+1 CHEMISTRY - NAME REACTIONS

Sabatier - Sanderson

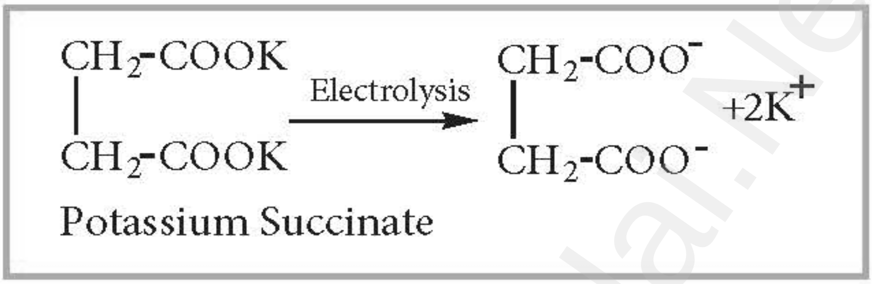
$$\underset{\text{ethene}}{CH_2=CH_2} + H_2 \xrightarrow[298K]{Ni} \underset{\text{ethane}}{CH_3-CH_3}$$

Preparation of Ethane by Kolbe's electrolytic method

$$\begin{array}{c} 2CH_3COONa+ 2H_2O \\ \downarrow \text{ Electrolysis} \\ \underbrace{H_3C-CH_3+ 2CO_2}_{\text{at Anode}}+\underbrace{H_2+2NaOH}_{\text{at Cathode}} \end{array}$$

(5) Preparation of ethene by kolbe's electrolytic method:

When an aqueous solution of potassium succinate is electrolyzed between two platinum electrodes, ethene is produced at the anode.

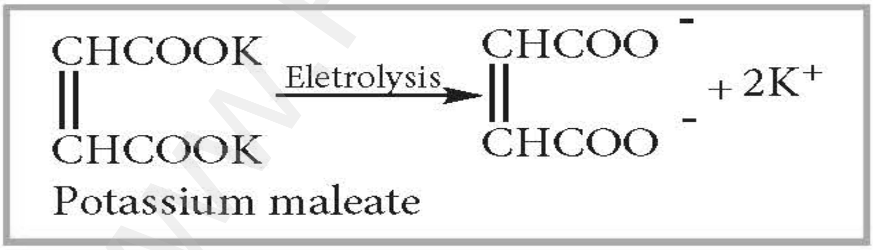


$$\begin{array}{l}CH_2\text{-}COOK\\ |\\ CH_2\text{-}COOK\end{array} \xrightarrow{\text{Electrolysis}} \begin{array}{l}CH_2\text{-}COO^-\\ |\\ CH_2\text{-}COO^-\end{array} + 2K^+$$

Potassium Succinate

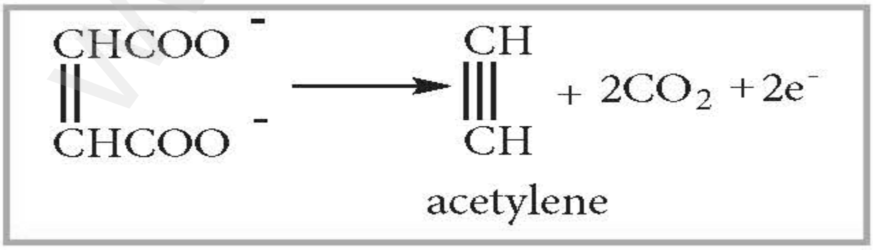
3. Preparation of alkynes from electrolysis of salts of unsaturated dicarboxylic acids. (Kolbe's electrolytic method)

Electrolysis of sodium or potassium salt of maleic or fumaric acid yields alkynes.



$$\begin{array}{l}CHCOOK\\ \|\\ CHCOOK\end{array} \xrightarrow{\text{Eletrolysis}} \begin{array}{l}CHCOO^-\\ \|\\ CHCOO^-\end{array} + 2K^+$$

Potassium maleate



$$\begin{array}{l}CHCOO^-\\ \|\\ CHCOO^-\end{array} \longrightarrow \begin{array}{l}CH\\ |||\\ CH\end{array} + 2CO_2 + 2e^-$$

acetylene

ii) Wurtz reaction

When a solution of halo alkanes in dry ether is treated with sodium metal, higher alkanes are produced. This reaction is used to prepare higher alkanes with even number of carbon atoms.

for example:

$$\underset{\text{methyl bromide}}{CH_3\text{-}Br} + 2Na + Br\text{—}CH_3 \xrightarrow[\text{ether}]{\text{dry}} \underset{\text{ethane}}{CH_3\text{-}CH_3} + 2NaBr$$

(c) Wurtz – Fittig Reaction:

When a solution of bromo benzene and iodo methane in dry ether is treated with metallic sodium, toluene is formed.

$$\underset{\text{Bromo benzene}}{C_6H_5Br} + 2Na + \underset{\text{Iodo methane}}{ICH_3} \xrightarrow{\text{ether}} \underset{\text{Toluene}}{C_6H_5\text{-}CH_3} + NaBr + NaI$$

iii) Corey – House Reaction

An alkyl halide and lithium di alkyl copper are reacted to give higher alkane.

for example:

$$\underset{\text{ethyl bromide}}{CH_3CH_2Br} + (CH_3)_2CuLi \longrightarrow CH_3CH_2CH_3 + CH_3Cu + LiBr$$

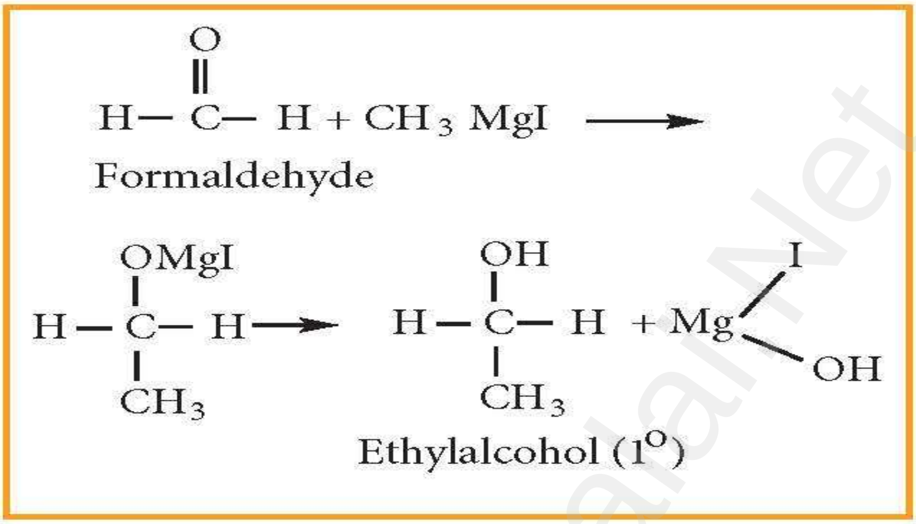
Grignard Reaction

$$\underset{\text{chloromethane}}{CH_3\text{—}Cl} + Mg \xrightarrow{\text{Dry ether}} \underset{\text{methyl magnesium chloride}}{CH_3MgCl}$$

$$CH_3MgCl + H_2O \longrightarrow \underset{\text{methane}}{CH_4} + Mg(OH)Cl$$

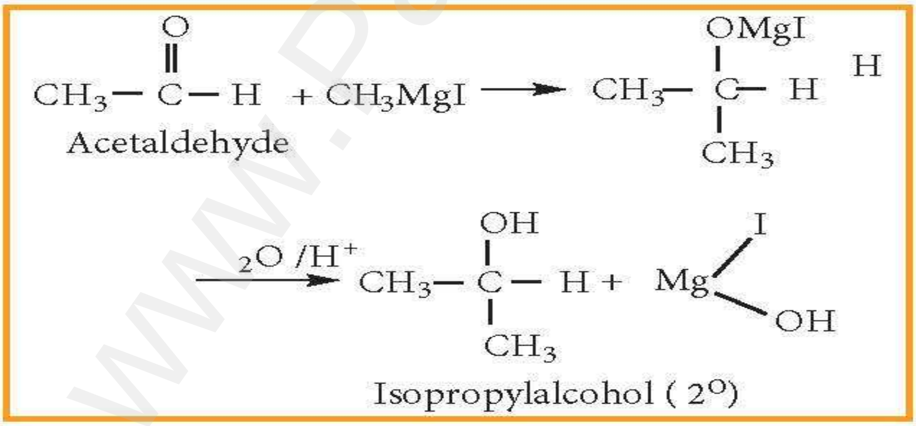
(1) Preparation of primary alcohol

Formaldehyde reacts with Grignard reagent to give addition products which on hydrolysis yields primary alcohol.



2) Preparation of secondary alcohol

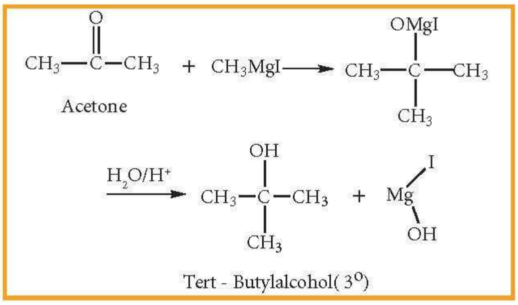
Aldehydes other than formaldehyde, react with Grignard reagent to give addition product which on hydrolysis yields secondary alcohol.



3) Preparation of Tertiary alcohol

Ketone reacts with Grignard reagent to give an addition product which on hydrolysis yields tertiary alcohols.

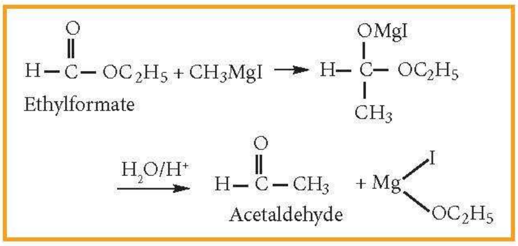
Example



(4) Preparation of aldehyde

Ethyl formate reacts with Grignard reagent to form aldehyde. However, with excess of Grignard reagent it forms secondary alcohol.

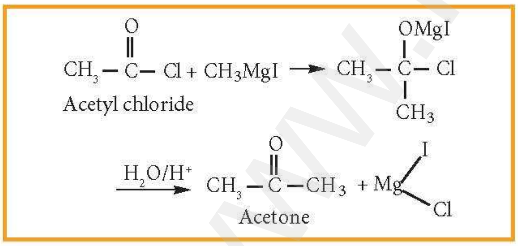
Example



(5) Preparation of ketone

Acid chloride reacts with Grignard reagent to form ketones. However, with excess of Grignard reagent it forms tertiary alcohol.

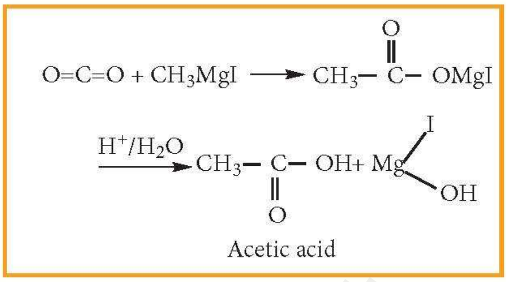
Example



6) Preparation of carboxylic acids

Solid carbon dioxide reacts with Grignard reagent to form addition product which on hydrolysis yields carboxylic acids.

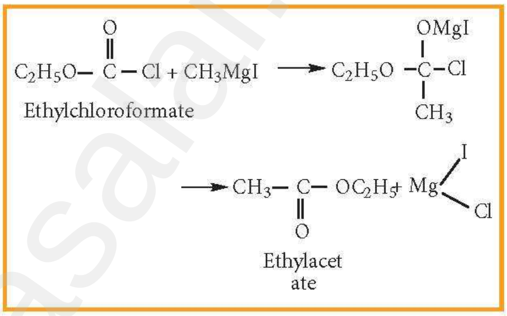
For Example



7) Preparation of esters

Ethylchloroformate reacts with Grignard reagent to form esters.

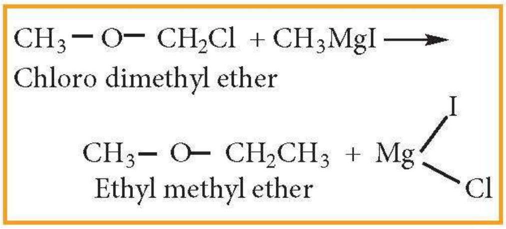
Example



8) Preparation of higher ethers

Lower halogenated ether reacts with Grignard reagent to form higher ethers.

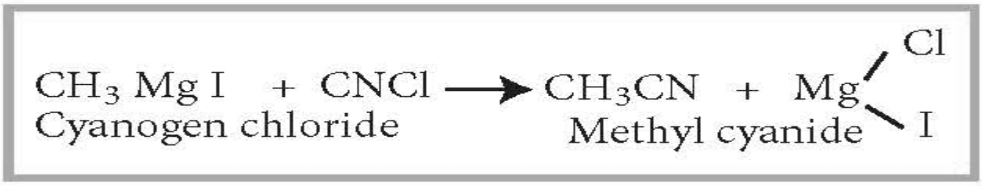
Example



9) Preparation of alkyl cyanide

Grignard reagent reacts with cyanogen chloride to from alkyl cyanide

Example



$$\underset{\text{Cyanogen chloride}}{CH_3MgI + CNCl} \longrightarrow \underset{\text{Methyl cyanide}}{CH_3CN} + Mg\begin{smallmatrix} Cl \\ I \end{smallmatrix}$$

10) Preparation of Alkanes

Compounds like water, alcohols and amines which contain active hydrogen atom react with Grignard reagents to form alkanes.

Example

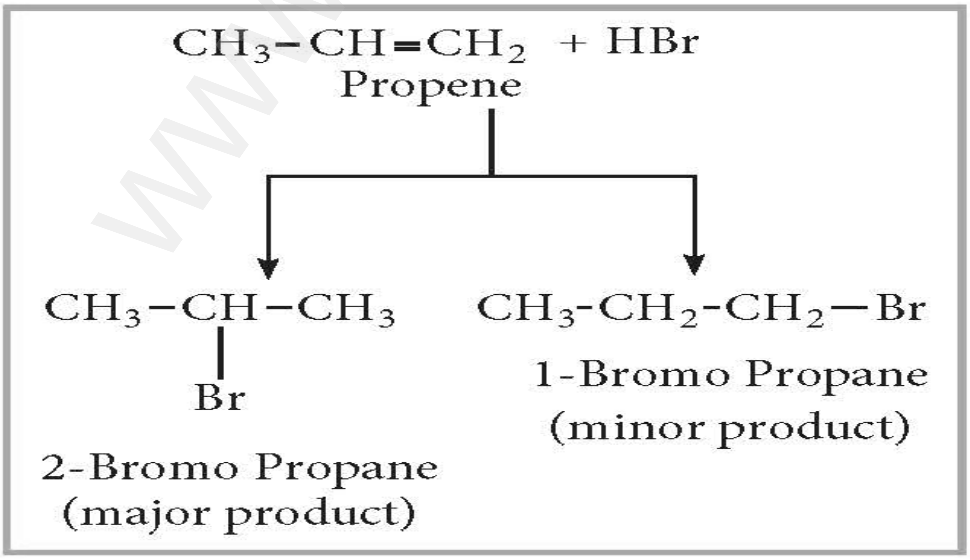
$$CH_3MgI + HO-H \longrightarrow CH_4 + MgI(OH)$$

$$CH_3MgI + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow{\Delta} \underset{\text{methane}}{CH_4} + MgI(OC_2H_5)$$

Markonikoff's Rule

(b) Addition HBr to unsymmetrical alkene:

In the addition of hydrogen halide to an unsymmetrical alkene, two products are obtained.



Anti-Markovnikoff's Rule (Or) Peroxide Effect (Or) KharaschAddition

The addition of HBr to an alkene in the presence of organic peroxide, gives the anti Markovnikoff's product. This effect is called peroxide effect.

$$CH_3-CH=CH_2 + HBr \xrightarrow[(C_6H_5CO)_2O_2]{\text{Peroxide}} CH_3-CH_2-CH_2-Br$$

propene

1-bromopropane

(d) Friedel Craft's Reaction:

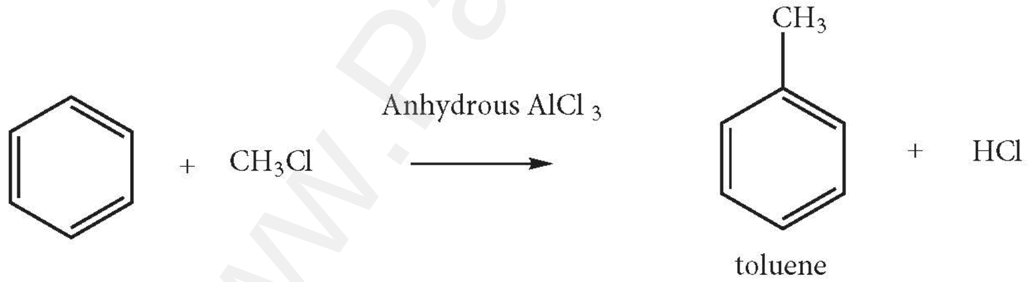
When benzene is treated with methyl chloride in the presence of anhydrous aluminium chloride, toluene is formed.

$$C_6H_6 + CH_3Cl \xrightarrow{\text{anhydrous } AlCl_3} C_6H_5CH_3 + HCl$$

Benzene chloromethane toluene

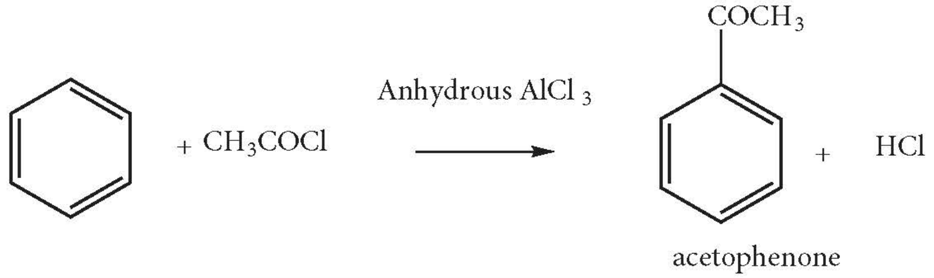
(d) Friedel Craft's Alkylation: (Methylation)

When benzene is treated with an alkyl halide in the presence of only AlCl3, alkyl benzene is formed.



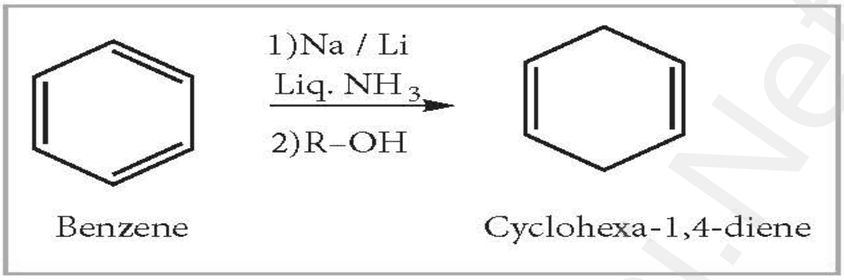
(e) Friedel Craft's Acylation : Acetylation

When benzene is treated with acetyl chloride in the presence of AlCl3, acyl benzene is formed.



b. Birch reduction:

Benzene can be reduced to 1, 4-cyclohexadiene by treatment with Na or Li in a mixture of liquid ammonia and alcohol. It is the convenient method to prepare cyclic dienes.



4) Halogen exchange reactions

a) Finkelstein reaction

Chloro or bromoalkane on heating with a concentrated solution of sodium iodide in dry acetone gives iodo alkanes. This reaction is called Finkelstein reaction, (S_N2 reaction).

$$\underset{\text{Bromoethane}}{CH_3CH_2Br + NaI} \xrightarrow[\Delta]{\text{Acetone}} \underset{\text{Iodoethane}}{CH_3CH_2I + NaBr}$$

b) Swarts reaction

Chloro or bromo alkanes on heating with metallic fluorides like AgF, SbF_3 or Hg_2F_2 gives fluoro alkanes. This reactions is called Swarts reaction.

Example

$$\underset{\text{Bromo ethane}}{CH_3CH_2Br + AgF} \xrightarrow{\Delta} \underset{\text{Fluoro ethane}}{CH_3CH_2F + AgBr}$$

vii) Williamson ether synthesis

Haloalkane, when boiled with sodium alkoxide gives corresponding ethers.

Example

This method can be used to prepare mixed (unsymmetrical) ethers also.

$CH_3CH_2Br + NaOCH_2CH_3$

Bromo ethane Sodium ethoxide

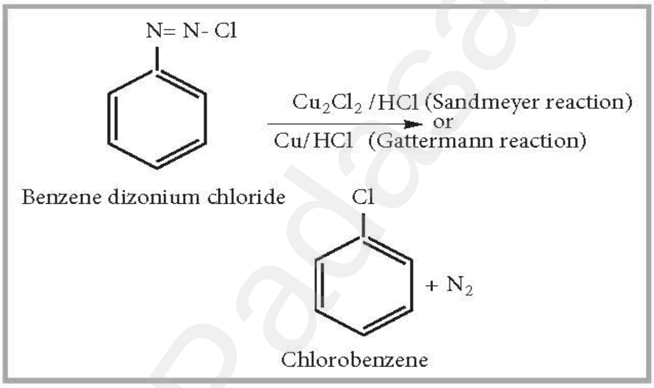
$\downarrow \Delta$

$CH_3CH_2OCH_2CH_3 + NaBr$

diethyl ether

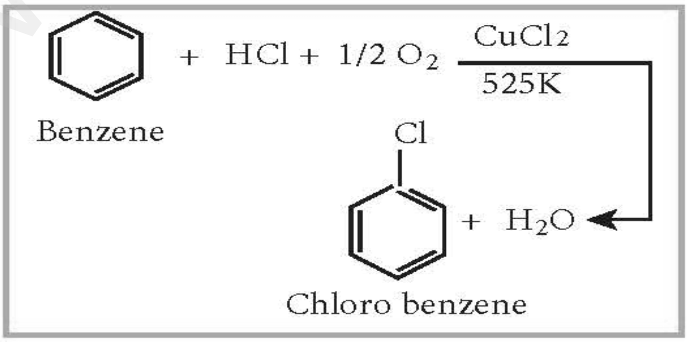
(i) Sandmeyer reaction

When aqueous solution of benzene diazonium chloride is warmed with Cu_2Cl_2 in HCl gives chloro benzene



5) Commercial preparation of chloro benzene (Raschig process)

Chloro benzene is commercially prepared by passing a mixture of benzene vapour, air and HCl over heated cupric chloride .This reaction is called Raschig process.

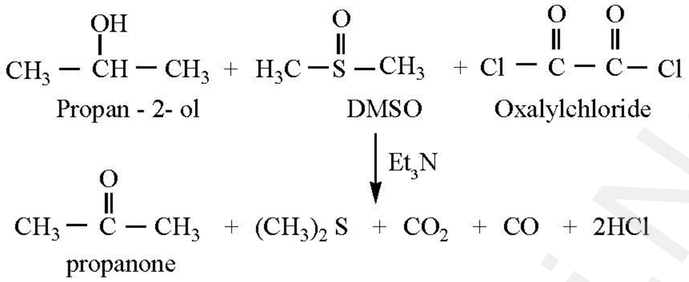


+2 CHEMISTRY - NAME REACTIONS

Swern oxidation

In this method, dimethyl sulfoxide (DMSO) is used as the oxidising agent, which converts alcohols to ketones / aldehydes.

In this method an alcohol is treated with DMSO and oxalyl chloride followed by the addition of triethylamine.

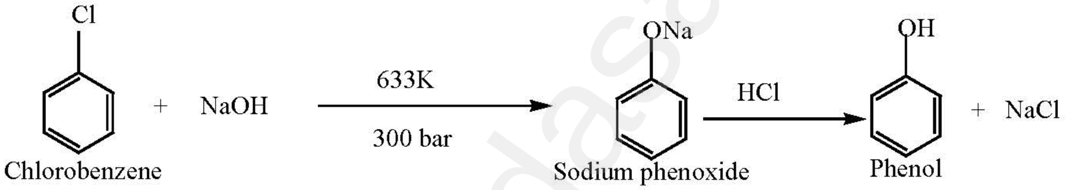


$$CH_3-\overset{OH}{CH}-CH_3 + H_3C-\overset{O}{\overset{\|}{S}}-CH_3 + Cl-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{Et_3N} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + (CH_3)_2S + CO_2 + CO + 2HCl$$

Preparation of Phenols

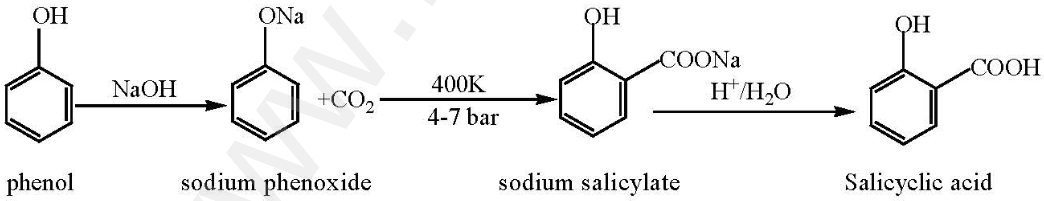
a) From halo arenes(Dows process)

When Chlorobenzene is hydrolysed with 6-8% NaOH at 300 bar and 633K in a closed vessel,sodium phenoxide is formed which on treatment with dilute HCl gives phenol.



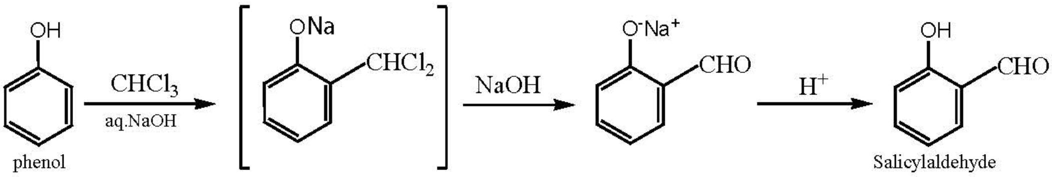
v) Kolbe's (or) Kolbe's Schmit reaction:

In this reaction, phenol is first converted into sodium phenoxide which is more reactive than phenol towards electrophilic substitution reaction with CO_2. Treatment of sodium phenoxide with CO_2 at 400K, 4-7 bar pressure followed by acid hydrolysis gives salicylic acid.



vi) Riemer – Tiemann Reaction:

On treating phenol with $CHCl_3$/NaOH, a -CHO group is introduced at ortho position. This reaction proceeds through the formation of substituted benzal chloride intermediate.



2. Williamsons synthesis:

When an alkyl halide is heated with an alcoholic solution of sodium alkoxide, the corresponding ethers are obtained. The reaction involves SN^2 mechanism.

$$CH_3\text{-}ONa + Br\text{-}C_2H_5 \xrightarrow{\Delta} CH_3\text{-}O\text{-}C_2H_5 + NaBr$$

Mechanism:

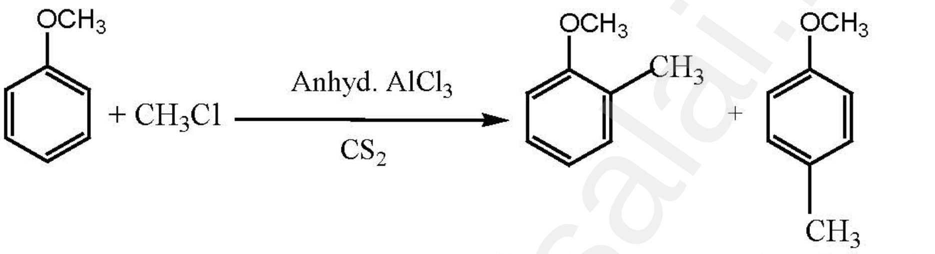
$$CH_3-O^-Na^+ + CH_3-CH_2-Br \xrightarrow[\Delta]{-NaBr} CH_3-CH_2-\ddot{\underset{\cdot\cdot}{O}}-CH_3$$

methoxyethane

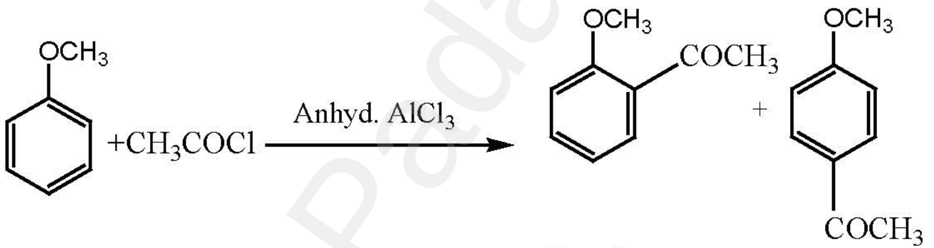
We know that primary alkyl halides are more susceptible for SN^2 reaction. Hence for the preparation of mixed ether having primary and tertiary alkyl group, primary alkyl halide and tertiary alkoxide are used. On the other hand, if we use tertiary alkyl halide and primary alkoxide, elimination dominates and succeeds over substitution to form an an alkene.

iii) Friedel Craft's reaction:

Anisole undergoes Fridel Craft's reaction in presence of anhydrous $AlCl_3$ as a catalyst.



2-methoxy toluene(minor) 4-methoxy toluene (major)



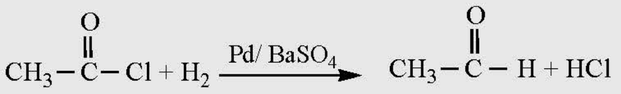
2-methoxy acetophenone (minor) 4-methoxy Acetophenone (major)

B. Preparation of aldehydes

1) Rosenmund reduction

a) **Aldehydes** can be prepared by the hydrogenation of acid chloride, in the presence of palladium supported by barium sulphate. This reaction is called **Rosenmund reduction**.

Example



$$CH_3-\overset{\overset{\large O}{\|}}{C}-Cl + H_2 \xrightarrow{Pd/\,BaSO_4} CH_3-\overset{\overset{\large O}{\|}}{C}-H + HCl$$

Acetyl chloride Acetaldehyde

In this reaction, barium sulphate act as a catalytic poison to palladium catalyst, so that aldehyde cannot be further reduced to alcohol.

Formaldehyde and ketones cannot be prepared by this method.

2. Stephen's reaction

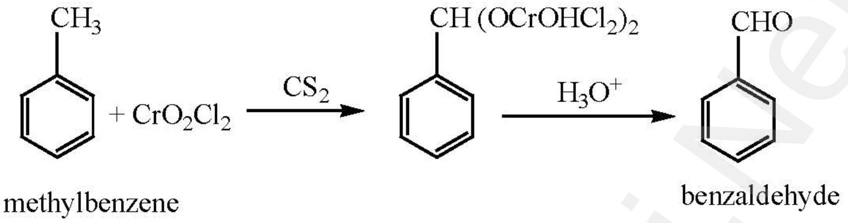
When alkylcyanides are reduced using $SnCl_2/HCl$, imines are formed, which on hydrolysis gives corresponding aldehyde.

$$CH_3-C\equiv N\xrightarrow[(H)]{SnCl_2/HCl}CH_3-CH=NH\xrightarrow{H_3O^+}CH_3-CHO+NH_3$$

C) Preparation of benzaldehyde

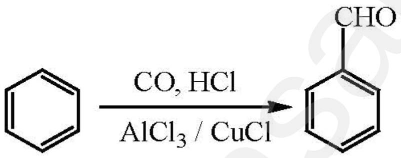
1. **Side chain oxidation of toluene and its derivatives** by strong oxidising agents such as $KMnO_4$ gives benzoic acid.

When chromylchloride is used as an oxidising agent, toluene gives benzaldehyde. This reaction is called **Etard reaction**. Acetic anhydride and CrO_3 can also be used for this reaction.



2) Gattermann – Koch reaction

This reaction is a variant of Friedel – Crafts acylation reaction. In this method, reaction of carbon monoxide and HCl generate an intermediate which reacts like formyl chloride.

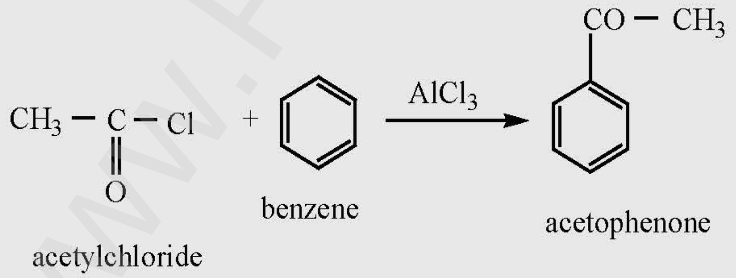


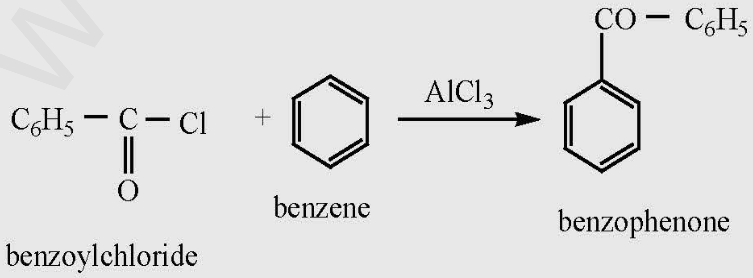
2) Preparation of phenyl ketones

Friedel – Crafts acylation

It is the best method for preparing alkyl aryl ketones or diaryl ketones. This reaction succeeds only with benzene and activated benzene derivatives.

Example





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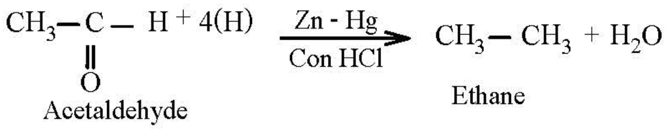
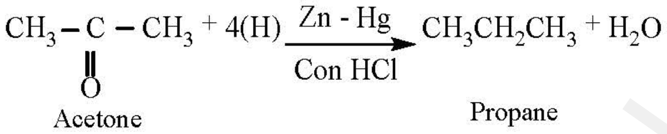
a) Clemmensen reduction

Aldehydes and Ketones when heated with zinc amalgam and concentrated hydrochloric acid gives hydrocarbons.

Example



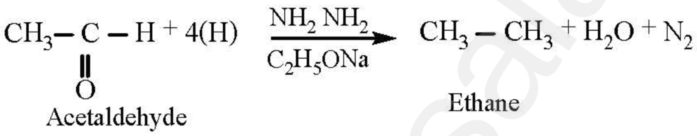
$$\underset{\text{Acetaldehyde}}{CH_3-\underset{\underset{O}{\|}}{C}-H} + 4(H) \xrightarrow[\text{Con HCl}]{\text{Zn - Hg}} \underset{\text{Ethane}}{CH_3-CH_3} + H_2O$$



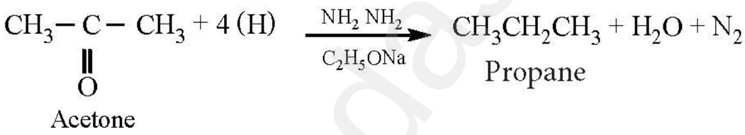
$$\underset{\text{Acetone}}{CH_3-\underset{\underset{O}{\|}}{C}-CH_3} + 4(H) \xrightarrow[\text{Con HCl}]{\text{Zn - Hg}} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O$$

b) Wolf Kishner reduction Aldehydes and Ketones when heated with hydrazine (NH_2NH_2) and sodium ethoxide, hydrocarbons are formed Hydrazine acts as a reducing agent and sodium ethoxide as a catalyst.

Example

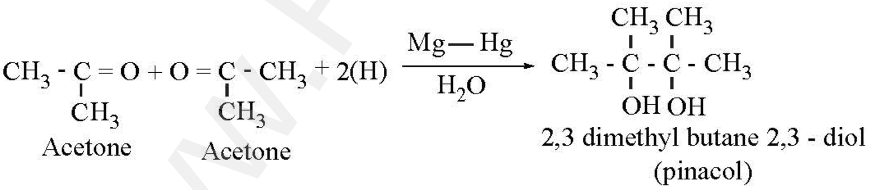


$$\underset{\text{Acetaldehyde}}{CH_3-\underset{\underset{O}{\|}}{C}-H} + 4(H) \xrightarrow[C_2H_5ONa]{NH_2\,NH_2} \underset{\text{Ethane}}{CH_3-CH_3} + H_2O + N_2$$



$$\underset{\text{Acetone}}{CH_3-\underset{\underset{O}{\|}}{C}-CH_3} + 4\,(H) \xrightarrow[C_2H_5ONa]{NH_2\,NH_2} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O + N_2$$

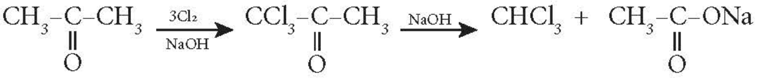
Aldehyde (or) ketones is first converted to its hydrazone which on heating with strong base gives hydrocarbons.



$$\underset{\text{Acetone}}{CH_3-\underset{\underset{CH_3}{|}}{C}=O} + \underset{\text{Acetone}}{O=\underset{\underset{CH_3}{|}}{C}-CH_3} + 2(H) \xrightarrow[H_2O]{Mg-Hg} \underset{\text{2,3 dimethyl butane 2,3 - diol (pinacol)}}{CH_3-\overset{CH_3}{\underset{OH}{C}}-\overset{CH_3}{\underset{OH}{C}}-CH_3}$$

D) Haloform reaction

Acetaldehyde and methyl ketones, containing $CH_3-\underset{\underset{O}{\|}}{C}-$ group, when treated with halogen and alkali give the corresponding haloform. This is known as Haloform reaction.



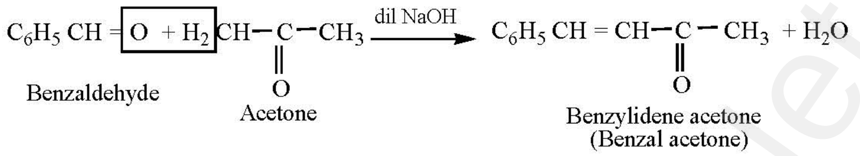
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[NaOH]{3Cl_2} CCl_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{NaOH} CHCl_3 + CH_3-\underset{\underset{O}{\|}}{C}-ONa$$

i) Claisen – Schmidt Condensation

Benzaldehye condenses with aliphatic aldehyde or methyl ketone in the presence of dil. alkali at room temperature to form unsaturated aldehyde or ketone. This type of reaction is called Claisen – Schmidt condensation.

Example

$$\underset{\text{Benzaldehyde}}{C_6H_5\,CH=}\boxed{O\ +H_2}\underset{\text{Acetaldehyde}}{CH-CHO} \xrightarrow{\text{dil NaOH}} \underset{\text{Cinnamaldehyde}}{C_6H_5\,CH=CH-CHO} + H_2O$$



$$C_6H_5\,CH=\boxed{O\ +H_2}CH-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 \xrightarrow{\text{dil NaOH}} C_6H_5\,CH=CH-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 + H_2O$$

Benzaldehyde Acetone Benzylidene acetone (Benzal acetone)

ii) Cannizaro reaction

In the presence of concentrated aqueous or alcoholic alkali, aldehydes which do not have α - hydrogen atom undergo self oxidation and reduction (disproportionation) to give a mixture of alcohol and a salt of carboxylic acid. This reaction is called **Cannizaro reaction**.

Benzaldehyde on treatment with concentrated NaOH (50%) gives benzyl alcohol and sodium benzoate.

$$\begin{array}{c} C_6H_5CHO \\ + \\ C_6H_5CHO \\ \text{Benzaldehyde} \end{array} \xrightarrow{\text{50\% NaOH}} \begin{array}{c} C_6H_5CH_2OH \\ \text{Benzylalcohol} \\ + \\ C_6H_5COONa \\ \text{Sodiumbenzoate} \end{array}$$

This reaction is an example disproportionation reaction

Crossed Cannizaro reaction

When Cannizaro reaction takes place between two different aldehydes (neither containing an α hydrogen atom), the reaction is called as crossed cannizaro reaction.

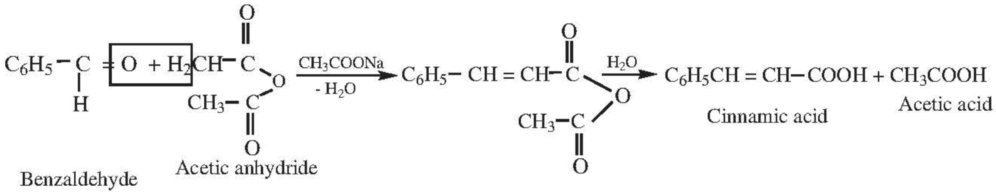
$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Formaldehyde}}{HCHO} \xrightarrow{\text{NaOH}} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{sodium formate}}{HCOONa}$$

In crossed cannizaro reaction more reactive aldehyde is oxidized and less reactive aldehyde is reduced.

4) Perkins' reaction

When an aromatic aldehyde is heated with an aliphatic acid anhydride in the presence of the sodium salt of the acid corresponding to the anhydride, condensation takes place and an α, β unsaturated acid is obtained. This reaction is known as **Perkin's reaction**.

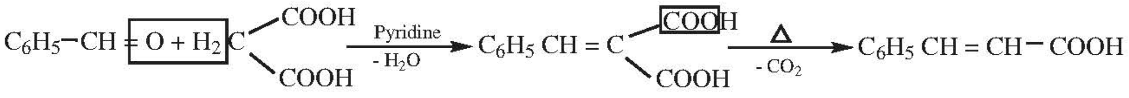
Example:



$$C_6H_5-\underset{H}{C}=\boxed{O\ +H_2}CH-\overset{O}{\overset{\|}{C}}-O-\underset{O}{\underset{\|}{C}}-CH_3 \xrightarrow[-H_2O]{CH_3COONa} C_6H_5-CH=CH-\overset{O}{\overset{\|}{C}}-O-\underset{O}{\underset{\|}{C}}-CH_3 \xrightarrow{H_2O} C_6H_5CH=CH-COOH + CH_3COOH$$

Benzaldehyde Acetic anhydride Cinnamic acid Acetic acid

5) Knoevenagal reaction

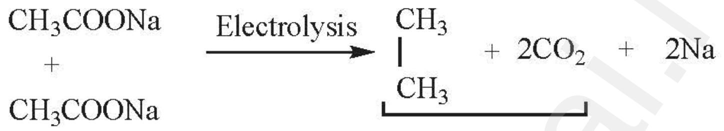


Benzaldehyde Malonic acid Cinnamic acid

Benzaldehyde condenses with malonic acid in presence of pyridine forming cinnamic acid, Pyridine act as the basic catalyst.

3) Kolbe's electrolytic decarboxylation

The aqueous solutions of sodium or potassium salts of carboxylic acid on electrolysis gives alkanes at anode. This reaction is called kolbes electrolysis.



$$\begin{matrix} CH_3COONa \\ + \\ CH_3COONa \end{matrix} \xrightarrow{\text{Electrolysis}} \begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} + 2CO_2 + 2Na$$

Sodium acetate Anode Cathode

Sodium formate solution on electrolysis gives hydrogen

4) Hoff mann's degradation

Amides reacts with bromine in the presence of caustic alkali to form a primary amine carrying one carbon less than the parent amide.

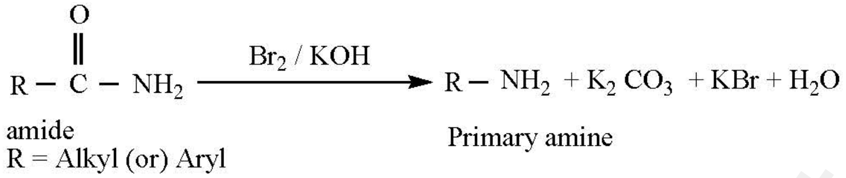
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4\,KOH \xrightarrow{\Delta} CH_3NH_2 + K_2CO_3 + 2KBr + 2H_2O$$

Acetamide Methyl amine

b) Hoffmann's degradation reaction

When Amides are treated with bromine in the presence of aqueous or ethanolic solution of KOH, primary amines with one carbon atom less than the parent amides are obtained.

Example:



$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{Br_2\,/\,KOH} R-NH_2 + K_2CO_3 + KBr + H_2O$$

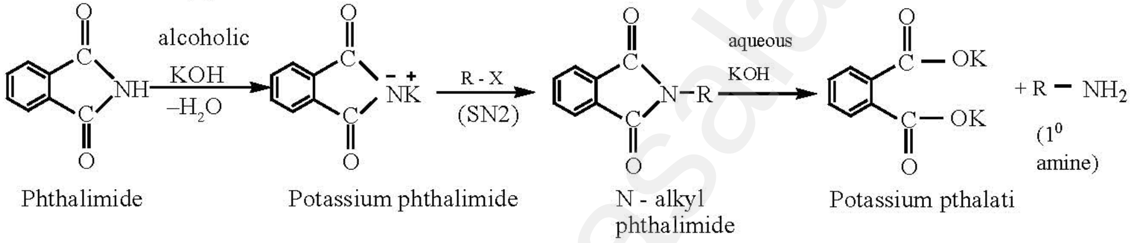
amide
R = Alkyl (or) Aryl

Primary amine

4) From alkyl halides

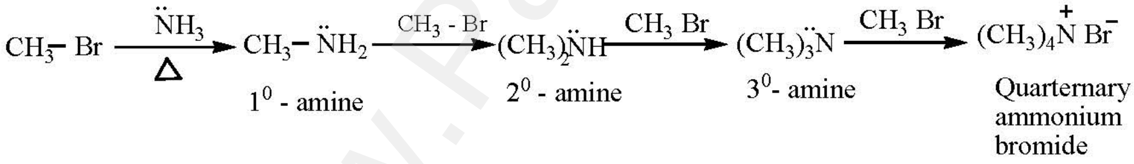
a) Gabriel phthalimide synthesis

Gabriel synthesis is used for the preparation of Aliphatic primary amines. Phthalimide on treatment with ethanolic KOH forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis gives primary amine. Aniline cannot be prepared by this method because the arylhalides do not undergo nucleophilic substitution with the anion formed by phthalimide



b) Hoffmann's ammonolysis

When Alkyl halides (or) benzylhalides are heated with alcoholic ammonia in a sealed tube, mixtures of 1^0, 2^0 and 3^0 amines and quaternary ammonium salts are obtained.



$$CH_3-Br \xrightarrow[\Delta]{\ddot{N}H_3} CH_3-\ddot{N}H_2 \xrightarrow{CH_3-Br} (CH_3)_2\ddot{N}H \xrightarrow{CH_3Br} (CH_3)_3\ddot{N} \xrightarrow{CH_3Br} (CH_3)_4\overset{+}{N}Br^-$$

1^0 - amine 2^0 - amine 3^0- amine Quarternary ammonium bromide

This is a nucleophilic substitution , the halide ion of alkyl halide is substituted by the $-NH_2$ group. The product primary amine so formed can also has a tendency to act as a nucleophile and hence if excess alkyl halide is taken, further nucleophilic substitution takes place leading

3) Schotten – Baumann reaction

Aniline reacts with benzoylchloride (C_6H_5COCl) in the presence of NaOH to give N – phenyl benzamide. This reaction is known as Schotten – Baumann reaction. The acylation and benzoylation are nucleophilic substitutions.

5) Carbylamine reaction

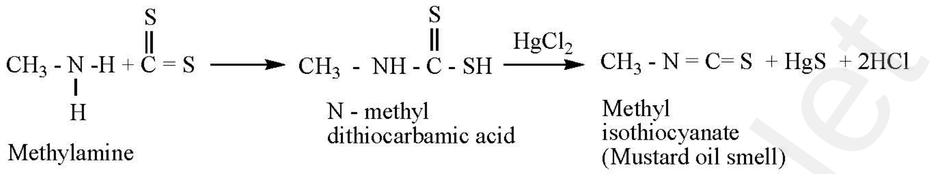
Aliphatic (or) aromatic primary amines react with chloroform and alcoholic KOH to give isocyanides (carbylamines), which has an unpleasant smell. This reaction is known as carbylamine test. This test used to identify the primary amines.

$$C_2H_5-NH_2 + CHCl_3 + 3KOH \longrightarrow C_2H_5-NC + 3KCl + 3H_2O$$

Ethylamine Chloroform Ethylisocyanide

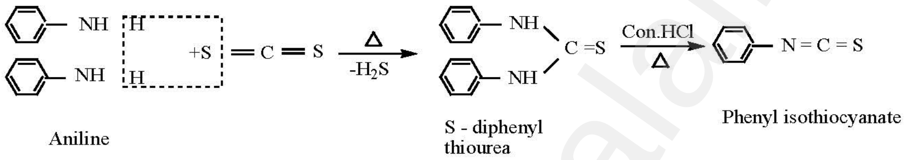
6) Mustard oil reaction

i) When primary amines are treated with carbon disulphide (CS_2), N - alkyldithio carbomic acid is formed which on subsequent treatment with $HgCl_2$, give an alkyl isothiocyanate.



$$CH_3-\underset{\displaystyle H}{\underset{|}{N}}-H + \overset{\displaystyle S}{\overset{\|}{C}}=S \longrightarrow CH_3-NH-\overset{\displaystyle S}{\overset{\|}{C}}-SH \xrightarrow{HgCl_2} CH_3-N=C=S + HgS + 2HCl$$

ii) When aniline is treated with carbon disulphide, or heated together, S- diphenylthio urea is formed, which on boiling with strong HCl, phenyl isothiocyanate (phenyl mustard oil), is formed.



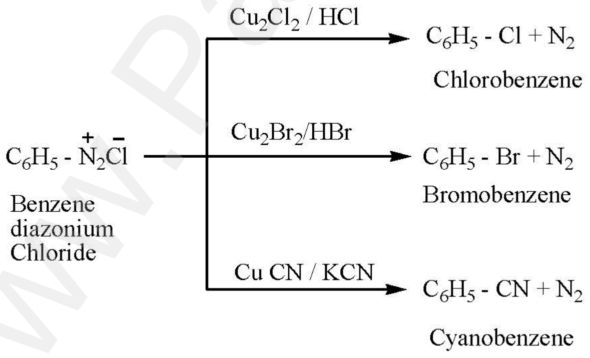
These reactions are known as Hofmann – Mustard oil reaction. This test is used to identify the primary amines.

2. Replacement by Chlorine, Bromine, Cyanide group

a) Sandmeyer reaction

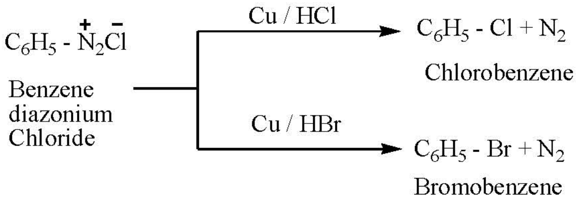
On mixing freshly prepared solution of benzene diazonium chloride with cuprous halides (chlorides and bromides), aryl halides are obtained. This reaction is called Sandmeyer reaction.

When diazonium salts are treated with cuprous cyanide, cyanobenzene is obtained.



b) Gattermann reaction

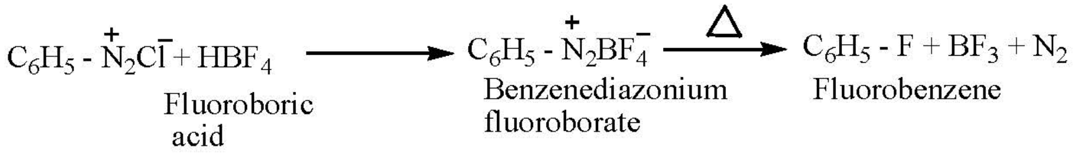
Conversion of benzene diazonium chloride into chloro / bromo arenes can also be effected using hydrochloric / hydrobromic acid and copper powder. This reaction is called Gattermann reaction.



The yield in Sandmeyer reaction is found to be better than the Gattermann reaction.

4. Replacement of fluorine (Baltz – schiemann reaction)

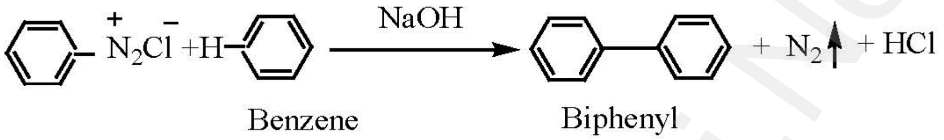
When benzene diazonium chloride is treated with fluoroboric acid, benezene diazonium tetra fluoroborate is precipitated which on heating decomposes to give fluorobenzene.



$$C_6H_5-\overset{+}{N}_2\bar{Cl}+HBF_4 \longrightarrow C_6H_5-\overset{+}{N}_2\bar{BF_4} \xrightarrow{\Delta} C_6H_5-F+BF_3+N_2$$

7. Replacement by aryl group (Gomberg reaction)

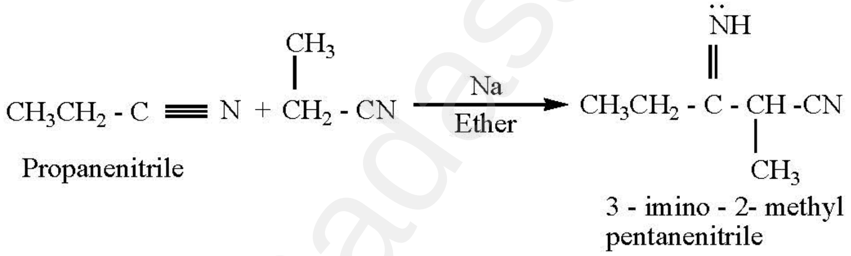
Benzene diazonium chloride reacts with benzene in the presence of sodium hydroxide to give biphenyl. This reaction in known as the Gomberg reaction.



3. Condensation reaction

a) Thorpe nitrile condensation

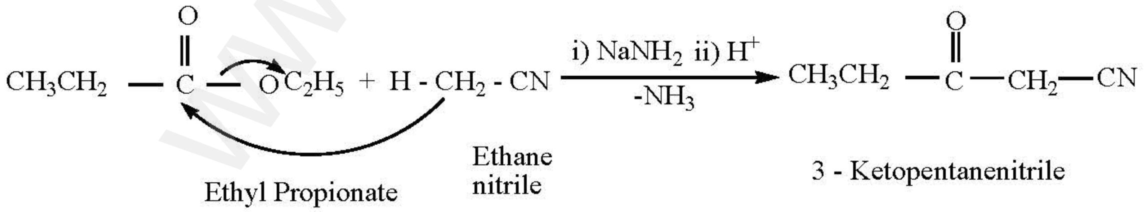
Self condensation of two molecules of alkyl nitrile (containing α–H atom) in the presence of sodium to form iminonitrile.



$$CH_3CH_2-C\equiv N + \underset{CH_3}{CH_2}-CN \xrightarrow[Ether]{Na} CH_3CH_2-\overset{\ddot{N}H}{\overset{\|}{C}}-\underset{CH_3}{CH}-CN$$

b) The nitriles containing α - **hydrogen** also undergo condensation with esters in the presence of sodamide in ether to form ketonitriles. This reaction is known as " Levine and Hauser" acetylation

This reaction involves replacement of ethoxy (OC_2H_5) group by methylnitrile $(-CH_2CN)$ group and is called as cyanomethylation reaction.



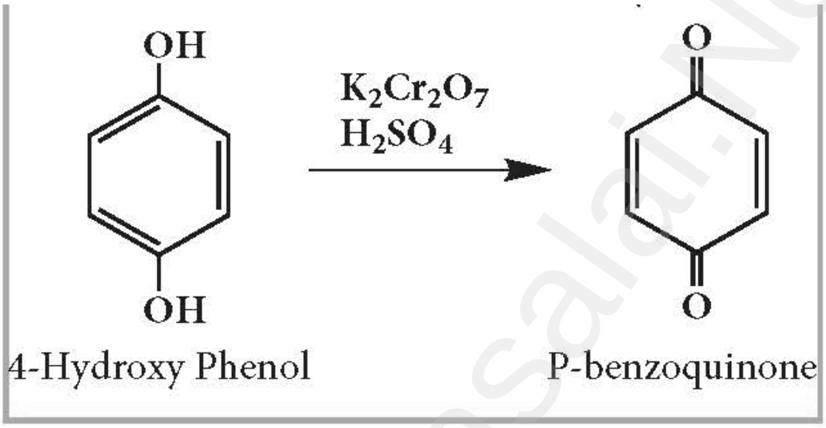
$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 + H-CH_2-CN \xrightarrow[-NH_3]{i)\ NaNH_2\ ii)\ H^+} CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CN$$

+1 & +2 OXIDATION REACTIONS

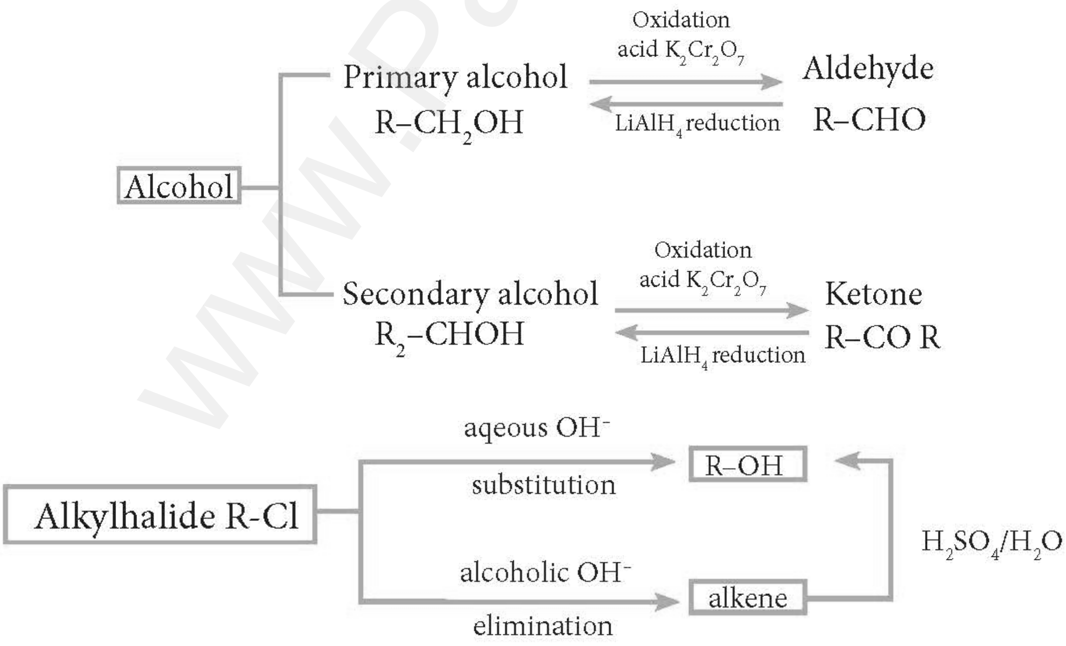
Oxidation

Examples:

$$\underset{\text{Acetaldihyde}}{CH_3CHO} \xrightarrow[\text{Acidic dichromate}]{(o)} \underset{\text{Acetic acid}}{CH_3COOH}$$



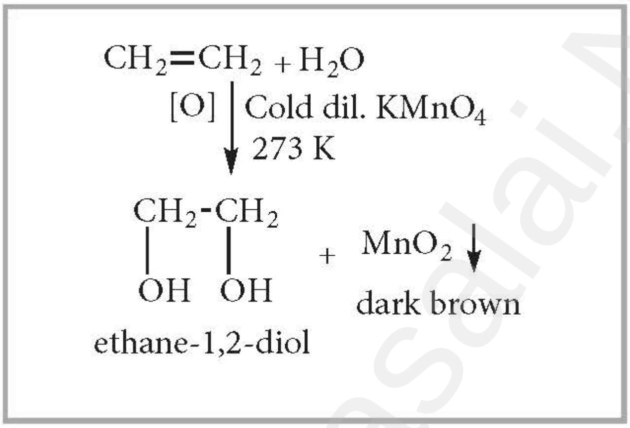
Some of the important functional group interconversions of Organic compounds summarised in the below mentioned Flow chart.



(2) Oxidation:

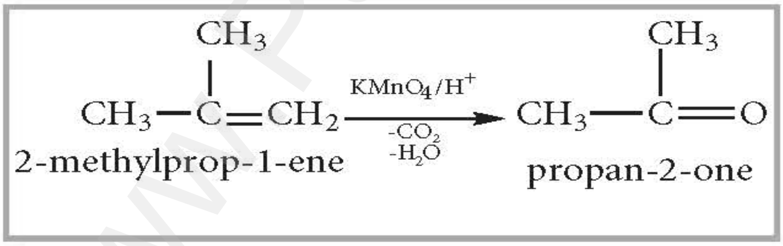
(i) With cold dilute alkaline KMnO4 solution (Baeyer's Reagent)

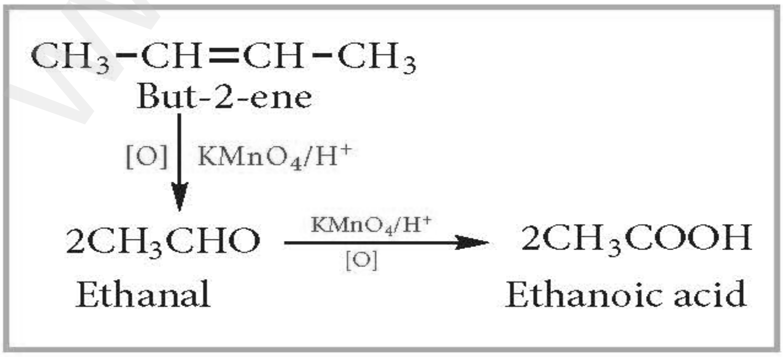
Alkenes react with Baeyer's reagent to form vicinal diols. The purple solution (Mn^{7+}) becomes dark green (Mn^{6+}), and then produces a dark brown precipitate (Mn^{4+}).

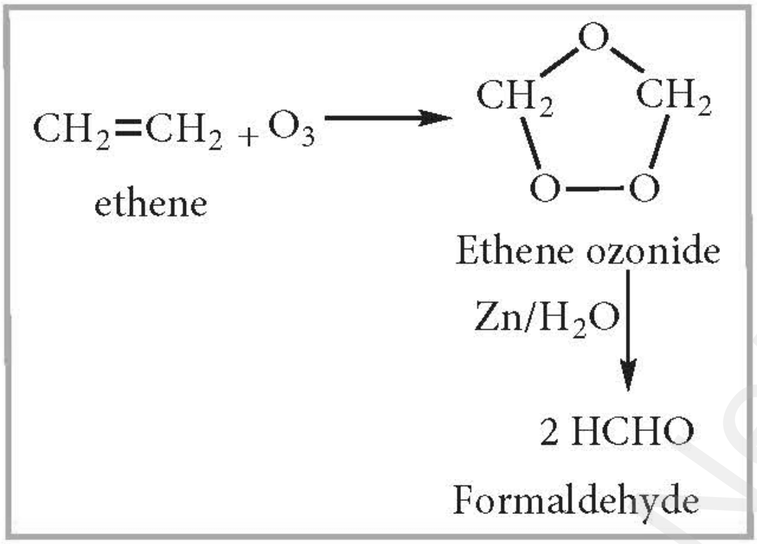


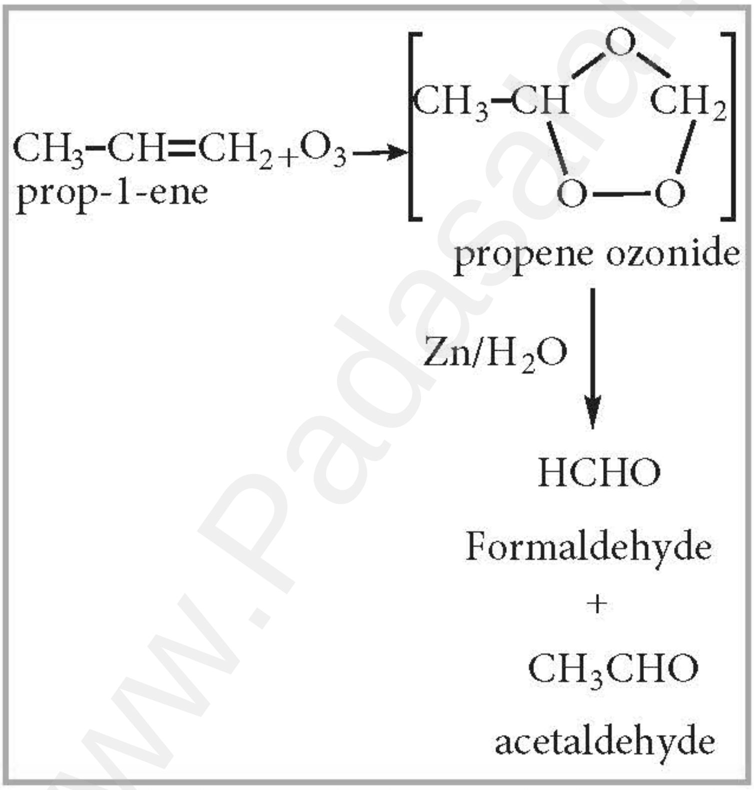
(ii) With acidified $KMnO_4$ Solution

Alkenes react with acidified $KMnO_4$ solution and are oxidiwed to ketones or carboxylic acid depends on the substituent at the olefinic carbon atom. The purple solution becomes colourless. This is one of the test for unsaturation.



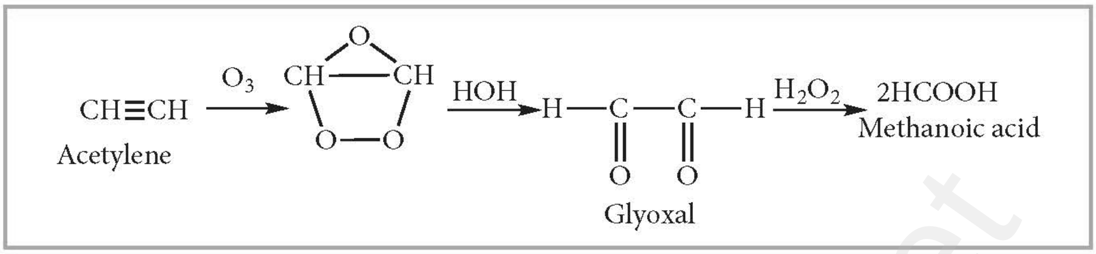


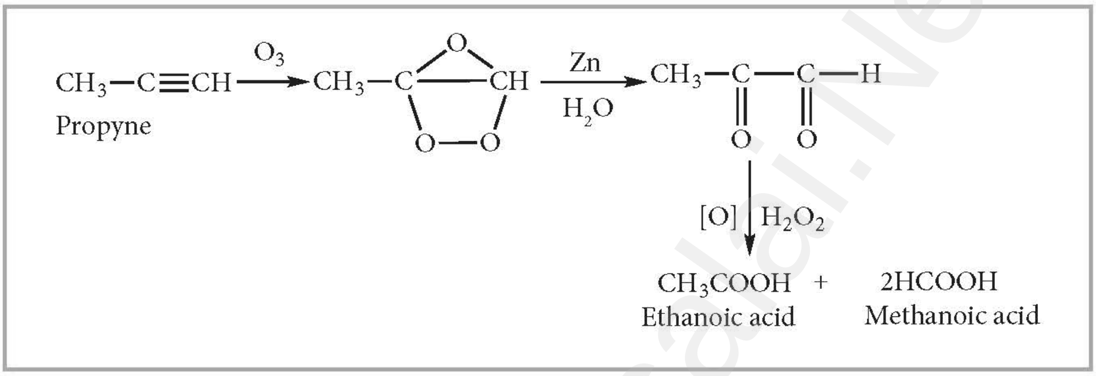

CH2=CH2 + O3
ethene
O
CH2
CH2
O
O
Ethene ozonide
Zn/H2O
2 HCHO
Formaldehyde


CH3-CH=CH2+O3
prop-1-ene
O
CH3-CH
CH2
O
O
propene ozonide
Zn/H2O
HCHO
Formaldehyde
+
CH3CHO
acetaldehyde

3. Ozonolysis:

Ozone adds to carbon-carbon triple bond of alkynes to form ozonides. The ozonides are hydrolyzed by water to form carbonyl compounds. The hydrogen peroxide (H_2O_2) formed in the reaction may oxidise the carbonyl compound to carboxylic acid.

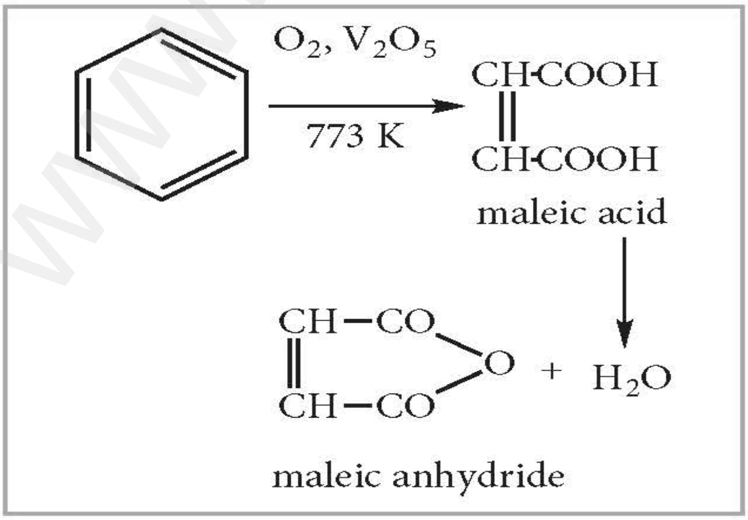




(iii) Oxidation:

a. Vapour – phase oxidation:-

Although benzene is very stable to strong oxidizing agents, it quickly undergoes vapour phase oxidation by passing its vapour mixed with oxygen over V_2O_5 at 773k. The ring breaks to give maleic anhydride.



Chemical properties

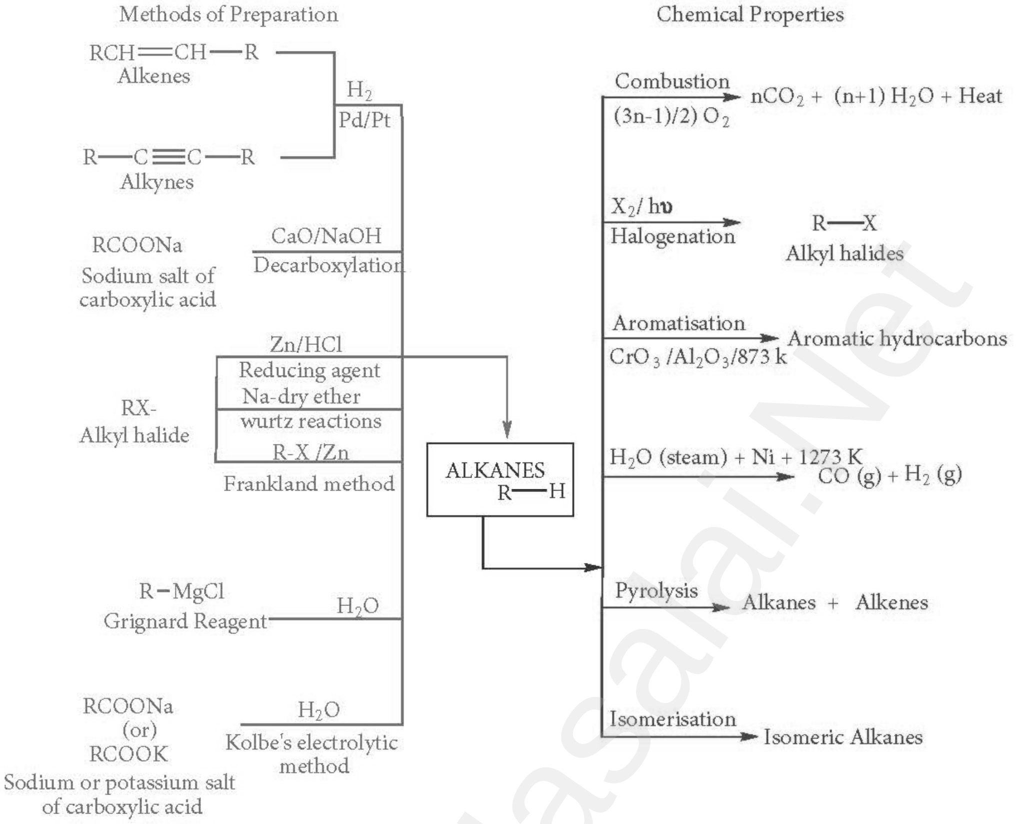
1) Oxidation

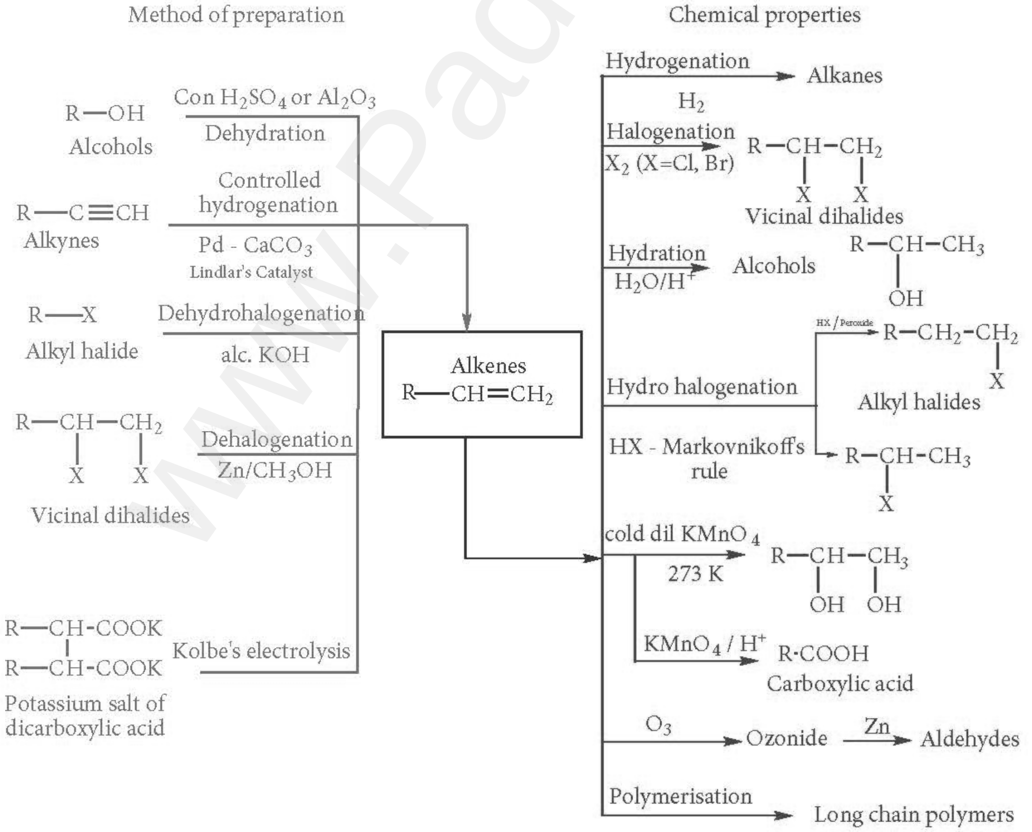
Chloroform undergoes oxidation in the presence of light and air to form phosgene (carbonyl chloride)

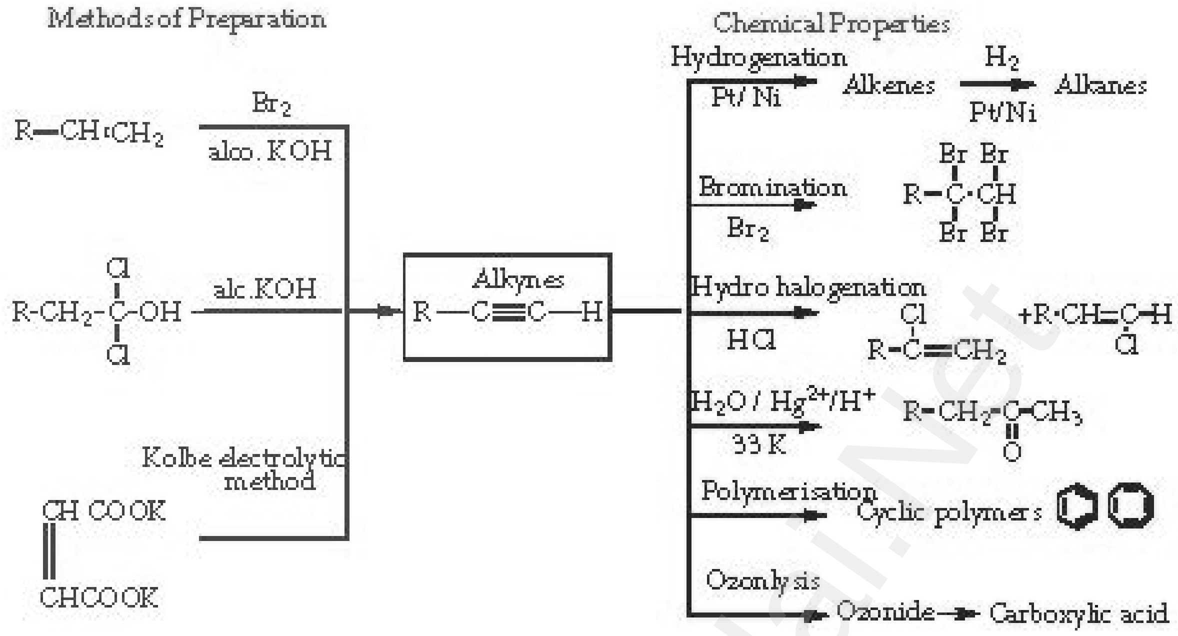
$$\underset{\text{Chloroform}}{CHCl_3} + \frac{1}{2} O_2 \xrightarrow[\text{light}]{\text{air}} \underset{\text{Phosgene}}{COCl_2} + HCl$$

Since phosgene is very poisonous, its presence makes chloroform unfit for use as anaesthetic.

FLOWCHART AND REACTION SUMMARY OF HYDROCARBON

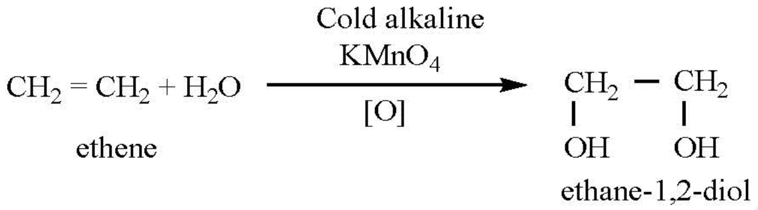





Methods of Preparation
R–CH=CH₂
Br₂
alco. KOH
Cl
R-CH₂-C-OH
Cl
alc.KOH
Kolbe electrolytic method
CH COOK
CHCOOK
Alkynes
R—C≡C—H
Chemical Properties
Hydrogenation
Pt/ Ni
Alkenes
H₂
Pt/Ni
Alkanes
Bromination
Br₂
Br Br
R–C-CH
Br Br
Hydro halogenation
HCl
Cl
R-C=CH₂
+R-CH=C-H
Cl
H₂O / Hg²⁺/H⁺
33 K
R-CH₂-C-CH₃
O
Polymerisation
Cyclic polymers
Ozonlysis
Ozonide
Carboxylic acid

Preparation of glycol

We have already learnt that the hydroxylation of ethylene using cold alkaline solution of potassium permanganate (Baeyer's reagent) gives ethylene glycol.



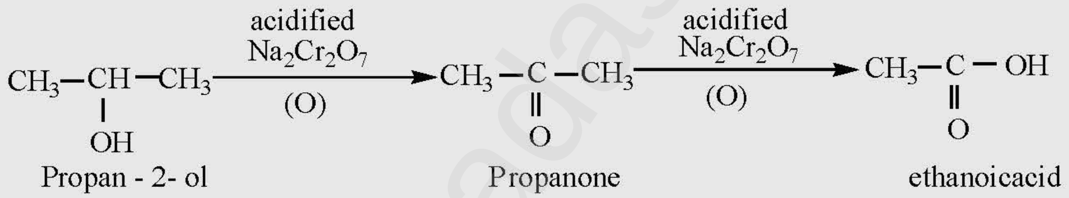
$$\underset{\text{ethene}}{CH_2 = CH_2 + H_2O} \xrightarrow[\text{[O]}]{\text{Cold alkaline } KMnO_4} \underset{\text{ethane-1,2-diol}}{\underset{OH}{CH_2} - \underset{OH}{CH_2}}$$

Oxidation of alcohols

The important reactions of alcohols are their oxidation to give carbonyl compounds. The commonly used oxidising agent is acidified sodiumdichromate. Oxidation of primary alcohols give an aldehyde which on further oxidation gives the carboxylic acids. To stop the oxidation reaction at the aldehyde / ketone stage, pyridinium chlorochromate (PCC) is used as an oxidising agent.

Example

$$\underset{\text{ethanol}}{CH_3 - CH_2 - OH} \xrightarrow[\text{(O)}]{\text{acidified } Na_2Cr_2O_7} \underset{\text{ethanal}}{CH_3 - CHO} \xrightarrow[\text{(O)}]{\text{acidified } Na_2Cr_2O_7} \underset{\text{ethanoicacid}}{CH_3 - COOH}$$



$$\underset{\text{Propan - 2- ol}}{CH_3 - \underset{OH}{CH} - CH_3} \xrightarrow[\text{(O)}]{\text{acidified } Na_2Cr_2O_7} \underset{\text{Propanone}}{CH_3 - \underset{O}{\overset{}{\underset{\|}{C}}} - CH_3} \xrightarrow[\text{(O)}]{\text{acidified } Na_2Cr_2O_7} \underset{\text{ethanoicacid}}{CH_3 - \underset{O}{\underset{\|}{C}} - OH}$$

$$\underset{\text{Propan - 1- ol}}{CH_3 - CH_2 - CH_2 - OH} \xrightarrow{\text{PCC}} \underset{\text{Propanal}}{CH_3 - CH_2 - CHO}$$

Tertiary alcohols do not undergo oxidation reaction under normal conditions, but at elevated temperatures, under strong oxidising agent cleavage of C –C bond takes place to give a mixture of carboxylic acid.

Biological oxidation

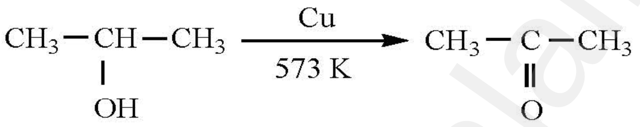
The fermentation of the food consumed by an animal produces alcohol. To detoxify the alcohol, the liver produces an enzyme called alcohol dehydrogenase (ADH). Nicotinamide adenine dinucleotide (NAD) present in the animals act as an oxidising agent and ADH catalyses the oxidation of toxic alcohols into non-toxic aldehyde.

$$\underset{\text{ethanol}}{CH_3CH_2OH} + NAD^+ \xrightarrow{ADH} \underset{\text{ethanal}}{CH_3CHO} + NADH + H^+$$

Catalytic dehydrogenation

When the vapours of a primary or a secondary alcohol are passed over heated copper at 573K, dehydrogenation takes place to form aldehyde or ketone.

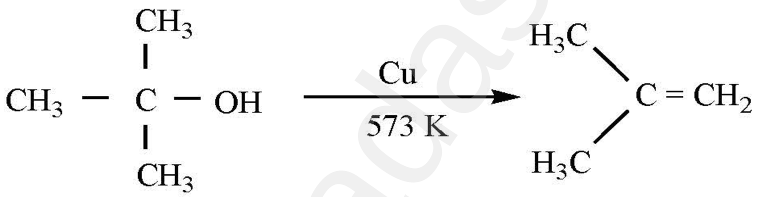
$$\underset{\text{ethanol}}{CH_3-CH_2-OH} \xrightarrow[573\ K]{Cu} \underset{\text{ethanal}}{CH_3-CHO}$$



$$CH_3-\underset{\substack{|\\ OH}}{CH}-CH_3 \xrightarrow[573\ K]{Cu} CH_3-\underset{\substack{\|\\ O}}{C}-CH_3$$

Propan - 2- ol propanone

Tertiary alcohols undergo dehydration reaction to give alkenes.

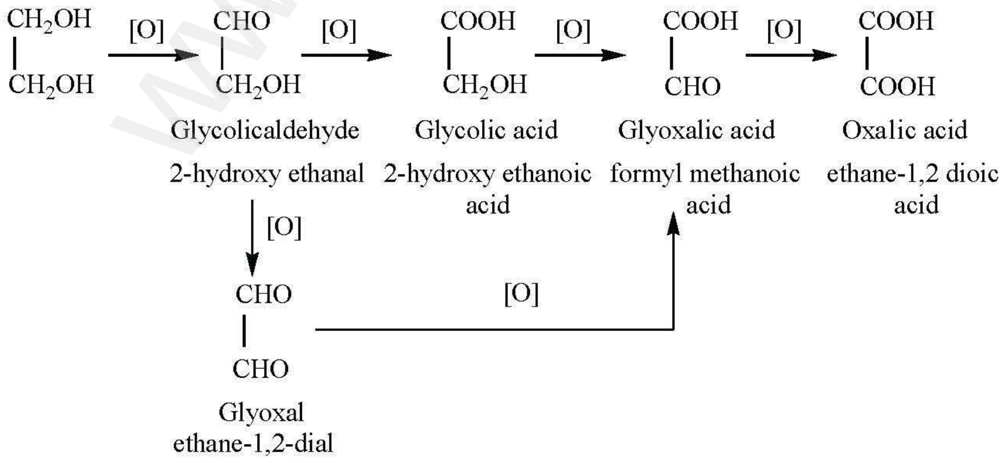


2 - methylpropan - 2- ol 2 - methylprop - 1- ene

Oxidation of glycol

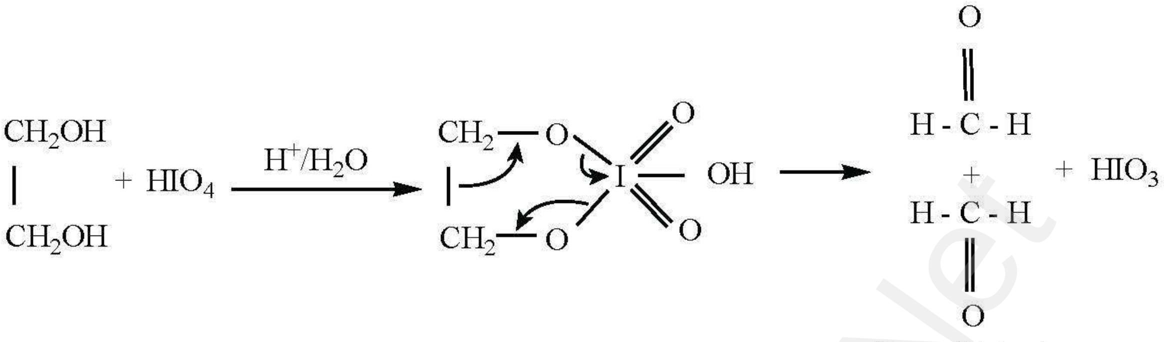
On oxidation, glycol gives a variety of products depending on the nature of oxidizing agent and other reaction conditions.

i) When nitric acid (or) alkaline potassium permanganate is used as the oxidizing agent, the following products are obtained.



ii) Oxidation of glycol with periodic acid

Ethylene glycol on treatment with periodic acid gives formaldehyde. This reaction is selective for vicinal 1,2 – diols and it proceeds through a cyclic periodate ester intermediate.



Formaldehyde

Oxidation

Glycerol can give rise to a variety of oxidation products depending on the nature of the oxidising agent used for oxidation.

a) Oxidation of glycerol with dil. HNO_3 gives glyceric acid and tartronic acid.

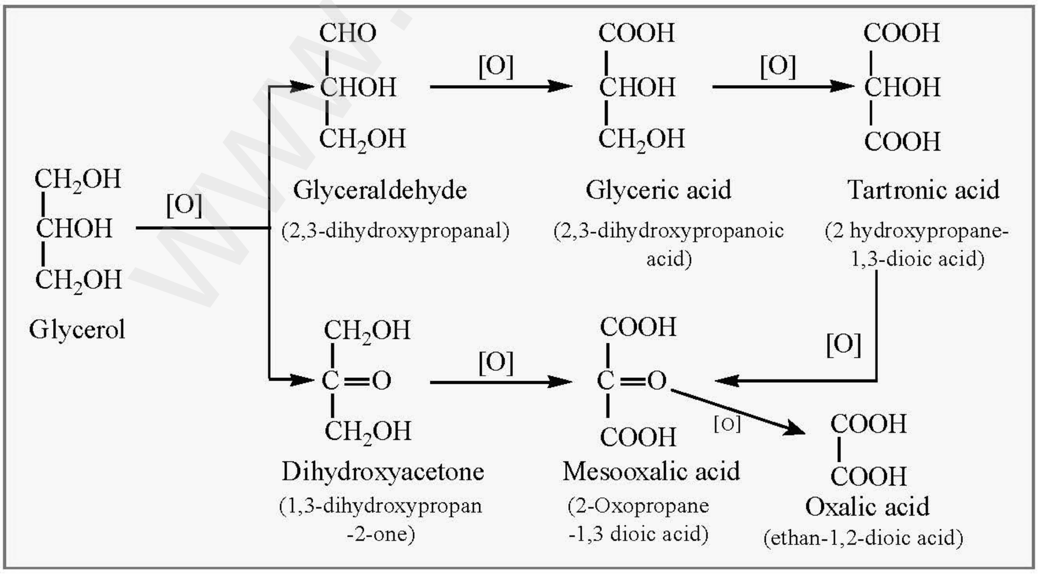
b) Oxidation of glycerol with Conc. HNO_3 gives mainly glyceric acid.

c) Oxidation of glycerol with bismuth nitrate gives as meso oxalic acid.

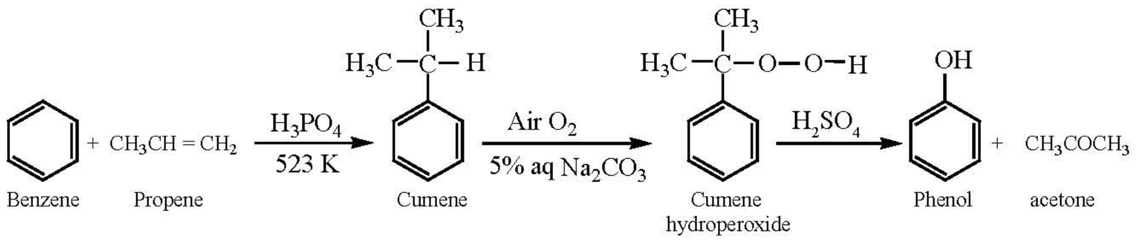
d) Oxidation of glycerol with Br_2/H_2O (or) NaOBr (or) Fenton's reagent ($FeSO_4 + H_2O_2$) gives a mixture of glyceraldehyde and dihydroxy acetone(This mixture is named as glycerose).

e) On oxidation with HIO_4 or Lead tetra acetate (LTA) it gives formaldehyde and formic acid.

f) Acidified $KMnO_4$ oxidises glycerol into oxalicacid.

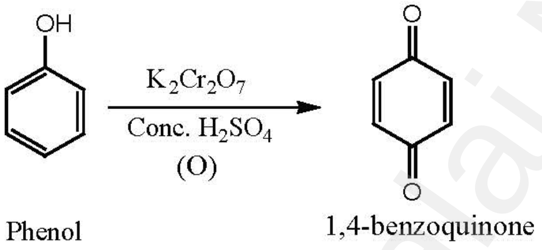


Oxidation of Benzene



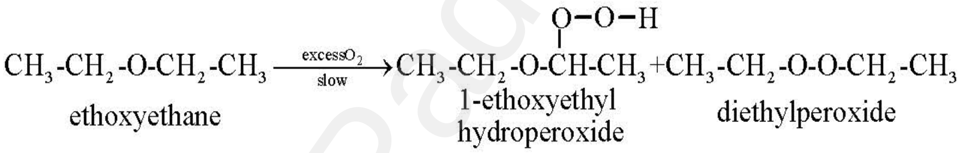
d) Oxidation:

Phenol undergoes oxidation with air or acidified $K_2Cr_2O_7$ with conc. H_2SO_4 to form 1,4-benzoquinone.



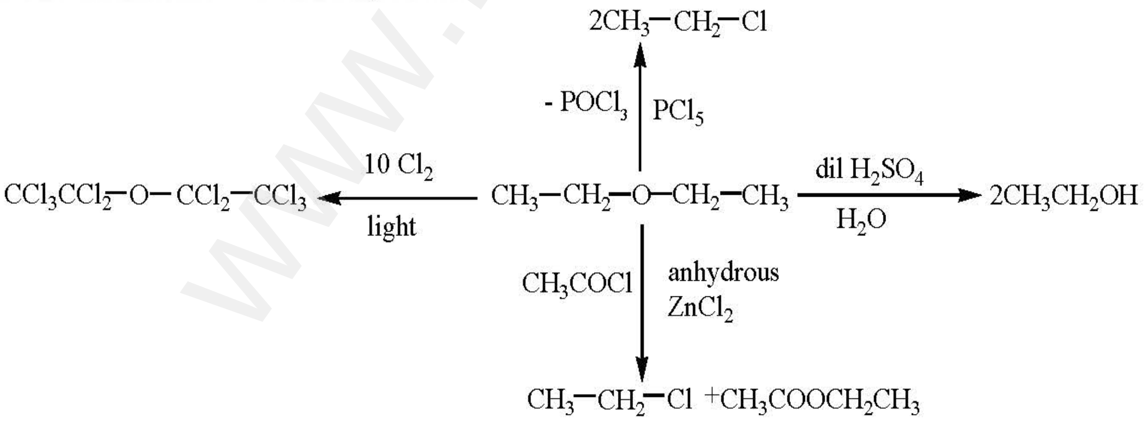
Autooxidation of ethers:

When ethers are stored in the presence of atmospheric oxygen, they slowly oxidise to form hydroperoxides and dialkylperoxides. These are explosive in nature. Such a spontaneous oxidation by atmospheric oxygen is called autooxidation.



$$CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3 \xrightarrow[\text{slow}]{\text{excess}O_2} CH_3\text{-}CH_2\text{-}O\text{-}\overset{O-O-H}{\overset{|}{C}}H\text{-}CH_3 + CH_3\text{-}CH_2\text{-}O\text{-}O\text{-}CH_2\text{-}CH_3$$

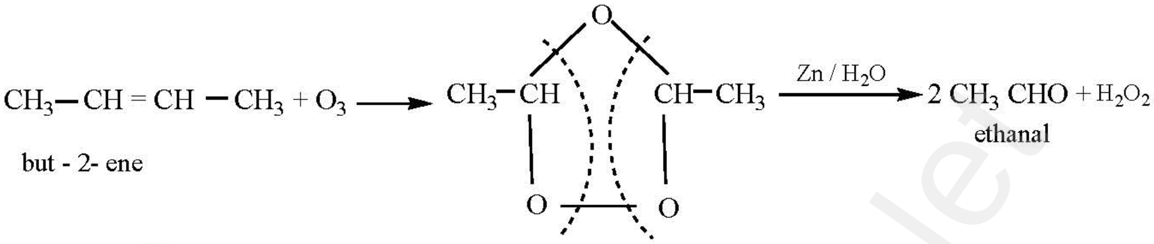
Some of the reaction of diethyl ether.

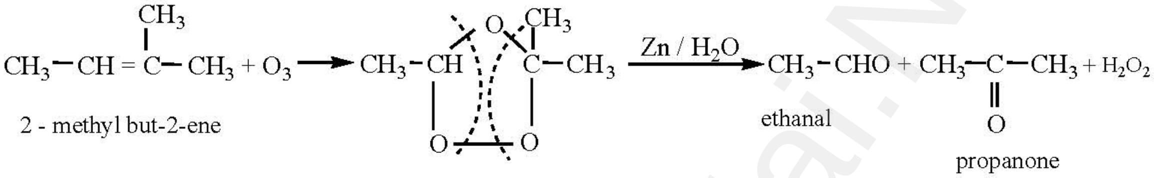


2.) Ozonolysis of alkenes

We have already learnt in XI th standard that the reductive ozonolysis of alkenes gives aldehydes and ketones.

Alkenes react with ozone to form ozonide which on subsequent cleavage with zinc and water gives aldehydes and ketones. Zinc dust removes H_2O_2 formed, which otherwise can oxidise aldehydes / ketones.



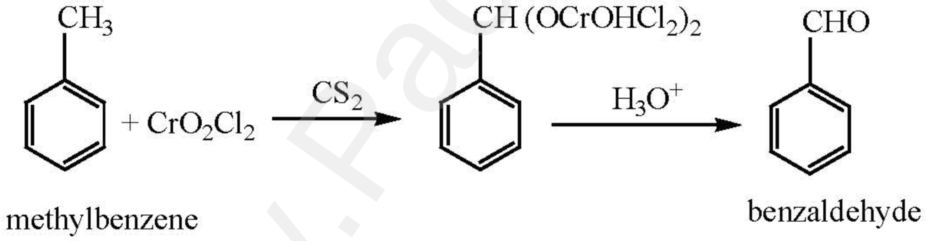


Terminal olefines give formaldehyde as one of the product.

C) Preparation of benzaldehyde

1. **Side chain oxidation of toluene and its derivatives** by strong oxidising agents such as $KMnO_4$ gives benzoic acid.

When chromylchloride is used as an oxidising agent, toluene gives benzaldehyde. This reaction is called **Etard reaction**. Acetic anhydride and CrO_3 can also be used for this reaction.

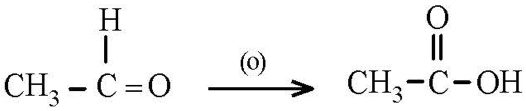


B) Oxidation of aldehydes and ketones

a) Oxidation of aldehydes

Aldehydes are easily oxidised to carboxylic acid containing the same number of carbon atom, as in parent aldehyde. The common oxidising agents are acidified $K_2Cr_2O_7$, acidic or alkaline $KMnO_4$ or chromic oxide.

Example

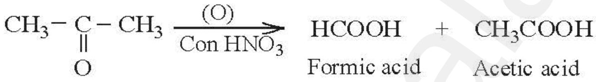


$$CH_3-\overset{\overset{\displaystyle H}{|}}{C}=O \xrightarrow{(o)} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Acetaldehyde Aceticacid

b) Oxidation of ketone

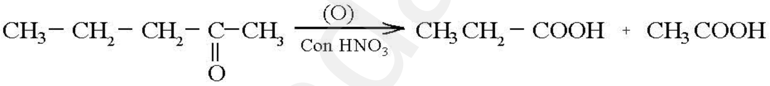
Ketones are not easily oxidised. Under drastic condition or with powerful oxidising agent like Con.HNO_3, $H^+/KMnO_4$, $H^+/K_2Cr_2O_7$, cleavage of carbon-carbon bond takes place to give a mixture of carboxylic acids having less number of carbon atom than the parent ketone.



$$CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[\text{Con } HNO_3]{(O)} HCOOH + CH_3COOH$$

Formic acid Acetic acid

The oxidation of unsymmetrical ketones is governed by **Popoff's rule**. It states that during the oxidation of an unsymmetrical ketone, a (C–CO) bond is cleaved in such a way that the keto group stays with the smaller alkyl group.



$$CH_3-CH_2-CH_2-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[\text{Con } HNO_3]{(O)} CH_3CH_2-COOH + CH_3COOH$$

pentan – 2 – one Propanoic acid ethanoic acid

1. From Primary alcohols and aldehydes

Primary alcohols and aldehydes can easily be oxidised to the corresponding carboxylic acids with oxidising agents such as potassium permanganate (in acidic or alkaline medium), potassium dichromate (in acidic medium)

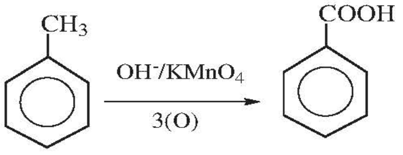
Example

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[(O)]{H^+/K_2Cr_2O_7} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[(O)]{} \underset{\text{Acetic acid}}{CH_3COOH}$$

6. Oxidation of alkyl benzenes

Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzene with chromic acid or acidic or alkaline potassium permanganate. The entire side chain is oxidised to –COOH group irrespective of the length of the side chain.

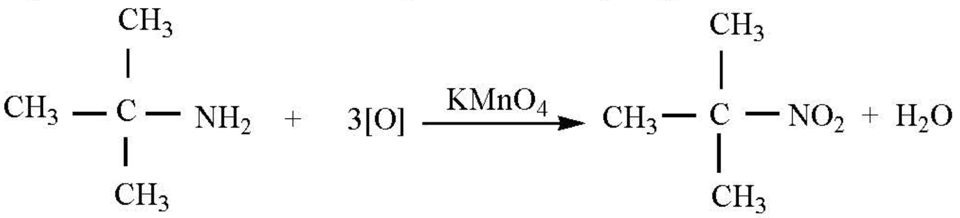
Example



Toluene Benzoic acid

4) Oxidation of tert – alkyl amines

tert – butyl amine is oxidised with aqueous $KMnO_4$ to give tert – nitro alkanes.



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-NH_2 + 3[O] \xrightarrow{KMnO_4} CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-NO_2 + H_2O$$

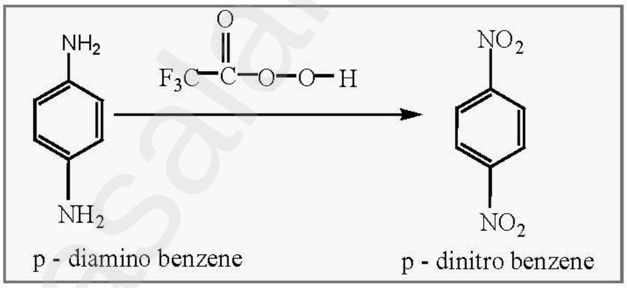
tert-butylamine 2 - methyl - 2 - nitro propane

5) Oxidation of Oximes

Oxidation of acetaldoxime and acetoneoxime with trifluoroperoxy acetic acid gives nitroethane (1^0) and 2 – nitropropane (2^0) respectively.

$$\underset{\text{Acetaldoxime}}{CH_3\text{-}CH{=}N\text{-}OH} \xrightarrow[{[O]}]{CF_3COOOH} \underset{\text{Nitroethane}}{CH_3CH_2\text{-}NO_2}$$

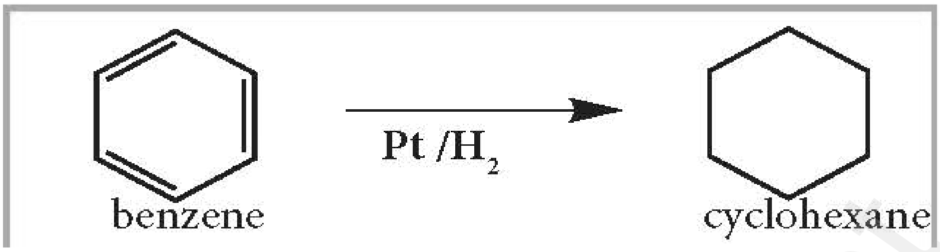
Amino group can be directly converted into nitro group, using caro's acid (H_2SO_5) (or) persulphuric acid ($H_2S_2O_8$) (or) peroxytrifluro acetic acid ($F_3C.CO_3H$) as oxidising agent.



p - diamino benzene p - dinitro benzene

+1 & +2 - REDUCTION REACTIONS

Reduction



1. Preparation of alkanes from catalytic reduction of unsaturated hydrocarbons.

When a mixture hydrogen gas with alkene or alkyne gas is passed over a catalysts such as platinum or palladium at room temperature, an alkane is produced. This process of addition of H_2 to unsaturated compounds is known as hydrogenationThe above process can be catalysed by nickel at 298K. This reaction is known as Sabatier-Sendersens reaction

for example:

$$\underset{\text{propene}}{CH_3-CH=CH_2} + H_2 \xrightarrow{Pt} \underset{\text{propane}}{CH_3-CH_2-CH_3}$$

$$\underset{\text{ethene}}{CH_2=CH_2} + H_2 \xrightarrow[298K]{Ni} \underset{\text{ethane}}{CH_3-CH_3}$$

$$\underset{\text{prop-1-yne}}{CH_3-C\equiv CH} + 2H_2 \xrightarrow{Pt} \underset{\text{propane}}{CH_3-CH_2-CH_3}$$

3.Preparation of alkanes using alkyl halides (or) halo alkanes

i) By reduction with nascent hydrogen

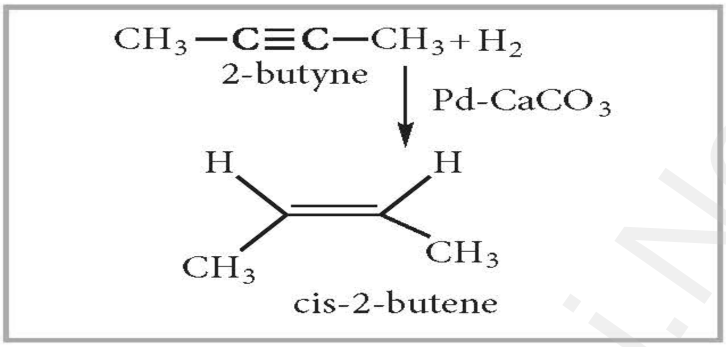
Except alkyl fluorides, other alkyl halides can be converted to alkanes by reduction with nascent hydrogen. The hydrogen for reduction may be obtained by using any of the following reducing agents: $Zn+HCl$, $Zn+CH_3COOH$, Zn-Cu couple in ethanol, $LiAlH_4$ etc.,

for example:

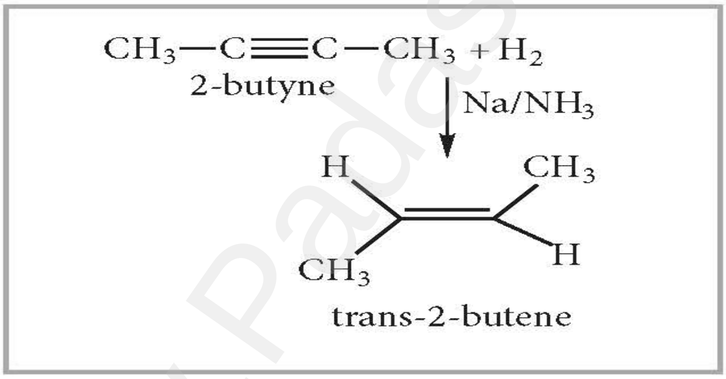
$$\begin{array}{c} CH_3\text{-}CH_2\text{-}CH_2\text{—}Cl \\ \text{chloro propane} \\ [H]\Big\downarrow Zn/HCl \\ CH_3\text{-}CH_2\text{-}CH_3 + HCl \\ \text{propane} \end{array}$$

(2)Preparation of alkenes from alkynes:

Alkynes can be reduced to cis-alkenes using Lindlar's catalyst ($CaCO_3$ supported in palladuium partially deactivated with sulphur (or) gasoline). This reaction is stero specific giving only the cis- alkene.



Alkynes can also be reduced to trans-alkenes using sodium in liquid ammonia. This reaction is stereospecific giving only the trans-alkene.



(3) Preparation of alkenes by dehydro-halogenaton of halo alkanes.

Halo alkanes react with alcoholic KOH and eliminate hydrohalide resulting in the formation of alkene.

$$\underset{\text{1-bromopropane}}{CH_3\text{-}CH_2\text{-}CH_2-Br} \xrightarrow{\text{alc. KOH}} \underset{\text{prop-1-ene}}{CH_3-CH=CH_2} + KBr + H_2O$$

2. Addition reactions of alkynes

i) addition of hydrogen

$$\underset{\text{acetylene}}{CH\equiv CH} + H_2 \xrightarrow{Pt} \underset{\text{ethylene}}{CH_2=CH_2} \xrightarrow{H_2} \underset{\text{ethane}}{CH_3-CH_3}$$

II) addition of hydrogen:

Benzene can add on to three moles of hydrogen in the presence of nickel catalyst to give cyclohexane.

$$C_6H_6 + 3H_2 \xrightarrow{\text{Raney Ni}} \underset{\text{cyclohexane}}{C_6H_{12}}$$

(b) Preparation Of Benzene From Phenol

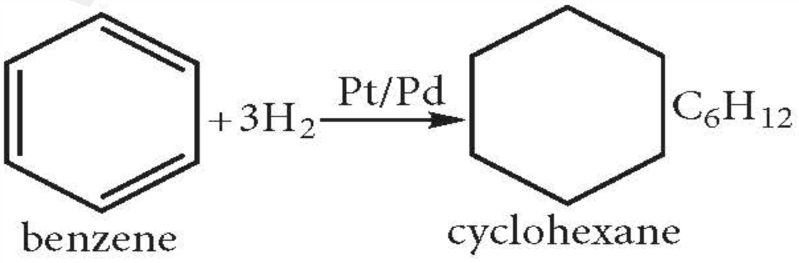
When phenol vapours are passed over zinc dust, then it is reduced to benzene.

$$\underset{\text{phenol}}{C_6H_5OH} + Zn \longrightarrow C_6H_6 + ZnO$$

(ii) Addition Reaction:

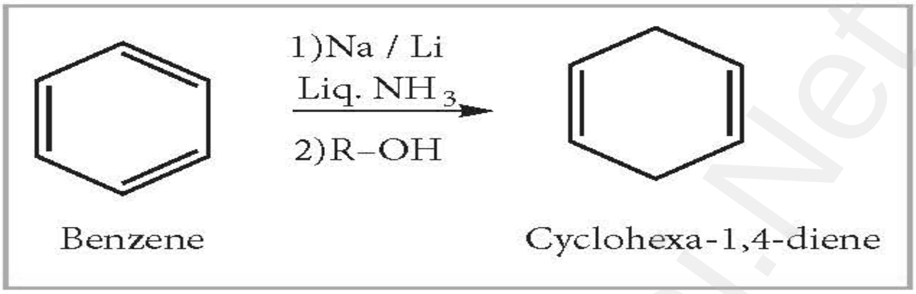
a. Hydrogenation of benzene:

Benzene reacts with hydrogen in the presence of Platinum or Palladium to yield Cyclohexane. This is known as hydrogenation.



b. Birch reduction:

Benzene can be reduced to 1, 4-cyclohexadiene by treatment with Na or Li in a mixture of liquid ammonia and alcohol. It is the convenient method to prepare cyclic dienes.



Toluene

4) Reduction

Haloarenes on reduction with Ni-Al alloy in the presence of NaOH gives corresponding arenes.

$$\underset{\text{Chloro benzene}}{C_6H_5Cl+2(H)} \xrightarrow[\text{NaOH}]{\text{Ni-Al}} \underset{\text{Benzene}}{C_6H_6} + HCl$$

4) Reduction reactions

Haloalkanes are reduced to alkanes by treating with H_2 in the presence of metal catalyst like nickel, palladium etc or with hydroiodic acid in the presence of red phosphorous.

$$\underset{\text{Bromo ethane}}{CH_3CH_2Br+H_2} \xrightarrow[\text{523 K}]{\text{Ni(or)Pd}} \underset{\text{Ethane}}{CH_3\text{-}CH_3}+HBr$$

$$\underset{\text{Iodo ethane}}{CH_3CH_2I + HI} \xrightarrow{\text{Red P}} \underset{\text{Ethane}}{CH_3 - CH_3} + I_2$$

1) Reduction of chloroform

a) Reduction of chloroform in the presence of Zn + HCl gives methylene chloride.

$$\underset{\text{chloro form}}{CHCl_3} \xrightarrow[2(H)]{Zn+HCl} \underset{\text{methylene chloride}}{CH_2Cl_2 + HCl}$$

b) Reduction of chloroform using H2/Ni

$$\underset{\text{chloro form}}{CHCl_3} \xrightarrow[Ni]{H_2} \underset{\text{methylene chloride}}{CH_2Cl_2 + HCl}$$

2) Reduction

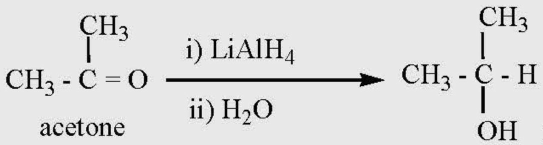
Chloroform undergoes reduction with zinc and HCl in the presence of ethyl alcohol to form methylene chloride.

$$\underset{\text{Chloroform}}{CHCl_3 + 2[H]} \xrightarrow[HCl]{Zn} \underset{\text{Methylene chloride}}{CH_2Cl_2 + HCl}$$

5. Reduction of carbonyl compounds:

Reduction of aldehydes/ketones with $LiAlH_4$ in the presence of solvents like THF (Tetrahydrofuran) followed by hydrolysis gives alcohols. Unlike other reducing agents such as Raney Ni, Na-Hg/H_2O, the lithium aluminium hydride does not reduce the carbon–carbon double bond present in unsaturated carbonyl compound and hence it is a best reagent to prepare unsaturated alcohols.

Examples



$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}}}=O \xrightarrow[\text{ii) } H_2O]{\text{i) } LiAlH_4} CH_3-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-H$$

acetone propan-2-ol

$$C_6H_5\text{-}COOH \xrightarrow[\text{(ii)}H_2O]{\text{(i)}LiAlH_4} C_6H_5CH_2OH$$

Benzoic acid Phenyl methanol(Benzyl alcohol)

$$CH_3COOCH_2CH_3 \xrightarrow[\text{(ii)}H_2O]{\text{(i)}LiAlH_4} 2CH_3CH_2OH$$

Ethyl ethanoate Ethanol

(ethyl acetate)

$$CH_3\text{-}CH{=}CH\text{-}CHO \xrightarrow[\text{(ii)}H_2O]{\text{(i)}LiAlH_4} CH_3\text{-}CH{=}CH\text{-}CH_2OH$$

crotonaldehyde crotyl alcohol

(but-2-enal) (but-2-en-1-ol)

When two or more functional groups are present in a molecule a less vigorous sodium borohydride is used as a reducing agent to reduce the more reactive group. For example, if a compound contains both carbonyl and carboxyl group, it preferentially reduces the carbonyl group.

$$RCOCH_2\,CH_2COOH \xrightarrow[H_3O^+]{NaBH_4} RCHOH\text{-}CH_2CH_2COOH$$

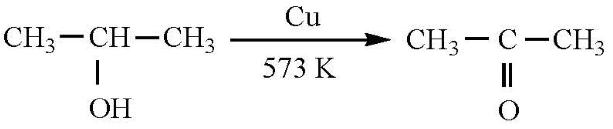
4-alkyl- 4- hydroxybutanoic acid

Catalytic dehydrogenation

When the vapours of a primary or a secondary alcohol are passed over heated copper at 573K, dehydrogenation takes place to form aldehyde or ketone.

$$CH_3-CH_2-OH \xrightarrow[573\ K]{Cu} CH_3-CHO$$

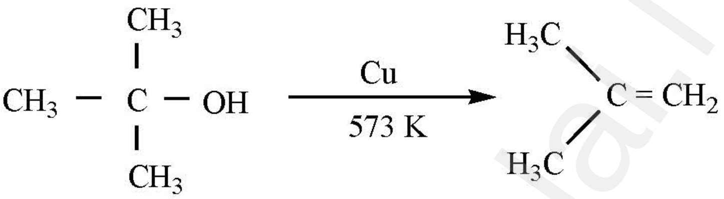
ethanol ethanal



$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[573\ K]{Cu} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

Propan - 2- ol propanone

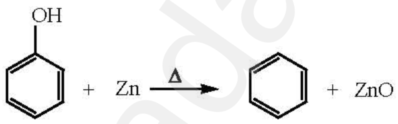
Tertiary alcohols undergo dehydration reaction to give alkenes.



2 - methylpropan - 2- ol 2 - methylprop - 1- ene

a) **Reaction with Zn dust:**

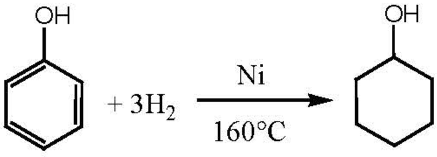
Phenol is converted to benzene on heating with zinc dust. In this reaction the hydroxyl group which is attached to the aromatic ring is eliminated.



phenol benzene

e) **Reduction:**

Phenol on catalytic hydrogenation gives cyclohexanol.



Phenol cyclohexanol

3. Selective reduction of cyanides

Diisobutyl aluminium hydride (DIBAL –H) selectively reduces the alkyl cyanides to form imines which on hydrolysis gives aldehydes.

Example

$$CH_3-CH=CH-CH_2-CH_2-CN \xrightarrow[ii)\ H_2O]{i)\ AlH(iso\text{-}butyl)_2} CH_3-CH=CH-CH_2-CH_2-CHO$$

hex - 4- ennitrile hex - 4- enal

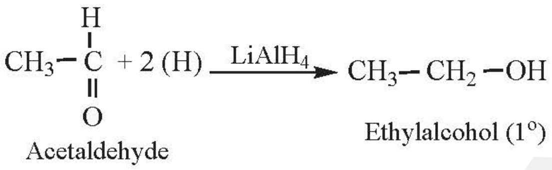
C) Reduction reactions

(i) Reduction to alcohols

We have already learnt that aldehydes and ketones can be easily reduced to primary and secondary alcohols respectively. The most commonly used reducing agents are Lithium Aluminium hydride ($LiAlH_4$), and Sodium borohydride ($NaBH_4$).

a) Aldehyde are reduced to primary alcohols.

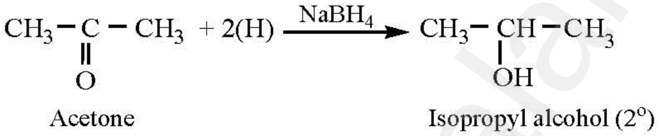
Example



$$CH_3-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{C}} + 2\,(H) \xrightarrow{LiAlH_4} CH_3-CH_2-OH$$

b) Ketone are reduced to Secondary alcohols.

Example

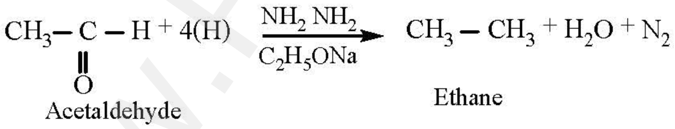


$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + 2(H) \xrightarrow{NaBH_4} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

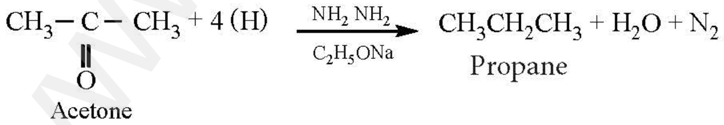
The above reactions can also be carried out with hydrogen in the presence of metal catalyst like Pt, Pd, or Ni. $LiAlH_4$ and $NaBH_4$ do not reduce isolated carbon – carbon double bonds and double bond of benzene rings. In case of α, β unsaturated aldehyde and ketones, $LiAlH_4$ reduces only C = O group leaving C = C bond as such.

b) **Wolf Kishner reduction** Aldehydes and Ketones when heated with hydrazine (NH_2NH_2) and sodium ethoxide, hydrocarbons are formed Hydrazine acts as a reducing agent and sodium ethoxide as a catalyst.

Example



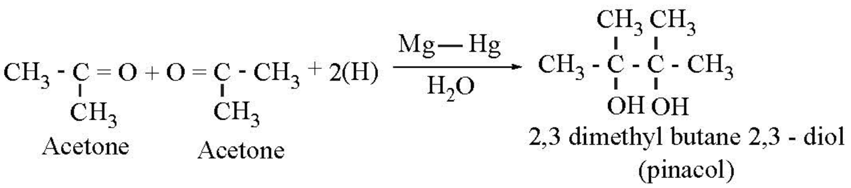
$$CH_3-\underset{\underset{O}{\|}}{C}-H + 4(H) \xrightarrow[C_2H_5ONa]{NH_2\,NH_2} CH_3-CH_3 + H_2O + N_2$$



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + 4\,(H) \xrightarrow[C_2H_5ONa]{NH_2\,NH_2} CH_3CH_2CH_3 + H_2O + N_2$$

Aldehyde (or) ketones is first converted to its hydrazone which on heating with strong base gives hydrocarbons.

(iii) **Reduction to pinacols:** Ketones, on reduction with magnesium amalgam and water, are reduced to symmetrical diols known as pinacol.



$$CH_3-\underset{\underset{CH_3}{|}}{C}=O + O=\underset{\underset{CH_3}{|}}{C}-CH_3 + 2(H) \xrightarrow[H_2O]{Mg-Hg} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

ii) Cannizaro reaction

In the presence of concentrated aqueous or alcoholic alkali, aldehydes which do not have α - hydrogen atom undergo self oxidation and reduction (disproportionation) to give a mixture of alcohol and a salt of carboxylic acid. This reaction is called **Cannizaro reaction**.

Benzaldehyde on treatment with concentrated NaOH (50%) gives benzyl alcohol and sodium benzoate.

$$\begin{array}{c} C_6H_5CHO \\ + \\ C_6H_5CHO \\ \text{Benzaldehyde} \end{array} \xrightarrow{50\%\ NaOH} \begin{array}{c} C_6H_5CH_2OH \\ \text{Benzylalcohol} \\ + \\ C_6H_5COONa \\ \text{Sodiumbenzoate} \end{array}$$

This reaction is an example disproportionation reaction

Crossed Cannizaro reaction

When Cannizaro reaction takes place between two different aldehydes (neither containing an α hydrogen atom), the reaction is called as crossed cannizaro reaction.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Formaldehyde}}{HCHO} \xrightarrow{NaOH} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{sodium formate}}{HCOONa}$$

In crossed cannizaro reaction more reactive aldehyde is oxidized and less reactive aldehyde is reduced.

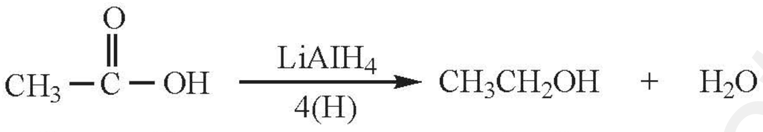
C) Reactions involving – COOH group

1) Reduction

i) Partial reduction to alcohols

Carboxylic acids are reduced to primary alcohols by $LiAlH_4$ or with hydrogen in the presence of copper chromite as catalyst. Sodium borohydride does not reduce the – COOH group.

Example



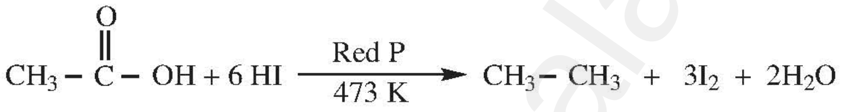
$$CH_3-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[4(H)]{LiAlH_4} CH_3CH_2OH + H_2O$$

ethanoicacid ethanol

ii) Complete reduction to alkanes

When treated with HI and red phosphorous, carboxylic acid undergoes complete reduction to yield alkanes containing the same number of carbon atoms.

Example

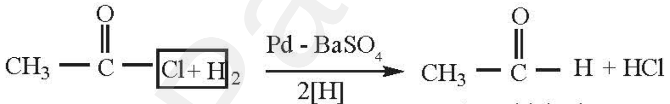


$$CH_3-\overset{\overset{O}{\|}}{C}-OH + 6\,HI \xrightarrow[473\ K]{Red\ P} CH_3-CH_3 + 3I_2 + 2H_2O$$

Acetic acid Ethane

(5) Reduction.

(a) When reduced with hydrogen in the presence of 'poisoned' palladium catalyst, they form aldehydes. This reaction is called Rosenmund reduction. We have already learnt this reaction under the preparation of aldehydes



$$CH_3-\overset{\overset{O}{\|}}{C}-\boxed{Cl+H}_2 \xrightarrow[2[H]]{Pd-BaSO_4} CH_3-\overset{\overset{O}{\|}}{C}-H + HCl$$

Acetyl chloride Acetaldehyde

(b) When reduced with $LiAlH_4$ gives primary alcohols.

$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + 4(H) \xrightarrow{LiAlH_4} CH_3-CH_2-OH + HCl$$

Ethyl alcohol

5) Reduction

Amides on reduction with $LiAlH_4$ or Sodium and ethyl alcohol to form corresponding amines.

$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + 4\,(H) \xrightarrow{LiAlH_4} CH_3-CH_2-NH_2 + H_2O$$

Acetamide Ethyl amine

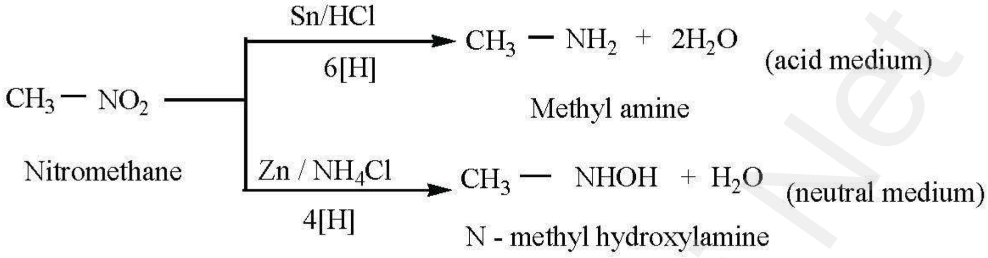
i. Reduction of nitroalkanes

Reduction of nitroalkanes has important synthetic applications. The various reduction stages of nitro group are given below.

$$CH_3-NO_2 \xrightarrow[-H_2O]{+2[H]} CH_3-N=O \xrightarrow{+2[H]} CH_3-NHOH \xrightarrow[-H_2O]{+2[H]} CH_3-NH_2$$

nitromethane nitroso methane N - methyl hydroxylamine methylamine

The final product depends upon the nature of reducing agent as well as the pH of the medium.

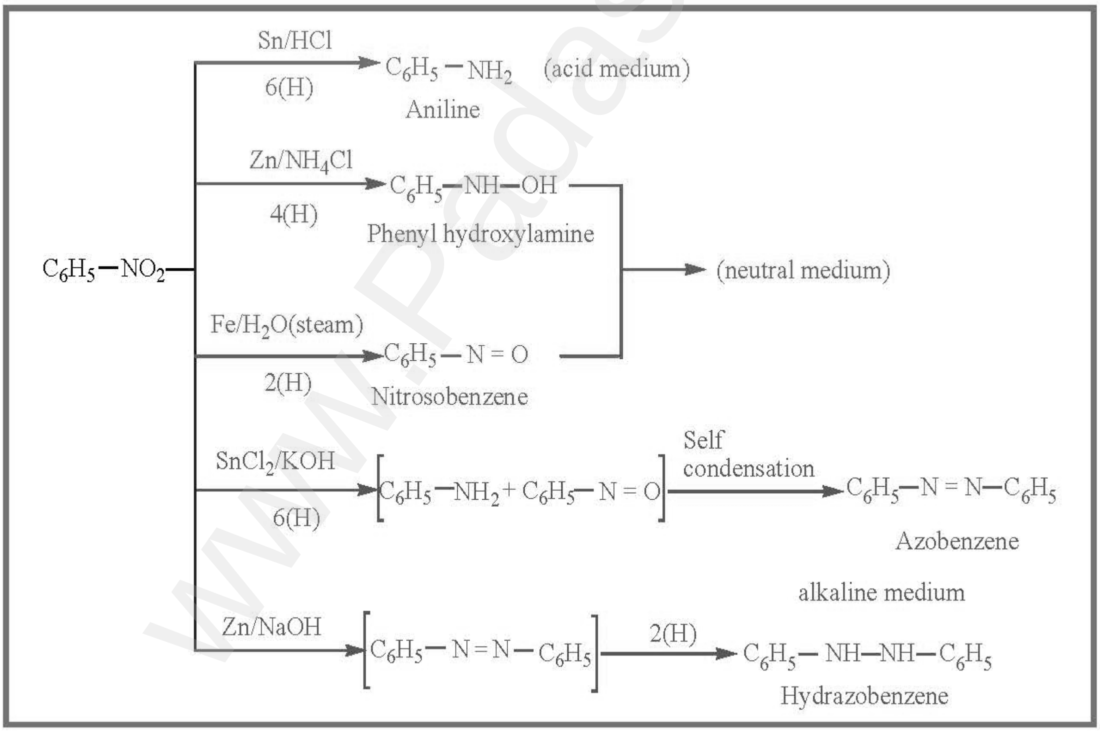


Reduction of alkyl nitrites

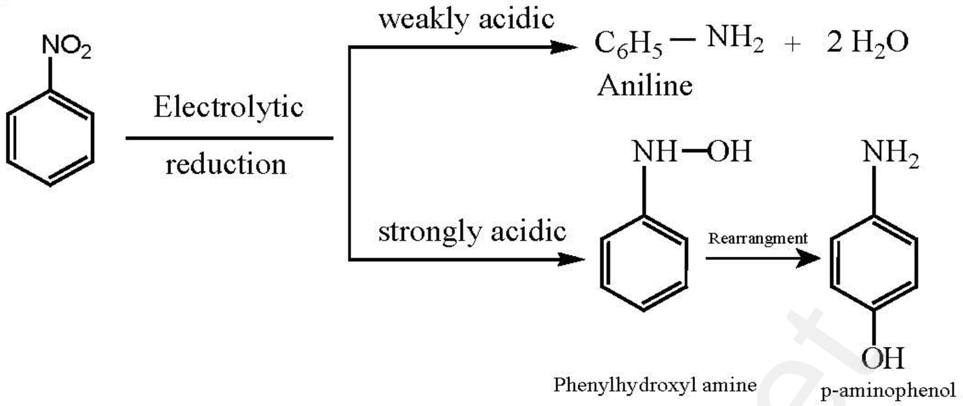
Ethylnitrite on reduction with Sn / HCl gives ethanol

$$CH_3CH_2-O-N=O + 6[H] \xrightarrow{Sn / HCl} CH_3CH_2-OH + NH_3 + H_2O$$

Chemical Properties of nitrobenzene



Electrolytic reduction:

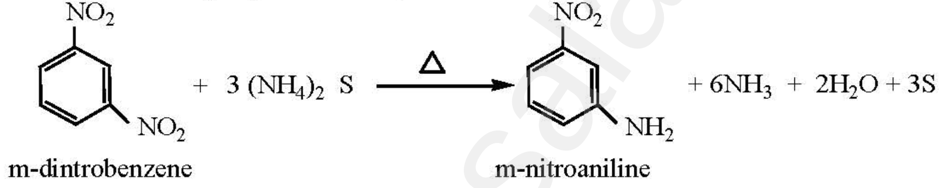


Reduction of catalytic and metal hydrides

Nitrobenzene reduction with Ni (or) Pt, (or) $LiAlH_4$ to give aniline

$$C_6H_5 - NO_2 + 6\,[H] \xrightarrow[\text{(or) } LiAlH_4]{\text{Ni (or) Pt / } H_2} C_6H_5 - NH_2 + 2\,H_2O$$

Selective reduction of polynitro compounds



1) From nitro compounds

Reduction of Nitro compounds using H_2 / Ni (or) Sn / HCl or Pd/H_2 gives primary amines.

$$\underset{\text{Nitroethane}}{CH_3CH_2 - NO_2} \xrightarrow[\text{Fe / HCl, 6 [H]}]{3H_2 \text{ / Ni (or)}} \underset{\text{ethanamine}}{CH_3CH_2 - NH_2} + 2\,H_2O$$

$$\underset{\text{Nitrobenzene}}{C_6H_5 - NO_2} \xrightarrow[\text{(or) Sn / HCl}]{3H_2 \text{ / Pt, 680 K}} \underset{\text{Aniline}}{C_6H_5 - NH_2} + 2\,H_2O$$

2) From nitriles

a) Reduction of alkyl or aryl cyanides with H_2/Ni (or) $LiAlH_4$ (or) Na / C_2H_5OH gives primary amines. The reduction reaction in which Na / C_2H_5OH is used as a reducing agent is called mendius reaction

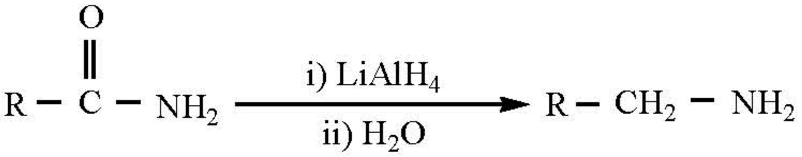
$$\underset{\text{ethanenitrile}}{CH_3 - CN} \xrightarrow[4\,[H]]{Na(Hg) / C_2H_5OH} \underset{\text{ethanamine}}{CH_3CH_2 - NH_2}$$

b) Reduction of isocyanides with sodium amalgam / C_2H_5OH gives secondary amines

$$\underset{\text{Methyl isocyanide}}{CH_3 - NC} \xrightarrow[4\,[H]]{Na(Hg) / C_2H_5OH} \underset{\text{N-methylmethanamine}}{CH_3 - NH - CH_3}$$

3) From amides

a) Reduction of amides with $LiAlH_4$ gives amines



$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[\text{ii) } H_2O]{\text{i) } LiAlH_4} R-CH_2-NH_2$$

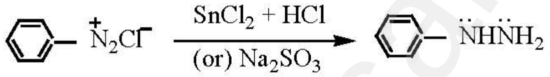
c) **Alkyl halide can also be converted to primary amine by treating it with sodium azide (NaN_3) followed by the reduction using lithium aluminium hydride.**

$$\underset{\text{Methylbromide}}{CH_3-Br} \xrightarrow{NaN_3} \underset{\text{Methyl azide}}{CH_3-N_3} \xrightarrow{LiAlH_4} \underset{\text{Methylamine}}{CH_3-NH_2} + N_2$$

B. Reactions involving retention of diazo group

9. Reduction to hydrazines

Certain reducing agents like $SnCl_2$ / HCl; Zn dust / CH_3COOH, sodium hydrosulphite, sodium sulphite etc. reduce benzene diazonium chloride to phenyl hydrazine.



2. Reduction

On reduction with $LiAlH_4$ (or) Ni / H_2, alkyl cyanides yields primary amines.

$$\underset{\text{Ethanenitrile}}{CH_3-CN + 2H_2} \xrightarrow{Ni} \underset{\text{Ethanamine}}{CH_3-CH_2-NH_2}$$

2. **Reduction:** When reduced catalytically (or) by nascent hydrogen, they give secondary amines.

$$\underset{\text{Methyl isocyanide}}{CH_3-NC} + 4[H] \xrightarrow[\text{(or) Ni / } H_2]{Na / C_2H_5OH} \underset{\text{Dimethylamine}}{CH_3-NH-CH_3}$$