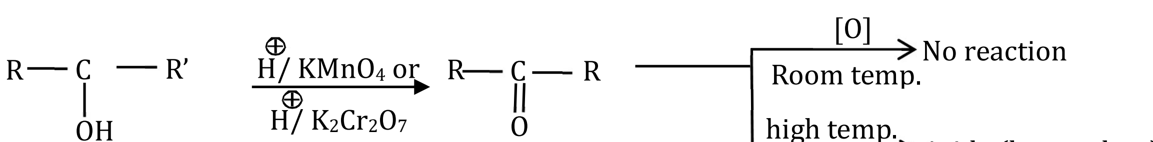


(t. alcohol) (Iso - butylene)

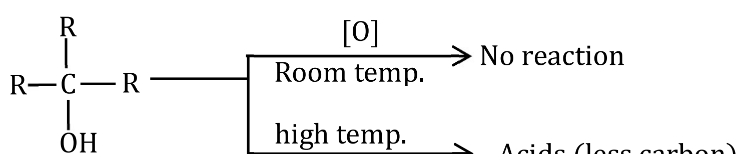
(iii) Oxidation: This reaction is useful in distinction of 1°, 2° and 3° alcohols.



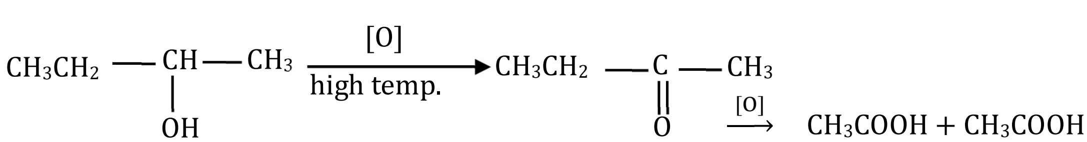
(p-alcohol) (same carbon acid)



(s- alcochol) (Same carbon)



(t-alcohol)



Carbonyl group goes with smaller alkyl group

(iv) Reaction with phosphorous pentasulphide

$R—OH + P_2S_5 \longrightarrow R—SH + P_2O_5$

Thio alcohol

(v) **Reaction with salts**

$$CH_3OH \xrightarrow{CuSO_4} CuSO_4.\,2CH_3OH$$
$$CH_3OH \xrightarrow{CaCl_2} CaCl_2.4CH_3OH$$
$$CH_3OH \xrightarrow{MgCl_2} MgCl_2.\,6CH_3OH$$

(vi) **Distinction between 1°, 2° and 3° alcohols**

(a) **Luca's test:** A mixture of HCl(conc.) and anhydrous $ZnCl_2$ is called Luca's 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 1 minute.

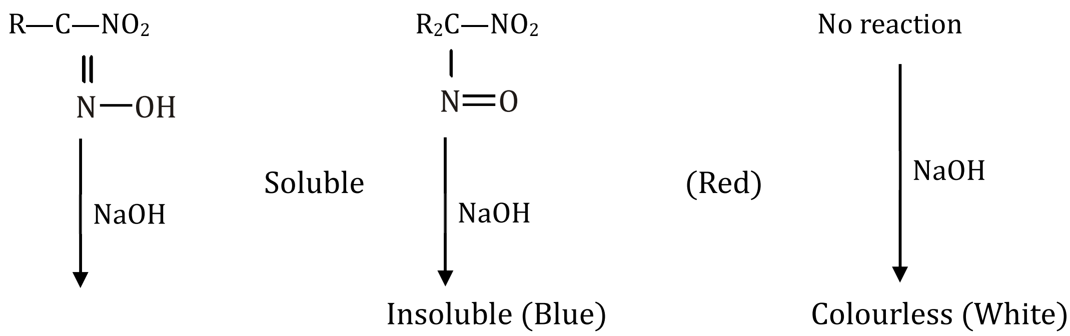
(b) **Victor - Meyer test:** This is colour test for alcohol (pri. sec. & tert.).

p-alcohol $\longrightarrow$ Red colour
s-alcohol $\longrightarrow$ Blue colour
t-alcohol $\longrightarrow$ No colour

$$R{-}CH_2{-}OH\ [1°] \xrightarrow{P+I_2} R{-}CH_2{-}I \xrightarrow{AgNO_2} RCH_2{-}NO_2 \xrightarrow{HNO_2}$$

$$R_2CH{-}OH\ [2°] \xrightarrow{P+I_2} R_2CH{-}I \xrightarrow{AgNO_2} R_2CH{-}NO_2 \xrightarrow{HNO_2}$$

$$R_3C{-}OH\ [3°] \xrightarrow{P+I_2} R_3C{-}I \xrightarrow{AgNO_2} R_3C{-}NO_2 \xrightarrow{HNO_2}$$



(vii) **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, No green

(viii) **Test of alcoholic group**

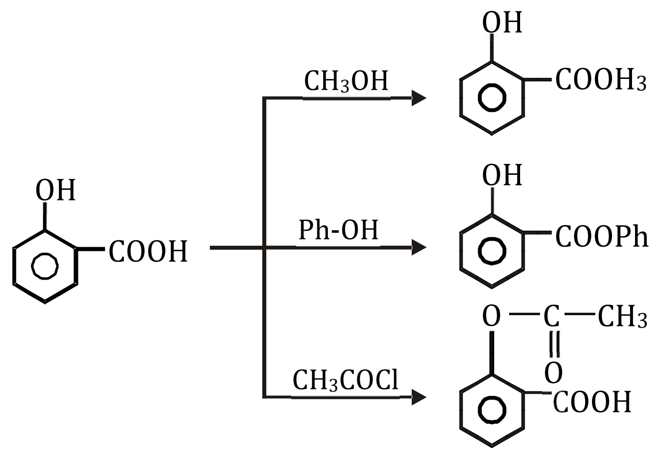
R—OH $\xrightarrow{Na}$ R—ONa + H_2 [effervescence of H_2]

R—OH $\xrightarrow{PCl_5}$ R—Cl + $POCl_3$ + HCl $\xrightarrow{NH_3}$ NH_4Cl [White fumes]

R—OH $\xrightarrow{\text{Cerric ammonium nitrate}}$ Red color

(ix) **Distinction between CH_3 – OH and C_2H_5OH**

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



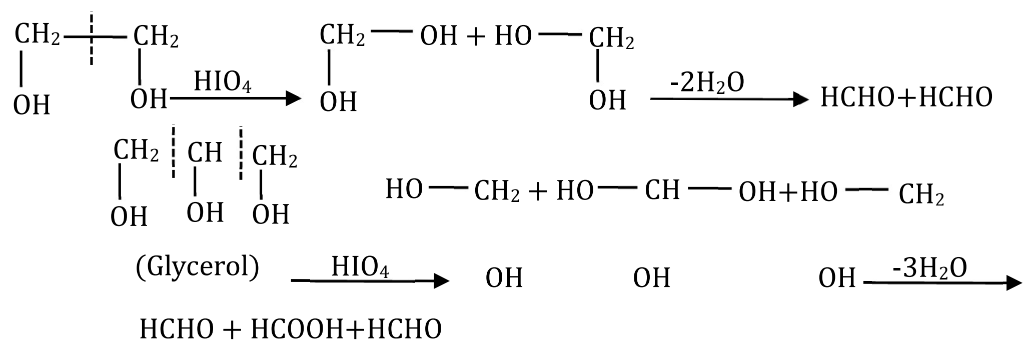
Methyl salicylate (Oil of wintergreen)

Phenyl salicylate Salol (Internal antiseptic)

Aspirin (Analgesic)

ADDITIONAL REACTIONS

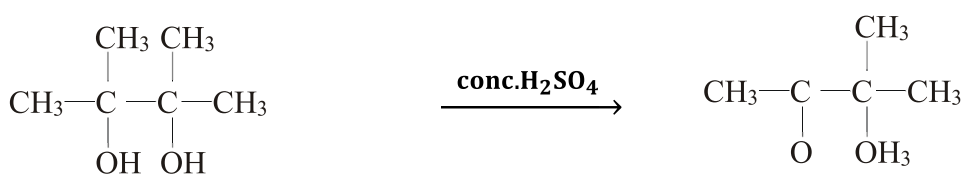
(a) Oxidation by HIO_4 [per iodic acid]



Condition for oxidation by HIO_4

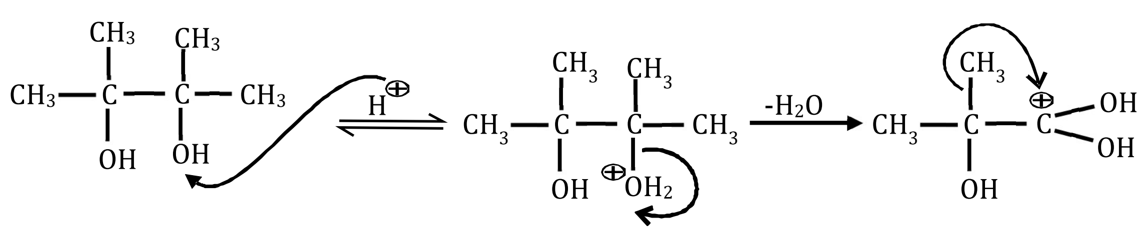
At least 2 —OH or 2 $>$C=O or 1 —OH and 1 $>$C=O should be at adjacent carbons.

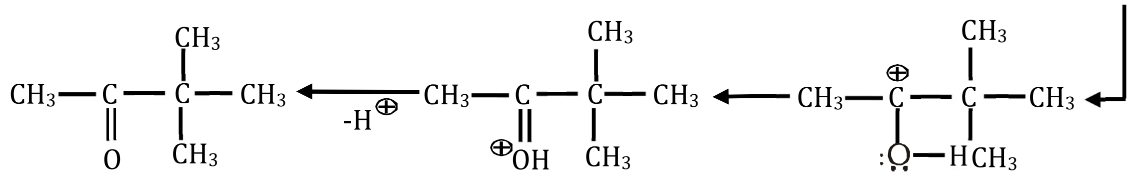
(b) Pinacole - Pinacolone Rearrangement



Pinacole Pinacolone

MECHANISM



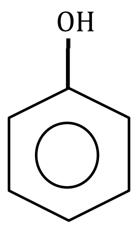


(Complete octet more stable)

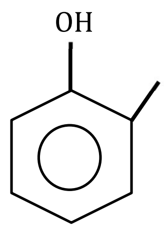
AROMATIC HYDROXY DERIVATIVES

Phenolic compounds

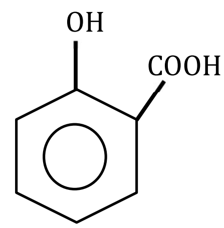
Compounds in which —OH group is directly attached to sp_2 C [Benzene ring]



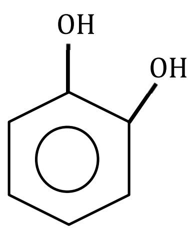
Phenol



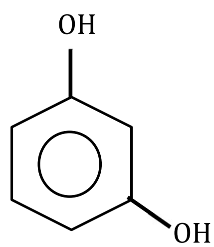
O-cresol



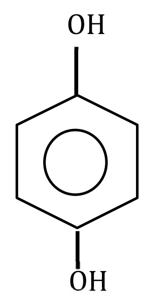
Salicylic acid



catechol



resorcinol



quinol

All phenolic compounds give characteristic colour with neutral $FeCl_3$.\

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

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