

B.Sc (Semester-IV)

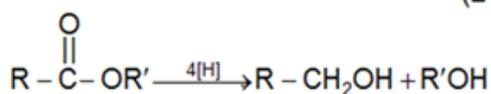
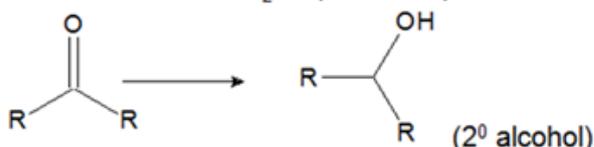
Study Material

ALCOHALS, PHENOLS AND ETHERS

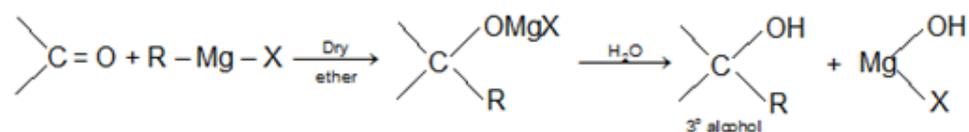
Alcohols

Preparation of Alcohols:

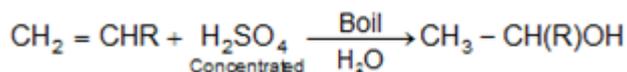
- By hydrolysis of haloalkanes : $R-X + \text{aq. KOH} \rightarrow \text{ROH} + \text{KX}$
- By reduction of Carbonyl compounds



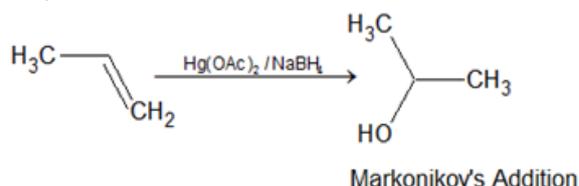
- By the action of Grignard's Reagent on aldehydes, ketones and esters



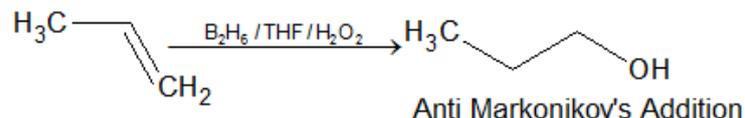
- By Aliphatic Primary Amines: $\text{RCH}_2\text{NH}_2 + \text{HNO}_2 \rightarrow \text{RCH}_2\text{OH} + \text{N}_2 + \text{H}_2\text{O}$
- Hydration of alkenes:



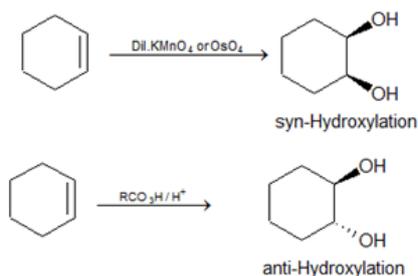
- Oxymercuration-demercuration:



- Hydroboration-oxidation:



- Hydroxylation of alkenes:



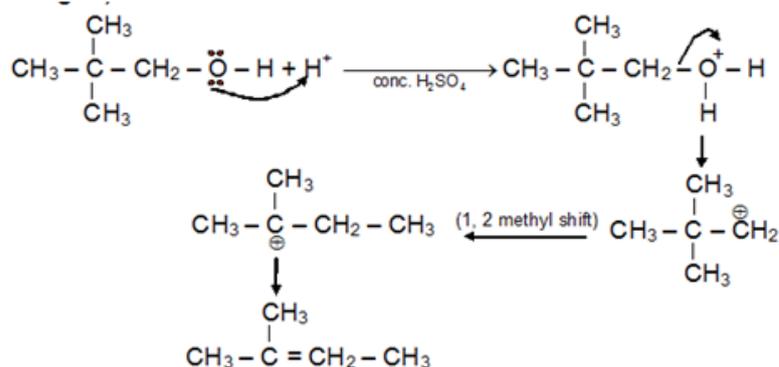
Physical Properties of Alcohol:

- Lower alcohols are liquid at room temperature while higher ones are solid.
- High boiling point due to presence of intermolecular hydrogen bonding. Order of Boiling Point: primary > secondary > tertiary
- Solubility in water decreases with increase in molecular mass due to decrease in extent of intermolecular hydrogen bonding.

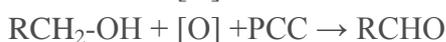
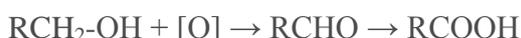
Chemical Properties of Alcohol:

- **Alcohol's reaction with metal:** $\text{ROH} + \text{Na} \rightarrow 2\text{RO}^+\text{Na}^- + \text{H}_2$
- **Formation of Halides:**
 - $3\text{ROH} + \text{P} + \text{I}_2 \rightarrow 3\text{RI} + \text{H}_3\text{PO}_3$
 - $\text{ROH} + \text{SOCl}_2/\text{PCl}_3/\text{PCl}_5 \rightarrow \text{RCl}$
 - $\text{ROH} + \text{HX} \rightarrow \text{RX}$
 - $\text{ROH} + \text{NaBr}, \text{H}_2\text{SO}_4 \rightarrow \text{R-Br}$
 - $\text{ROH} + \text{Zn} + \text{HCl} \rightarrow \text{R-Cl}$
 - $\text{R}_2\text{C-OH alcohol} + \text{HCl} \rightarrow \text{R}_2\text{CCl}$
- **Reaction with HNO₃:** $\text{R-OH} + \text{HO-NO}_2 \rightarrow \text{R-O-NO}_2$
- **Reaction with carboxylic acid (Esterification) :** $\text{R-OH} + \text{R}'\text{-COOH} + \text{H}^+ \leftrightarrow \text{R}'\text{-COOR}$
- **Reaction with Grignard reagent:** $\text{R}'\text{OH} + \text{RMgX} \rightarrow \text{RH} + \text{R}'\text{OMgX}$
- **Reduction of alcohol :** $\text{ROH} + 2\text{HI} + \text{Red P} \rightarrow \text{RH} + \text{I}_2 + \text{H}_2\text{O}$
- **Dehydration of Alcohol:** Dehydration of alcohols takes place in acidic medium. Intramolecular dehydration leads to the formation of alkene while inter molecular dehydration which forms ether. Ease of dehydration: $3^\circ > 2^\circ > 1^\circ$

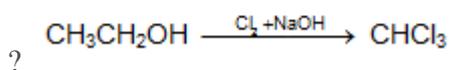
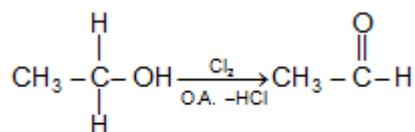
- **Satzyeff's Rule** : Elimination through b carbon containing minimum b hydrogen



- **Oxidation of Alcohol:**



- **Haloform Reaction:** Compound containing $\text{CH}_3\text{CO-}$ group (or compound on oxidation gives $\text{CH}_3\text{CO-}$ group) which is attached with a C or H, in presence of halogen and mild alkali gives haloform. $\text{CH}_3\text{-CH}_2\text{-COCH}_2\text{-CH}_3$, $\text{CH}_3\text{-CO-Cl}$, CH_3COOH will not respond to haloform reaction while $\text{CH}_3\text{CH}_2\text{OH}$ will respond to haloform Reaction.



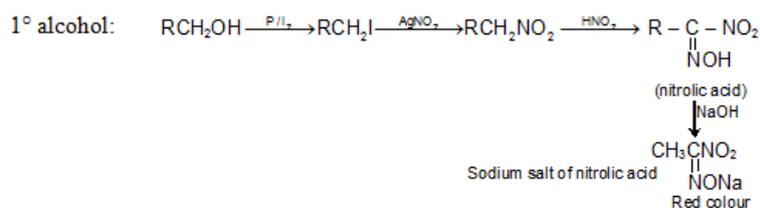
Test for Alcohols:

1. Lucas Test:

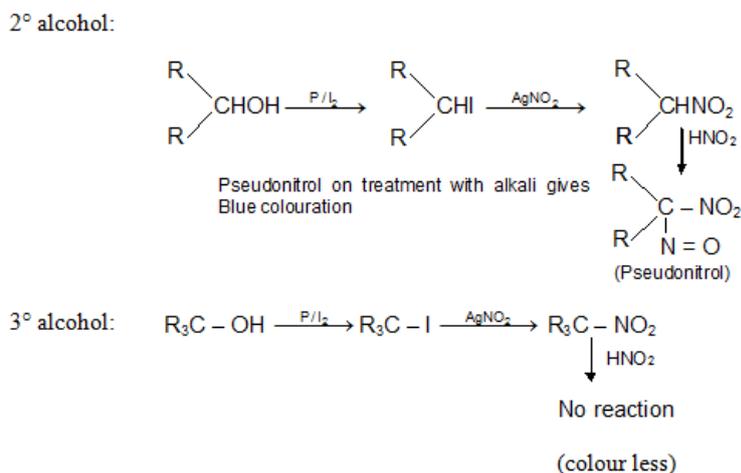


- 1° Alcohol: $\text{RCH}_2\text{OH} + \text{ZnCl}_2 + \text{HCl} \rightarrow$ No reaction at room temperature
- 2° Alcohol: $\text{R}_2\text{CHOH} + \text{ZnCl}_2 + \text{HCl} \rightarrow \text{R}_2\text{CHCl}$ White turbidity after 5-10 min.
- 3° Alcohol: $\text{R}_3\text{CHOH} + \text{ZnCl}_2 + \text{HCl} \rightarrow \text{R}_3\text{CHCl}$ white turbidity instantaneously.

2. Victor Meyer Test



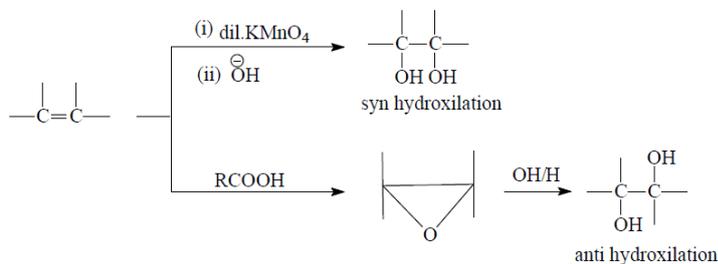
Nitrolic acid on treatment with alkali gives colouration



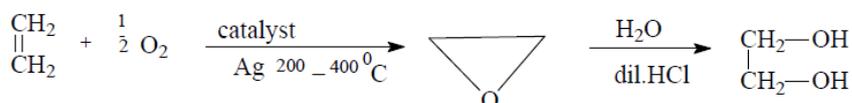
Dihydric Alcohol

Dihydric alcohols are prepared by following different methods:

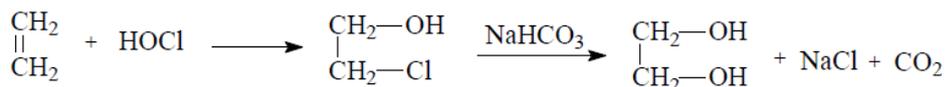
From ethylene: (a) through icy dilute alkaline solution of Bayer's reagent.



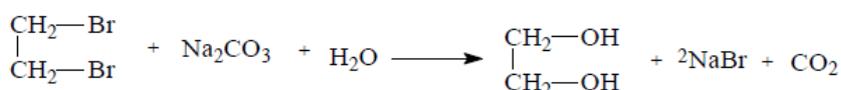
(b) With O₂ in presence of Ag :



(c) With HOCl followed by hydrolysis:



From 1, 2 dibromo ethane :



Physical properties of dihydric alcohol

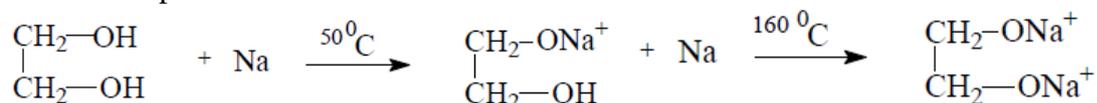
(i) It is a colourless, syrupy liquid and sweet in taste. Its boiling point is 197°C. melting point -11.50C

- (ii) It is miscible in water and ethanol in all proportions but is insoluble in ether.
- (iii) It is toxic as methanol when taken orally.
- (iv) It is widely used as a solvent and as an antifreeze agent.

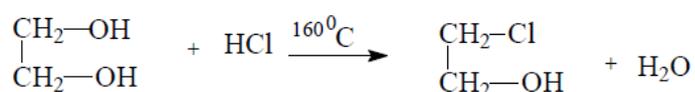
Chemical reactions of glycerol

Glycerol molecule is made up of two 1° alcohol groups joined together its chemical reactions are, therefore twice over those of 1° alcohols

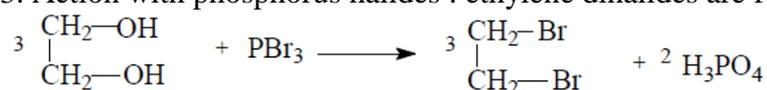
1. Action of Sodium: It reacts with Na at 50° C to form mono and dialkoxide at elevated temperature.



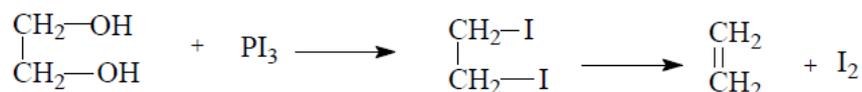
2. Reaction with HCl: Ethylene dichloride is formed in two successive steps at elevated Temperature



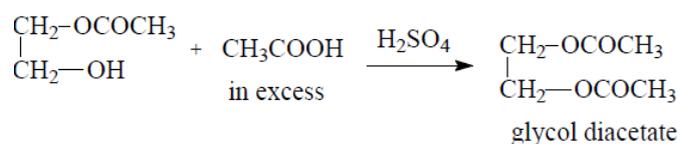
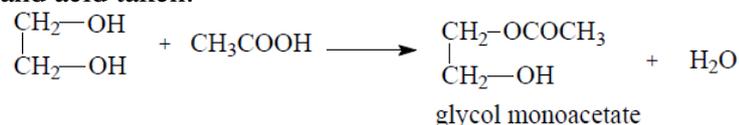
3. Action with phosphorus halides : ethylene dihalides are formed as follow:



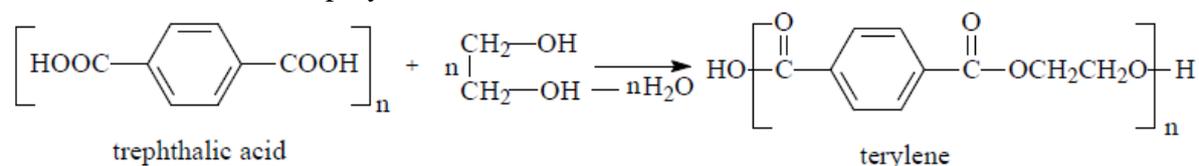
PI3 produce ethylene diiodide which is unstable and split into I2= and ethylene



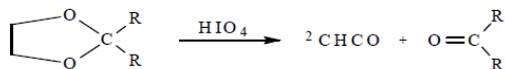
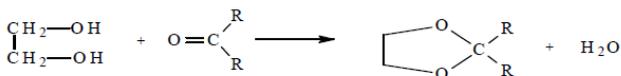
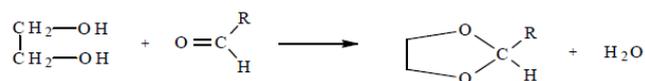
4. Reaction with carboxylic acid: Gives diester depending upon the amount of glycol and acid taken:



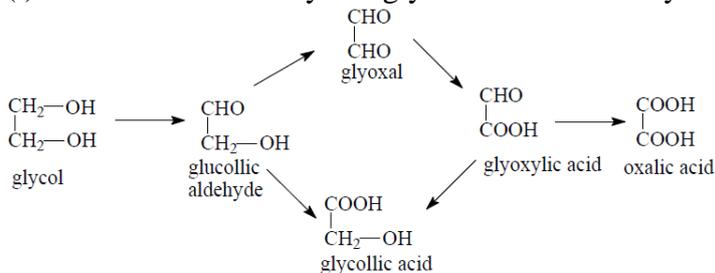
With dibasic acid it form polymer:



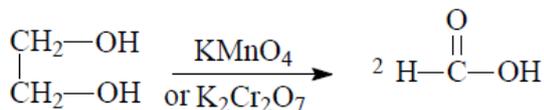
5. Reaction with aldehyde and ketones: Glycol reacts with aldehyde and ketones in presence of p- toluene sulphonic acid to give cyclic acetals/ketals which further may give ketone/aldehyde while treating with HIO4. This reaction thus can be useful to protect carbonyl group.



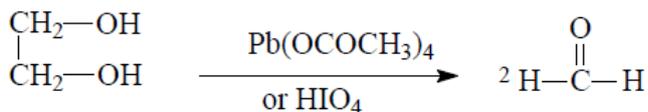
6. (i) The oxidation of ethylene glycol with HNO₃ to yields a number of substance as



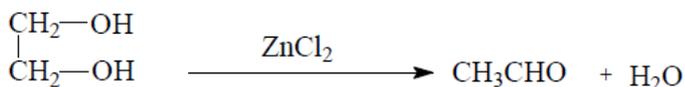
(ii) Oxidation with KMnO₄ or K₂Cr₂O₇ to form formic acid:



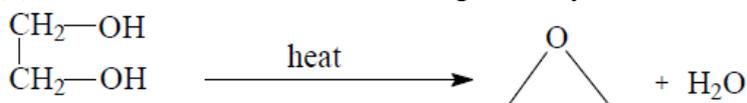
(iii) Oxidation with Pb(OCOCH₃)₄ or HIO₄ glycol gives formaldehyde.



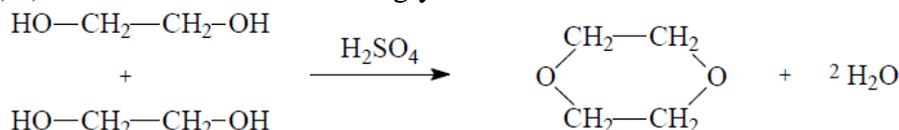
7. Dehydration: (i) Heating with ZnCl₂ glycol gives acetaldehyde



(ii) When heated alone at 500°C, it gives ethylene oxide.



(iii) Dioxane is obtained when glycol is heated with conc. H₂SO₄.



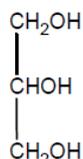
Uses of ethylene glycol:-

1. It is used as antifreeze substance which prevents the freezing of water in car radiators in cold countries.
2. Due it has a high viscosity, so it is used in the hydrolic break , printing ink ball, pen inks, organic solvents .
3. Used in the manufacture of Dacron, dioxane etc.
4. As a solvent and as a preservatives.
5. As a cooling agent in aeroplanes.
6. As an explosives in the form of dinitrate.

7. Large amounts of ethylene glycol are converted to polymers (such as polyethylene glycol) used in The manufacture of dacron fibers ,photographic films and cassette tapes.

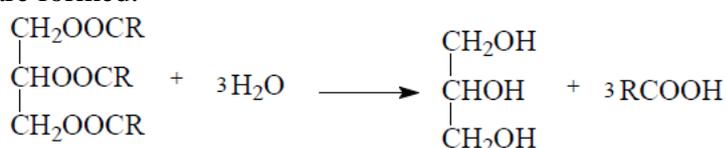
Trihydric Alcohol

It is a triol. The introduction of third –OH group in diol molecule raises the b.p. about 1000C, increase viscosity and make the alcohol more sweet. Viz; glycerol

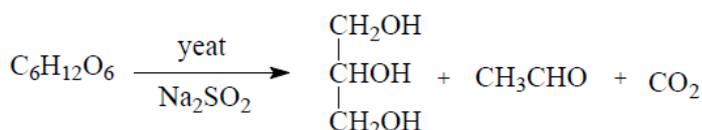


Glycerol can be synthesized by following different methods:

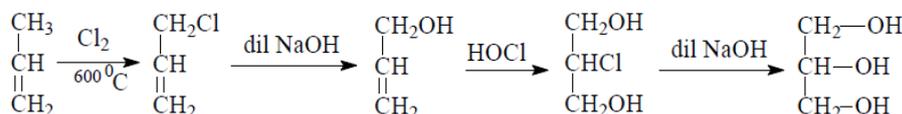
1. **From fats and oil:** On hydrolysis of fats and oils, glycerol and higher fatty acids are formed.



2. **By fermentation of sugars:** Alcoholic fermentation of sugar in the presence of sodium sulphite gives good yield of glycerol.



3. **Synthesis (from propene):** Today much of glycerol is obtained from propene.



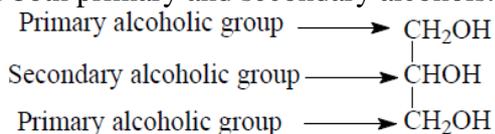
Physical properties: Glycerol is a colourless, odourless, viscous and hygroscopic liquid, sweet in taste and non-toxic in nature.

It is soluble in water and ethyl alcohol but insoluble in ether.

It has high boiling point, i.e., 290°C. The high viscosity and high boiling point of glycerol are due to association through hydrogen bonding purified in the lab by reduced pressure distillation or vacuum distillation.

Chemical reactions

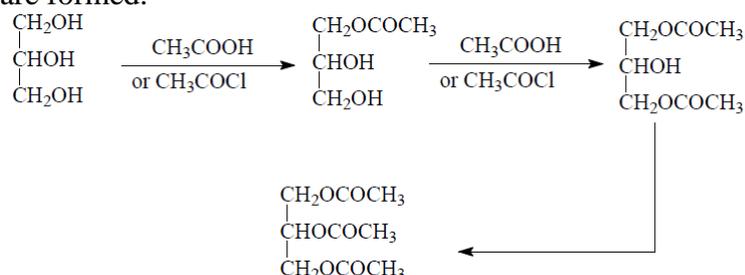
Glycerol molecule contains two 1° – OH groups and one 2° – OH group. Thus, it shows characteristics of both primary and secondary alcohols.



In general, 1° – OH groups are more reactive than 2° – OH group.

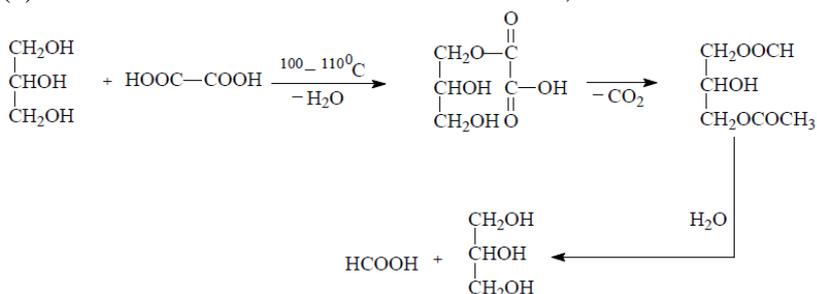
1. Reaction with sodium: Only primary alcoholic groups are attacked one by one and secondary alcoholic group is not attacked, Sodium forms monosodium glycerolate at room temperature and disodium glycerolate at higher temperature.

6. Reaction with acetic acid, acetic anhydride or acetyl chloride: Mono-, di- and triesters are formed.

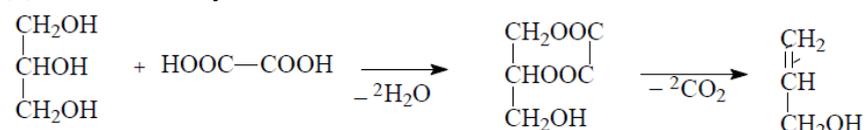


7. **Reaction with oxalic acid:** Different products are formed under different conditions.

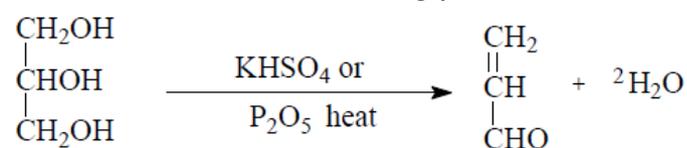
(a) At 100°C and with excess of oxalic acid, formic acid is formed



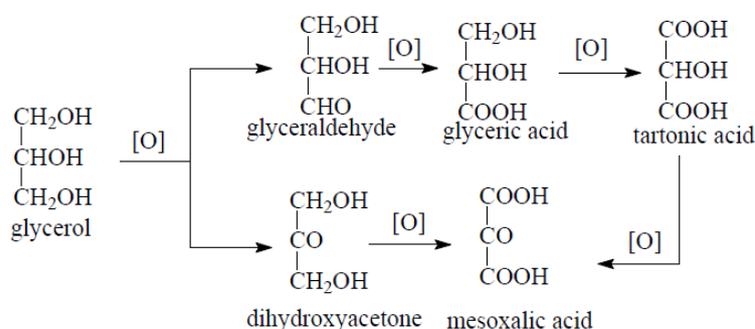
(b) At 260°C allyl alcohol is formed



8. Dehydration: Glycerol when heated alone or with dehydrating agents such as potassium hydrogen sulphate or phosphorus pentoxide or conc. sulphuric acid, acrolein or acrylaldehyde is formed which has a characteristic bad smell. This reaction can be used as a test of glycerol.



9. Oxidation: Glycerol gives different oxidation products depending on the nature of oxidizing agent. The following products may be obtained during oxidation of glycerol.



(a) Dilute HNO₃ gives mainly glyceric acid.

(b) Conc. HNO₃ oxidises glycerol into glyceric acid and tartaric acid.

(c) Bismuth nitrate gives mainly meso oxalic acid.

(d) Fenton's reagent (H₂O₂ + FeSO₄) or NaOBr or Br₂- water in presence of Na₂CO₃

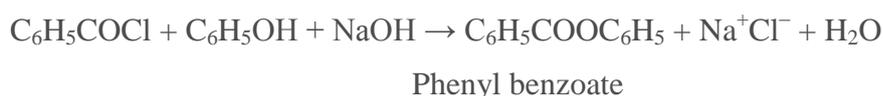
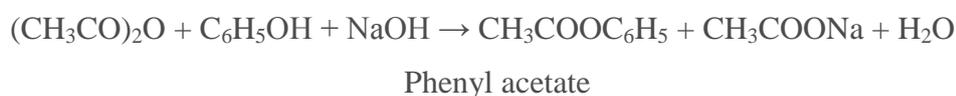
Physical Properties of Phenols

- Phenol is a colorless, toxic, corrosive, needle shaped solid.
- Phenol soon liquifies due to high hygroscopic nature.
- Phenol is less soluble in water, but readily soluble in organic solvents.
- Simplest phenols, because of hydrogen bonding have quite high boiling points.
- o-nitrophenol is, steam volatile and also is less soluble in water because of intramolecular hydrogen bonding

Chemical Properties of Phenols

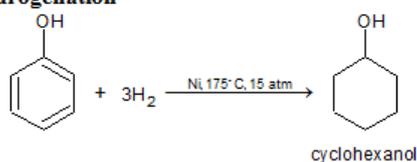
a) Formation of Esters

Phenyl esters (RCOOAr) are not formed directly from RCOOH. Instead, acid chlorides or anhydrides are reacted with ArOH in the presence of strong base

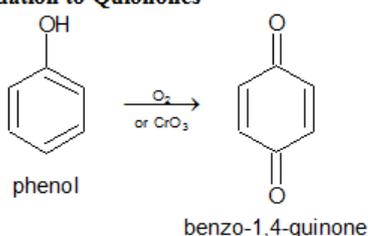


b) **Displacement of OH group:** $\text{ArOH} + \text{Zn} \xrightarrow{\Delta} \text{ArH} + \text{ZnO}$ (poor yields)

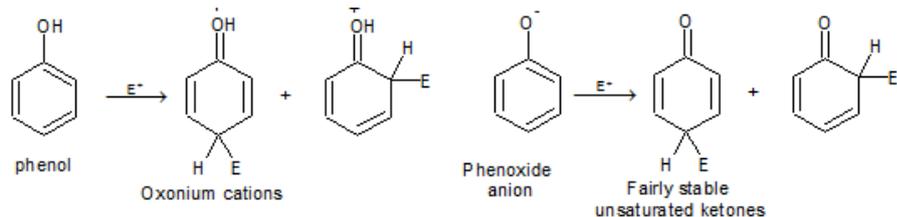
c) Hydrogenation



d) Oxidation to Quinones

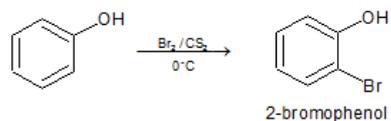
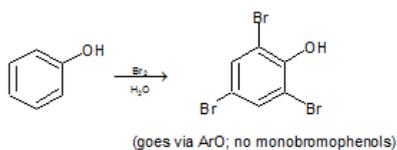


e) **Electrophilic Substitution** The —OH and even more so the —O(phenoxide) are strongly activating ortho, para - directing

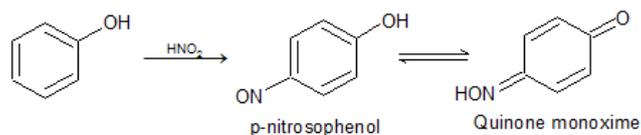


Special mild conditions are needed to achieve electrophilic monosubstitution in phenols because their high reactivity favors both polysubstitution and oxidation

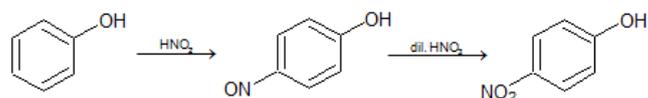
f) Halogenation



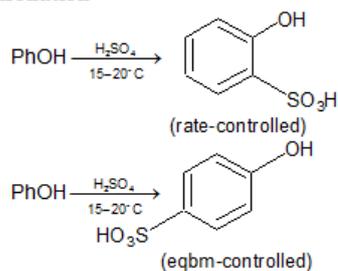
h) Nitrosation



i) Nitration

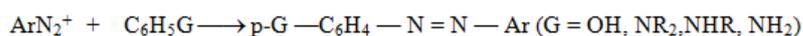


j) Sulfonation

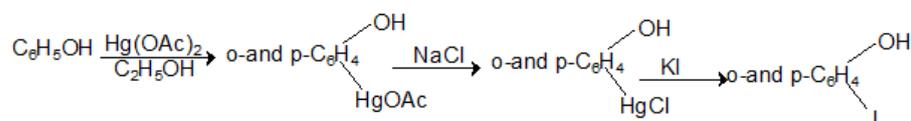


k) Diazonium salt coupling to form azophenols

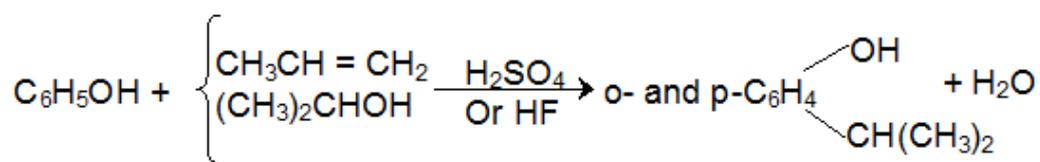
Coupling (G in ArG is an electron-releasing group)



l) Mercuration

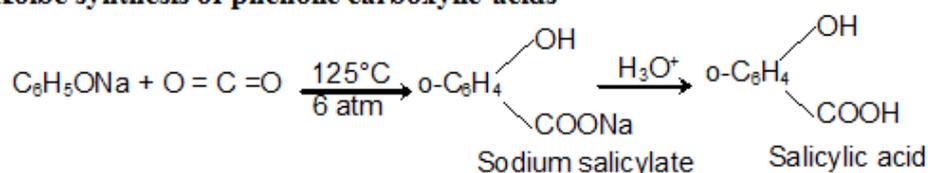


m) Ring alkylation



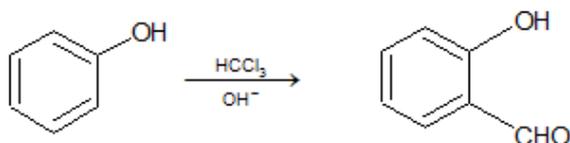
RX and AlCl₃ give poor yields because AlCl₃ coordinates with O.

n) Kolbe synthesis of phenolic carboxylic acids



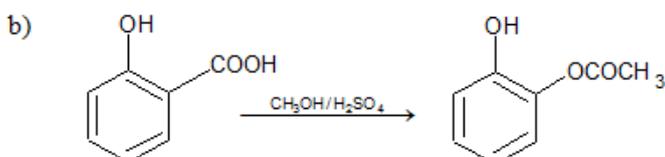
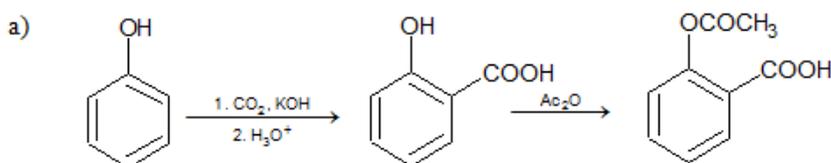
Phenoxide carbanion adds at the electrophilic carbon of CO₂, para product is also possible.

o) Reimer – Tiemann synthesis of phenolic aldehydes



The electrophile is the dichlorocarbene, CCl_2 , formation of carbene is an example of α -elimination. $\text{OH}^- + \text{HCCl}_3 \xrightarrow{-\text{HCl}} \text{:CCl}_2$

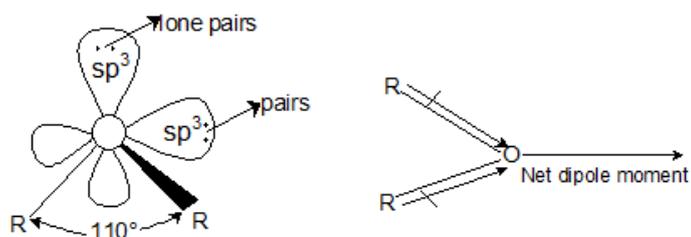
p) Synthesis of (a) aspirin (acetylsalicylic acid) (b) oil of wintergreen (methyl salicylate)



Ethers

Physical Properties of Ethers

- **Physical state, colour and odour:** Dimethyl ether and ethyl methyl ether is gas at ordinary temperature while the other lower homologues of ethers are colourless liquid with characteristic 'ether smell'.
- **Dipole nature:** Ethers have a tetrahedral geometry i.e., oxygen is sp³ hybridized. The C—O—C angle in ethers is 110°. Because of the greater electronegativity of oxygen than carbon, the C—O bonds are slightly polar and are inclined to each other at an angle of 110°, resulting in a net dipole moment.

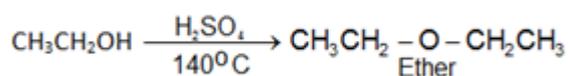


Bond angle of ether is greater than that of tetrahedral bond angle of 109°28'.

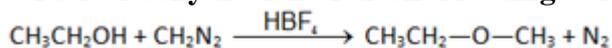
- **Solubility and boiling point:** Due to the formation of less degree of hydrogen bonding, ethers have lower boiling point than their corresponding isomeric alcohols and are slightly soluble in water.

Preparation of Ethers:

a) From alcohols:



Order of dehydration of alcohol leading to formation of ethers: 1° > 2° > 3°

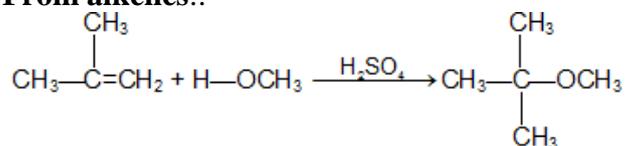


b) Williamson's synthesis:

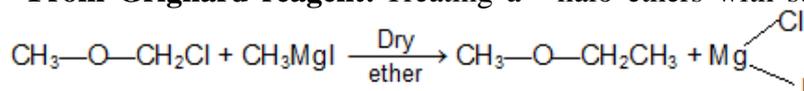


In case of tertiary substrate elimination occurs giving alkenes.

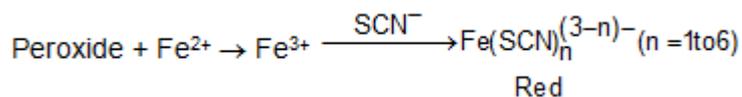
From alkenes:.



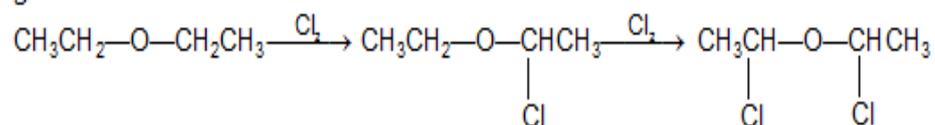
From Grignard reagent: Treating a - halo ethers with suitable Grignard reagents.



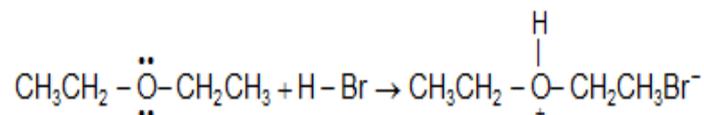
On standing in contact with air, most aliphatic ethers are converted slowly into unstable peroxides. The presence of peroxides is indicated by formation of a red colour when the ether is shaken with an aqueous solution of ferrous ammonium sulfate and potassium thiocyanate



f) Halogenation of ethers:



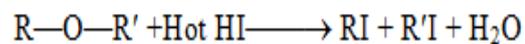
g) Ethers as base:



h) Reaction With Cold conc. HI/HBr:

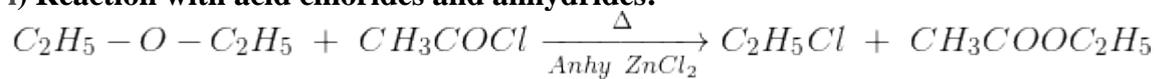


i) Hot conc. HI/HBr:

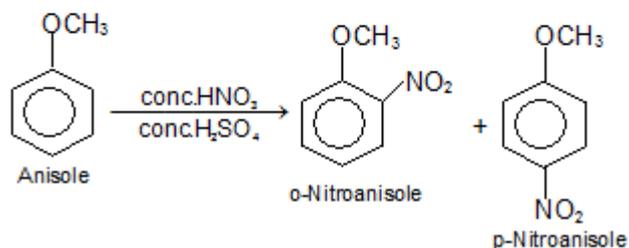
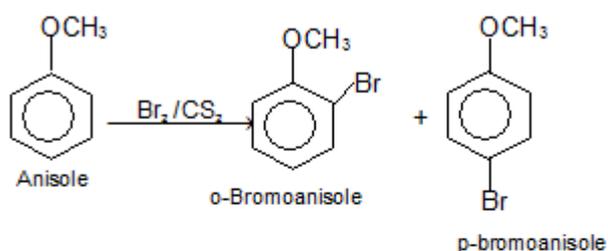


Case I:	<p> $\text{CH}_3\text{-O-CH(CH}_3\text{)-CH}_3 \xrightarrow{\text{HI}} \text{CH}_3\text{-O}^+\text{(H)-CH(CH}_3\text{)-CH}_3 \xrightarrow{\text{S}_\text{N}2} \text{CH}_3\text{I} + \text{CH}_3\text{-CH}_2\text{-OH}$ </p> <p>primary secondary</p>
Case II:	<p> $\text{CH}_3\text{-C(CH}_3\text{)}_3\text{-O-CH}_3 \xrightarrow{\text{HI}} \text{CH}_3\text{-C(CH}_3\text{)}_3\text{-O}^+\text{(H)-CH}_3 \xrightarrow{\text{I}^-, \text{S}_\text{N}1} \text{CH}_3\text{-C(CH}_3\text{)}_3\text{-I} + \text{CH}_3\text{-C(CH}_3\text{)}_3\text{-OH}$ </p> <p>secondary tertiary</p>
Case III:	<p> $\text{CH}_3\text{-O-C(CH}_3\text{)}_3 \xrightarrow[\text{Ether (i.e., aprotic polar/Non polar solvent) S}_\text{N}2]{\text{HI}} \text{CH}_3\text{I} + (\text{CH}_3)_3\text{C-OH}$ </p> <p> $\text{CH}_3\text{-O-C(CH}_3\text{)}_3 \xrightarrow[\text{Protic polar S}_\text{N}1]{\text{H}_2\text{O HI}} \text{CH}_3\text{-C(CH}_3\text{)}_3\text{-I} + \text{CH}_3\text{OH}$ </p> <p>primary tertiary</p>
Case IV:	<p> $\text{C}_6\text{H}_5\text{-O-CH}_3 \xrightarrow[\text{S}_\text{N}2]{\text{HI (aq)}} \text{CH}_3\text{I} + \text{C}_6\text{H}_5\text{-OH}$ </p> <p> $\text{C}_6\text{H}_5\text{-O-CH}_3 \xrightarrow[\text{S}_\text{N}1]{\text{Conc. HI}} \text{CH}_3\text{I} + \text{C}_6\text{H}_4(\text{OH})_2$ </p>

i) Reaction with acid chlorides and anhydrides:



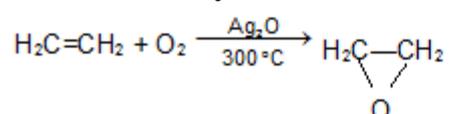
j) Electrophilic substitution reactions



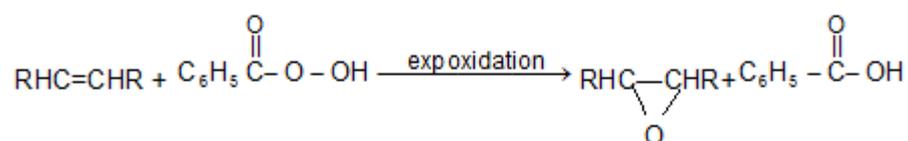
Epoxides or Oxiranes:

Preparation

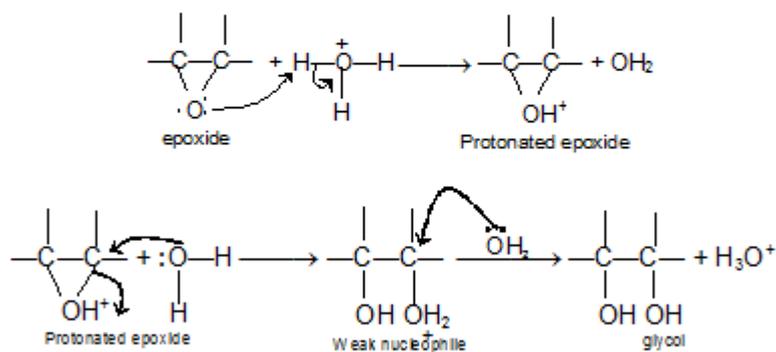
a) Oxidation of ethylene :



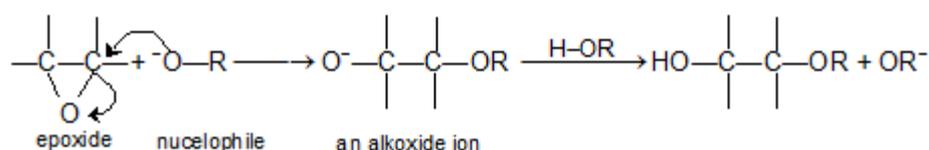
b) Expoxidation :



Acid catalysed ring opening



Base catalysed ring opening:



CARBONYL COMPOUNDS

Carbonyl Compounds are the organic compounds containing carbon-oxygen double bond ($>C=O$). $>C=O$ is the most important functional group of organic chemistry.

Carbonyl compounds in which carbonyl group is bonded to a carbon and hydrogen are known as aldehydes.

Carbonyl compounds in which carbonyl group is bonded to carbon atoms are known as ketons.

The carbonyl compounds in which carbonyl group is bonded to oxygen are known as carboxylic acids, and their derivatives (e.g. esters, anhydrides)

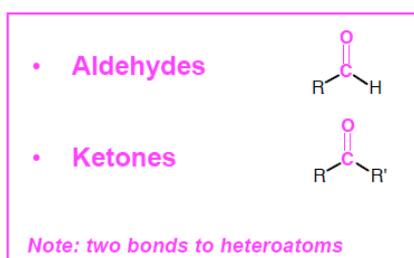
Carbonyl compounds where carbon is attached to nitrogen are called amides.

Carbonyl compounds where carbon is attached to halogen are called acyl halides.

In short, carbonyl compounds can be divided into two major groups

- **Aldehydes & Ketones**
- **Carboxylic Acid & Its derivatives**
 - Carbonyl compounds are molecules containing the carbonyl group, $C=O$.

These include:

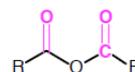


Carboxylic acid derivatives:

- Esters



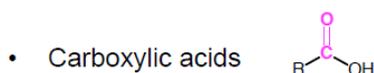
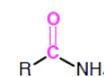
- Anhydrides



- Acid halides



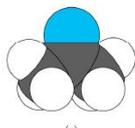
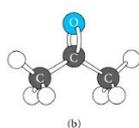
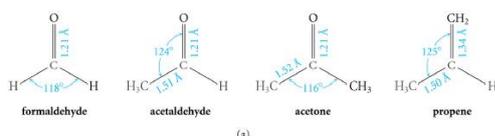
- Amides



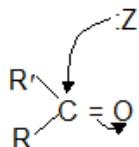
- Structure of Carbonyl Group

Carbonyl carbon is joined to three other atoms by σ bonds; since these bonds utilize sp^2 orbitals, they lie in a plane, and are 120° apart. The remaining p-orbitals of carbon overlaps a p-orbital of oxygen to form a π bond; carbon and oxygen are thus joined by a double bond. The part of the molecule immediately surrounding carbonyl carbon lies in a plane.

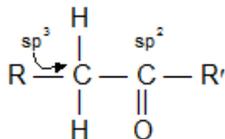
The electrons of a carbonyl double bond hold together atoms of quite different electronegativity and hence the electrons are not equally shared; in particular the polar π -cloud is pulled strongly towards the more electronegative atom, oxygen.



The carbonyl group, C = O, governs the chemistry of aldehydes and ketones. It does this in two ways: a) By providing a site for nucleophilic addition, and

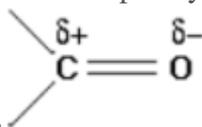


b) By increasing the acidity of hydrogen atoms attached to the alpha carbon.



Physical properties of carbonyl compounds

1. The boiling point of carbonyl compounds is higher than the alkanes with similar molecular weight.
2. The boiling point increases with increasing number of carbon atom. This is because there are more electrons, hence more temporary dipoles can be set up. More energy is required to

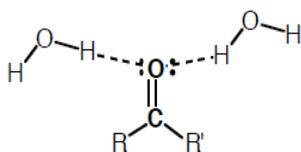


overcome these forces.

3. Besides temporary dipoles, permanent dipole-dipole forces are also present due to carbonyl compounds being polar

Methanal and ethanal are gases at room temperature, while others are liquids. Carbonyl compounds are soluble in water. This is because they are able to form hydrogen bond with water molecules.

Aldehydes and ketones are hydrogen bond acceptors; this makes them have considerable solubilities in water.



Ketones such as acetone are good solvents because they dissolve both aqueous and organic compounds
Recall that acetone is a **polar, aprotic** solvent.

The solubility decreases with increasing number of carbon atoms. This is because the long hydrocarbon chain disrupts the hydrogen bonding.

Preparation of Aldehyde and Ketone

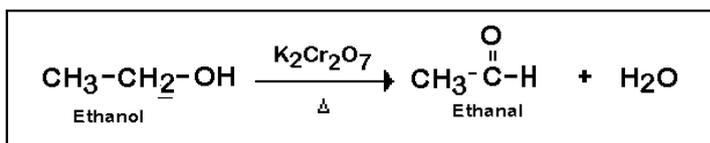
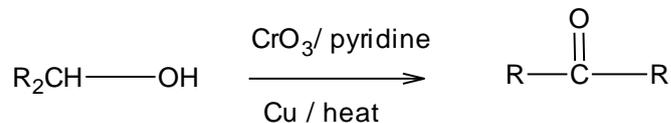
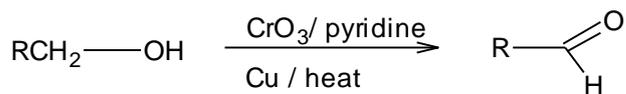
Aldehydes, synthesis:

- Oxidation of 1° alcohols
- Oxidation of methylaromatics
- Reduction of acid chlorides

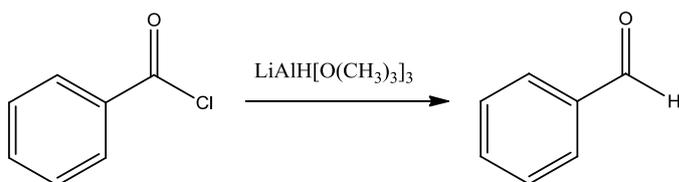
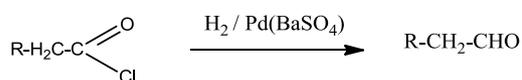
Ketones, synthesis:

- Oxidation of 2° alcohols
- Friedel-Crafts acylation
- Coupling of R_2CuLi with acid chloride

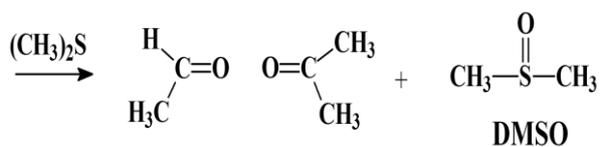
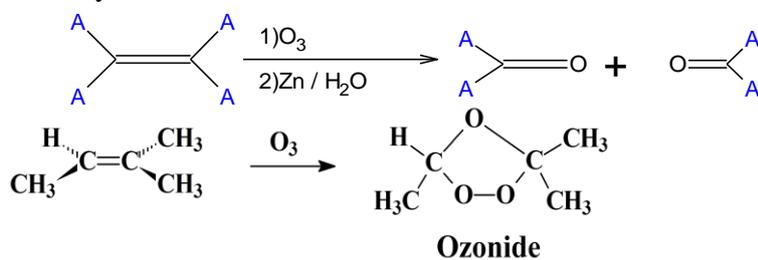
1- Oxidation of alcohols



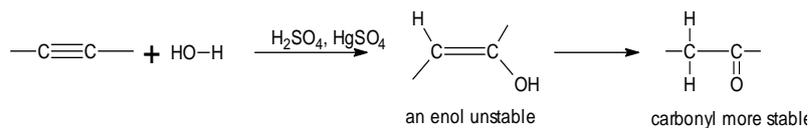
Reduction of acid chloride

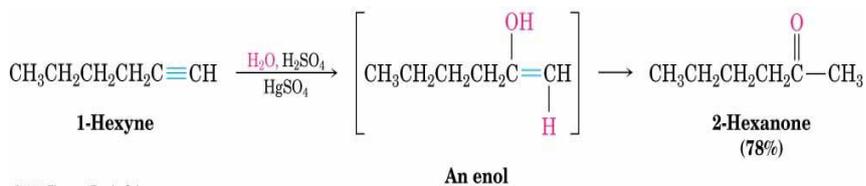


Ozonolysis of alkenes

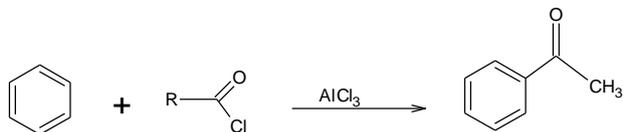


Hydration of alkynes

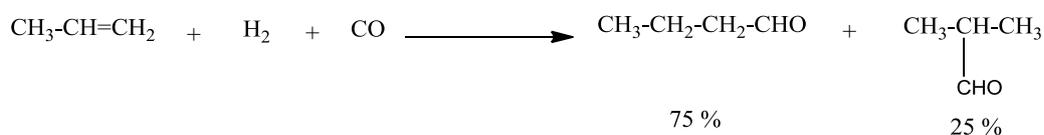




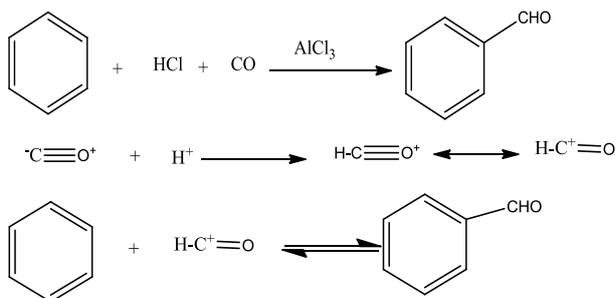
Friedel Crafts acylation



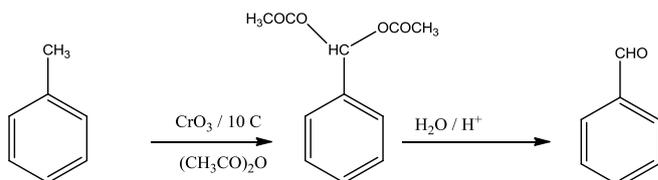
Oxo reaction - Hydroformylation reaction



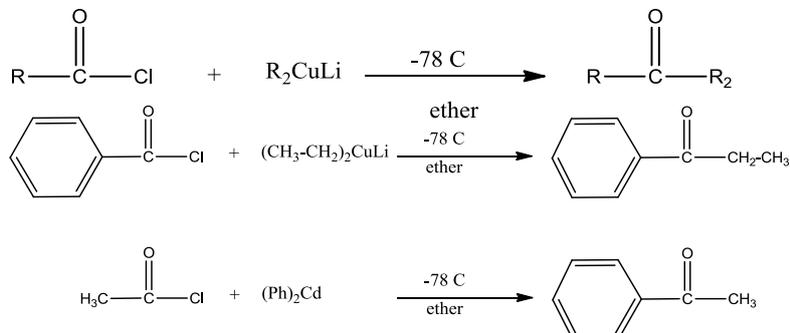
Gattermann-Koch reaction



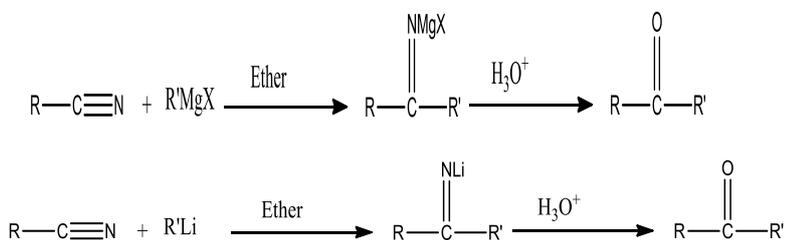
Oxidation of an Alkyl Side of aromatic ring



From acid chloride and lithium dialkyl cuprate or R₂Cd



From nitrile and Grignard reagent or alkyl lithium



Aldehydes and ketones are moderately reactive as electrophiles (electron acceptors) among the carboxylic acid derivatives.

acid chloride

acid anhydride

aldehyde

ketone

ester

carboxylic acid

amide

nitrile

carboxylate

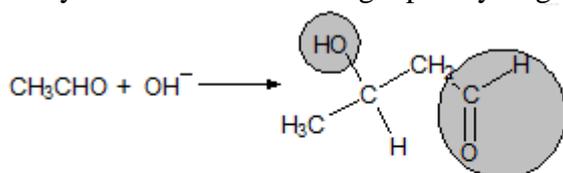
least

reactive

Reactions of Aldehydes and Ketones:

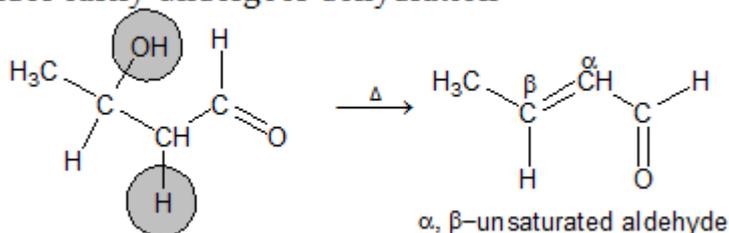
a) Aldol condensation

Aldehydes and ketones having alpha hydrogen atom: _____



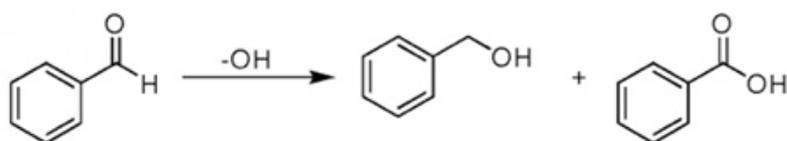
(Since it contains two functional groups aldehydes and alcohol)

Aldol easily undergoes dehydration

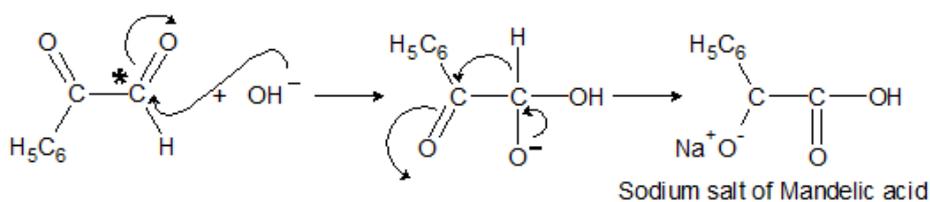


b) Cannizzaro reaction:

Aldehydes and ketones having no alpha hydrogen atom:

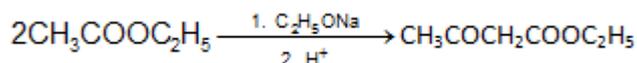


When two carbonyl groups are present within a molecule, think of intramolecular reaction. OH will attack more positively charged carbon. In this case, it is right >c=O group.



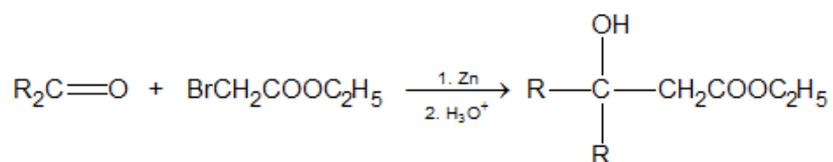
c) Formation of Keto Esters

Esters having α -hydrogen on treatment with a strong base e.g. $\text{C}_2\text{H}_5\text{ONa}$. Undergo self condensation to produce β -keto esters. This reaction is Claisen Condensation.



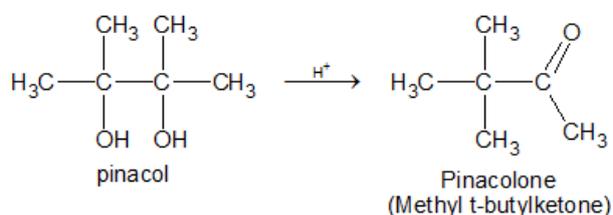
d) Reformatsky Reaction

This is the reaction of α -haloester, usually an α -bromoester with an aldehyde or ketone in the presence of Zinc metal to produce β -hydroxyester.



e) Pinacol-pinacolone Rearrangement

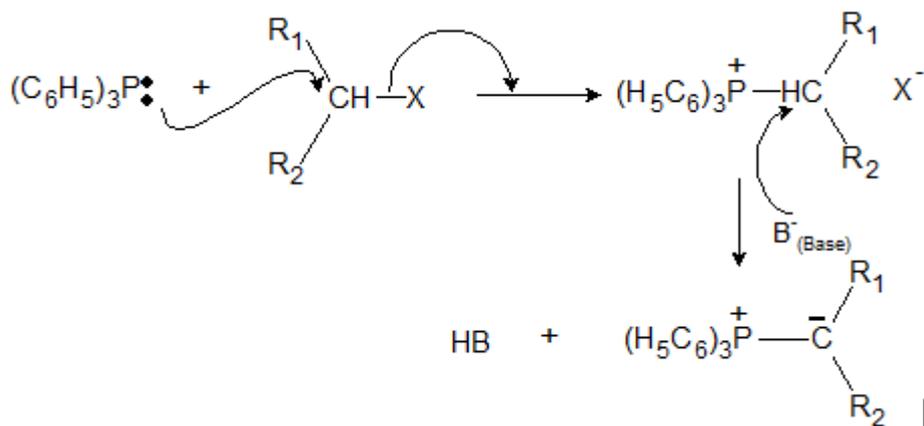
The acid catalysed rearrangement of 1,2 diols (Vicinal diols) to aldehydes or ketones with the elimination of water is known as pinacol pinacolone rearrangement.



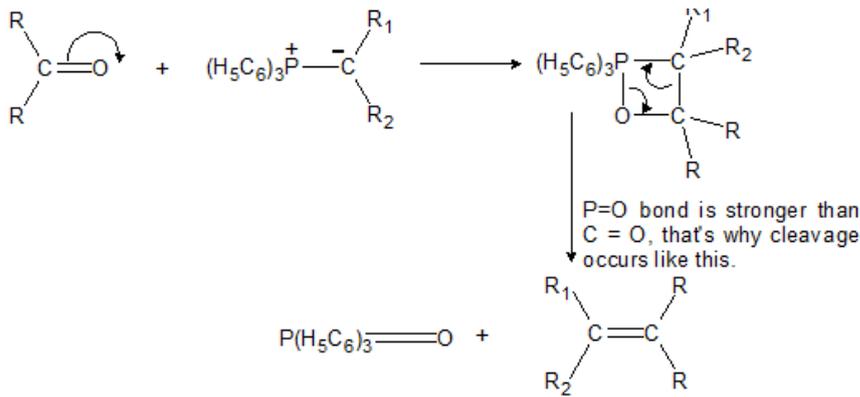
a) Wittig-Ylide Reaction

Aldehydes and Ketones react with phosphorus Ylides to yield alkenes and triphenyl phosphine oxide. An Ylide is a neutral molecule having a negative carbon adjacent to a positive hetero atom. Phosphorus ylides are also called phosphoranes.

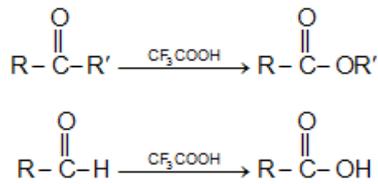
Preparation of Ylides



Reaction of Ylide with $>\text{C}=\text{O}$

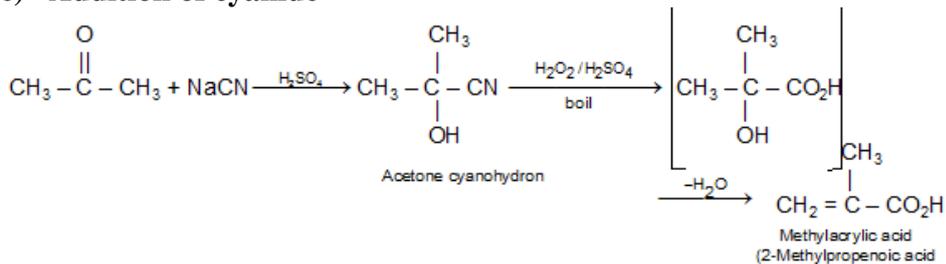


d) Baeyer-Villiger Oxidation

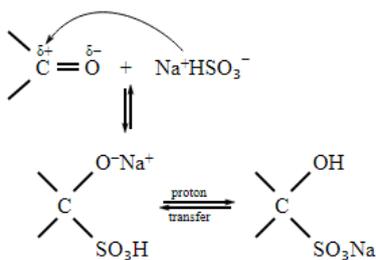


Above things happens in BVO (Bayer Villiger oxidation). Reagents are either per acetic acid or perbenzoic acid or pertrifluoroacetic acid or permonosulphuric acid.

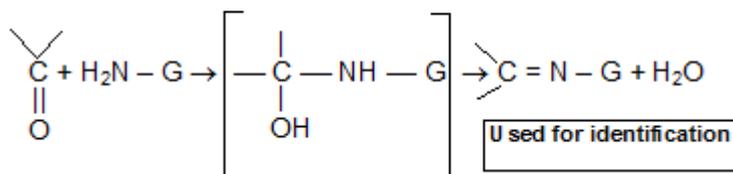
e) Addition of cyanide

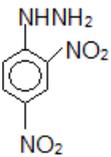
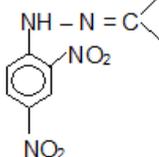


f) Addition of bisulfite:

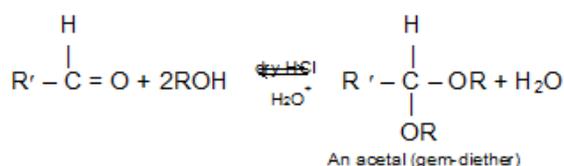


g) Addition of derivative of ammonia



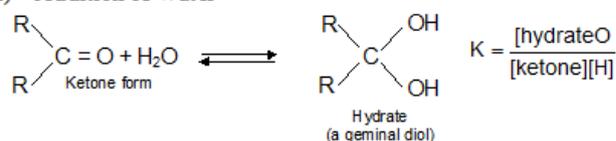
	$H_2N - G$	Product	
H_2NOH	Hydroxylamine	$>C = N - OH$	Oxime
$H_2N - NH_2$	Hydrazine	$>C = N - NH_2$	Hydrazone
$H_2N - NH - C_6H_5$	Phenylhydrazine	$>C = N - NHC_6H_5$	Phenylhydrazone
$H_2N - NH - CO - NH_2$	Semicarbazide	$>C = N - NHCONH_2$	Semicarbazone
	2, 4-Dinitrophenyl hydrazine		2, 4-dinitrophenylhydrazine (bright orange or yellow precipitate used for identifying aldehydes and ketones)

h) Addition of Alcohols; Acetal Formation

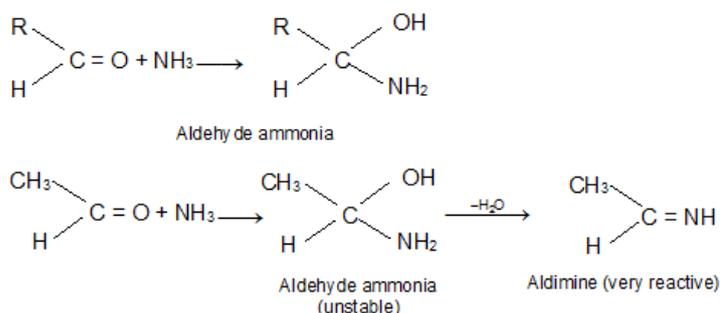


In H_3O^+ , RCHO is regenerated because acetals undergo acid catalyzed cleavage much more easily than do ethers. Since acetals are stable in neutral or basic media, they are used to protect the $-CH = O$ group.

i) Addition of Water

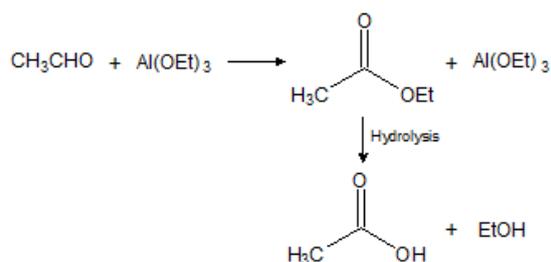


j) Addition of Ammonia:



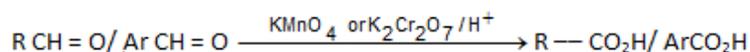
k) Tischenko reaction:

All aldehydes can be made to undergo the Cannizzaro reaction by treatment with *aluminium ethoxide*. Under these conditions the acids and alcohols are combined as the ester, and the reaction is then known as the Tischenko reaction; eg, acetaldehyde gives ethyl acetate, and propionaldehyde gives propyl propionate.



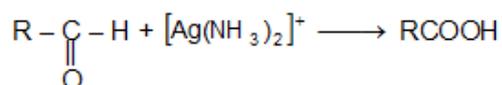
Oxidation of Aldehydes and Ketones

a)



b) Tollen's Reagent

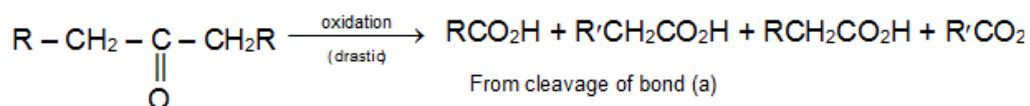
A specific oxidant for RCHO is $[\text{Ag}(\text{NH}_3)_2]^+$



Tollen's test chiefly used for the detection of aldehydes.

Tollen's reagent does not attack carbon-carbon double bonds.

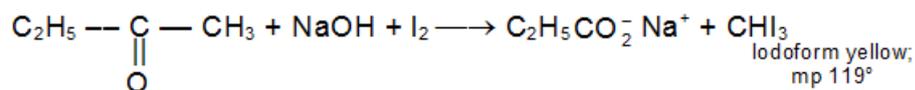
c) **Strong Oxidants:** Ketones resist mild oxidation, but with strong oxidants at high temperature they undergo cleavage of C – C bonds on either sides of the carbonyl group.



d) **Haloform Reaction**

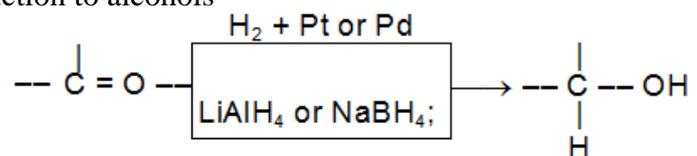
CH_3COR are readily oxidised by NaOI ($\text{NaOH} + \text{I}_2$) to iodoform, CHI_3 , and RCO_2Na

Example:



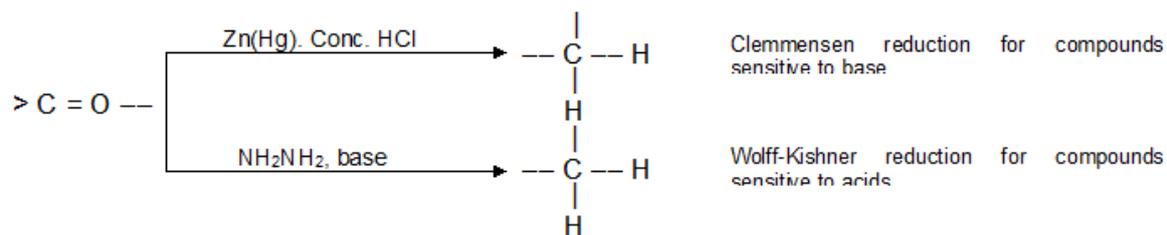
• **Reduction:**

a) Reduction to alcohols



Aldehydes \rightarrow 1 $^\circ$ alcohols; Ketones \rightarrow 2 $^\circ$ alcohols

b) Reduction to hydrocarbons



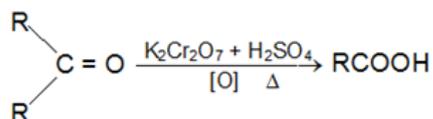
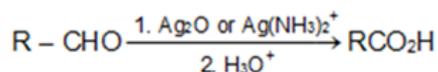
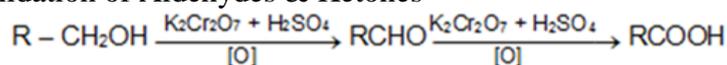
Carboxylic Acids

Physical Properties:

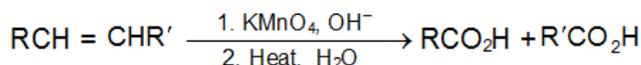
- The first three acids are colourless, pungent smelling liquids.
- First four members are miscible in water due to the intermolecular hydrogen bonding whereas higher members are miscible in non – polar solvents like ether.
- Benzene or ethanol but immiscible in water due to the increase in the size of lyophobic alkyl chain.
- The b.p. of carboxylic acids are higher than alcohols because carboxylic acids exist as dimers due to the presence of intermolecular H-bonding
- Increase in the number of Halogen atoms on α -position increases the acidity, eg. $\text{CCl}_3\text{COOH} > \text{CHCl}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{CH}_3\text{COOH}$
- Increase in the distance of Halogen from COOH decreases the acidity e.g. $\text{CH}_3 - \text{CH}_2 - \text{CH}(\text{Cl}) - \text{COOH} > \text{CH}_3 - \text{CH}(\text{Cl}) - \text{CH}_2 - \text{COOH} > \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{COOH}$
- Increase in the electro negativity of halogen increases the acidity. $\text{FCH}_2\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ICH}_2\text{COOH}$

Methods of Preparations of Carboxylic Acids

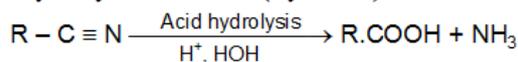
a. Oxidation of Aldehydes & Ketones



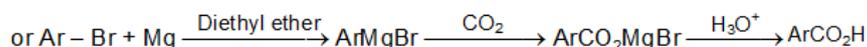
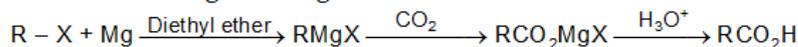
b. Oxidation of Alkanes:



c. Hydrolysis of Nitriles (Cyanides)

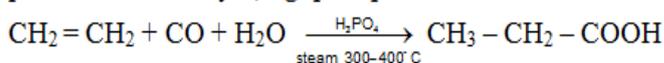


d. Carbonation of Grignard Reagents

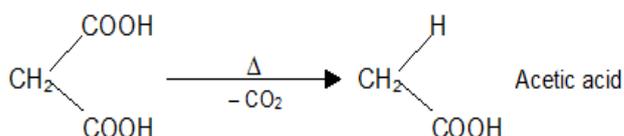


e. Koch Reaction:

An olefin is heated with carbon monoxide and steam under pressure at 300-400° in the presence of a catalyst, e.g. phosphoric acid.

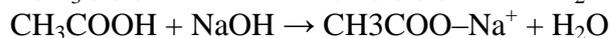
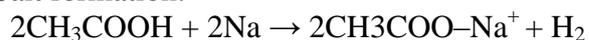


f. Heating Gem Dicarboxylic Acids:

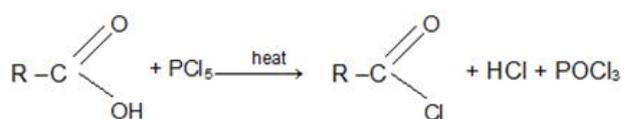
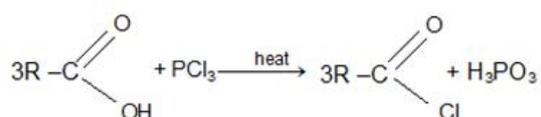
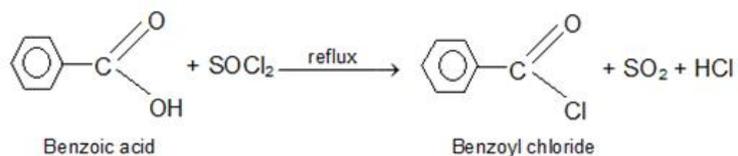


Chemical Reactions of Carboxylic Acids

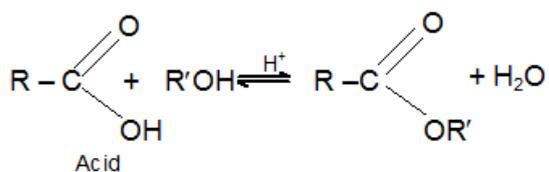
a. Salt formation:



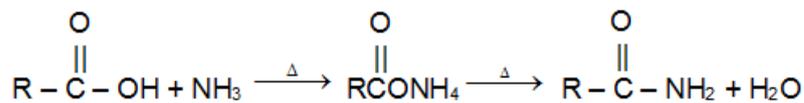
b. Conversion into Acid Chlorides:



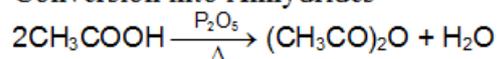
c. Conversion into Esters (Esterification)



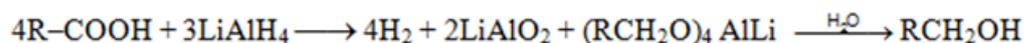
d. Conversion into Amides



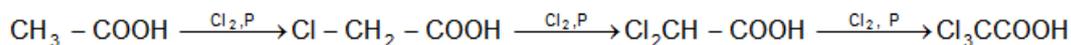
e. Conversion into Anhydrides



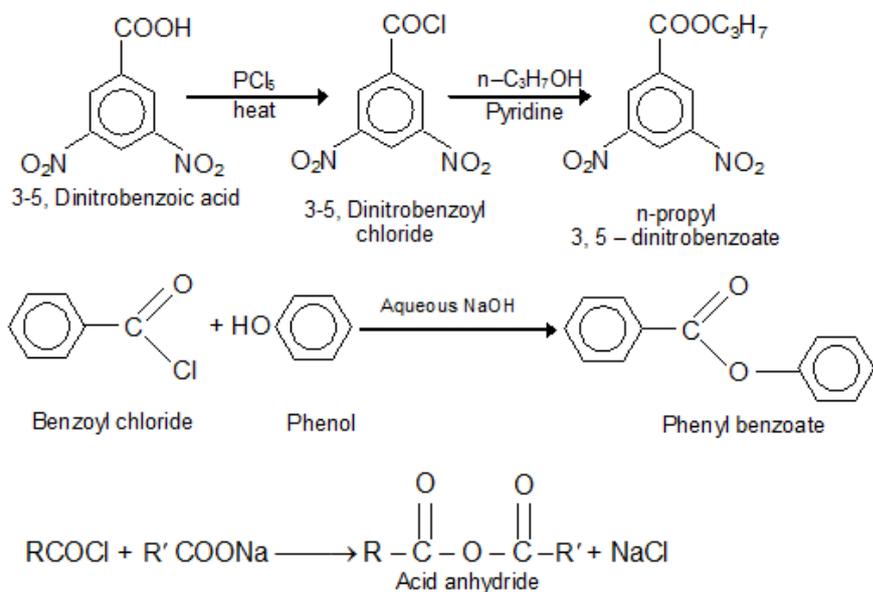
f. Reduction:



g. Halogenation:

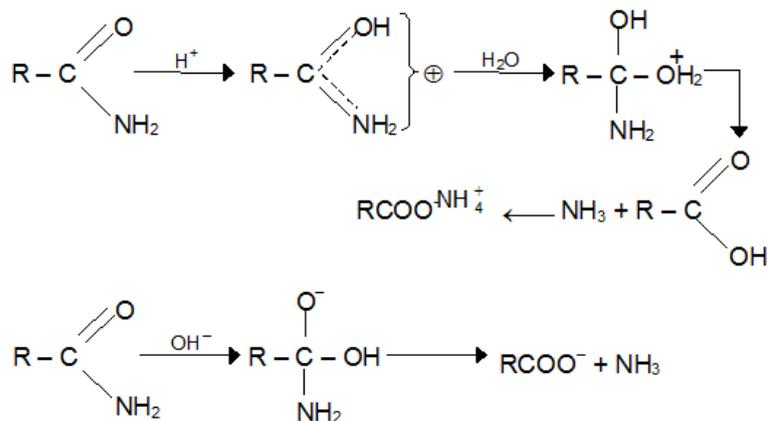


c) Conversion of Acid Chlorides into Acid Derivatives:

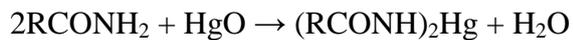


Amides

a. Hydrolysis:

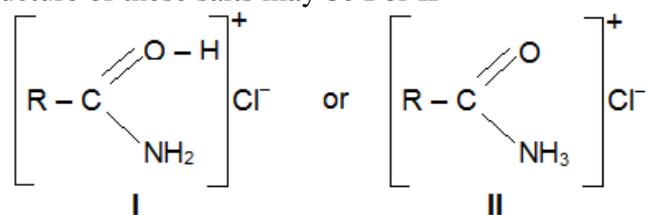


b. Acidic Character of Amides:

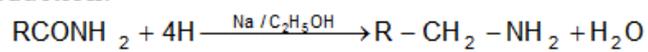


c. Basic Character of Amides:

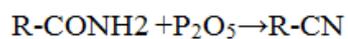
Amides are very feebly basic and form unstable salts with strong inorganic acids. e.g. RCONH_2HCl . The structure of these salts may be I or II



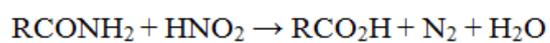
d. Reduction:



e. Reaction with Phosphorus Pentaoxide:



f. Reaction with Nitrous Acid:

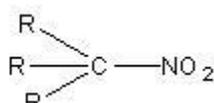
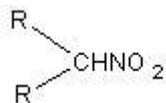
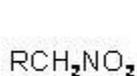


ORGANIC COMPOUNDS CONTAINING

NITROGEN

Nitro and Cyno Compounds

Nitro alkanes are derivatives of alkanes. They are isomeric to nitrites (esters) classified as primary, secondary and tertiary depending on the nature of carbon atom to which nitro group is linked.



Primary nitro alkane

Secondary Nitro alkane

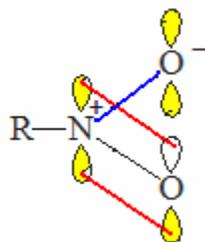
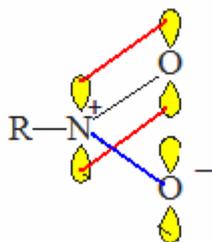
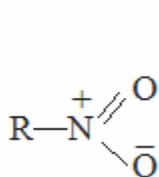
Tertiary nitro alkane

—NO₂ group is an ambident group. If it attacks through nitrogen. It is called nitro and if it attacks through oxygen atom, it is called nitrite. Hence nitrites and nitro compounds are isomers.

Ambident nucleophiles:

Nucleophiles which can attack from two sites such as CN⁻, NO₂⁻ are called ambident nucleophiles

Evidences show that nitrogen is attached to one of the oxygen atoms by a double bond and to the other by a dative bond. The resonance hybrid is shown as under which confirms the spectroscopic evidence that both nitrogen – oxygen bonds have same bond length.



Resonating forms

Hybrid structure

Out of three hybrid orbitals of nitrogen one overlaps with alkyl group and two with oxygens while the unhybridized p orbital of N – atom containing a pair of electrons and lying perpendicular to the plane of hybrid orbitals overlaps sideways with half filled 2p – orbitals of two oxygen atoms. This forms π-bond above and below the plane of molecule.

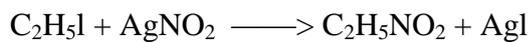
Preparation of Nitro Compounds

(i) From alkyl halides:

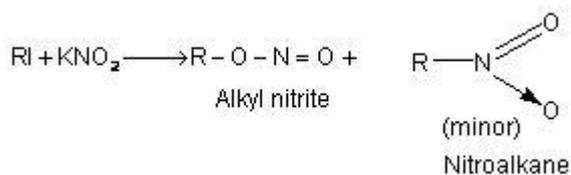
Alkyl halides react with silver nitrite in ethanolic solution to give nitro compounds. Alkyl nitrite is formed in minor quantity. This reaction is used to prepare 1° nitro compounds primarily while 2° and 3° halides give major proportion of alkenes due to β – elimination. Contrary to this alkali nitrites give alkyl nitrites as major product. This is due to ionic nature of alkali nitrite.

But if the reaction is carried out in solvents like DMF or DMSO, then even NaNO₂ or KNO₂ give good yield (about 60%) of nitro compound.

Reactions:

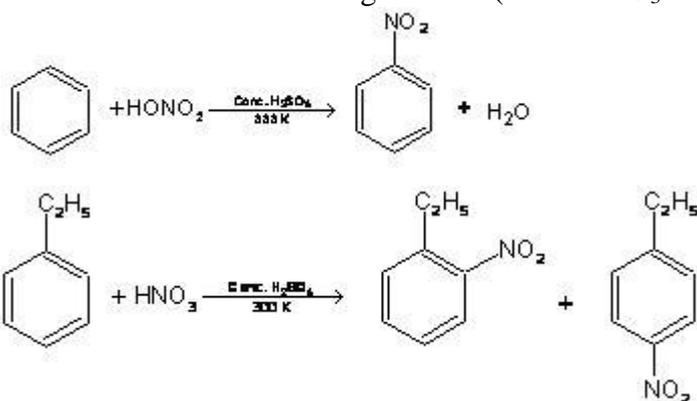


Nitroethane



(ii) Nitration:

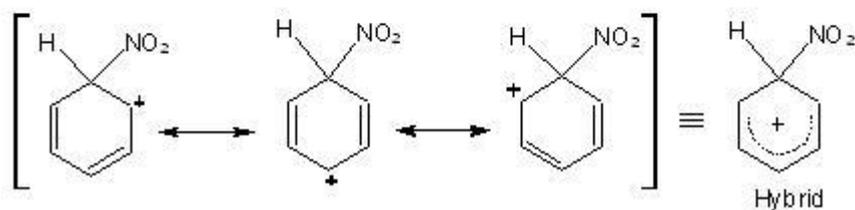
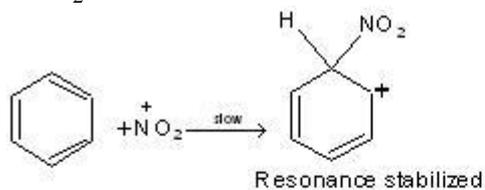
Nitro derivatives of aromatic compounds like nitrobenzene are produced when benzene is allowed to react with nitrating mixture. (conc. HNO_3 /conc. H_2SO_4).



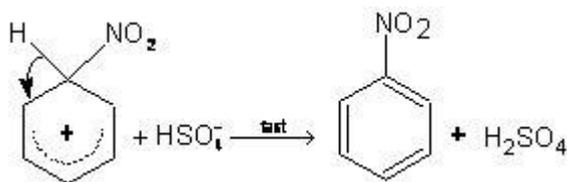
Mechanism:

Generation of nitronium ion

Attack of NO_2^+ on benzene molecule



Loss of proton:



Nitrobenzene

Direct nitration of alkane involves vapour phase nitration at high temperature.

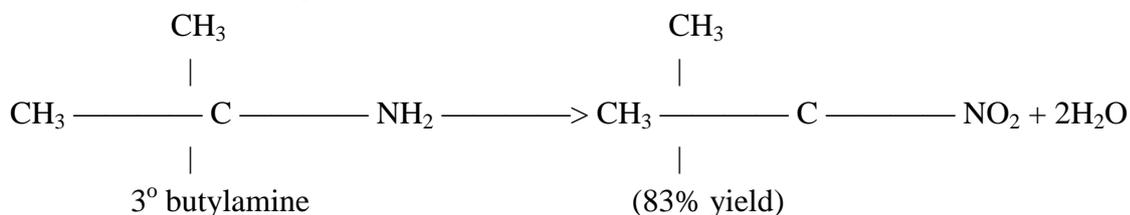


Problem faced in the method is that at such high temperature, a mixture of nitro alkanes is formed due to C – C cleavage.

e.g. $\text{CH}_3\text{CH}_2\text{CH}_3 + \text{HNO}_3 \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2 + \text{CH}_3\text{CH}_2\text{NO}_2 + \text{CH}_3\text{NH}_2 + \text{other products}$

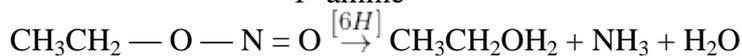
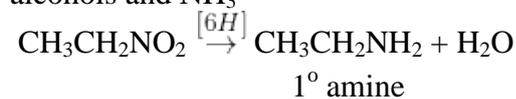
(iii) From amines:

3° nitroalkanes can be produced as follows:



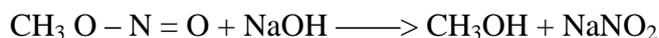
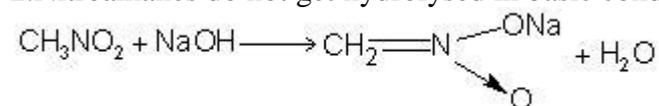
Distinguish test between nitroalkanes and alkyl nitrites

1. Nitroalkane on reduction with H_2/Ni produce 1° amines while alkyl nitrites produce alcohols and NH_3



Ethyl nitrite

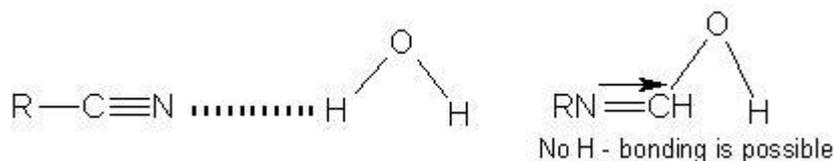
2. Nitroalkanes do not get hydrolysed in basic conditions while nitrites produce alcohols



Cyanides and Isocyanides

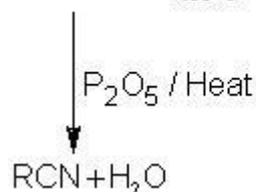
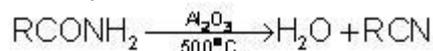
Both alkyl cyanides (RCN) and alkyl isocyanides (RNC) are organic derivatives of

hydrocyanic acid HCN. Alkali cyanides are ionic $\left(\text{:C} \equiv \text{N}^- \right)$ and cyanide ion is ambident in nature (can form covalent bond either from carbon or nitrogen). $\text{AgC} \equiv \text{N}$ is covalent, hence lone pair on nitrogen is mainly available for covalent bond formation, resulting in predominant formation of isocyanides.

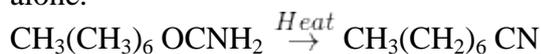


Methods of preparation of Cyanides

1. Dehydration of Amides:



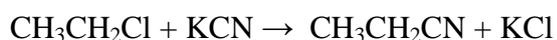
High molecular weight acid amides are dehydrated to the corresponding cyanide by heat alone.



2. From RX:



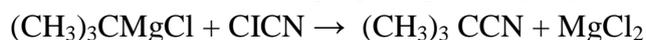
This method is satisfactory only if R is 1° or 2° group. If it is 3° group, then it is converted into alkene.



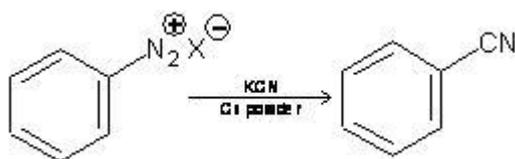
3. By Grignard's reagent and Cyanogen chloride reaction:



This is best method for preparing 3° alkyl cyanides.

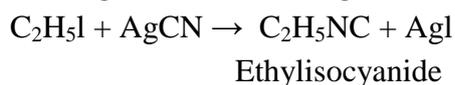


4. From Diazonium salt



Methods of Preparation of Isocyanides

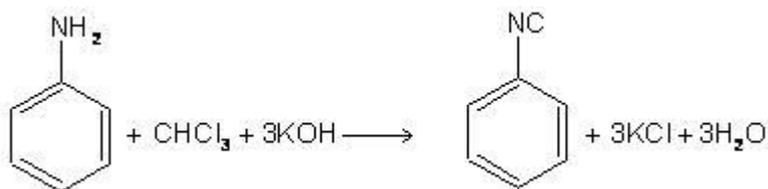
1. By heating an alkyl iodide with AgCN in aqueous ethanolic solution



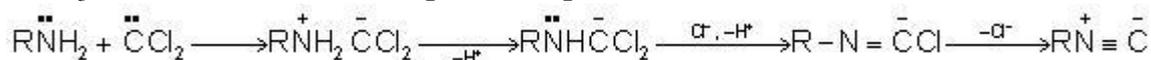
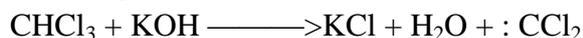
2. By carbylamine reaction

Heating a mixture of 1° amine and chloroform with ethanolic potassium hydroxide





Mechanism proceeds via intermediate formation of dichloromethylene or, dichloro carbene produced from chloroform in alkaline solution. (Via α -elimination)

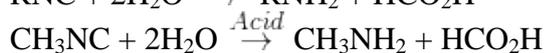
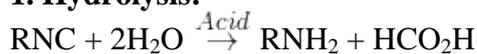


Properties of Isocyanides

1. Alkyl isocyanides are poisonous, unpleasant smelling, with lower boiling points than isomeric cyanides.
2. RNC are not very soluble in water, nitrogen atom not having a lone pair of electrons available for hydrogen bonding.

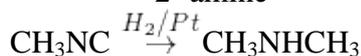
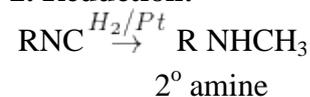
Reactions:

1. Hydrolysis:



RNC are not hydrolysed by alkalis.

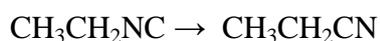
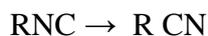
2. Reduction:



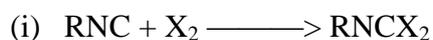
Methyl isocyanide Dimethyl amine

3. Rearrangement:

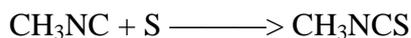
When alkyl isocyanides are heated for a long time, they arrange to form cyanide



4. Reaction with non metals:

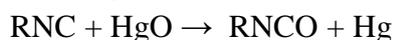


Alkyl isothiocyanates

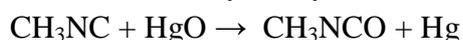


5. Oxidation:

with HgO:



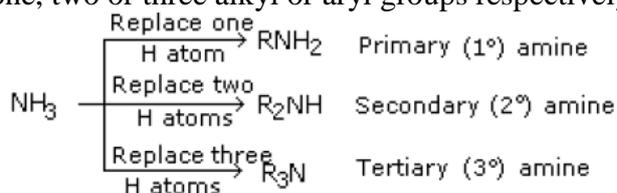
Alkyl isocyanates



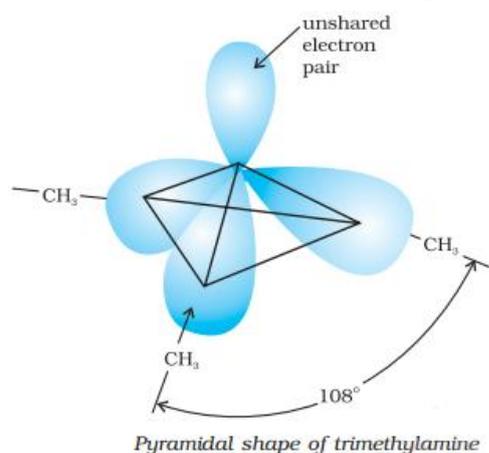
Amines

Introduction

Amines are organic compounds that are structurally related to inorganic ammonia and are basic in nature. They can be thought of as derivatives of ammonia in which one, two or all the three hydrogen atoms have been replaced by alkyl or aryl groups. They are classified into primary (1°), secondary (2°) or tertiary (3°) amines, depending on whether nitrogen is joined to one, two or three alkyl or aryl groups respectively.

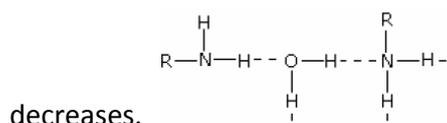


Structure of amines: Trigonal Pyramidal



Physical properties

- Physical state and smell** :The lower aliphatic amines are colourless gases, while those with four carbons or higher members are liquids.
- Aromatic amines** are generally **very toxic**; they are readily absorbed through the skin, often with fatal results. Aromatic amines are very easily oxidized by air.
- Boiling points** : Like ammonia, amines are polar compounds and, except for tertiary amines, can form **intermolecular hydrogen bonds**. As a result of this, amines have higher boiling points than the non-polar compounds of similar molecular masses.
- Solubility** :Amines of all three classes are capable of forming hydrogen bonds with water. amines of lower molecular masses (upto 6 carbon atoms) are soluble in water due to hydrogen bonding. As the molecular mass increases, the solubility in water



Basicity of Amines

1. Amines are stronger bases than alcohols, ethers, esters, etc.

It is because, nitrogen is less electronegative than oxygen, the lone pair is easily donated and can better accommodate the positive charge of the ion.

2. Alkyl amines are stronger bases than ammonia This can be explained in terms of an electron donating inductive effect of the alkyl groups. Alkyl groups, by their electron donating effect, increase the electron density of nitrogen and hence, make the lone pair of nitrogen more easily available to be given to acids.

3. Aryl amines are weaker bases than ammonia: This can be explained in terms of the electron withdrawing resonance and inductive effect of the aryl groups, which decrease the electron density of nitrogen and hence, make the lone pair of nitrogen less available to be given to acids.

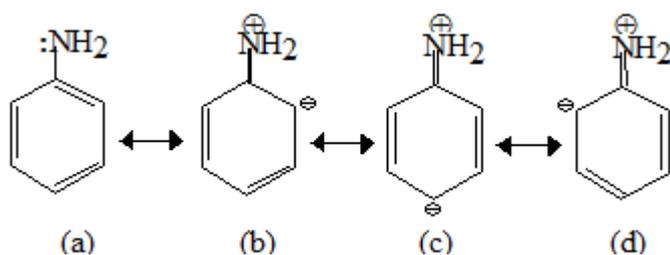
a) Aliphatic Amine:

Basic Strength: $\text{NH}_3 < \text{RNH}_2 < \text{R}_2\text{NH} < \text{R}_3\text{N}$,

b) Aromatic Amine:

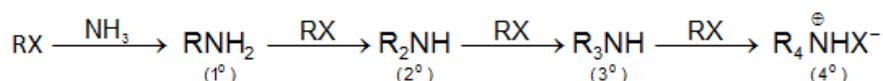
Basic Strength: $\text{NH}_3 > \text{Ar-NH}_2 > \text{Ar}_2\text{-NH}$

Benzene ring decreases the electron density over N atom due to resonance effect.

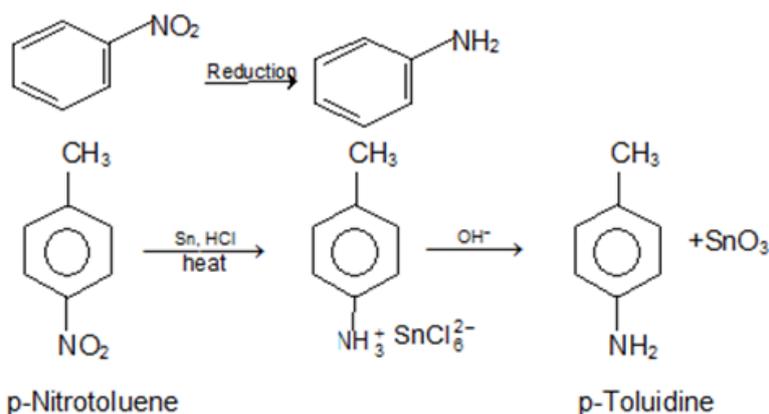


Preparation of Amines

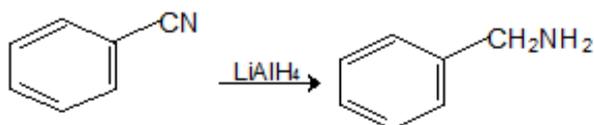
a) From Alkyl halides:



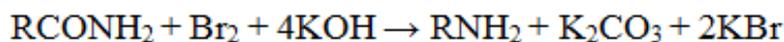
b) From Nitro Compounds:



c) **From Nitriles :**



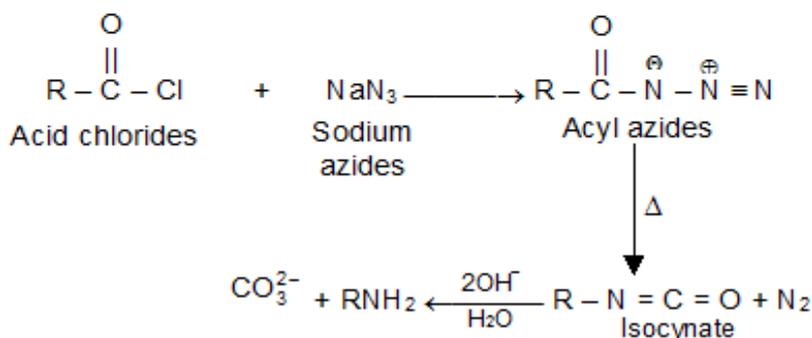
d) **Hofmann Bromamide or Hofmann degradation:**



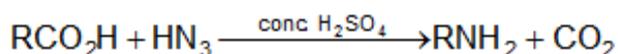
e) **From carbonyl compounds (Reductive Amination)**



f) **Curtius reaction:**



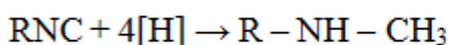
g) **Schmidt reaction :**



g) **Schmidt reaction :**



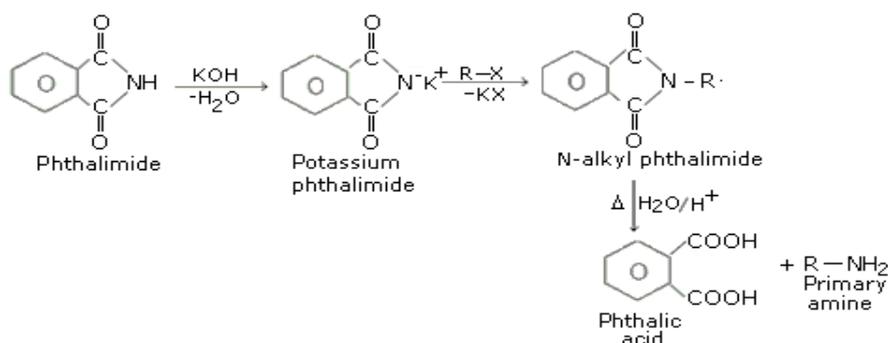
h) **Reduction of Alkyl isocyanide:**



i) **Preparation of tertiary amine:**



j) **Gabriel's phthalimide synthesis:** Gabriel's phthalimide synthesis is used to prepare pure primary aliphatic amines and thus provides an indirect method of carrying on the transformation of RX to RNH₂, without the formation of secondary or tertiary amines as by products. In this method, phthalimide is first converted into potassium phthalimide (a salt) by a reaction with KOH (or NaOH). Then, potassium phthalimide gives N-alkyl-phthalimide on treatment with alkyl halide, which gives a primary amine on hydrolysis with hydrochloric acid.



Chemical Reactions

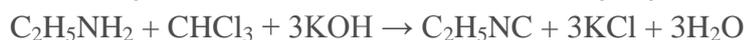
a) Acylation:



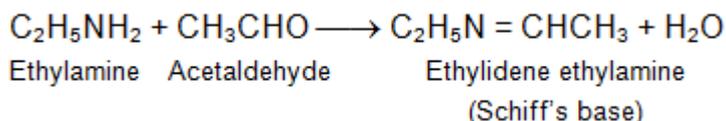
b) Benzoylation (Schotten Baumann Reaction)

Primary amine reacts with benzoyl chloride to give the acylated product

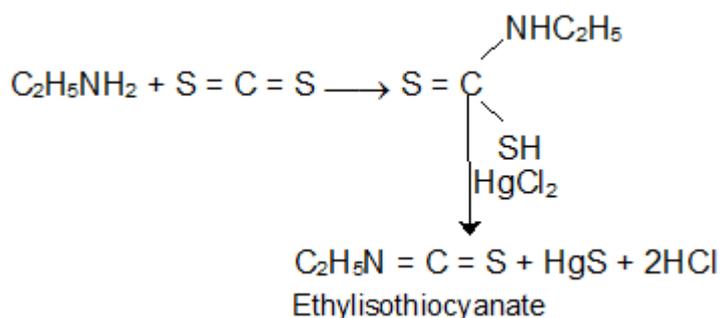
c) Carbylamine Reaction (Given Only by Primary Amines):



d) Action with Aldehyde and Ketone:

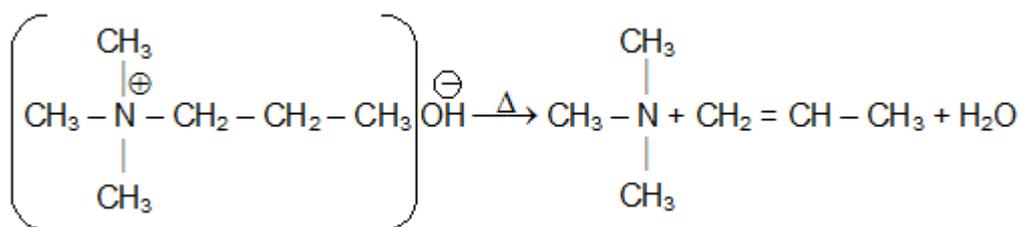


e) Hofmann Mustard Oil Reaction:

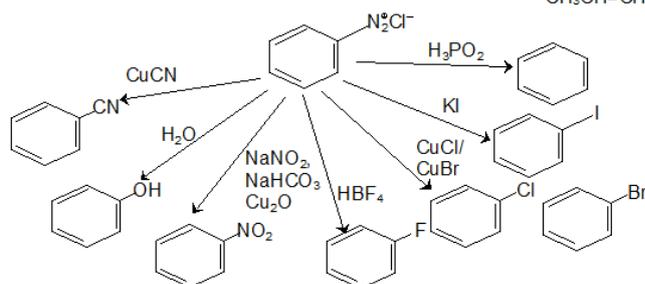
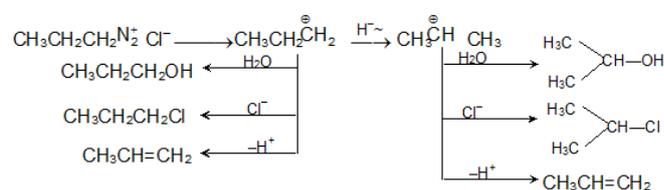
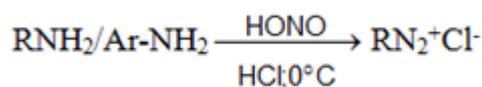


f) Reaction with Carbonyl Chloride: $C_2H_5 - NH_2 + COCl_2 \rightarrow C_2H_5NCO + 2HCl$

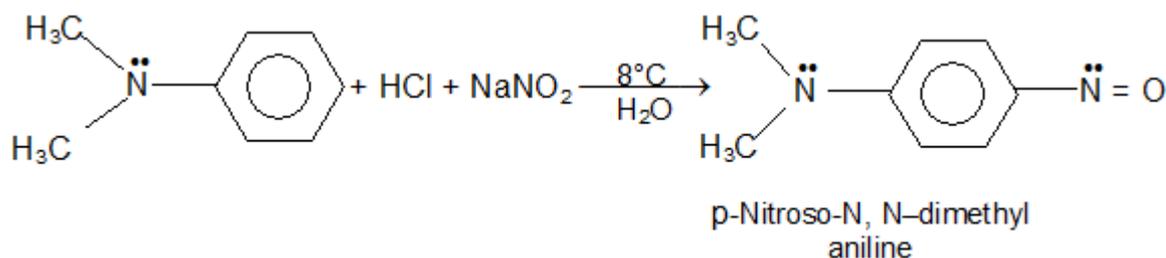
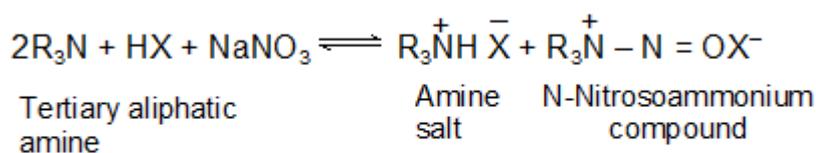
g) Hofmann Elimination: When a quaternary ammonium hydroxide is heated strongly (125° or higher) it decomposes to yield water, a tertiary amine and an alkene



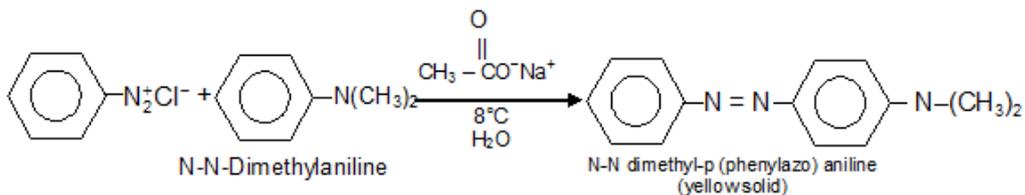
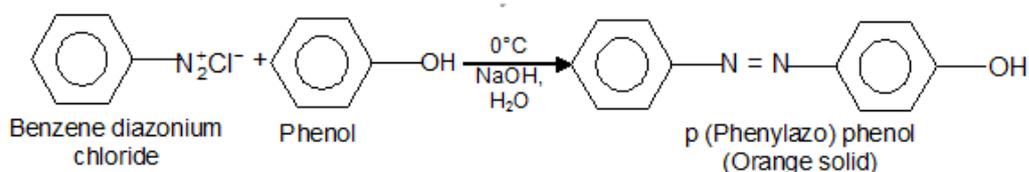
h) The diazonium salts of amines:



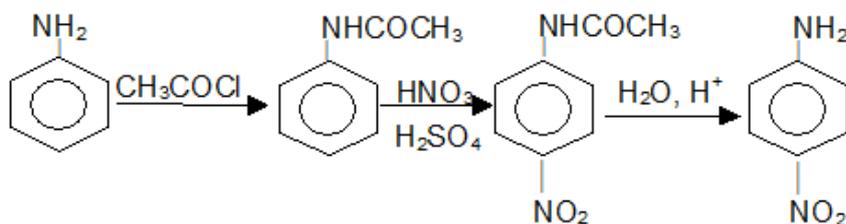
i) Reaction of Tertiary amines with Nitrous acid: When a tertiary aliphatic amine is mixed with nitrous acid, an equilibrium is established among the tertiary amine, its salt, and an N-Nitrosoammonium compound.



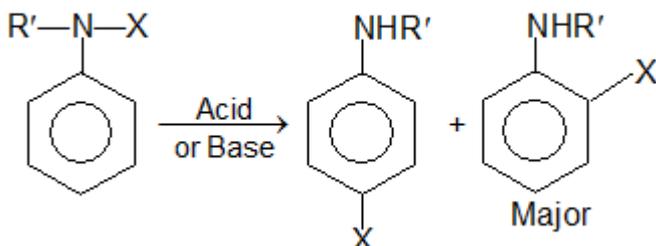
j) Coupling Reactions of Arene Diazonium Salts:



k) Ring Substitution in Aromatic Amines:

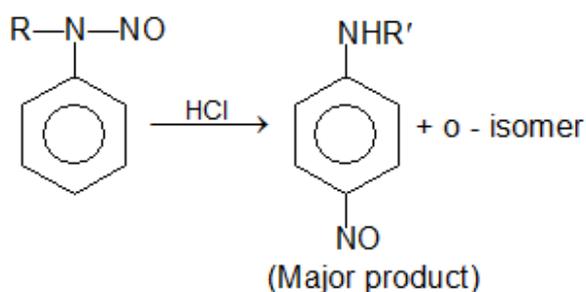


l) Aniline -X rearrangement:



Such compounds are not much stable so the group X migrates mainly at p-position.

1. Fisher-Hepp rearrangement



2. Phenylhydroxylamine - p-aminophenol rearrangement.

Separation of a Mixture of Amines:

a) Hinsberg's Method

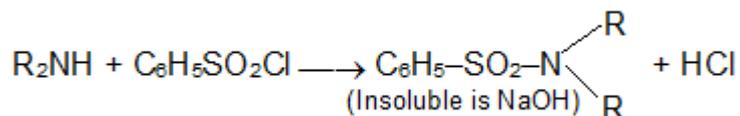
Primary amine:



$C_6H_5-SO_2-NH-R$: N-alkyl benzene sulfonamides

Dissolves in NaOH due to acidic H-attached to Nitrogen)

Secondary amine

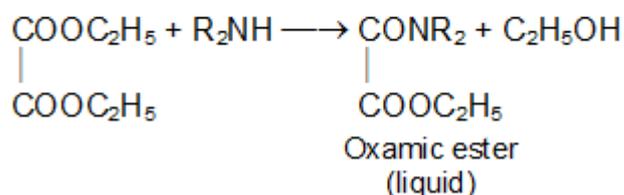
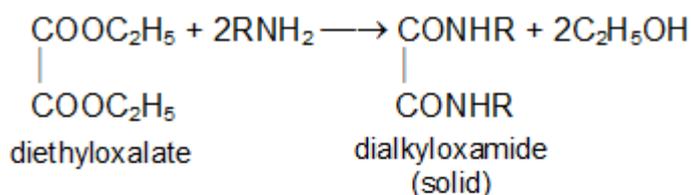


Tertiary amine :

Tertiary amines do not react with Hinsberg's reagent.

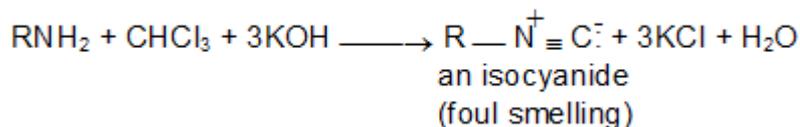
a) Hofmann's Method:

The mixture of amines is treated with diethyloxalate, which forms a solid oxamide with primary amine, a liquid oxime ester with secondary amine. The tertiary amine does not react.



Test for Amines

Carbylamine test: This test is used to identify primary amines (aliphatic as well as aromatic). In this test, the compound is warmed with chloroform in the presence of an alcoholic solution of potassium hydroxide. The primary amines give offensive-smelling



isocyanides.

Secondary amine is converted into nitrosoamine by treating the amine with nitrous acid. The resultant solutions warmed with phenol and concentrated H_2SO_4 , a brown or red colour is formed at first soon it changes to blue and then to green. The colour changes to red on dilution and further changes to greenish blue on treating with alkali.

Tertiary arylamines react with nitrous acid to form o-nitroso aromatic compound.