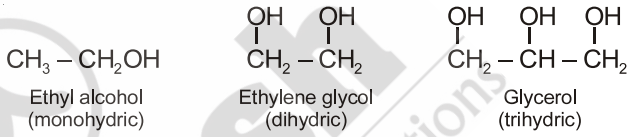
Chapter 14

Organic Compounds Containing Oxygen

ALCOHOLS

Molecules containing –OH group are termed as alcohols. Classification of alcohols they are classified as primary, secondary or tertiary alcohol according to the carbon that is bonded with –OH.

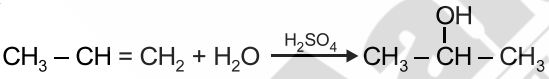
Again when any molecule contain 1, 2 or 3 –OH groups then it is called mono, di or tri hydric alcohols respectively. (as in case of alkyl halides)



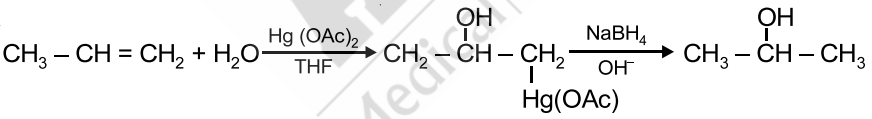
GENERAL METHODS OF PREPARATION

1. From Alkenes :

(i) **By Acid catalyzed hydrolysis :**

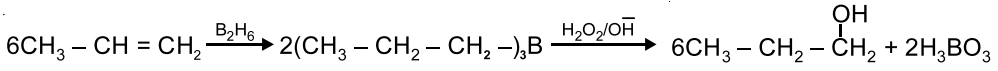


(ii) **Oxymercuration followed by demercuration :**



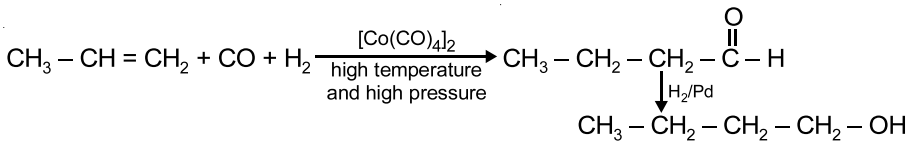
Overall result of above reaction is Markownikoff addition of water without rearrangement

(iii) **Hydroboration followed by oxidation :**



Overall result of above reaction is anti Markownikoff addition of water with no rearrangement.

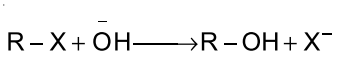
(iv) **Oxo process followed by hydrogenation :**



Product has one more carbon.

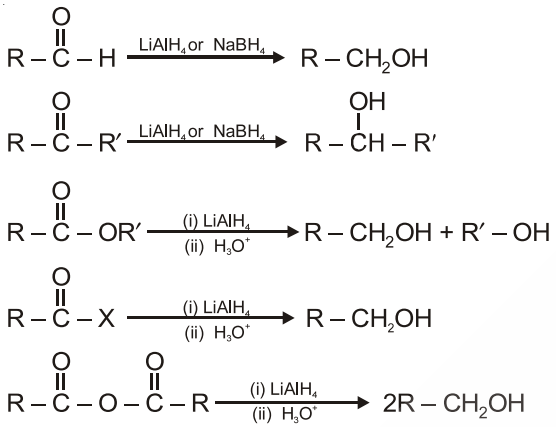
2. From Alkyl Halides :

When alkyl halides are treated with aq. KOH or aq. NaOH or moist Ag_2O, alcohols are formed.



$$R - X + \overline{O}H \longrightarrow R - OH + X^-$$

3. Reduction of Carbonyl Compounds, Carboxylic Acids and their Derivatives :



$$R-\overset{\overset{O}{\|}}{C}-H \xrightarrow{LiAlH_4 \text{ or } NaBH_4} R-CH_2OH$$

$$R-\overset{\overset{O}{\|}}{C}-R' \xrightarrow{LiAlH_4 \text{ or } NaBH_4} R-\overset{\overset{OH}{|}}{CH}-R'$$

$$R-\overset{\overset{O}{\|}}{C}-OR' \xrightarrow[(ii)\ H_3O^+]{(i)\ LiAlH_4} R-CH_2OH + R'-OH$$

$$R-\overset{\overset{O}{\|}}{C}-X \xrightarrow[(ii)\ H_3O^+]{(i)\ LiAlH_4} R-CH_2OH$$

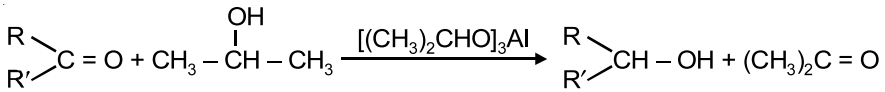
$$R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R \xrightarrow[(ii)\ H_3O^+]{(i)\ LiAlH_4} 2R-CH_2OH$$

Table : Reducing nature of different reagents

Group	Product	$LiAlH_4/H_2O$	$NaBH_4/C_2H_5OH$	B_2H_6/THF	H_2/Pt
$-\overset{\overset{O}{\|}}{C}-H$	$-CH_2-OH$	Yes	Yes	Yes	Yes
$>C=O$	$>CH-OH$	Yes	Yes	Yes	Yes
$-COOH$	$-CH_2OH$	Yes	No	Yes	Yes
$-\overset{\overset{O}{\|}}{C}-Cl$	$-CH_2OH$	Yes	Yes	No	Yes
$(R-\overset{\overset{O}{\|}}{C}-O)_2O$	$R-CH_2OH$	Yes	No	Yes	Yes
$-\overset{\overset{O}{\|}}{C}-OR$	$-CH_2OH + R-OH$	Yes	No	Yes	Yes
$>C=C<$	$>CH-CH<$	No ($LiAlH_4$ reduces) C = C only when it is conjugated with Phenylic system	No	Yes	Yes

Meerwein-Ponndorf-Verley Reduction (MPV Reduction) :

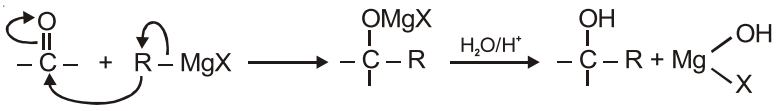
Ketones can be reduced to secondary alcohols with aluminium isopropoxide in 2-propanol solution.



$$R\diagdown \atop R'\diagup C=O + CH_3-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow{[(CH_3)_2CHO]_3Al} R\diagdown \atop R'\diagup CH-OH + (CH_3)_2C=O$$

4. Using Grignard Reagent :

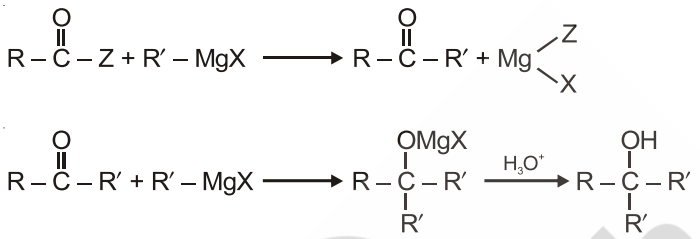
(i) From aldehydes or ketones :



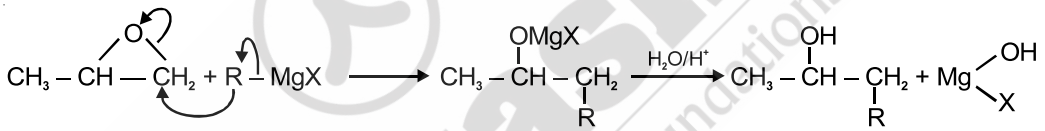
In this reaction

Formaldehyde gives	1°-alcohol
Other aldehydes give	2°-alcohol
Ketones give	3°-alcohol

(ii) From carboxylic acid and their derivatives :

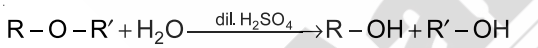


(iii) From epoxides :



5. Hydrolysis of Ether :

Ethers undergo acid hydrolysis with dilute H_2SO_4 under pressure to give corresponding alcohols.



Physical Properties

(i) Physical state : At ordinary temperature, lower members are colourless liquids with burning taste and pleasant smell.

(ii) Boiling Point : The boiling point of alcohols rise regularly with the rise in the molecular weight. Amongst isomeric alcohols, the boiling point decrease in the order.

$1° > 2° > 3°$

Alcohols have high boiling point then hydrocarbons and haloalkanes of similar molecular mass due to intermolecular hydrogen bonding.

(iii) Solubility : The extent of solubility of any alcohol in water depends upon the capability of its molecules to form hydrogen bonds with water molecule.

(iv) Alcohols are lighter than water, however, the density increases with the increase in molecular mass.

Chemical Properties

1. Reactions involving cleavage of O – H Bond

Alcohols are acidic in nature but they are less acidic than water hence they do not give H^+ in aqueous solution. They do not change the colour of litmus paper.

Their acidic strength increases by increasing–I strength of the groups attached and decreases by increasing +I strength of the groups.

(i) Alcohols do not react with aqueous alkali, as they do not give H^+ in aqueous solution.

(ii) Action of active metal : When alcohols are treated with active metal they form alkoxides with the liberation of H_2 gas.

$$2ROH + 2Na \longrightarrow 2R - \overset{-}{O}\overset{+}{Na} + H_2 \uparrow$$

(iii) Esterification : When carboxylic acid is treated with alcohols in the presence of acid as catalyst, esters are formed.

Alcohol reactivity order 1° > 2° > 3°.

$$R - \overset{O}{\overset{\|}{C}} - OH + H - O - R' \underset{}{\overset{H^+}{\rightleftharpoons}} R - \overset{O}{\overset{\|}{C}} - OR' + HOH$$

Its acid catalysed revsersible reaction.

Note : *(a) OH is removed from carboxylic acid and H is removed from alcohol.*

(b) Overall reaction is S_N2 in which alcohol acts as nucleophile.

(iv) Reaction with Grignard Reagent : When Grignard reagents are treated with alcohol (or any proton donor) they form alkanes.

$$R - MgX + H - OR' \longrightarrow R - H + R' - OMgX$$

Other proton donors can be carboxylic acids, phenols, alkynes, H_2O, Amines, NH_3 etc.

2. Reactions Involving Cleavage of C– O Bond

(i) Reaction with HX : Most alcohols undergo S_N1.

(a) $$R - OH + HCl(g) \xrightarrow{\text{Anhyd. } ZnCl_2} R - Cl + H_2O$$

Note : *HCl + anhyd. $ZnCl_2$ is called Lucas reagent. Lucas test is used to distinguish primary, secondary and tertiary alcohols.*

(b) $$R - OH + HBr \xrightarrow[\text{conc.}]{H^+/H_2SO_4} R - Br + H_2O$$

(c) $$R - OH + HI \xrightarrow[\text{conc.}]{H^+/H_2SO_4} R - I + H_2O$$

Reactivity order of HX is

HI > HBr > HCl

(ii) Alkyl chlorides can also be prepared by following methods :

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

$$3R - OH + PCl_3 \longrightarrow 3R - Cl + H_3PO_3$$

$$R - OH + SOCl_2 \longrightarrow R - Cl + SO_2 + HCl \text{ (Darzen's process)}$$

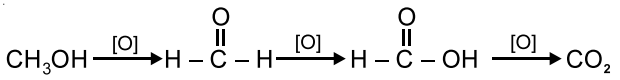
Darzen's process is the best method as the other by-products are gases.

3. Reduction :

Alcohols are reduced to alkanes when they are treated with red P + HI.

$$R - OH \xrightarrow{HI + \text{red P}} R - H + ZnO$$

4. Oxidation :



3°-alcohols can't be oxidised.

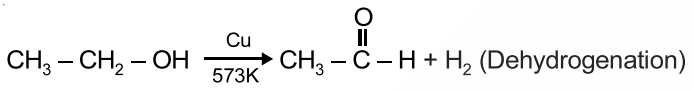
(i) Strong oxidising agent like $KMnO_4$ or $K_2Cr_2O_7$ cause maximum oxidation as above.

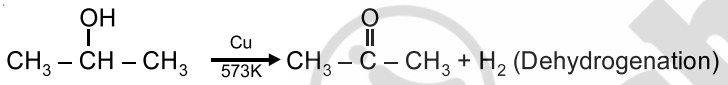
(ii) PCC (Pyridinium chlorochromate) is used to convert primary and secondary alcohol into corresponding carbonyl compound.

(iii) 2°-alcohol can be converted to ketone best by PCC + CH_2Cl_2 or CrO_3 or H_2CrO_4 in aq. acetone (Jones reagent).

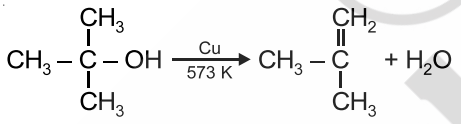
(iv) MnO_2 selectively oxidises the –OH group of allylic and benzylic 1° and 2° alcohols to aldehydes and ketones respectively.

5. Action of Heated Copper :

(i) 

(ii) 

(iii) Tertiary alcohols undergo dehydration to give alkene under similar condition.



Distinction Between 1°, 2° and 3° Alcohols

Lucas Test :

Any alcohol is treated with Lucas reagent (HCl + anhyd. $ZnCl_2$) at room temperature if

(i) Solution becomes cloudy immediately, alcohol is 3°.

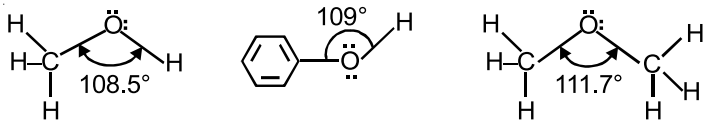
(ii) Solution becomes cloudy after 5-min, alcohol is 2°.

(iii) In solution cloud does not form at room temperature, alcohol is 1°.

PHENOLS

and their derivatives are called phenols. In phenol R– of alcohol is replaced by aryl ring.

Comparison of bond Angles in Phenols, Alcohols and Ethers :

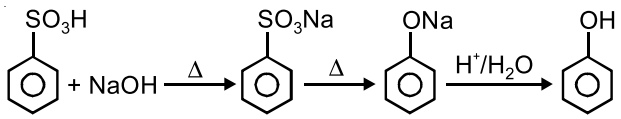


Bond angle increases with the increase in hindrance.

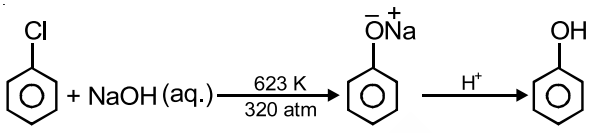
Method of Preparation

1. From Aryl Sulphonic Acids (Industrial Method):

When aryl sulphonic acids are fused with NaOH at 570 – 620 K followed by hydrolysis phenols are formed.

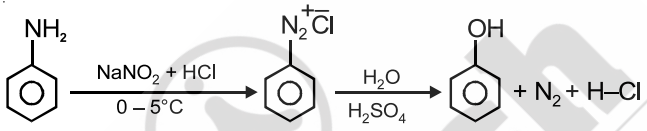


2. From Haloarenes : (Dow's process)

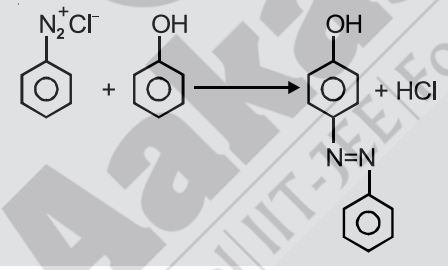


Note : *Condition of reaction become less vigorous when –M groups are present at ortho or para or both position to the chlorine atom.*

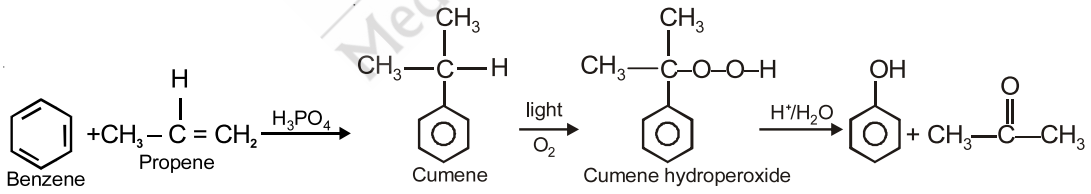
3. From Benzene Diazonium Salts (Lab Method) :



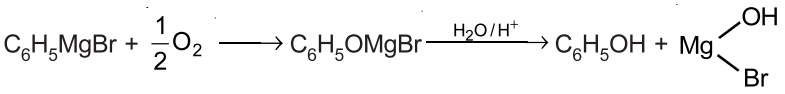
Note : *In the absence of H_2SO_4 diazocoupling will also take place.*



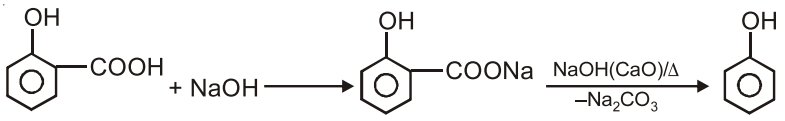
4. Cumene Process :



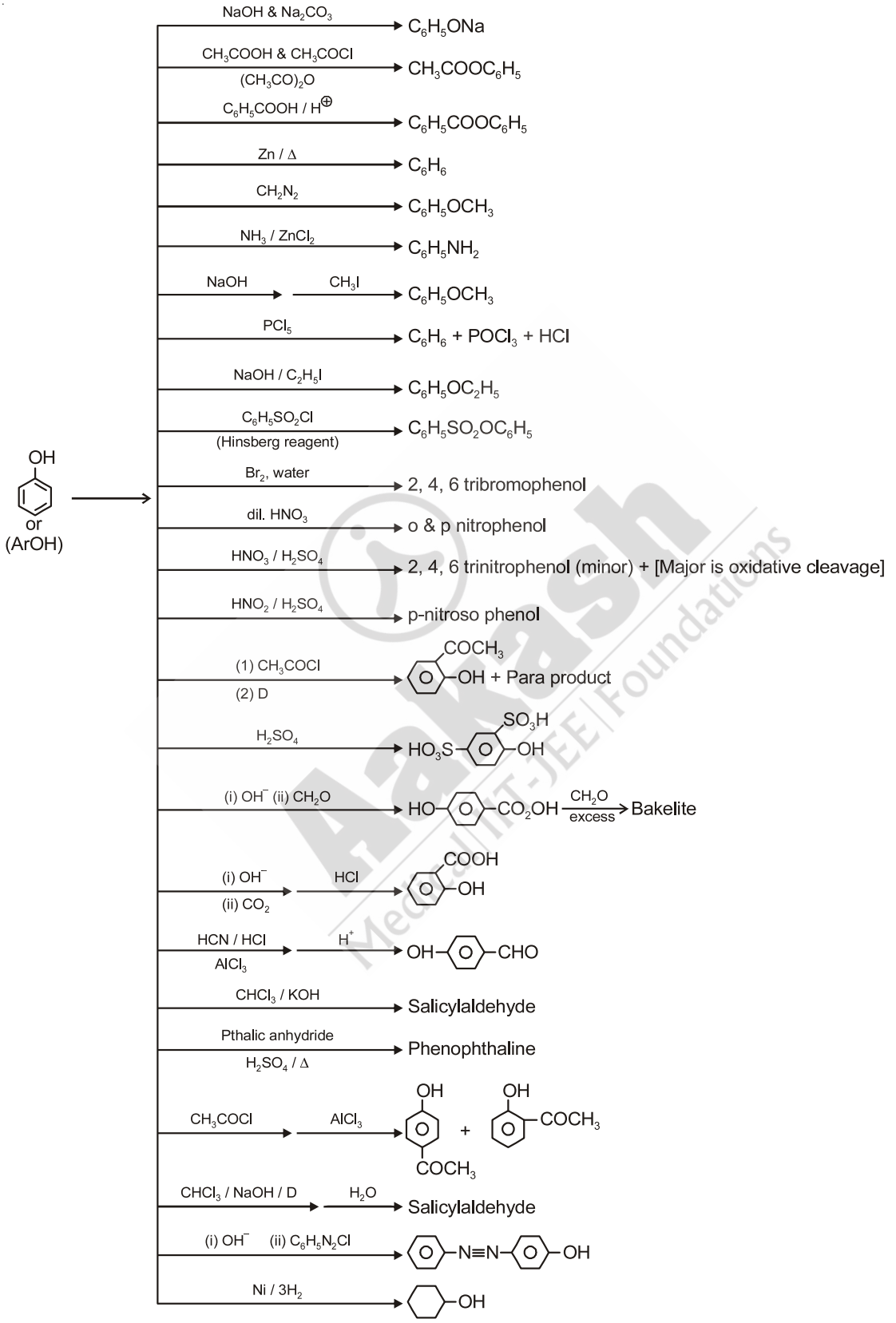
5. Grignard's Synthesis :



6. From Salicylic Acid :



Chemical Properties



ETHERS

Ethers are those organic compounds which contain two alkyl groups attached to an oxygen atom, *i.e.*, R–O–R. They are regarded as dialkyl derivatives of water or anhydrides of alcohols.

$$\underset{\text{Water}}{H-O-H} \xrightarrow[+2R]{-2H} \underset{\text{Ether}}{R-O-R} \xleftarrow{-H_2O} \underset{\text{Alcohol (2 moles)}}{R-OH + HO-R}$$

Ethers may be of two types : (i) **Symmetrical or simple ethers** are those in which both the alkyl groups are identical and (ii) **unsymmetrical or mixed ethers** are those in which the two alkyl groups are different.

$CH_3–O–CH_3$; $C_6H_5–O–C_6H_5$ $CH_3–O–C_2H_5$; $CH_3–O–C_6H_5$
Symmetrical (simple) ethers Unsymmetrical (mixed)ethers

Like water, ether has two unshared pair of electrons on oxygen atom, yet its angle is greater than normal tetrahedral (109°28′) and different from that in water (105°). This is because of the fact that in ethers the repulsion between lone pairs of electrons is overcome by the repulsion between the bulky alkyl groups.

Preparation of Ethers :

1. **By dehydrating excess of alcohols :** Simple ethers can be prepared by heating an excess of primary alcohols with conc. H_2SO_4 at 413K. Alcohol should be taken in excess so as to avoid its dehydration to alkenes.

$$\underset{\text{Ethanol (2 molecules)}}{C_2H_5-OH + HO-C_2H_5} \xrightarrow[413K]{\text{Conc. } H_2SO_4} \underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5} + H_2O$$

Dehydration may also be done by passing alcohol vapours over heated catalyst like alumina under high pressure and temperature of 200 – 250°C.

2. **By heating alkyl halide with dry silver oxide** (only for simple ethers) :

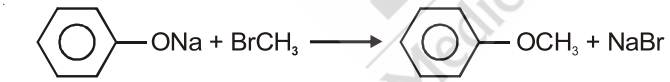
$$C_2H_5I + \underset{\text{Dry}}{Ag_2O} + IC_2H_5 \rightarrow C_2H_5OC_2H_5 + 2AgI$$

Remember that reaction of alkyl halides with moist silver oxide ($Ag_2O + 2H_2O = 2AgOH$) give alcohols

$C_2H_5I + Ag_2O$ (moist) $\rightarrow C_2H_5OH + AgI$

3. **By heating alkyl halide with sod. or pot. alkoxides** (Williamson synthesis):

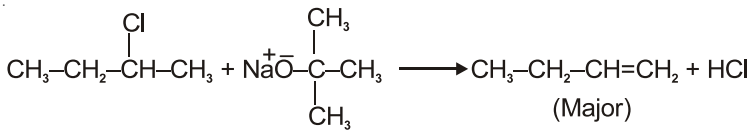
$C_2H_5ONa + ICH_3 \rightarrow C_2H_5OCH_3 + NaI$



Sod. phenoxide Methoxybenzene (Anisole)

However $CH_3–Cl + NaO–C(CH_3)_3 \rightarrow CH_3–O–C(CH_3)_3 + NaCl$

If alkyl halide is other than methyl halide and it is treated with tertiary alkoxide ion, Hofmann elimination takes place instead of Williamson's ether synthesis.



Limitations :

1. In this reaction alkoxide ion may be 1°, 2°, 3°.
2. Alkyl halide must be 1°.
3. In the case of 3° alkyl halide elimination occurs to produce alkene as major product.
4. In the case of 2° alkyl halide both elimination and substitution products are obtained.

Chemical Properties :

A. Properties due to carbon-oxygen bond :

1. Hydrolysis :

$$C_2H_5 - O - C_2H_5 + H_2O \xrightarrow{H_2SO_4} \underset{\text{Ethyl alcohol}}{2C_2H_5OH}$$

The hydrolysis may also be effected by boiling the ether with water or by treating it with steam.

Note : *Ethers can never be hydrolysed in alkaline medium.*

2. Action of conc. sulphuric acid :

$$C_2H_5 - O - C_2H_5 + H_2SO_4\ (\text{conc.}) \rightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4}$$

$$C_2H_5OH + H_2SO_4(\text{conc.}) \rightarrow C_2H_5HSO_4 + H_2O$$

3. Action of hydroiodic or hydrobromic acid :

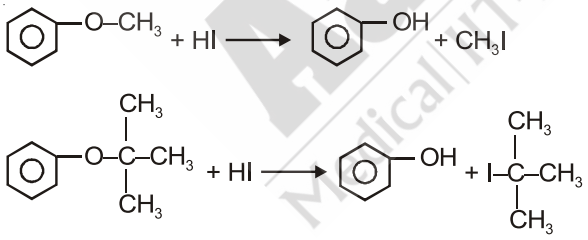
In cold, ether react with HI or HBr to give the corresponding alkyl halide and alcohol. In case of mixed ethers, the halogen atom attaches itself to the smaller alkyl group.

$$\underset{\text{Ethyl ether}}{C_2H_5 - O - C_2H_5} + HI \rightarrow \underset{\text{Ethyl iodide}}{C_2H_5I} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

The order of reactivity of halogen acids is :

HI > HBr > HCl

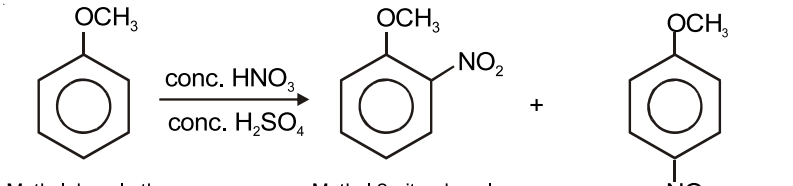
If one of the group around oxygen is aryl group then I^- will always attack on the group other than aryl group.



B. Properties Due to Benzene Nucleus :

Alkoxy group, being o-, p- directing, anisole undergoes substitution in o- and p- positions. However, –OR group is less activating than the phenolic group.

(i) Nitration :

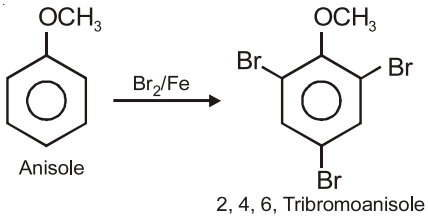


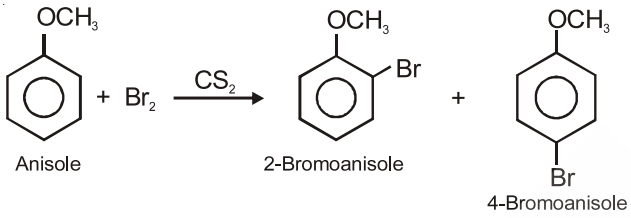
Methylphenyl ether (Anisole)

Methyl 2-nitrophenyl ether or o-Nitroanisole

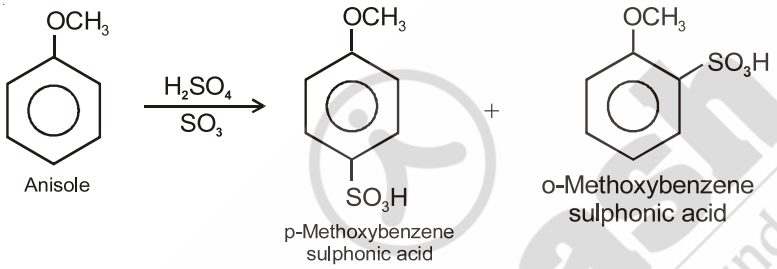
Methyl 4-nitrophenyl ether or p-Nitroanisole

(ii) Bromination :





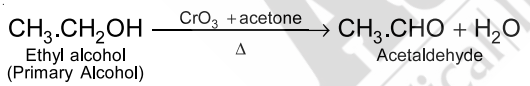
(iii) Sulphonation :

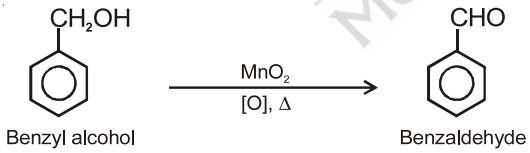


GENERAL METHODS OF PREPARATION OF ALDEHYDES AND KETONES

1. From Alcohols :

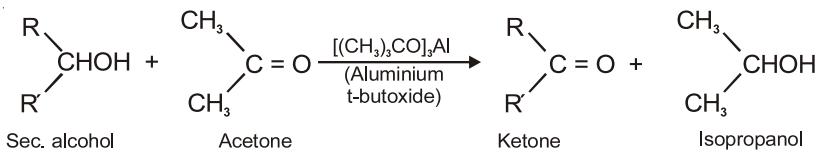
(i) By Oxidation : Primary alcohols gives aldehydes, while secondary alcohols give ketones.



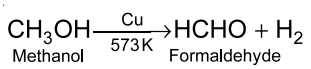


Controlled oxidation of 1°- alcohol and 2° - alcohol with PCC + CH_2Cl_2 or CrO_3 forms aldehyde and ketone respectively.

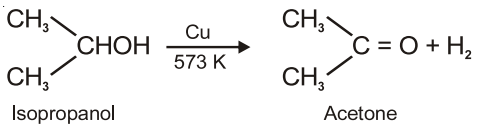
Ketones in good yield can be prepared by **Oppenauer oxidation of secondary alcohols.**



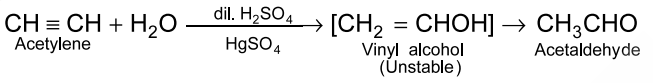
(ii) By catalytic dehydrogenation of alcohols : 1° Alcohols yield aldehyde in this method.

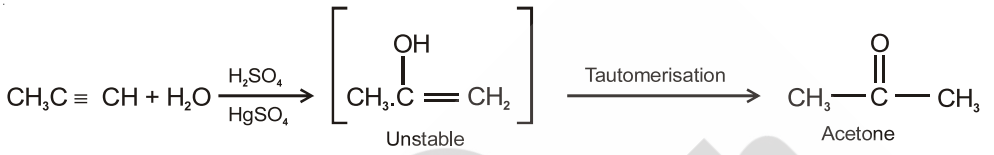


Secondary alcohols, on similar treatment, give ketones.

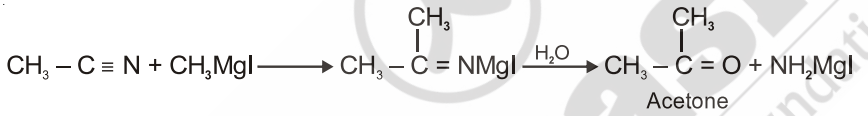


2. From Alkynes :



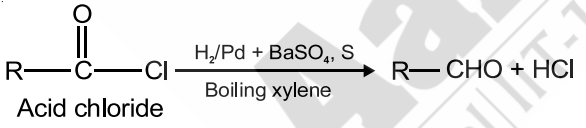


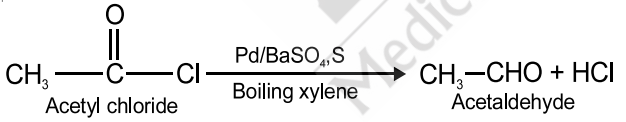
3. From Grignard Reagents :



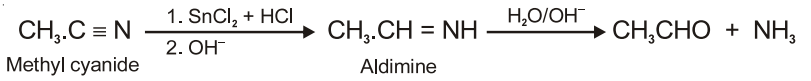
4. Methods giving only Aldehydes :

(a) From Acid Chlorides (Rosenmund Reduction) :



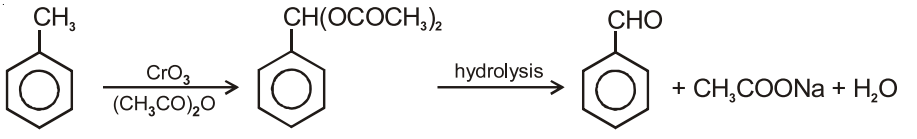


(b) From nitriles (Stephen's reduction) :



5. Methods for Aromatic Aldehydes and Ketones :

(a) Aromatic Aldehydes :



(b) Aromatic Ketones : (Friedel-Craft's acylation)

(i) $\underset{\text{Benzene}}{C_6H_6} + CH_3COCl \xrightarrow[AlCl_3]{\text{anhy.}} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + HCl$

Here instead of acid chloride we can use anhydrides also

(ii) $C_6H_6 + C_6H_5COCl \xrightarrow[AlCl_3]{\text{anhy.}} \underset{\text{Benzophenone}}{C_6H_5COC_6H_5} + HCl$

Trend of Boiling Point

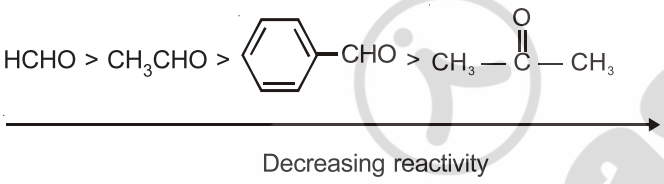
$$CH_3–CH_3–OH > CH_3CH_2CHO > CH_3\overset{\overset{O}{\|}}{C}CH_3 > CH_3–O–CH_2–CH_3 > CH_3–CH_2–CH_2–CH_3$$

Chemical Properties

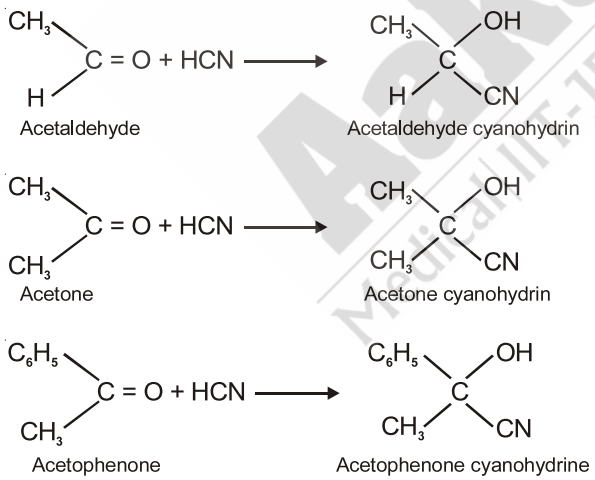
Both aldehydes and ketones contain a carbonyl group in the structure and hence show marked similarity in their chemical behaviour.

(a) Nucleophilic addition reactions

Reactivity of carbonyl compounds towards nucleophilic addition reaction is governed by ELECTRONIC FACTOR and STERIC FACTOR. Aldehydes are more reactive than ketones.



(1) Addition of hydrogen cyanide : Aldheydes and ketones react with hydrogen cyanide to form **cyanohydrins**.

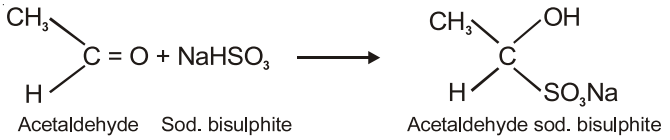


Benzophenone does not react with hydrogen cyanide because of steric hindrance. On the other hand, aromatic aldehydes (e.g., C_6H_5CHO) when refluxed with alcoholic potassium cyanide solution undergo dimerization to form benzoin.

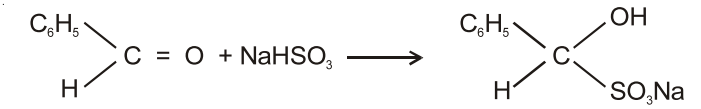
$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} \xrightarrow[\text{ethanol}]{CN^-} \underset{\text{Benzoin}}{C_6H_5–\overset{\overset{OH}{|}}{CH}–\overset{\overset{O}{\|}}{C}–C_6H_5}$$

Above reaction is known as benzoin condensation.

(2) Addition of sodium bisulphite : Aldehydes and methyl ketones react with a saturated aqueous solution of bisulphite to form crystalline sodium bisulphite derivatives.



Acetaldehyde Sod. bisulphite Acetaldehyde sod. bisulphite

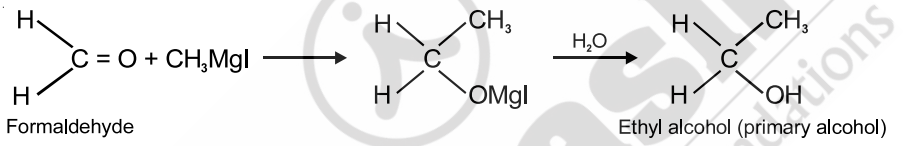


Benzaldehyde Benzaldehyde sod. bisulphite

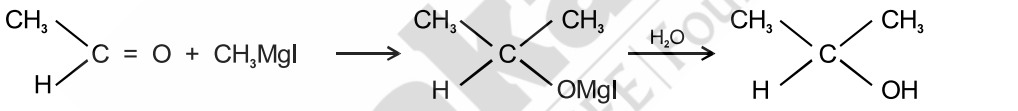
Aromatic ketones and aliphatic ketones having higher alkyl groups do not react with sodium bisulphite. This is due to the fact that the large SO_3^{2-} ion cannot attack the carbonyl carbon atom when it is surrounded by larger substituents (steric hindrance).

Thus $C_2H_5COC_2H_5$, $C_6H_5COCH_3$, $C_6H_5COC_6H_5$ do not react with sodium bisulphite. Methyl ketones give this reaction.

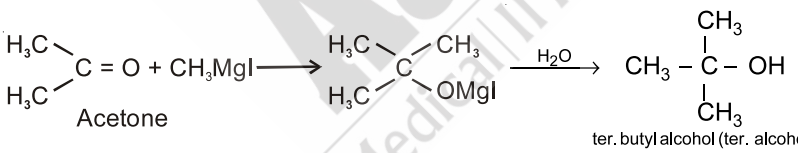
(3) Addition of Grignard reagents :



Formaldehyde Ethyl alcohol (primary alcohol)

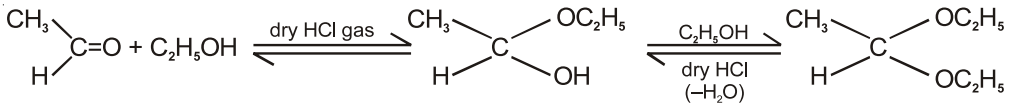


Acetaldehyde Isopropyl alcohol (Sec. alcohol)

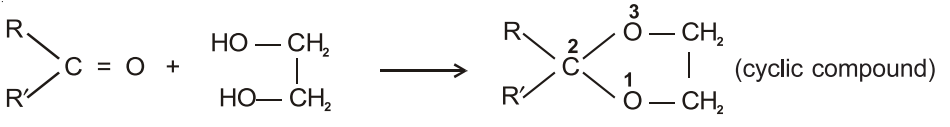


Acetone ter. butyl alcohol (ter. alcohol)

(4) Addition of alcohols (Acetal formation) : Aldehydes (not Ketones) react with alcohols in presence of dry HCl gas to form **hemi-acetals** (hemi means half) which being unstable immediately react with another molecule of alcohol to form stable acetals. For example,

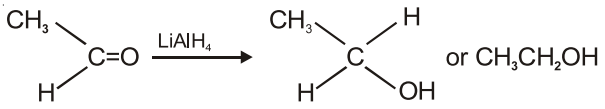


Acetaldehyde hemiacetal (1-Ethoxyethanol) Acetaldehyde acetal (1, 1-diethoxyethane, Gem diether)



Ethanol Ethylene glycol Ethylene glycol acetal

(5) Reduction by metal hydrides such as lithium aluminium hydride



Acetaldehyde Ethyl alcohol

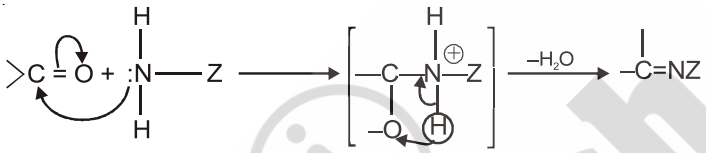
Similar product are also formed by $NaBH_4$, H_2 — Pt, H_2 — Ni or metal-acid.

However, aldehydes and ketones can be reduced to the corresponding alkanes by means of red phosphorus and hydroiodic acid, or amalgamated zinc and concentrated hydrochloric acid (**Clemmensen reduction**) or reacting hydrazine solution followed by treatment with alkaline solution of ethylene glycol (**Wolff-Kishner reduction**). The basic reaction in all these reductions is the reduction of carbonyl group to methylene group.

(1) Replacement of Carbonyl Oxygen :

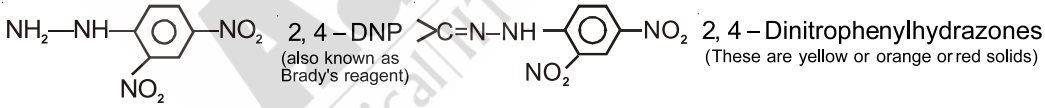
(i) Reaction with Ammonia Derivatives : Aldehydes and ketones react with a number of ammonia derivatives like NH_2OH, NH_2NH_2, $C_6H_5NHNH_2$ etc. in weakly acidic medium.

Such reactions take place in slightly acidic medium and involve nucleophilic addition of the ammonia derivative followed by dehydration.



Ammonia der. Addition product

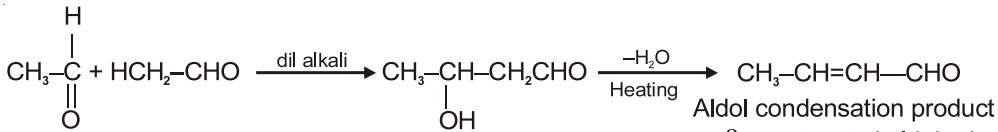
Ammonia derivatives	Final products
H_2N — OH Hydroxylamine	$>C = NOH$ Oximes
H_2N — NH_2 Hydrazine	$>C = NNH_2$ Hydrazones
H_2N — NHC_6H_5 Phenylhydrazine	$>C = NNHC_6H_5$ Phenylhydrazones
H_2N — $NHCONH_2$ Semicarbazide	$>C = NNHCONH_2$ Semicarbazones



(ii) Reaction with thioalcohols (mercaptans) : Aldehydes and ketones react with thioalcohols and form thioacetals (mercaptals) and thioketals (mercaptals) respectively.

(2) Reactions involving α-hydrogen of carbonyl groups :

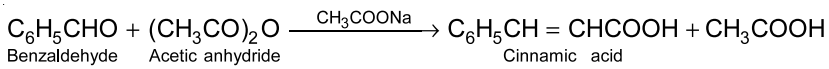
Aldol condensation :



β-hydroxybutyraldehyde (Aldol) Addition product

Aldol condensation product
α, β-unsaturated aldehyde

Perkin reaction : Condensation of an aromatic aldehyde with acid anhydride in presence of base (sodium salt of the acid from which the anhydride is derived) to form α, β-unsaturated acid is known as **Perkin reaction**. For example,



Benzaldehyde Acetic anhydride Cinnamic acid

(a) Oxidation reactions :

Aldehydes are oxidised not only by strong oxidising agents like $KMnO_4$ and $K_2Cr_2O_7$ but also by much milder oxidising agents like bromine water, Tollen's reagent, Fehling's solution and Benedict's solution.

Tollen's reagent : Tollen's reagent is Ammoniacal silver nitrate solution

$$R.CHO + \underset{\text{(Tollen's reagent)}}{2[Ag(NH_3)_2]OH} \rightarrow RCO\overset{-}{O}\overset{+}{N}H_4 + \underset{\text{Silver mirror}}{2Ag\downarrow} + H_2O + 3NH_3$$

Fehling solution : [Alkaline solution of copper sulphate containing sodium potassium tartarate (Rochelle salt)]

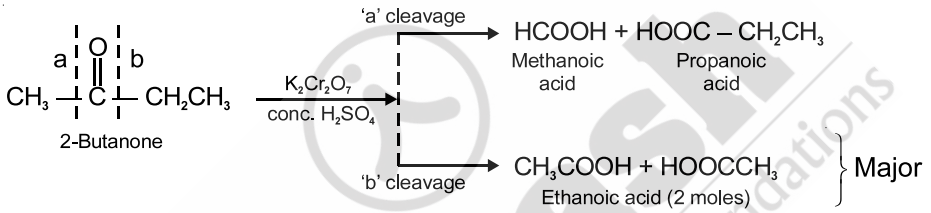
$$R{-}CHO + 2Cu^{2+} + 5OH^- \longrightarrow R{-}COO^- + \underset{\text{(Reddish brown)}}{Cu_2O} + 3H_2O$$

Benedict Solution : Its a solution of $CuSO_4$, sodium citrate and sodium carbonate. When heated with aldehyde it gives a reddish brown ppt. of Cu_2O.

> ***Note :*** *Benzaldehyde although reduces Tollen's reagent, it does not reduce Fehling and Benedict solutions*

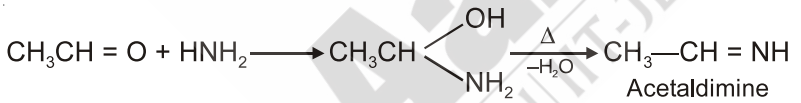
Ketones are not oxidised by mild oxidising agents.

Oxidation in drastic condition



Oxidation of mixed ketones is governed by **Popoff's rule** according to which the carbonyl group of the ketone goes with the smaller alkyl group. Thus in the above case 'b' type of cleavage will decide major products.

(b) Reaction with Ammonia :



$$6HCHO + 4NH_3 \rightarrow \underset{\substack{\text{Hexamethylene}\\-\text{tetramine}\\\text{(Urotropine)}}}{(CH_2)_6N_4} + 6H_2O$$

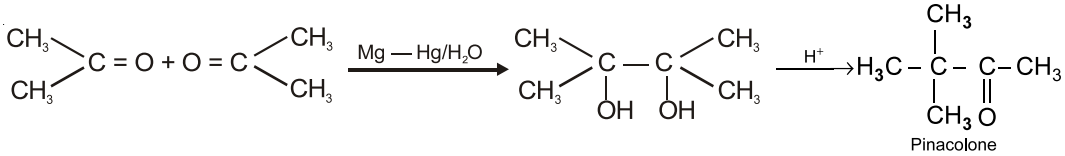
(c) Cannizzaro reaction : This reaction is preferentially given by those aldehydes which do not contain α-hydrogen. In Cannizzaro reaction, one molecule of the aldehyde is oxidised to acid at the expense of the other which is reduced to alcohol *i.e.*, disproportionation reaction takes place. The reaction occurs in the presence of concentrated solution of any base.

$$\underset{\text{Formaldehyde}}{2HCHO} + NaOH \rightarrow \underset{\text{Sod. formate}}{HCOONa} + \underset{\text{Methyl alcohol}}{CH_3OH}$$

(d) Reaction given only by Ketones :

(1) Reduction in Neutral or Alkaline medium :

To form Pinacol which undergoes Pinacol - Pinacolone rearrangement in acidic medium

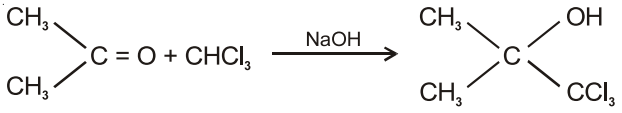


Ketones can be reduced to secondary alcohols with aluminum isopropoxide in 2-propanol solution

$$R_2C=O \xrightarrow[Me_2CHOH]{[Me_2CHO]_3Al} R_2CHOH$$ (Meerwein Ponndorf's verley reduction)

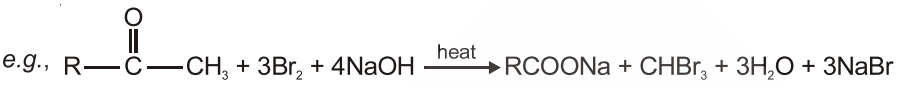
$$R_2C=O \xrightarrow[Me_2CHOH]{[Me_2CHO]_3Al} R_2CHOH$$

(2) Condensation with chloroform :



1, 1, 1-Trichloro-2-methylpropanol-2
(Chloretone) used as hypnotic drug

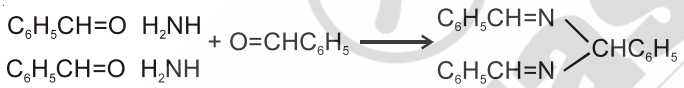
Haloform reaction : Methyl ketones or alcohols which can be oxidized to methyl ketone gives this test.



Bromoform
(reddish brown ppt.)

(e) Special Reactions of Aromatic Aldehydes and Ketones :

(i) Reaction with Ammonia :

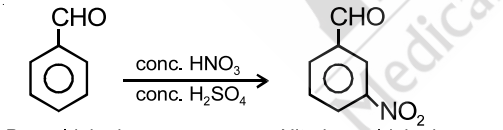


Hydrobenzamide

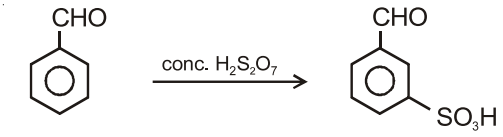
(ii) Reaction with amines :

Benzylidene aniline.
(Benzal aniline)

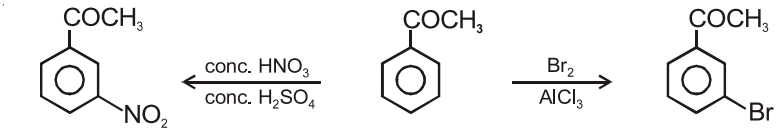
(iii) Reaction of benzene nucleus



Benzaldehyde m-Nitrobenzaldehyde



Benzaldehyde 3-Benzaldehyde sulphonic acid

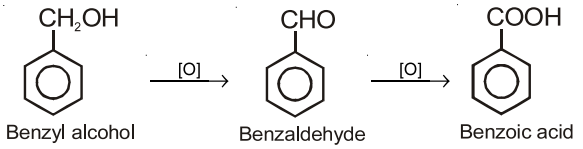


3-Nitroacetophenone Acetophenone 3-Bromoacetophenone

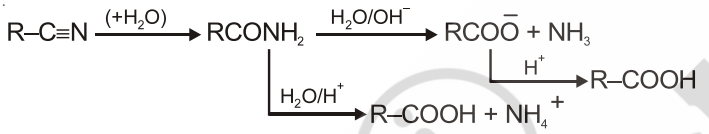
CARBOXYLIC ACIDS

Preparation :

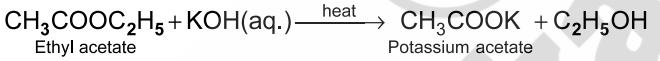
1. By the oxidation of primary alcohols and aldehydes

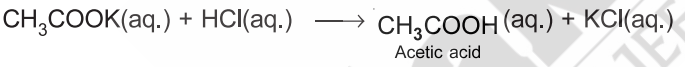


2. By the hydrolysis of cyanides (nitriles)

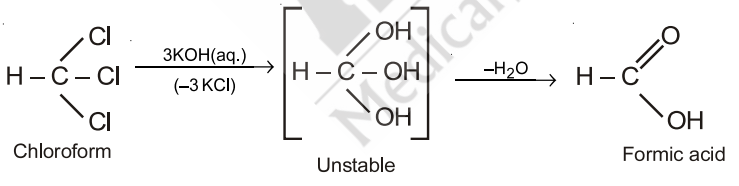


3. By the hydrolysis of esters

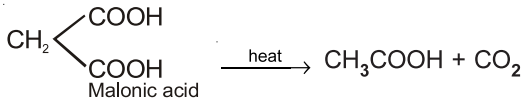




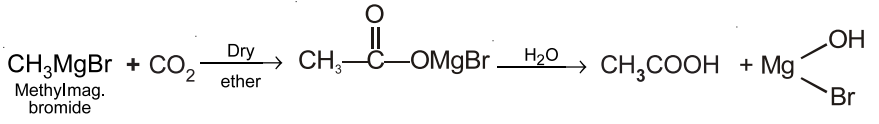
4. By the hydrolysis of trihalogen derivatives of alkanes

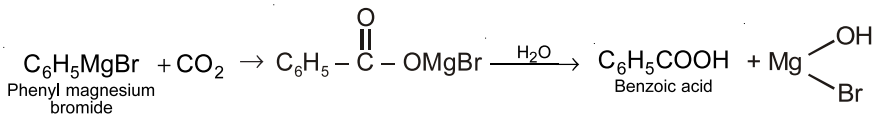


5. By heating malonic acid and their derivative acids.



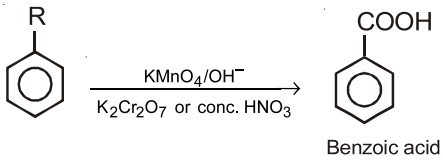
6. By the reaction of Grignard reagent with CO_2





Product in above reactions have one more carbon than that in Grignard reagent taken.

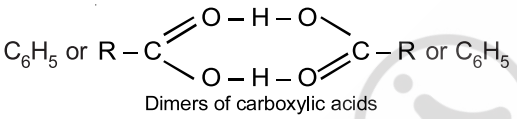
7. By oxidation of alkyl benzenes



Physical properties

1. The first three members (C_1 to C_3) are colourless, pungent smelling liquids, the next three (C_4 to C_6) have unpleasant odours. Acids with 7 or more carbon atoms have no distinct smell because of low volatility.

   Two molecules of carboxylic acids are held together not by one but by two strong hydrogen bonds.



Dimers of carboxylic acids

   The behaviour of **formic acid is exceptional.** It exists as a dimer in vapour state and a polymer in liquid and solid states.

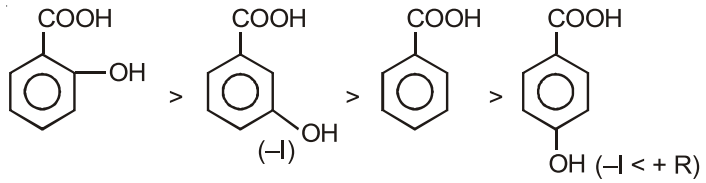
2. In normal carboxylic acids, the even members have markedly higher melting points than the odd members preceding or following it.

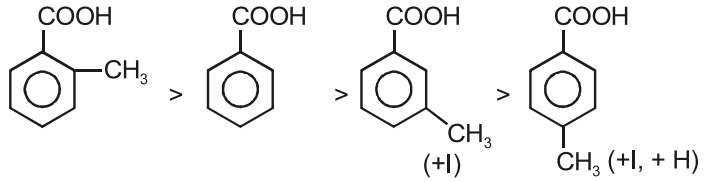
   Effect of Substituents on Acidity :

   e.g., the acidic strength of the corresponding halogen acids also follows the same order *i.e.*

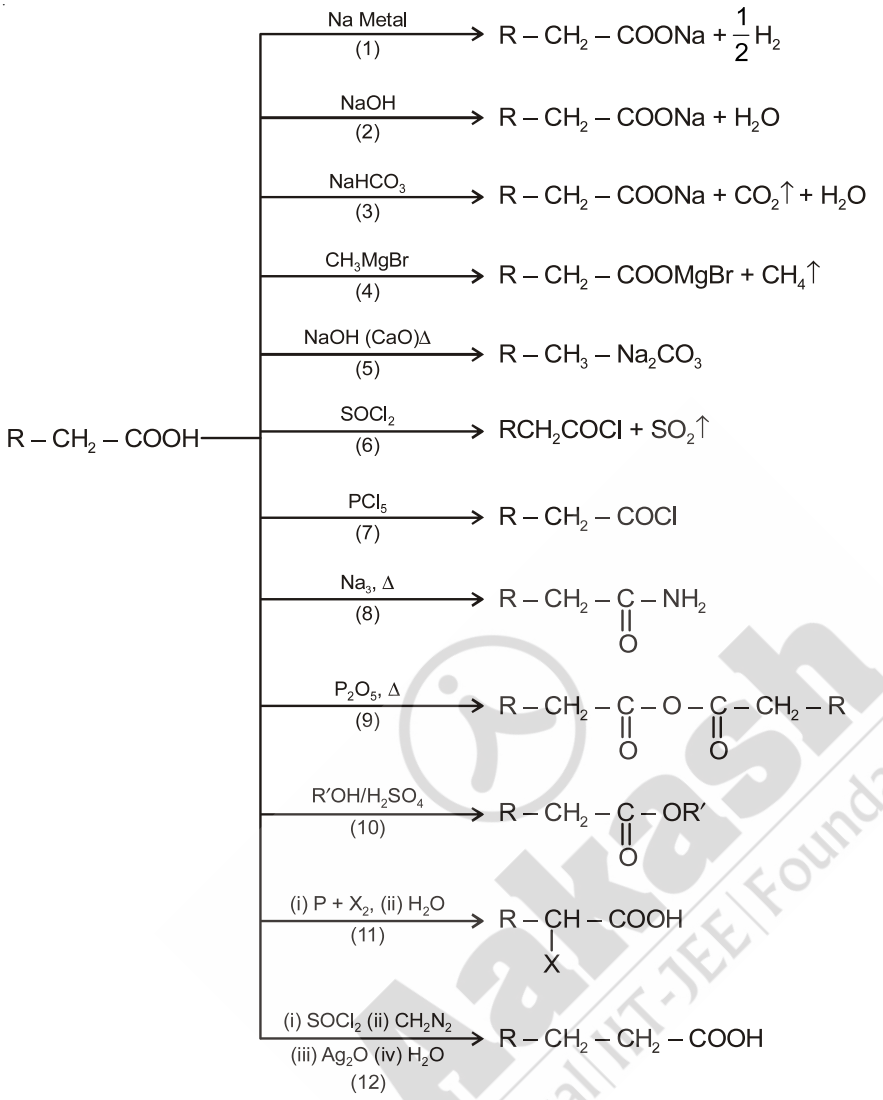
   Ortho effect : Among derivative of aromatic carboxylic acid, ortho derivative is the most acidic. This effect is known as ortho effect.

e.g.,





Chemical Properties

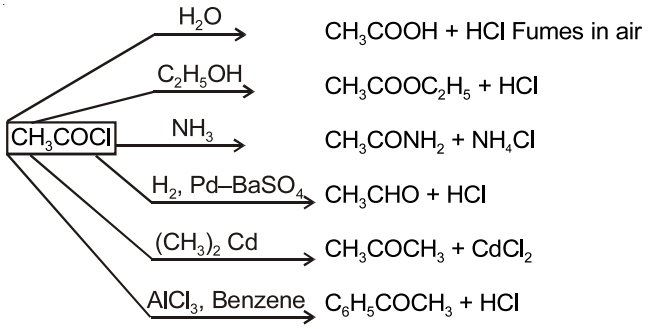


Derivatives of carboxylic acids : These are formed by the replacement of –OH group of acid by some other suitable group e.g. RCOCl, $RCONH_2$, RCOOR′ and $(RCO)_2O$.

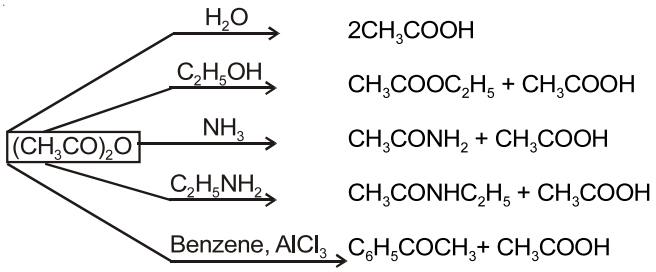
Order of Reactivity Towards Nucleophilic Substitution Reaction :

Carboxylic acid derivatives reacts with a nucleophile through addition/elimination mechanism via tetrahedral intermediate over all substitution product is obtained.

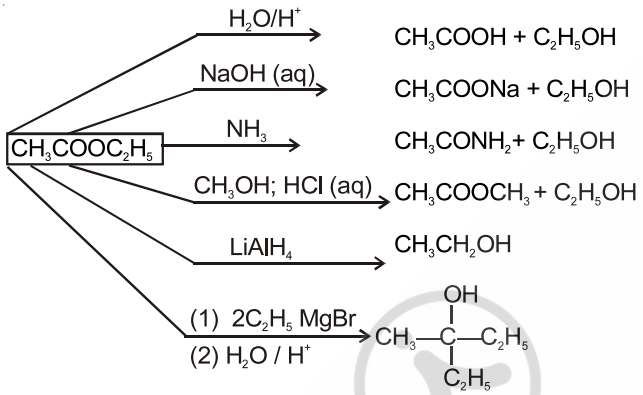
Properties :



Acid Anhydrides : $(RCO)_2O$, prepared by dehydration of carboxylic acid.

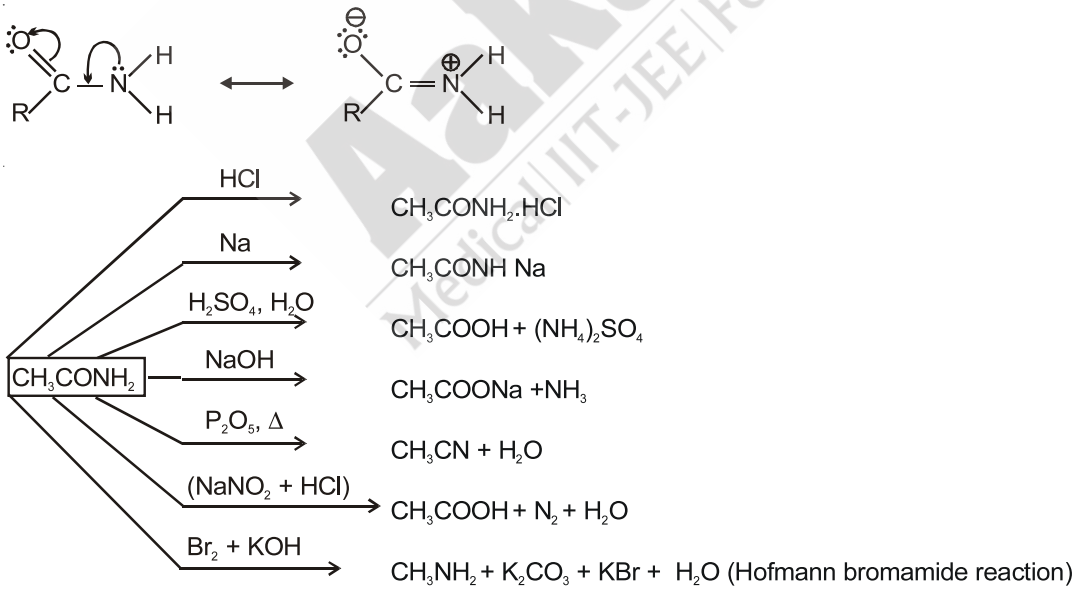


Esters : RCOOR prepared by reaction of acid with alcohol or acid chloride or anhydrides with alcohol.



Acid amides : $RCONH_2$ – It is prepared by reaction of carboxylic acid or its derivatives with NH_3. It is amphoteric in nature.

Acid amides act as weak acids as well as weak bases. Lone pair of N is delocalised with π electrons of C = O group.



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