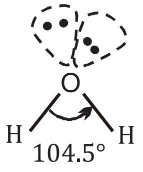
Chapter 10

Alcohols, Phenols and Ethers

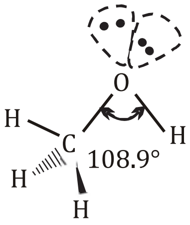
INTRODUCTION OF ALCOHOL, PREPARATION AND PROPERTIES

Introduction of Alcohol

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.



water



Methyl alcohol

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

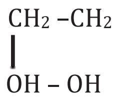
(II) **Aromatic Hydroxy Derivatives**
Hydroxy derivatives in which —OH is directly attached to sp^2 C or benzene ring (Phenolic compounds).

Aliphatic Hydroxy Derivatives

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

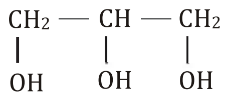
(i) Monohydric [one –OH] ⟶ $CH_3CH_2—OH$

(ii) Dihydric [two –OH] ⟶



$$\underset{OH}{CH_2}-\underset{OH}{CH_2}$$

(iii) Trihydric [three –OH ⟶



$$\underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2}$$

(IV) Polyhydric [N –OH] ⟶

$$\underset{OH}{CH_2} - \underset{OH}{CH} \text{------------} \underset{OH}{CH_2}$$

(b) Classification according to nature of carbon

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

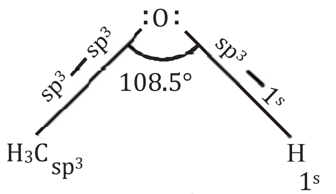
(ii) s or 2° – alcohol ⟶ $(CH_3)_2CH - OH$

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

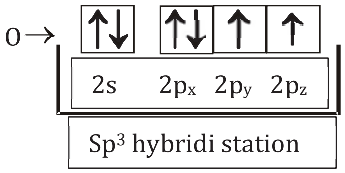
Alcohols

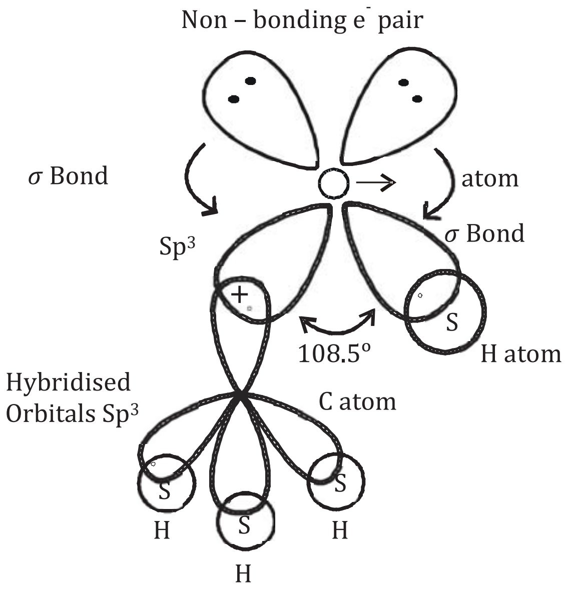
Structure of Alcohol

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





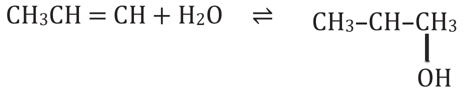
Out of these four orbitals, two contain one electron each, while the other two contain two electrons each. The orbitals with two electrons do not actively participate in bonding. The remaining two half-filled orbitals form sigma (σ) bonds with the s-orbitals of hydrogen atoms and the hybridized orbital 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.

Oxygen Containing Compound

An oxygen-containing compound is a chemical substance that incorporates oxygen atoms within its molecular structure. These compounds can be organic or inorganic and serve various purposes in nature, industry, and everyday life.

Organic oxygen-containing compounds include alcohols, ethers, aldehydes, ketones, carboxylic acids, esters, and more. These compounds are characterized by the presence of oxygen atoms bonded to carbon atoms.

When subjected to water in the presence of an acid catalyst, alkene undergoes a chemical reaction resulting in the formation of alcohol. In instances involving unsymmetrical alkenes, the resultant alcohol conforms to the principles outlined by Markovnikov's rule.



$$CH_3CH = CH + H_2O \rightleftharpoons CH_3\text{–}\underset{\substack{|\\OH}}{CH}\text{–}CH_3$$

For example, ethanol (C_2H_5OH) is a common alcohol, while acetone (CH_3COCH_3) is a widely used ketone.

Inorganic oxygen-containing compounds include oxides, peroxides, and hydroxides, among others. These compounds typically involve oxygen bonded to elements other than carbon.

For instance, magnesium oxide (MgO) is an inorganic oxide commonly used in manufacturing processes, while hydrogen peroxide (H_2O_2) is a well-known inorganic peroxide with disinfectant properties.

The presence of oxygen in these compounds often imparts specific properties and reactivities, such as acidity, oxidation potential, and solubility.

General Methods of Preparation

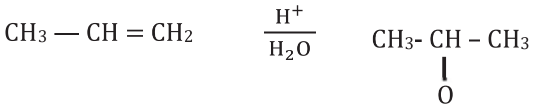
Monohydric Alcohol

(a) From alkanes (By oxidation)

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

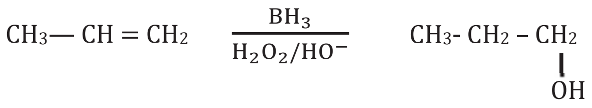
(b) From alkenes

(i) By hydration



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

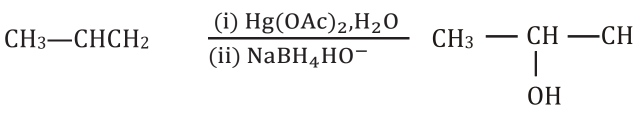
(ii) By hydroboration oxidation



$$CH_3 — CH = CH_2 \xrightarrow[H_2O_2/HO^-]{BH_3} CH_3\text{-}CH_2\text{–}\underset{\substack{|\\OH}}{CH_2}$$

(1° alcohol)

(iii) By oxymercuration demarcation



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

(c) From Alkyl Halides (By hydrolysis)

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

(d) From Carbonyl Compounds (By reduction)

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

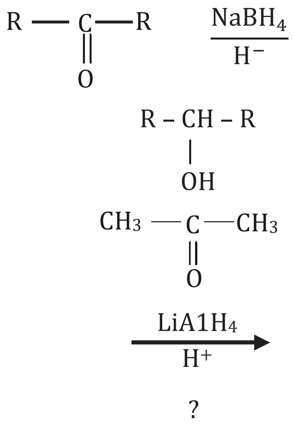
Reducing agents may be, $LiAlH_4/H^{\oplus}$, $NaBH_4/H^{\oplus}$

Na + EtOH [Bouveault-blanc Reduction]

NaH [Darzen reduction]

Ni / H_2

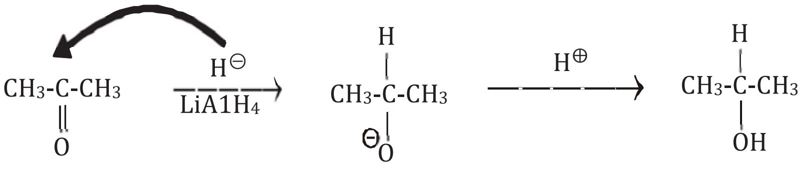
$$R— CHO \xrightarrow[H^-]{LiAlH_4} R—CH_2—OH$$

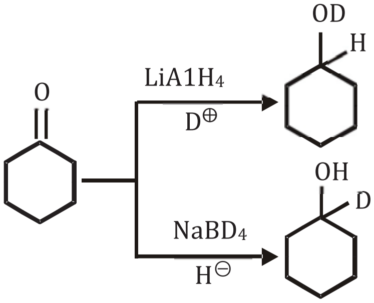


$$R-\underset{\underset{O}{\|}}{C}-R \xrightarrow[H^-]{NaBH_4} R-\underset{\underset{OH}{|}}{CH}-R$$

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[H^+]{LiA1H_4} ?$$

Mechanism





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

Crotonaldehyde

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

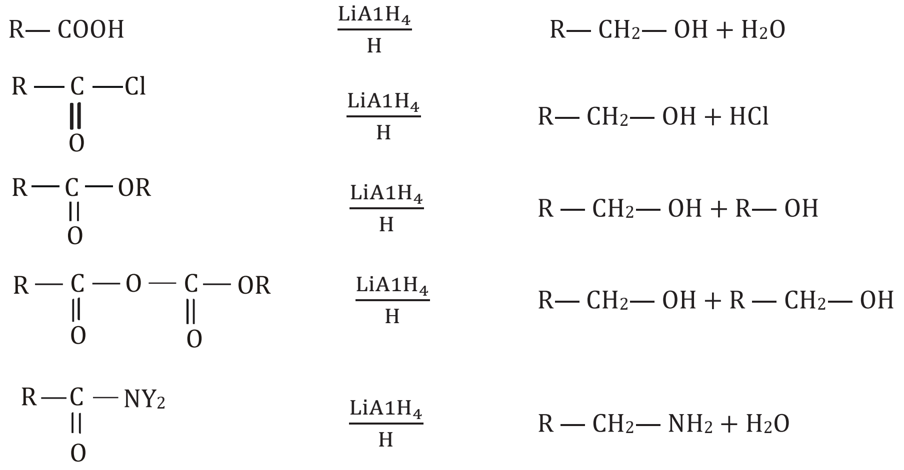
Cinnamaldehyde

(e) From Ethers

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

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

(f) From Acid and Derivatives (By reduction)



$$R-COOH \xrightarrow[H]{LiA1H_4} R-CH_2-OH + H_2O$$

$$R-\overset{\overset{}{}}{\underset{\underset{O}{\|}}{C}}-Cl \xrightarrow[H]{LiA1H_4} R-CH_2-OH + HCl$$

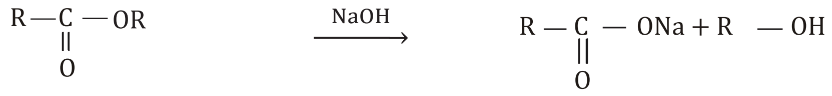
$$R-\underset{\underset{O}{\|}}{C}-OR \xrightarrow[H]{LiA1H_4} R-CH_2-OH + R-OH$$

$$R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-OR \xrightarrow[H]{LiA1H_4} R-CH_2-OH + R-CH_2-OH$$

$$R-\underset{\underset{O}{\|}}{C}-NY_2 \xrightarrow[H]{LiA1H_4} R-CH_2-NH_2 + H_2O$$

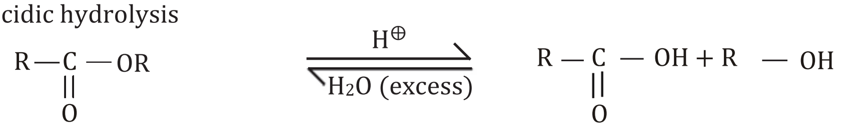
(g) From Esters (By hydrolysis)

(i) By alkaline hydrolysis

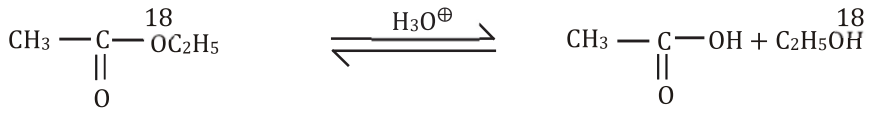


$$R-\underset{\underset{O}{\|}}{C}-OR \xrightarrow{NaOH} R-\underset{\underset{O}{\|}}{C}-ONa + R-OH$$

(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.

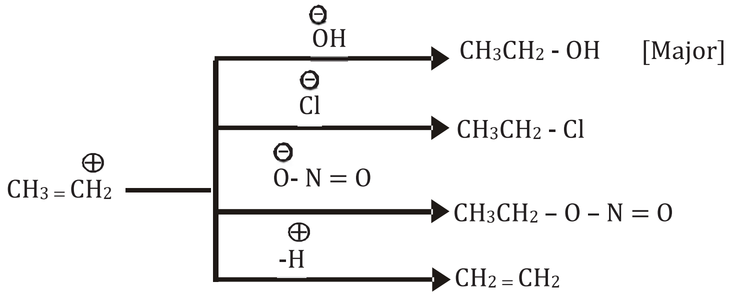
(h) From p-amines

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

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

Mechanism

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

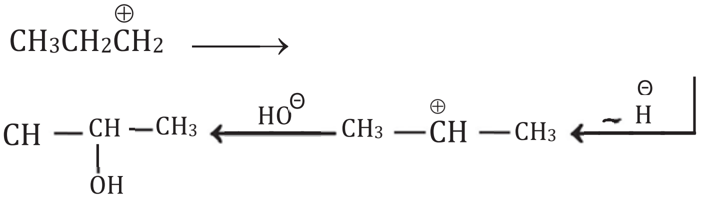


Inter mediate is carbocation so rearrangement may be possible.

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

Sol. Mechanism

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



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

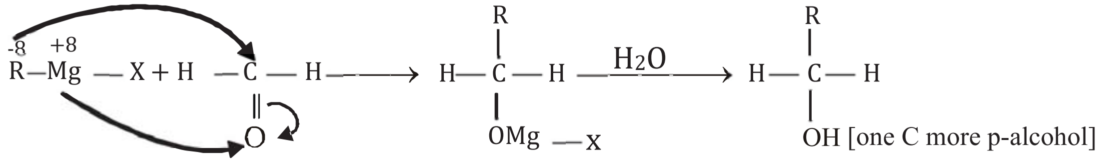
$$CH—\underset{OH}{CH}—CH_3 \xleftarrow{HO^{\ominus}} CH_3—\overset{\oplus}{C}H—CH_3 \xleftarrow{\sim \overset{\ominus}{H}}$$

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

From Grignard Reagent

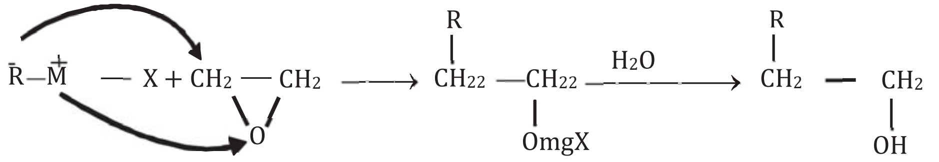
(i) **p-alcohol**

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



$$\overset{-\delta}{R}—\overset{+\delta}{Mg}—X + H—\underset{O}{\overset{}{C}}—H \longrightarrow H—\underset{OMg—X}{\overset{R}{C}}—H \xrightarrow{H_2O} H—\underset{OH}{\overset{R}{C}}—H$$

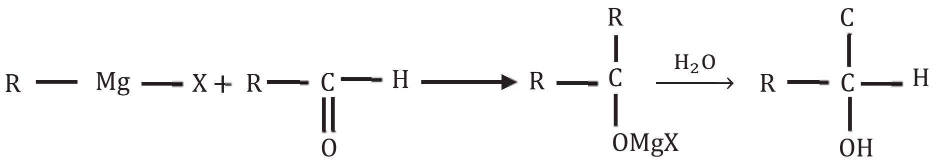
[one C more p-alcohol]



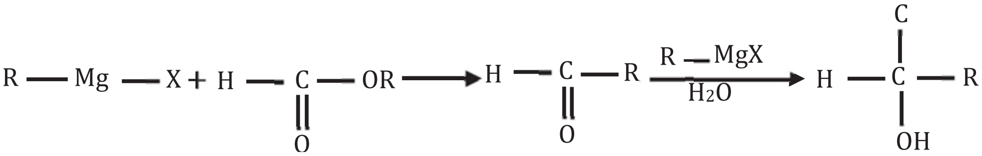
$$\overset{-}{R}—\overset{+}{M}—X + CH_2—CH_2 (O) \longrightarrow \overset{R}{C}H_{22}—\underset{OmgX}{CH_{22}} \xrightarrow{H_2O} \overset{R}{C}H_2—\underset{OH}{CH_2}$$

Two C more p-alcohol

(ii) **s-alcohol**

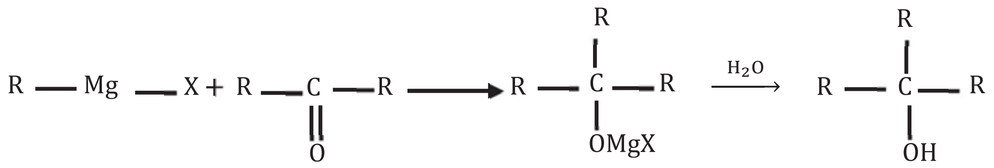


$$R—Mg—X + R—\underset{\|\ O}{C}—H \longrightarrow R—\underset{OMgX}{\overset{R}{C}} \xrightarrow{H_2O} R—\underset{OH}{\overset{C}{C}}—H$$

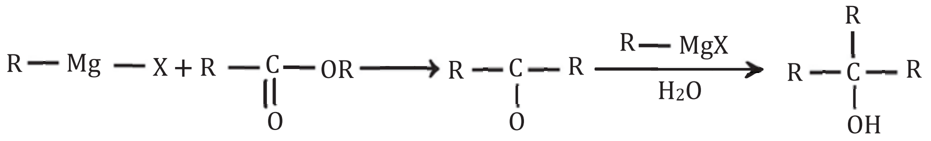


$$R—Mg—X + H—\underset{\|\ O}{C}—OR \longrightarrow H—\underset{\|\ O}{C}—R \xrightarrow[H_2O]{R—MgX} H—\underset{OH}{\overset{C}{C}}—R$$

(iii) **t-alcohol**



$$R-Mg-X + R-\underset{\underset{O}{\|}}{C}-R \longrightarrow R-\underset{OMgX}{\overset{R}{C}}-R \xrightarrow{H_2O} R-\underset{OH}{\overset{R}{C}}-R$$



$$R-Mg-X + R-\underset{\underset{O}{\|}}{C}-OR \longrightarrow R-\underset{\underset{O}{|}}{C}-R \xrightarrow[H_2O]{R-MgX} R-\underset{OH}{\overset{R}{C}}-R$$

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.

Solubility

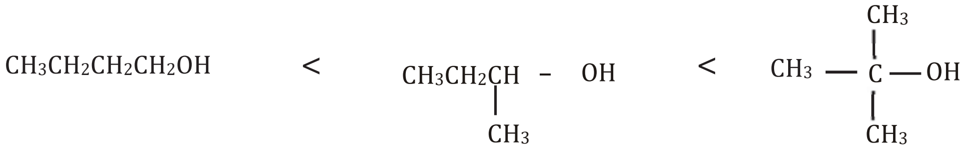
- The initial three members can fully dissolve in water, whereas the higher members are nearly insoluble in water but can dissolve in organic solvents such as benzene and ether.
- The solubility of lower alcohols arises from the formation of hydrogen bonds between the polar O–H groups of alcohol molecules 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.

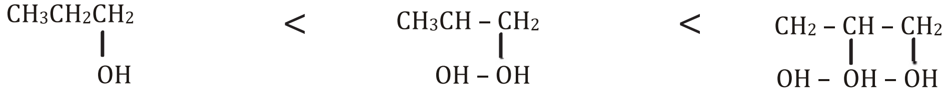
$$\text{solubility} \propto \text{No. of side chains} \propto \frac{1}{\text{Molecular weight}}$$

Order of Solubility

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



$$CH_3CH_2CH_2CH_2OH \quad < \quad CH_3CH_2\underset{CH_3}{\underset{|}{CH}} - OH \quad < \quad CH_3-\underset{CH_3}{\underset{|}{\overset{\overset{CH_3}{|}}{C}}}-OH$$

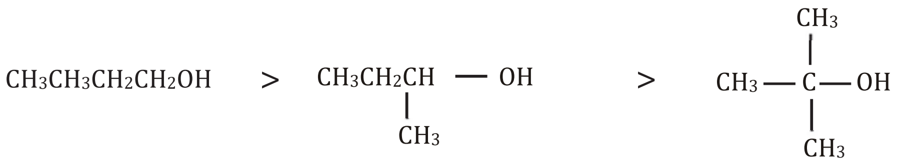


$$\underset{OH}{\underset{|}{CH_3CH_2CH_2}} \quad < \quad \underset{OH\ -\ OH}{CH_3CH-CH_2} \quad < \quad \underset{OH\ -\ OH\ -\ OH}{CH_2-CH-CH_2}$$

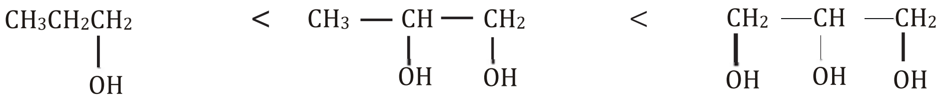
[Number of —OH increases, H-bonding increases]
Boiling points: B.P. $\propto$ molecular weight
If molecular wt. is same then B.P. $\propto \frac{1}{\text{branching}}$

Order of BP

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



$$CH_3CH_3CH_2CH_2OH > \underset{\underset{\displaystyle CH_3}{|}}{CH_3CH_2CH}-OH > CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH$$



$$\underset{\underset{\displaystyle OH}{|}}{CH_3CH_2CH_2} < CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-\underset{\underset{\displaystyle OH}{|}}{CH_2} < \underset{\underset{\displaystyle OH}{|}}{CH_2}-\underset{\underset{\displaystyle OH}{|}}{CH}-\underset{\underset{\displaystyle OH}{|}}{CH_2}$$

[Number of OH increases, H-bonding increases]

Chemical Properties of Alcohol

Monohydric alcohol shows following reactions

(A) Reaction involving cleavage of $O \wr H$

(B) Reaction involving cleavage of $C \wr OH$

(C) Reaction involving complete molecule of alcohol

(A) Reaction involving cleavage of $O \wr H$

Reactivity order (Acidic nature) is

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

(i) **Acidic nature**

$$H_2O > R—OH > CHCH > NH_3 \quad \text{(Acidic strength)}$$

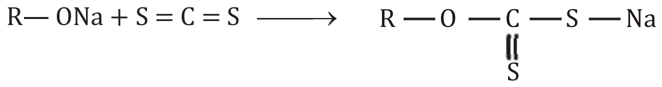
Alcohols are less acidic than H_2O and neutral for litmus paper and gives H_2 with active metals (Na, K)

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

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

(ii) **Reaction with CS_2**

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



$$R—ONa + S = C = S \longrightarrow R—O—\underset{\underset{\displaystyle S}{\|}}{C}—S—Na$$

Sodium alkyl xanthate (Used as floating agent)

(iii) **Alkylation**

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

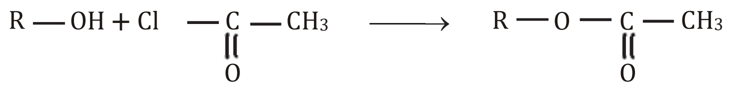
$$R—OH \xrightarrow{Na} R—ONa \xrightarrow{R-X} R—O—R$$

(Williamson synthesis)

(iv) **Acylation**

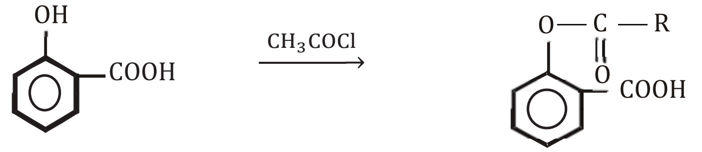
$$R—OH + Cl—\underset{\underset{\displaystyle O}{\|}}{C}—R \longrightarrow R—O—\underset{\underset{\displaystyle O}{\|}}{C}—R$$

(Acylation)



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

(Acetylation)



Salicylic acid

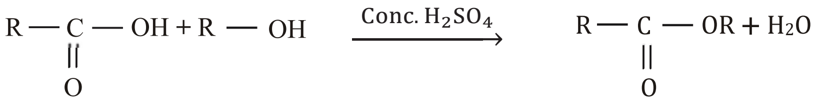
Acetoxy benzoic acid
Acetyl salicylic acid
Aspirin [Used as analgesic]

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

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

(Benzoylation)

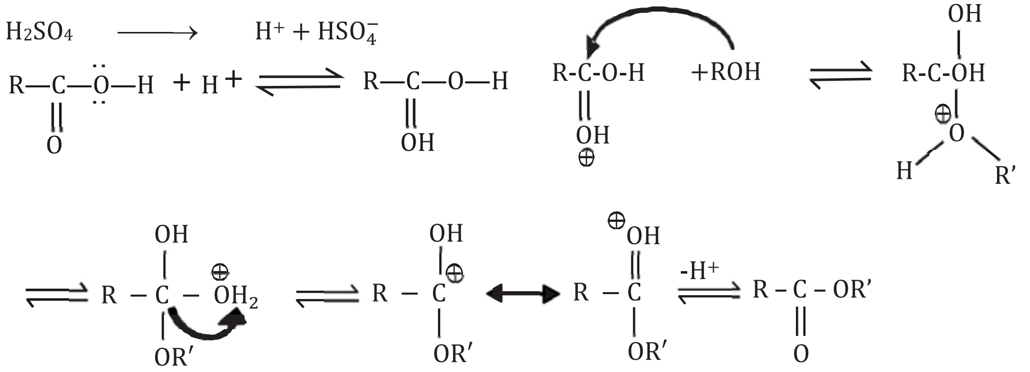
(vi) Esterification: Conc. H_2SO_4 is used as catalyst and dehydrating agent**.**



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

Mechanism

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

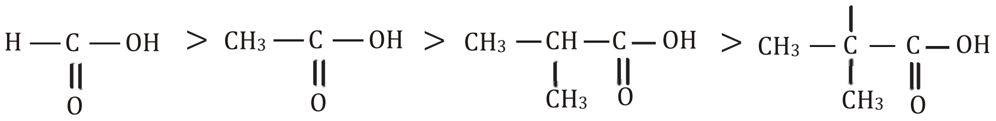


Note: This is a laboratory method to prepare ester.

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

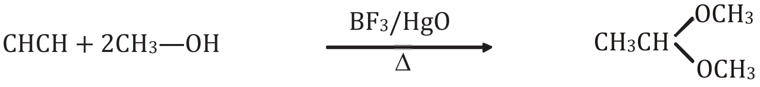
(ii) Reactivity of R – OH [If acid is same]: $CH_3-OH > 1° > 2° > 3°$ alcohol

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

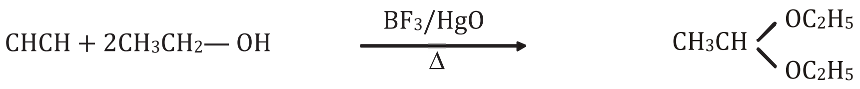


$$H-\underset{\underset{O}{\|}}{C}-OH > CH_3-\underset{\underset{O}{\|}}{C}-OH > CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OH > CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{O}{\|}}{C}-OH$$

(vii) Reaction with CHCH



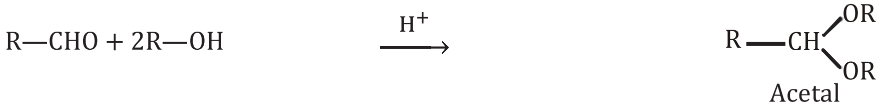
Methylal



$$CHCH + 2CH_3CH_2\text{—}OH \xrightarrow[\Delta]{BF_3/HgO} CH_3CH\begin{matrix} OC_2H_5 \\ OC_2H_5 \end{matrix}$$

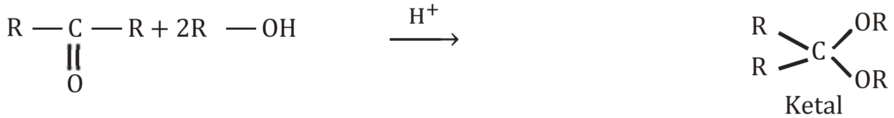
Ethylal

(viii) Reaction with carbonyl compounds



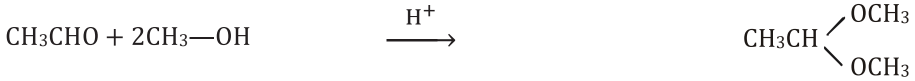
$$R\text{—}CHO + 2R\text{—}OH \xrightarrow{H^+} R\text{—}CH\begin{matrix} OR \\ OR \end{matrix}$$

Acetal



$$R\text{—}\underset{O}{\underset{\|}{C}}\text{—}R + 2R\text{—}OH \xrightarrow{H^+} \begin{matrix} R \\ R \end{matrix}C\begin{matrix} OR \\ OR \end{matrix}$$

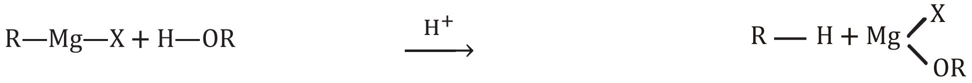
Ketal



$$CH_3CHO + 2CH_3\text{—}OH \xrightarrow{H^+} CH_3CH\begin{matrix} OCH_3 \\ OCH_3 \end{matrix}$$

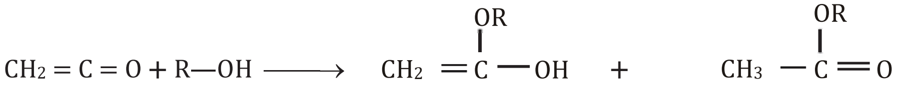
Methylal

(ix) Reaction with Grignard reagent

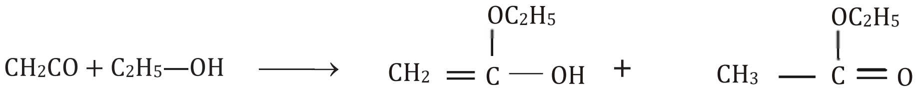


$$R\text{—}Mg\text{—}X + H\text{—}OR \xrightarrow{H^+} R\text{—}H + Mg\begin{matrix} X \\ OR \end{matrix}$$

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



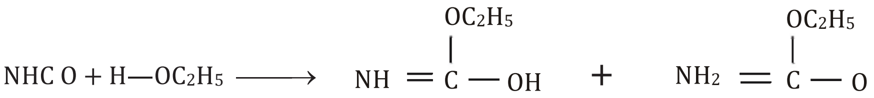
$$CH_2 = C = O + R\text{—}OH \longrightarrow CH_2 = \overset{OR}{\overset{|}{C}}\text{—}OH + CH_3\text{—}\overset{OR}{\overset{|}{C}} = O$$



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

Ethyl acetate

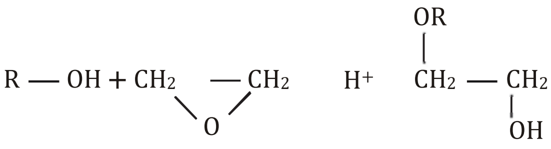
(xi) Reaction with isocyanic acid: Ethyl urethane is used in preparation of urea.



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

Ethyl urethane

(xii) Reaction with oxirane



$$R\text{—}OH + \underset{\diagdown O \diagup}{CH_2\text{—}CH_2} \quad H^+ \quad \overset{OR}{\overset{|}{CH_2}}\text{—}\underset{OH}{\underset{|}{CH_2}}$$

(B) Reaction involving cleavage of $C\text{—}\wr\text{—}OH$

Reactivity order or basic nature is

$$CH_3\text{—}OH < CH_3CH_2\text{—}OH < (CH_3)_2CH\text{—}OH < (CH_3)_3\,C\text{—}OH$$

(i) Reaction with halogen acid

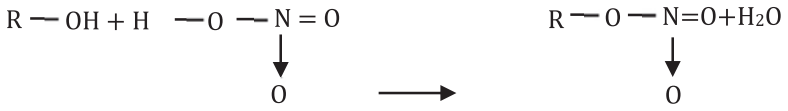
$$R-CH_2-OH + HCl \xrightarrow[\Delta]{ZnCl_2} R-CH_2-Cl + H_2O$$

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

2^0 alcohols

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

(ii) Reaction with inorganic acids



$$R-OH + H-O-\underset{\overset{\downarrow}{O}}{N}=O \longrightarrow R-O-\underset{\overset{\downarrow}{O}}{N}=O+H_2O$$

Nitric acid Alkyl nitrate

$$R-OH + HHSO_4 \longrightarrow R-HSO_4 + H_2O$$

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 ($SOCl_2$)

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

(gas)

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

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

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

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

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

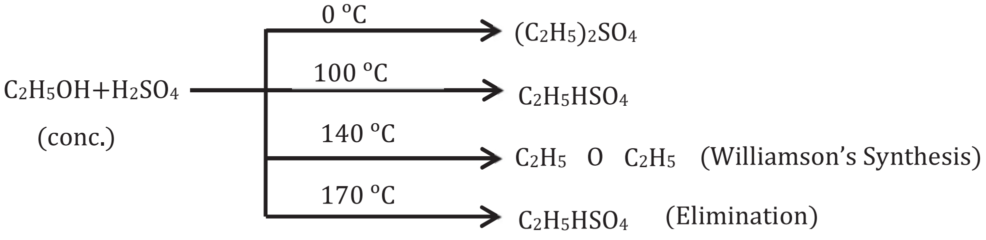
chloral

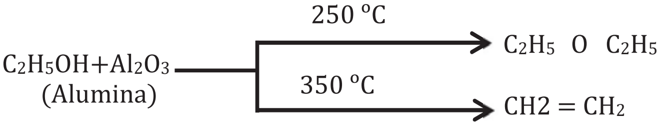
(C) Reaction involving complete molecule of alcohol

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

(a) Intermolecularly removal of H_2O [form ether]

(b) Intramolecularly removal of H_2O [form alkene]

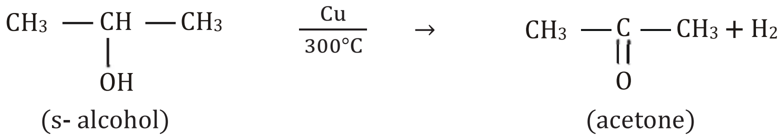




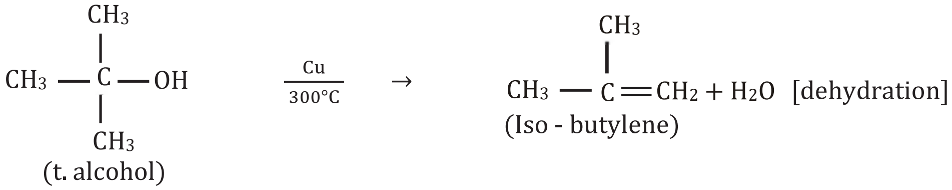
Ease of dehydration follow the order: 3° ROH > 2° ROH > 1° ROH > CH_3OH

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

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



$$\underset{\text{(s- alcohol)}}{CH_3-CH(OH)-CH_3} \xrightarrow[300°C]{Cu} \underset{\text{(acetone)}}{CH_3-C(=O)-CH_3} + H_2$$

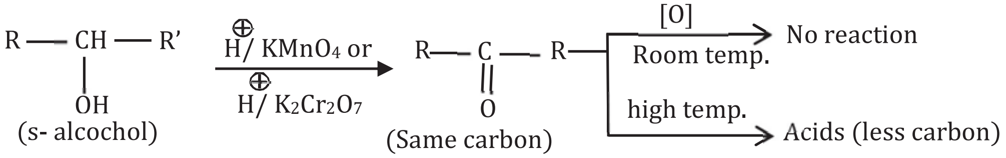


$$\underset{\text{(t. alcohol)}}{(CH_3)_3C-OH} \xrightarrow[300°C]{Cu} \underset{\text{(Iso - butylene)}}{CH_3-C(CH_3)=CH_2} + H_2O \quad \text{[dehydration]}$$

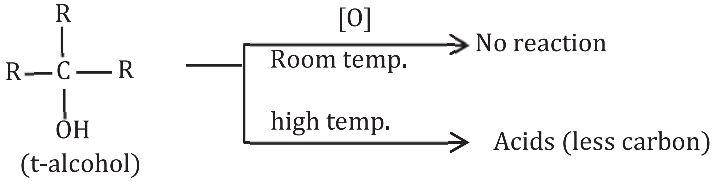
(iii) Oxidation: This reaction is useful in distinction of 1°, 2° and 3° alcohols.

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

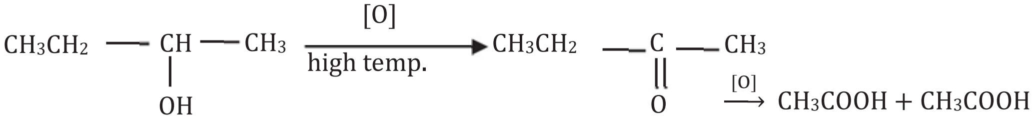
(same carbon acid)



$$\underset{\text{(s- alcochol)}}{R-CH(OH)-R'} \xrightarrow[\overset{\oplus}{H}/K_2Cr_2O_7]{\overset{\oplus}{H}/KMnO_4 \text{ or}} \underset{\text{(Same carbon)}}{R-C(=O)-R} \begin{cases} \xrightarrow[\text{Room temp.}]{[O]} \text{No reaction} \\ \xrightarrow{\text{high temp.}} \text{Acids (less carbon)} \end{cases}$$



$$\underset{\text{(t-alcohol)}}{R_3C-OH} \begin{cases} \xrightarrow[\text{Room temp.}]{[O]} \text{No reaction} \\ \xrightarrow{\text{high temp.}} \text{Acids (less carbon)} \end{cases}$$



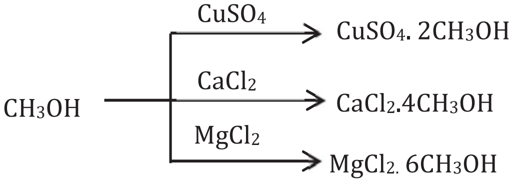
$$CH_3CH_2-CH(OH)-CH_3 \xrightarrow[\text{high temp.}]{[O]} CH_3CH_2-C(=O)-CH_3 \xrightarrow{[O]} CH_3COOH + CH_3COOH$$

Carbonyl group goes with smaller alkyl group

(iv) Reaction with phosphorous pentasulphide

$$R-OH + P_2S_5 \longrightarrow \underset{\text{Thio alcohol}}{R-SH} + P_2O_5$$

(v) Reaction with salts



$$CH_3OH \begin{cases} \xrightarrow{CuSO_4} CuSO_4.\ 2CH_3OH \\ \xrightarrow{CaCl_2} CaCl_2.4CH_3OH \\ \xrightarrow{MgCl_2} MgCl_2.\ 6CH_3OH \end{cases}$$

(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.

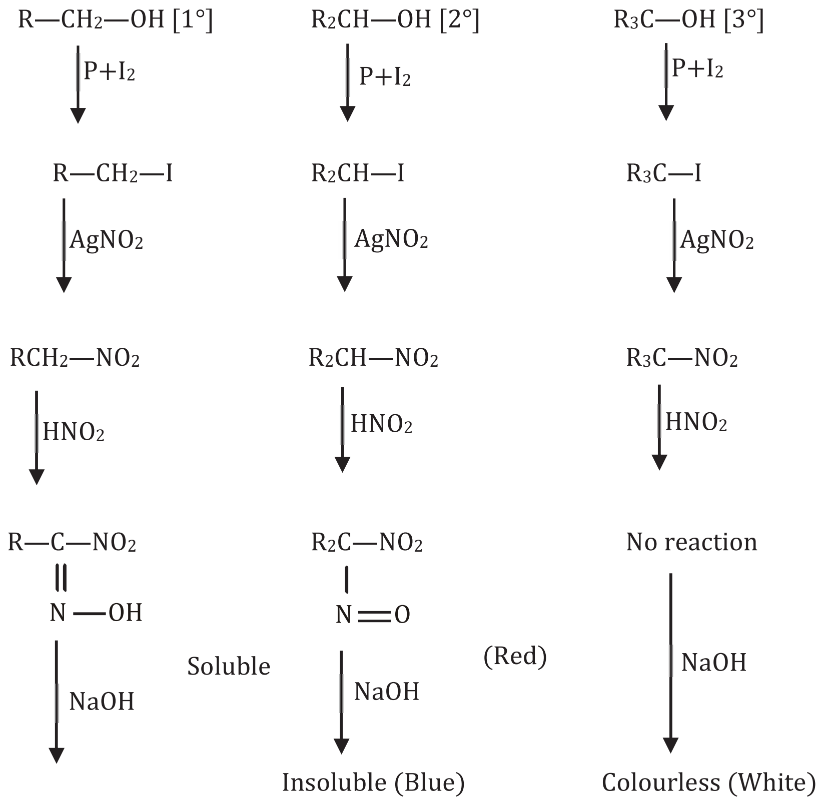
p-alcohol $\xrightarrow{ZnCl_2+HCl}$ No turbidity at room temp. [On heating within 30 minutes.]

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



(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]

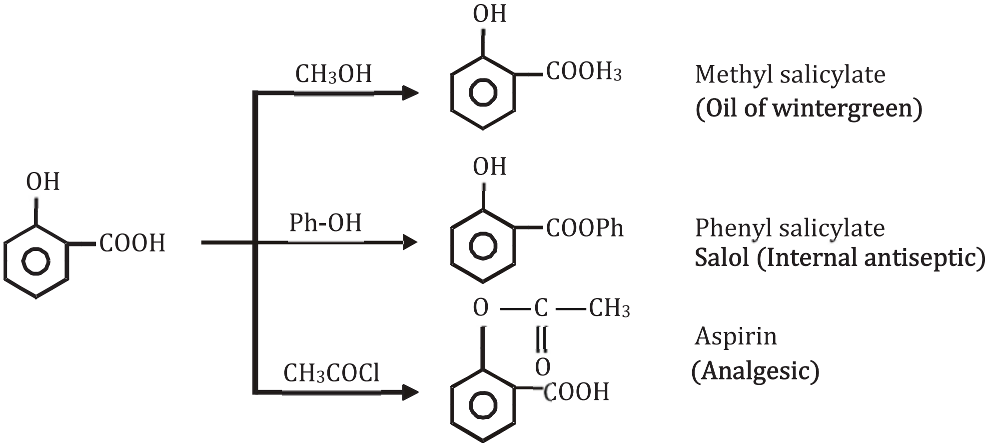
$$R{-}OH \xrightarrow{PCl_5} R{-}Cl + POCl_3 + HCl \xrightarrow{NH_3} NH_4Cl$$

[White fumes]

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

(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



Differentiation Methods of Alcohol

Distinguishing between various categories of alcohols can be achieved through a variety of approaches, rooted in their distinctive chemical and physical attributes.

Below are several commonly utilized methods for differentiation:

Classification by Carbon Substitution

Alcohols are categorized into primary, secondary, and tertiary types, contingent upon the carbon atom where the hydroxyl (-OH) group is affixed.

Primary alcohol: The -OH group is linked to a carbon atom bonded solely to another carbon atom.

Secondary alcohol: The -OH group is attached to a carbon atom bonded to two other carbon atoms.

Tertiary alcohol: The -OH group is connected to a carbon atom bonded to three other carbon atoms.

Distillation

Employed extensively, distillation serves as a prevalent means of segregating alcohols by exploiting their differing boiling points. Variances in molecular weights and intermolecular forces engender distinct boiling points among alcohols. Consequently, upon heating a blend of alcohols, separation is achieved as those with lower boiling points vaporize initially.

Chromatography

A diverse array of chromatographic techniques, encompassing gas chromatography (GC) and high-performance liquid chromatography (HPLC), is deployed to fractionate and scrutinize alcohols based on factors such as polarity, size, and other inherent physical and chemical characteristics.

Infrared Spectroscopy (IR)

IR spectroscopy facilitates the identification of functional groups present within molecules, including the hydroxyl (-OH) group in alcohols. Unique functional group absorption patterns at characteristic frequencies enable the differentiation of various alcohol types.

Oxidation Reactions

Alcohols manifest different oxidation behaviors, aiding in their differentiation:
Primary alcohols undergo oxidation to yield aldehydes, subsequently oxidizing to carboxylic acids.
Secondary alcohols oxidize to form ketones.
Tertiary alcohols typically resist oxidation under standard conditions.

NMR Spectroscopy

NMR spectroscopy stands as a potent tool for elucidating the structural compositions of organic compounds, including alcohols. Each alcohol variant exhibits distinctive NMR spectra due to variations in molecular structures and chemical environments.