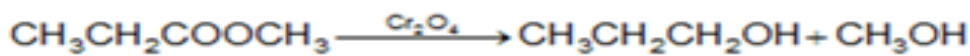
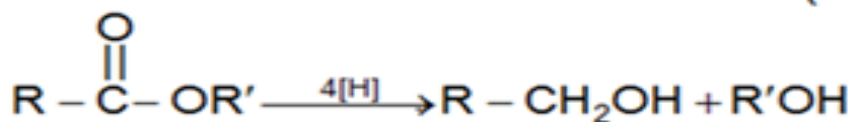
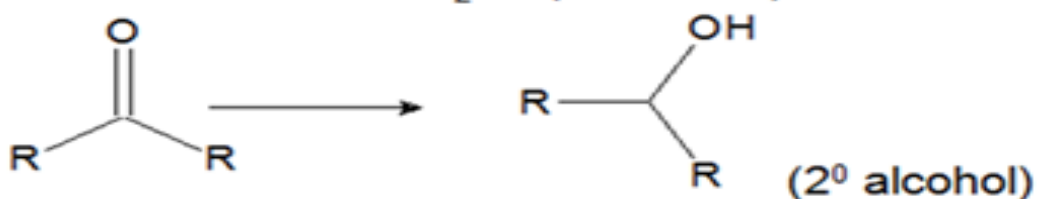


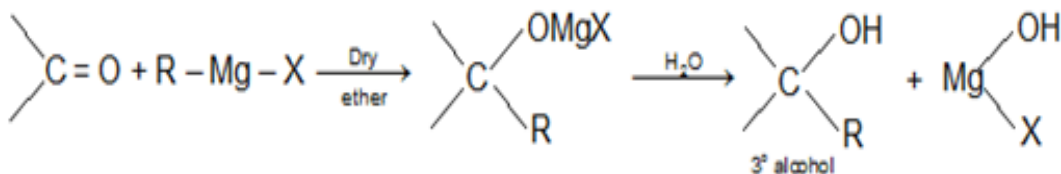
Alcohols, Phenols and Ether Alcohols

Preparation of Alcohols:-

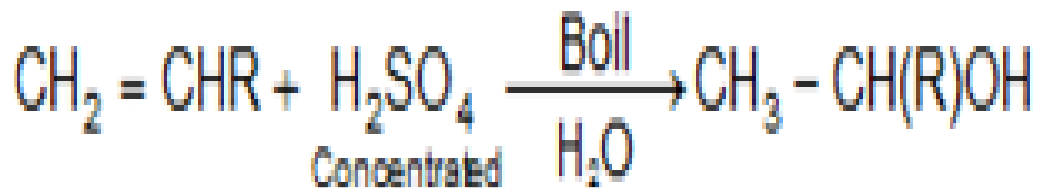
- By hydrolysis of haloalkanes : $R-X + \text{aq. KOH} \rightarrow \text{ROH} + \text{KX}$
- By reduction of Carbonyl compounds



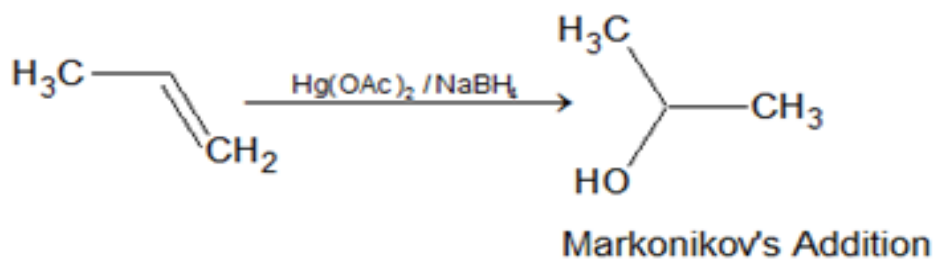
- By the action of Grignard's Reagent on aldehydes, ketones and esters



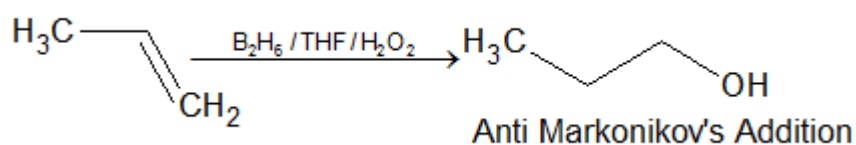
- By Aliphatic Primary Amines: $\text{RCH}_2\text{NH}_2 + \text{HNO}_2 \rightarrow \text{RCH}_2\text{OH} + \text{N}_2 + \text{H}_2\text{O}$
- Hydration of alkenes:



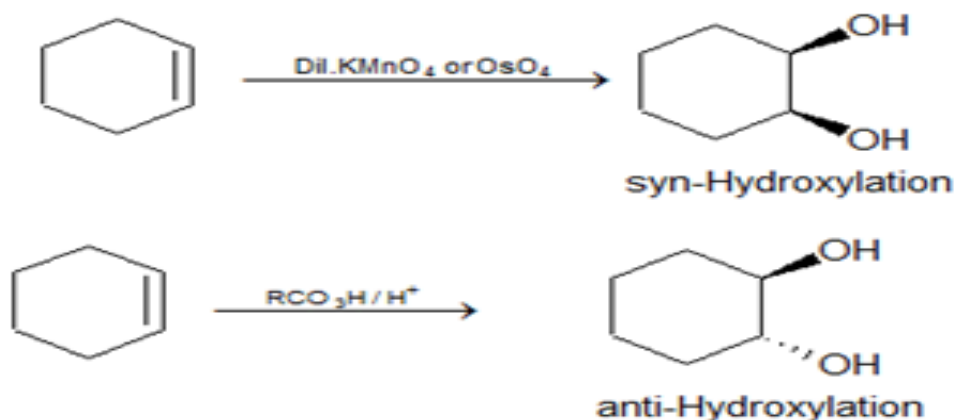
- Oxymercuration-demercuration:



- Hydroboration-oxidation:



- Hydroxylation of alkenes:

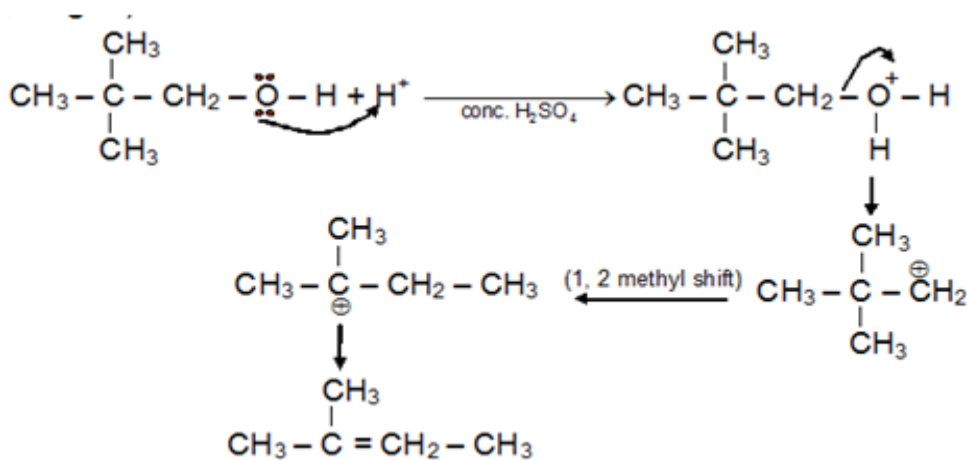


Physical Properties of Alcohol:

- 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 HNO_3 :** $\text{R-OH} + \text{HO-NO}_2 \rightarrow \text{R-O-NO}_2$
- **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. Intra-molecular 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 β carbon containing minimum β hydrogen

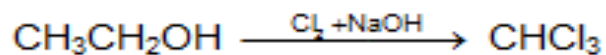
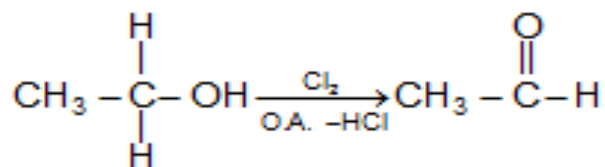


- **Oxidation of Alcohol:**

$$\text{RCH}_2\text{-OH} + [\text{O}] \rightarrow \text{RCHO} \rightarrow \text{RCOOH}$$

$$\text{RCH}_2\text{-OH} + [\text{O}] + \text{PCC} \rightarrow \text{RCHO}$$
- **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.



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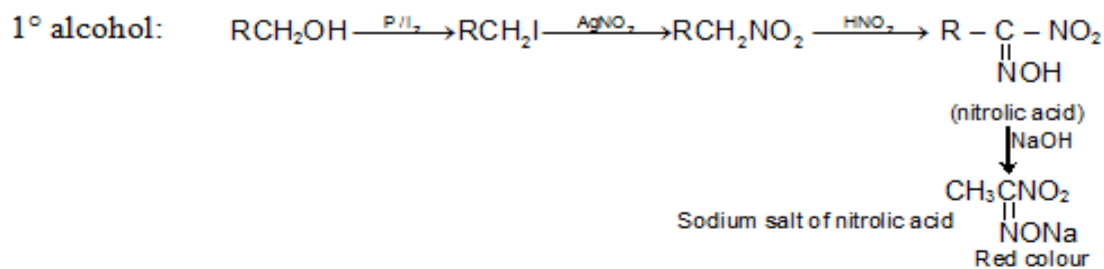
Test for Alcohols:

1. Lucas Test:

Alcohols + ZnCl_2 + HCl

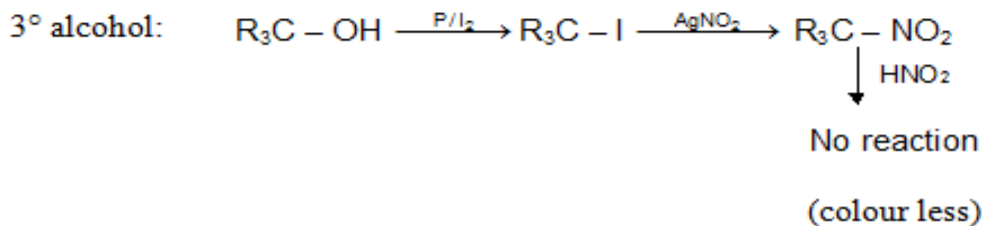
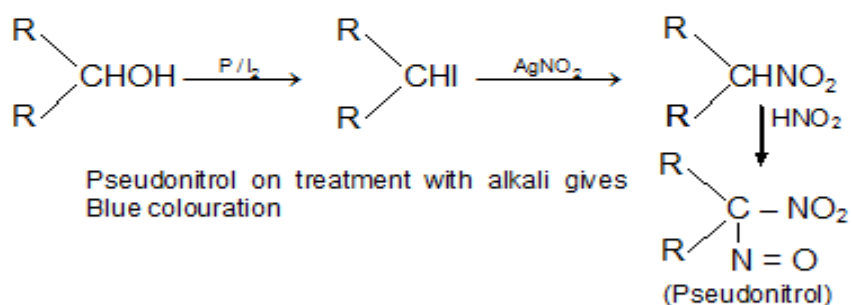
- 1° Alcohol: $\text{RCH}_2\text{OH} + \text{ZnCl}_2 + \text{HCl} \rightarrow$ No reaction at room temperature
- 2° Alcohol: $\text{R}_2\text{CHOH} + \text{ZnCl}_2 + \text{HCl} \rightarrow \text{R}_2\text{CHCl}$ White turbidity after 5-10 min.
- 3° Alcohol: $\text{R}_3\text{CHOH} + \text{ZnCl}_2 + \text{HCl}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

2. Victor Meyer Test



Nitric acid on treatment with alkali gives colouration

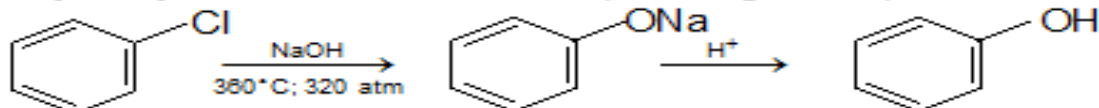
2° alcohol:



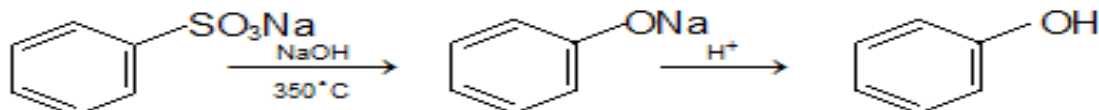
Phenols

Preparation:

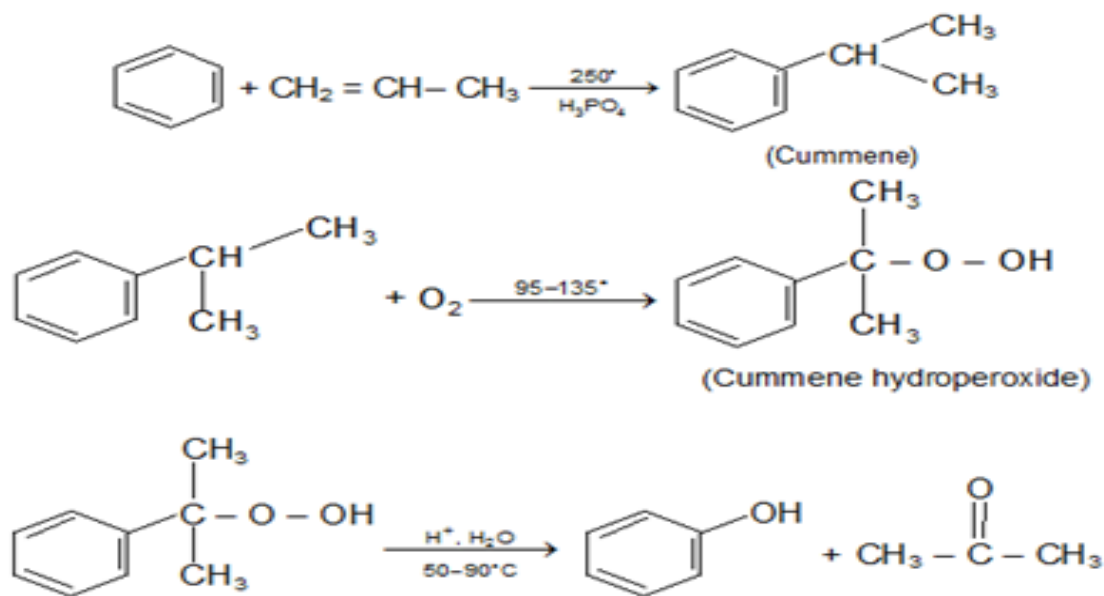
a. Hydrolysis of chlorobenzene: (Dow's process)



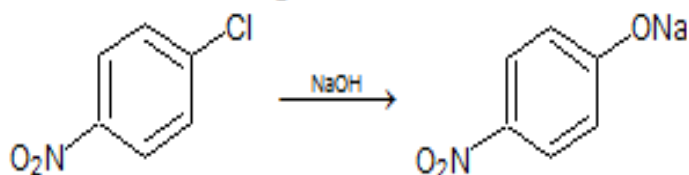
b. Alkali fusion of Sodium benzene sulfonate



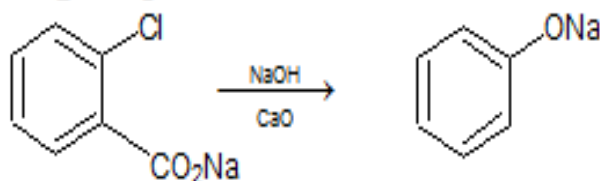
c. From Cumene Hydroperoxide



d. Aromatic Nucleophilic Substitution of Nitro Aryl Halides



e. Distillation of phenolic acids with soda-lime produces phenols, e.g. sodium salicylate gives phenol.



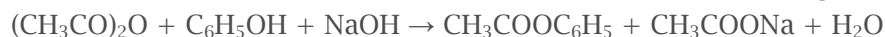
Physical Properties of Phenols

- 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



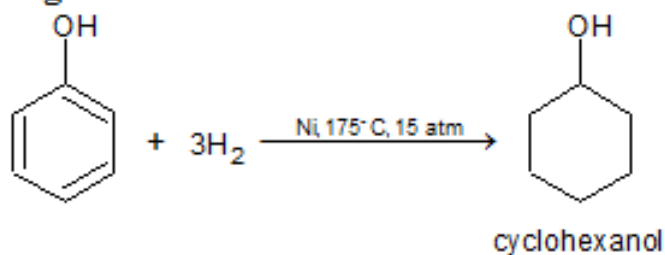
Phenyl acetate



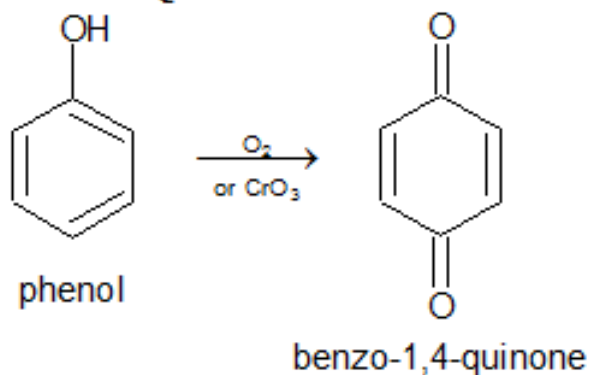
Phenyl benzoate

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

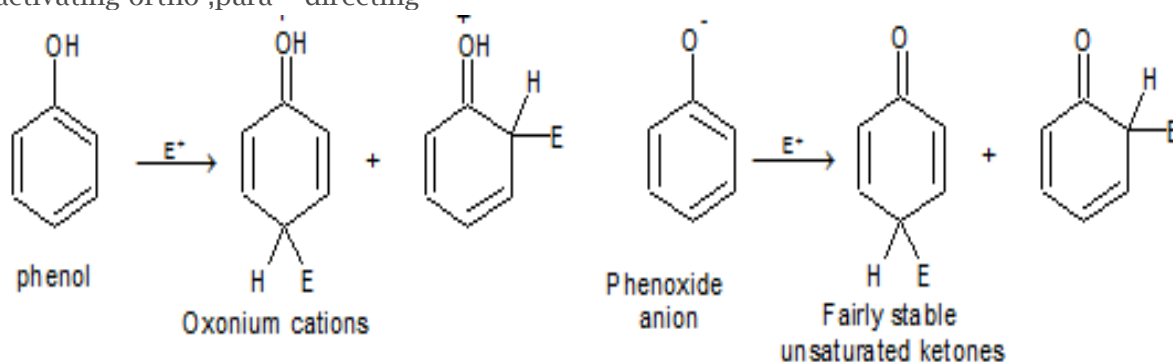
c) Hydrogenation



d) Oxidation to Quinones

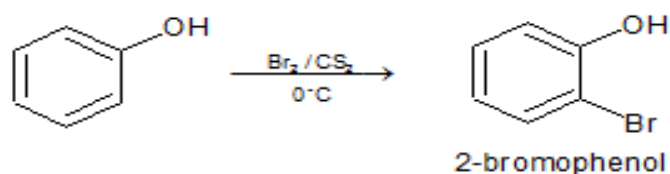
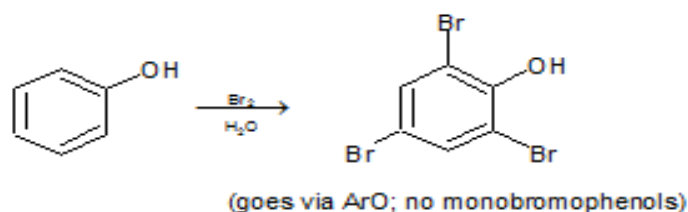


e) Electrophilic Substitution The $-\text{OH}$ and even more so the $-\text{O}(\text{phenoxide})$ are strongly activating ortho, para - directing

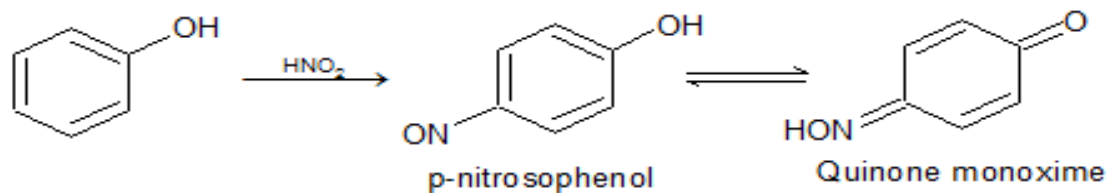


Special mild conditions are needed to achieve electrophilic monosubstitution in phenols because their high reactivity favors both polysubstitution and oxidation

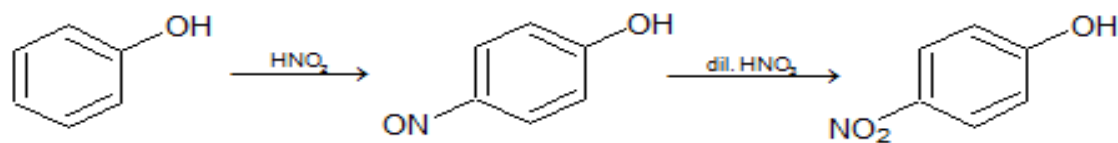
f) Halogenation



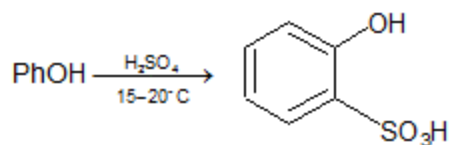
h) Nitrosation



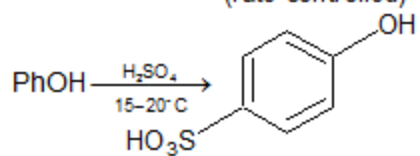
i) Nitration



j) Sulfonation



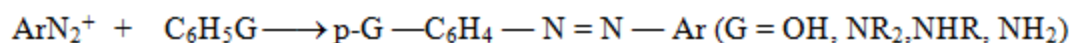
(rate-controlled)



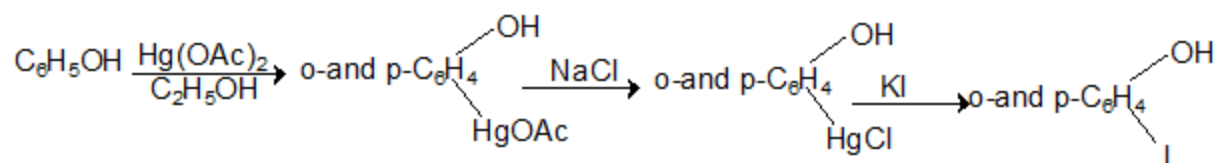
(eqbm-controlled)

k) Diazonium salt coupling to form azophenols

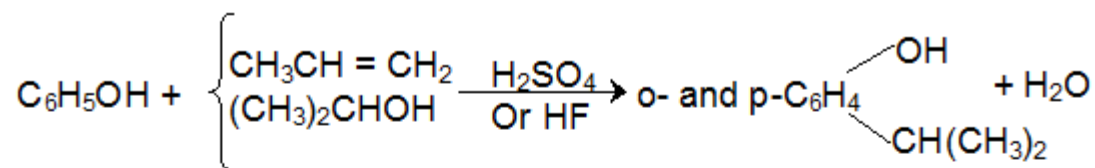
Coupling (G in ArG is an electron – releasing group)



l) Mercuration

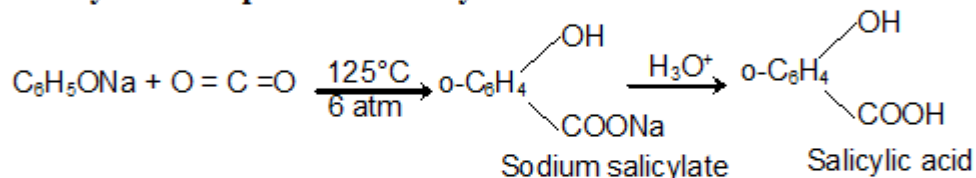


m) Ring alkylation



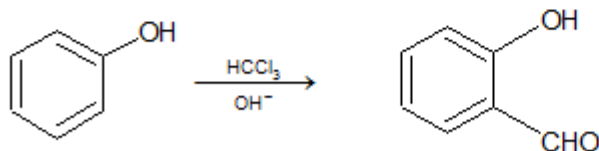
RX and AlCl_3 give poor yields because AlCl_3 coordinates with O.

n) Kolbe synthesis of phenolic carboxylic acids



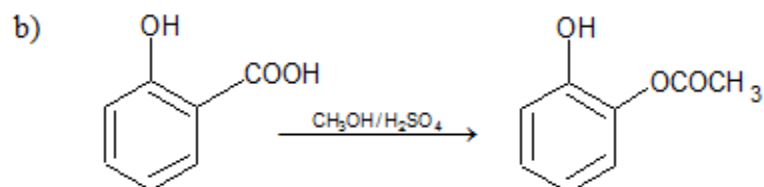
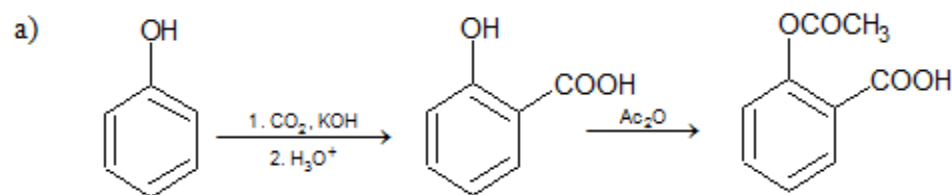
Phenoxide carbanion adds at the electrophilic carbon of CO_2 , para product is also possible.

o) Reimer – Tiemann synthesis of phenolic aldehydes



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

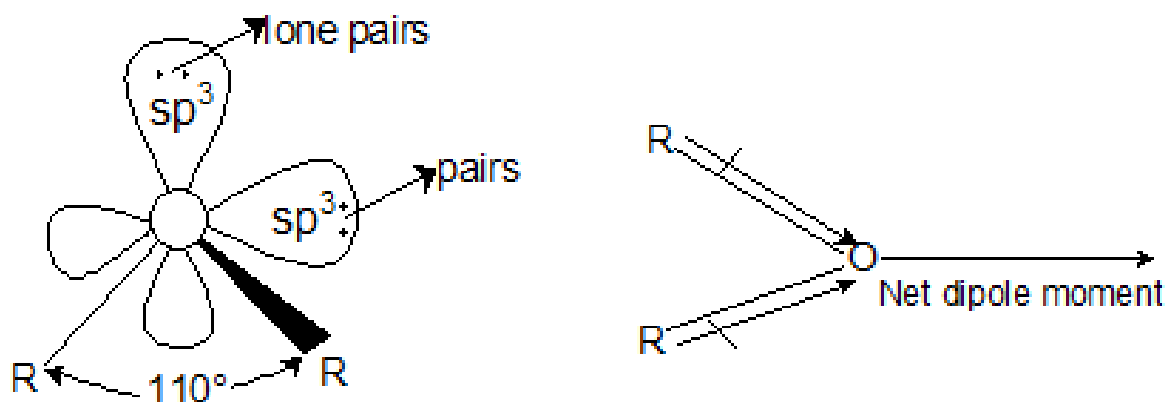
p) Synthesis of (a) aspirin (acetylsalicylic acid) (b) oil of wintergreen (methyl salicylate)



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 sp^3 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.

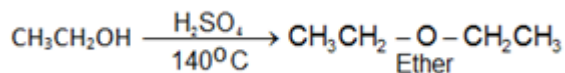


Bond angle of ether is greater than that of tetrahedral bond angle of $109^\circ 28'$.

- **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:

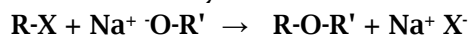
a) From alcohols:



Order of dehydration of alcohol leading to formation of ethers: $1^\circ > 2^\circ > 3^\circ$

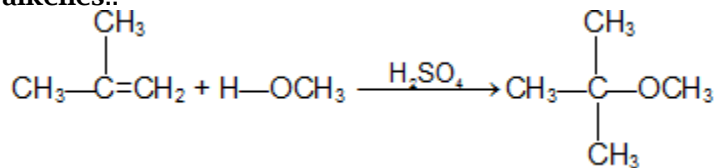


b) Williamson's synthesis:

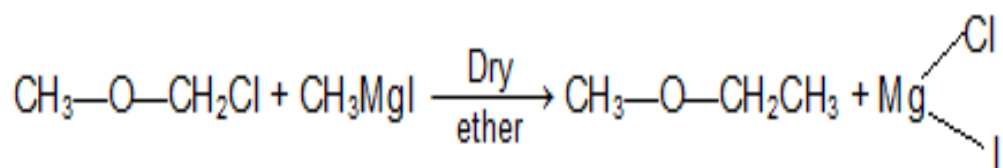


In case of tertiary substrate elimination occurs giving alkenes.

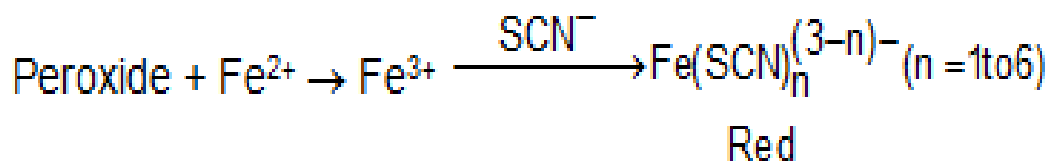
From alkenes:



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

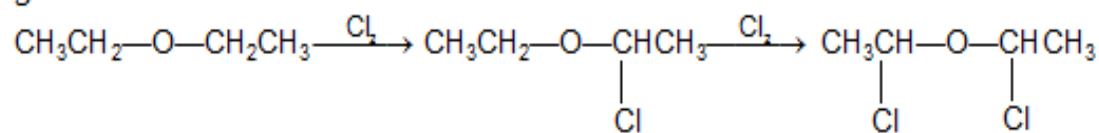


On standing in contact with air, most aliphatic ethers are converted slowly into unstable peroxides. The presence of peroxides is indicated by formation of a red colour when the ether is shaken with an aqueous solution of ferrous ammonium sulfate and potassium thiocyanate

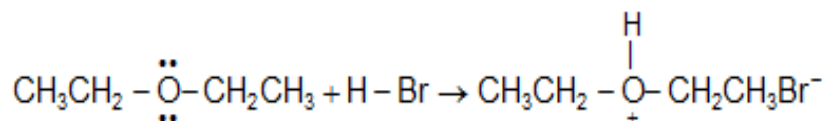


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f) Halogenation of ethers:



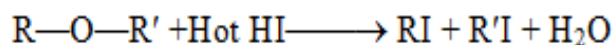
g) Ethers as base:



h) Reaction With Cold conc. HI/HBr:



i) Hot conc. HI/HBr:

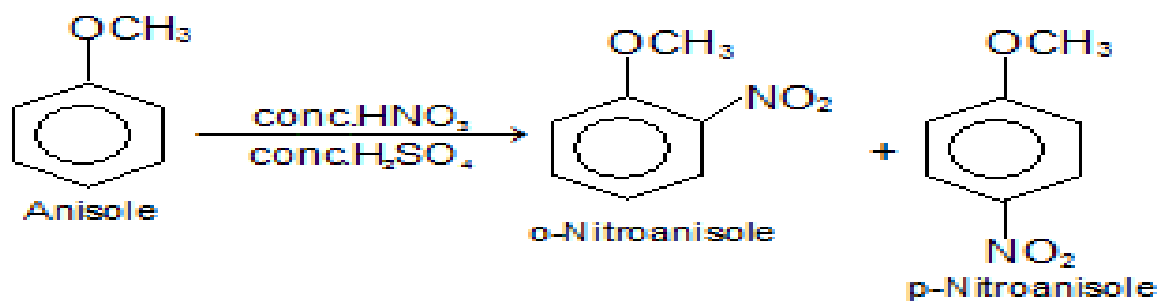
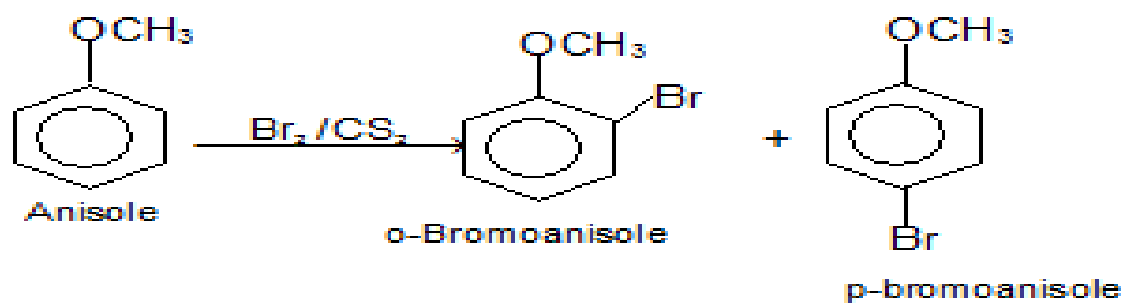


Case I:	<p> $\text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-CH}_3 \xrightarrow{\text{HI}} \text{CH}_3\text{-I} + \text{CH}_3\text{-CH}_2\text{-OH}$ </p> <p>primary secondary</p>
Case II:	<p> $\text{CH}_3\text{-CH(O-CH(CH}_3\text{))}_2 \xrightarrow{\text{HI}} \text{CH}_3\text{-CH(OH)-CH}_3 + \text{(CH}_3\text{)}_3\text{C-I}$ </p> <p>secondary tertiary</p>
Case III:	<p> $\text{CH}_3\text{-O-C(CH}_3\text{)}_3 \xrightarrow[\text{Ether (i.e., aprotic polar/Non polar solvent) S}_N2]{\text{HI}} \text{CH}_3\text{I} + \text{(CH}_3\text{)}_3\text{C-OH}$ </p> <p> $\text{CH}_3\text{-O-C(CH}_3\text{)}_3 \xrightarrow[\text{Protic polar S}_N1]{\text{H}_2\text{O HI}} \text{(CH}_3\text{)}_3\text{C-I} + \text{CH}_3\text{OH}$ </p> <p>primary tertiary</p>
Case IV:	<p> $\text{C}_6\text{H}_5\text{-O-CH}_3 \xrightarrow[\text{S}_N2]{\text{HI (g)}} \text{CH}_3\text{I} + \text{C}_6\text{H}_5\text{-OH}$ </p> <p> $\text{C}_6\text{H}_5\text{-O-CH}_3 \xrightarrow[\text{S}_N1]{\text{Conc HI}} \text{CH}_3\text{I} + \text{C}_6\text{H}_5\text{-OH}$ </p>

i) Reaction with acid chlorides and anhydrides:



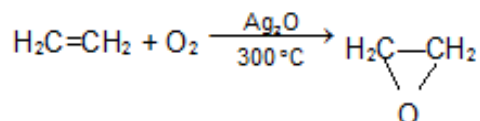
j) Electrophilic substitution reactions



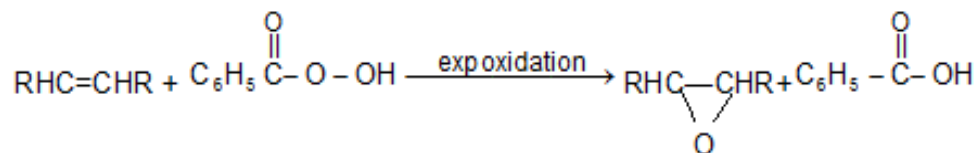
Epoxides or Oxiranes:

Preparation

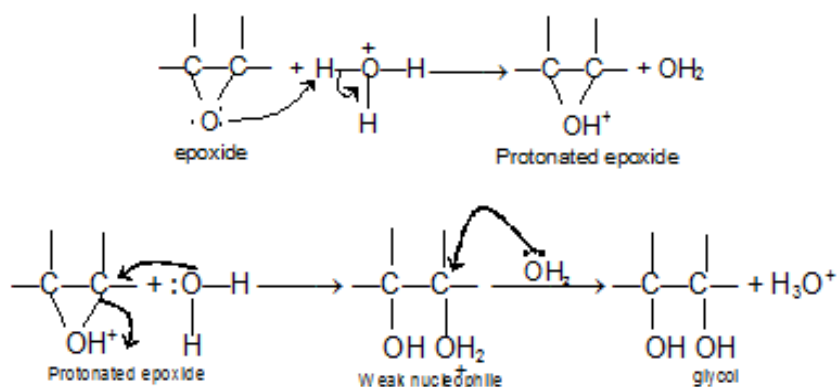
a) Oxidation of ethylene :



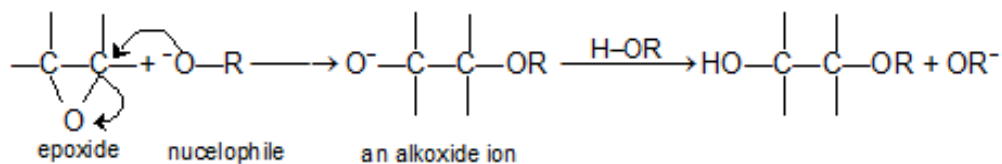
b) Epoxidation :



Acid catalysed ring opening



Base catalysed ring opening:

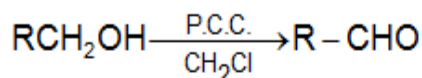
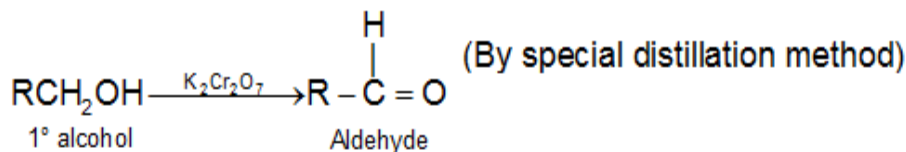


Aldehyde, Ketones and Carboxylic Acids

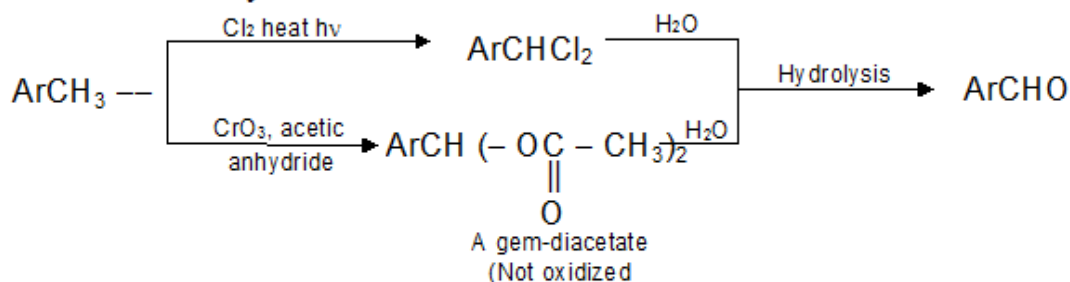
Aldehyde and Ketones

Preparation of Aldehydes

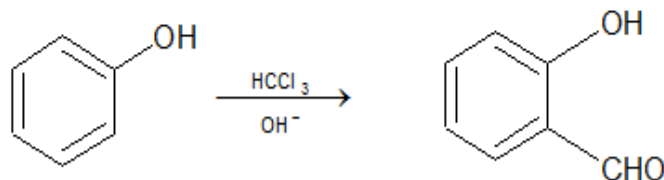
a. Oxidation of primary alcohols



b. Oxidation of methyl benzenes



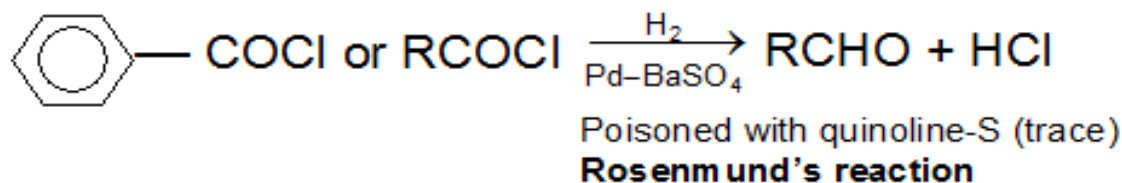
c. Reimer – Tiemann synthesis of phenolic aldehydes



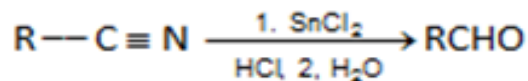
The electrophile is the dichlorocarbene, :CCl_2 , formation of carbene is an example of α -

elimination. $\text{OH}^- + \text{HCCl}_3 \xrightarrow{-\text{HCl}} \text{:CCl}_2$

d. Reduction of acid chlorides

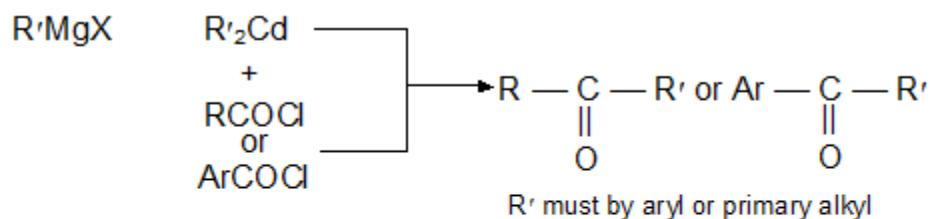


e. Stephen's Method

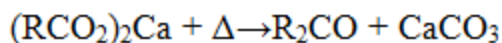


H_2O (Hydrolysis of intermediate) $\text{RCH}=\text{NH}$ to RCHO and NH_3

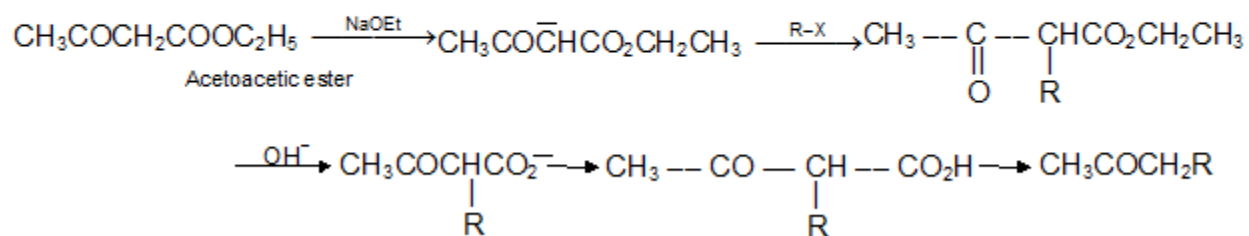
Preparation of Ketones:



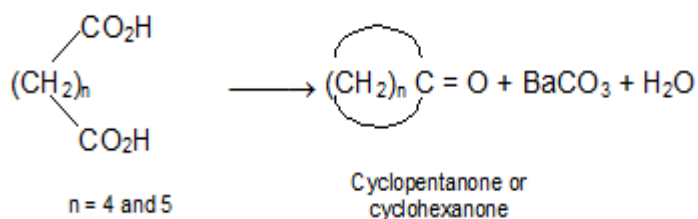
e) By heating the calcium salt of any monocarboxylic acid other than formic acid



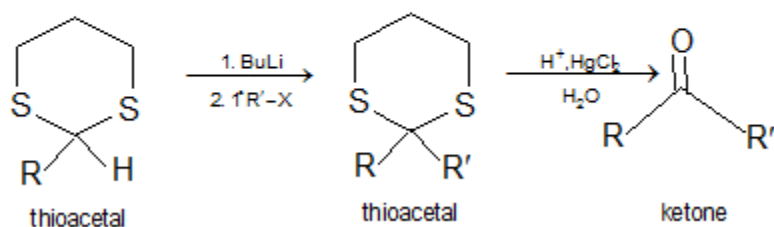
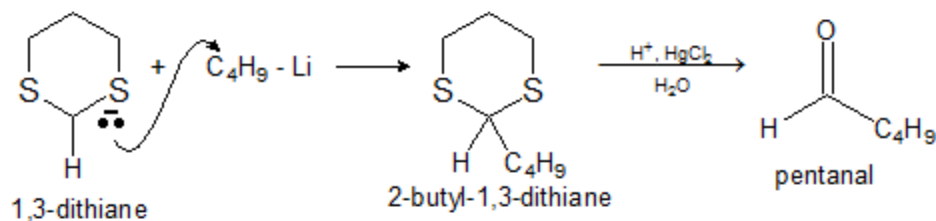
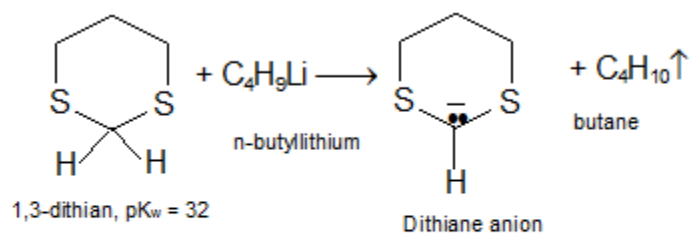
f) Acetoacetic ester synthesis of ketones



g) Ring Ketones from Dicarboxylic acids and their Derivatives:



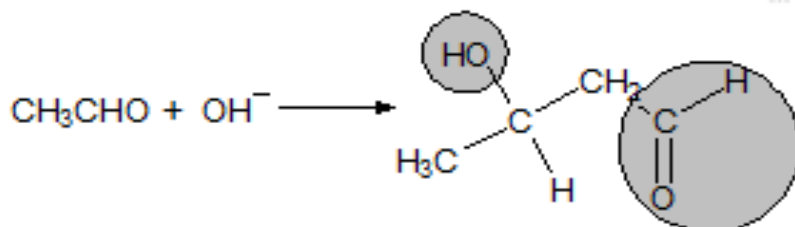
h) Synthesis of Ketones and Aldehydes Using 1,3-Dithianes:



Reactions of Aldehydes and Ketones:

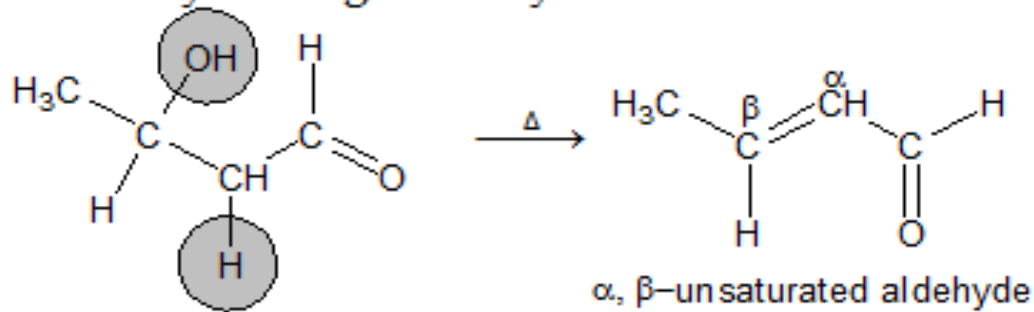
a) Aldol condensation

Aldehydes and ketones having alpha hydrogen atom:



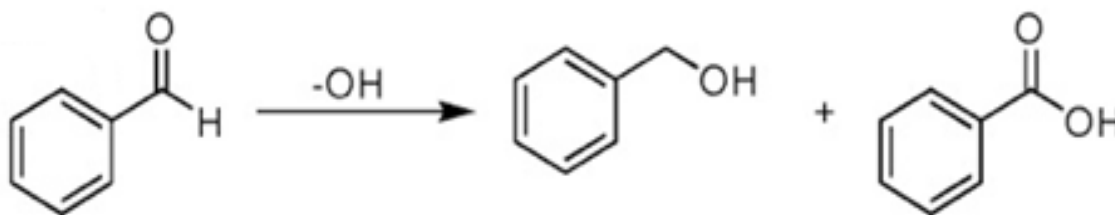
(Since it contains two functional groups aldehydes and alcohol)

Aldol easily undergoes dehydration

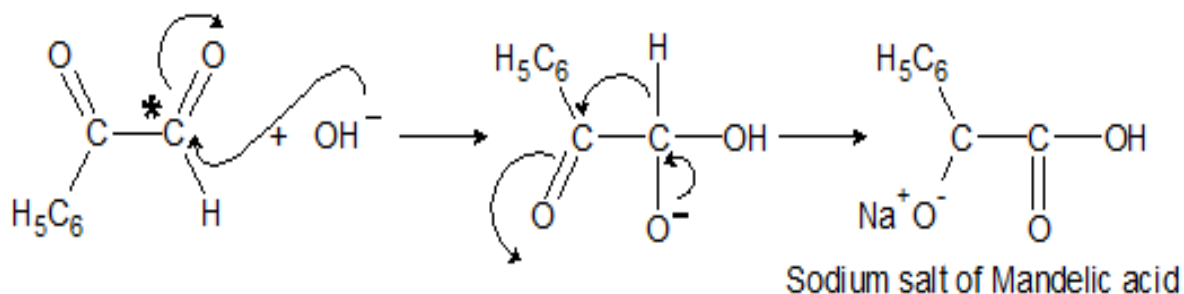


b) Cannizzaro reaction:

Aldehydes and ketones having no alpha hydrogen atom:

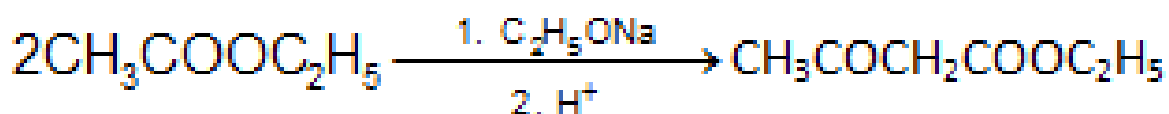


When two carbonyl groups are present within a molecule, think of intramolecular reaction. OH⁻ will attack more positively charged carbon. In this case, it is right >c=O group.



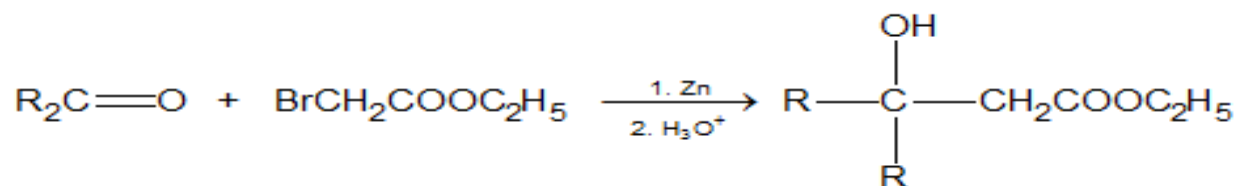
c) Formation of Keto Esters

Esters having α -hydrogen on treatment with a strong base e.g. C₂H₅ONa. Undergo self condensation to produce β -keto esters. This reaction is Claisen Condensation.



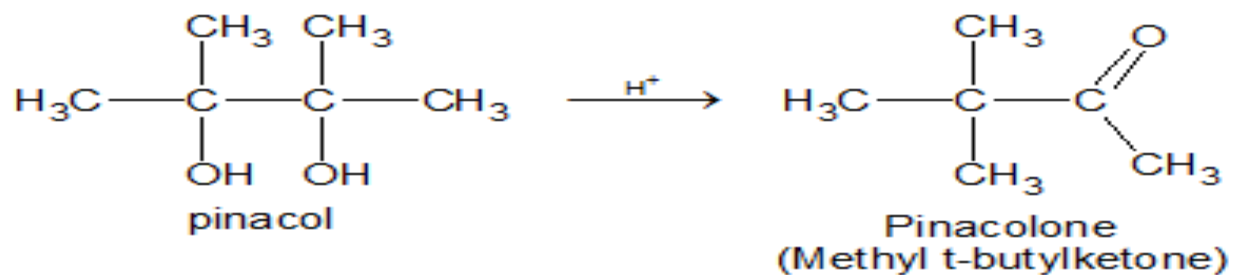
d) Reformatsky Reaction

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

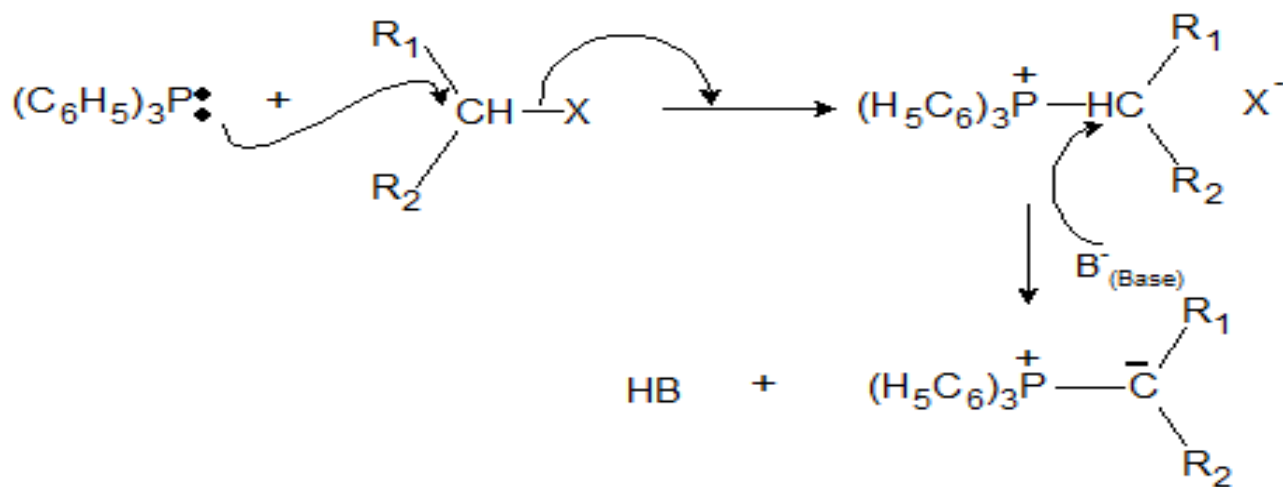
The acid catalysed rearrangement of 1,2 diols (Vicinal diols) to aldehydes or ketones with the elimination of water is known as pinacol pinacolone rearrangement.



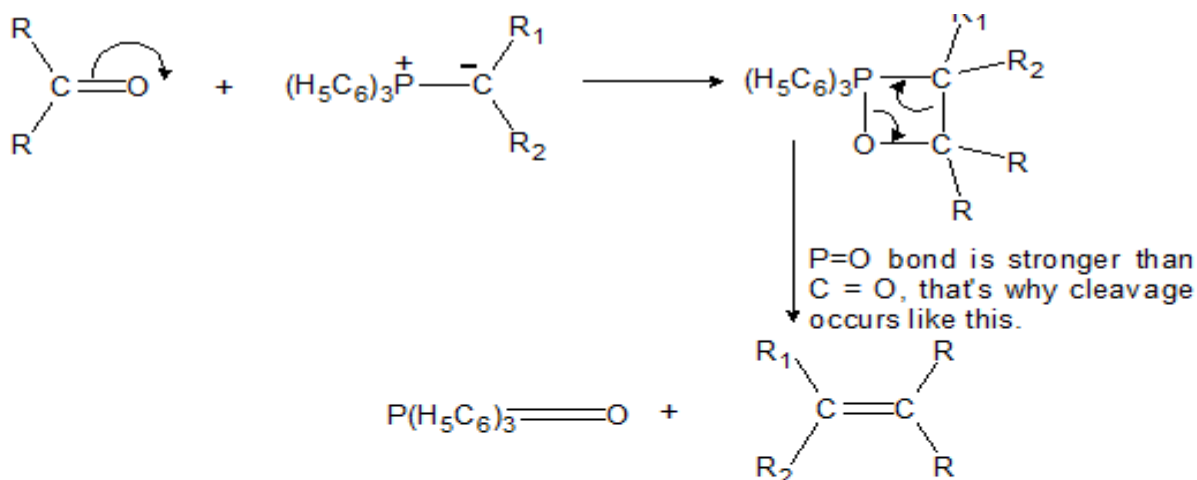
a) Wittig-Ylide Reaction

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.

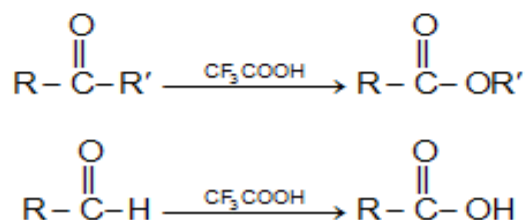
Preparation of Ylides



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

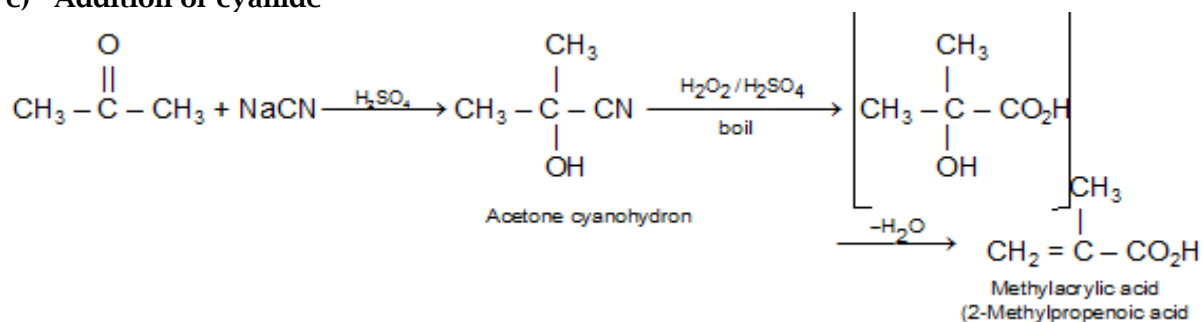


d) Baeyer-Villiger Oxidation

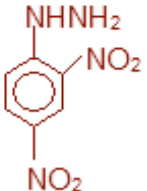
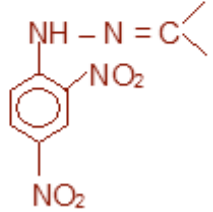


Above things happens in BVO (Bayer Villiger oxidation). Reagents are either per acetic acid or perbenzoic acid or pertrifluoroacetic acid or permonosulphuric acid.

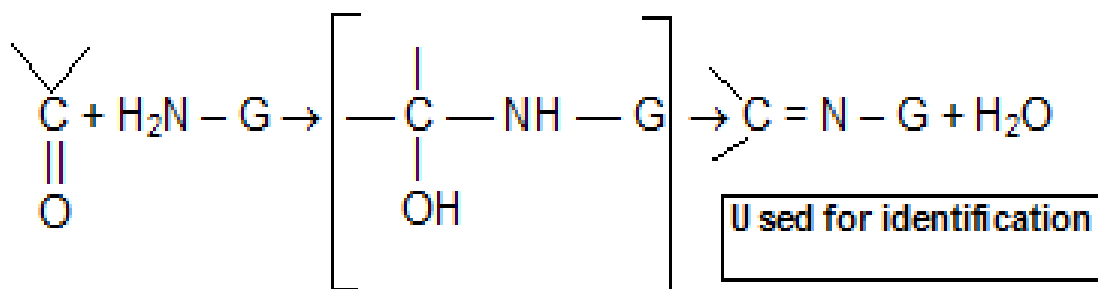
e) Addition of cyanide



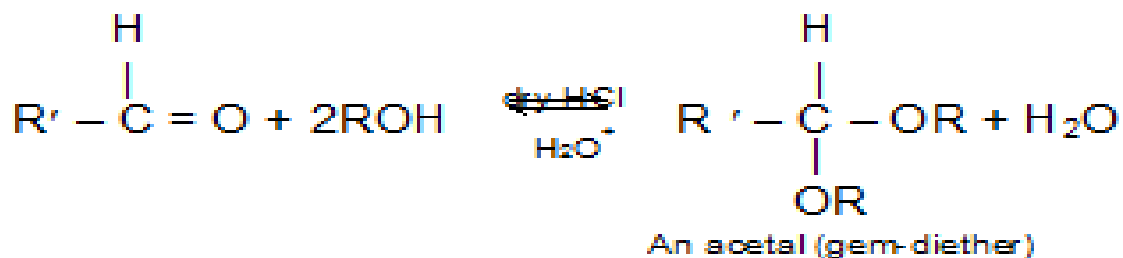
f) Addition of bisulfite:

	$H_2N - G$	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-dinitrophenylhydrazone (bright orange or yellow precipitate used for identifying aldehydes and ketones)

g) Addition of derivative of ammonia

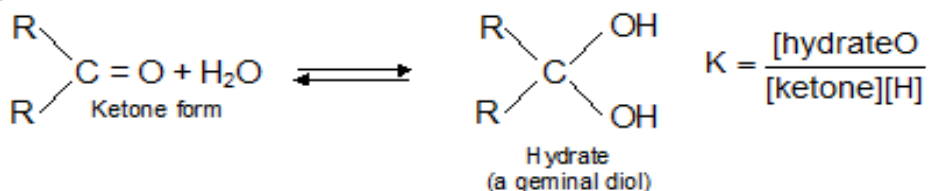


h) Addition of Alcohols; Acetal Formation

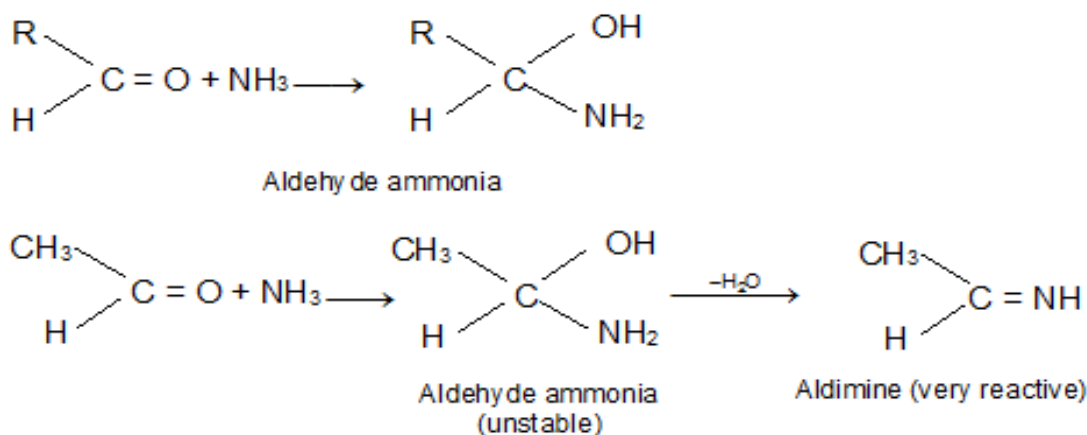


In H_3O^+ , RCHO is regenerated because acetals undergo acid catalyzed cleavage much more easily than do ethers. Since acetals are stable in neutral or basic media, they are used to protect the $\text{C}=\text{O}$ group.

i) Addition of Water

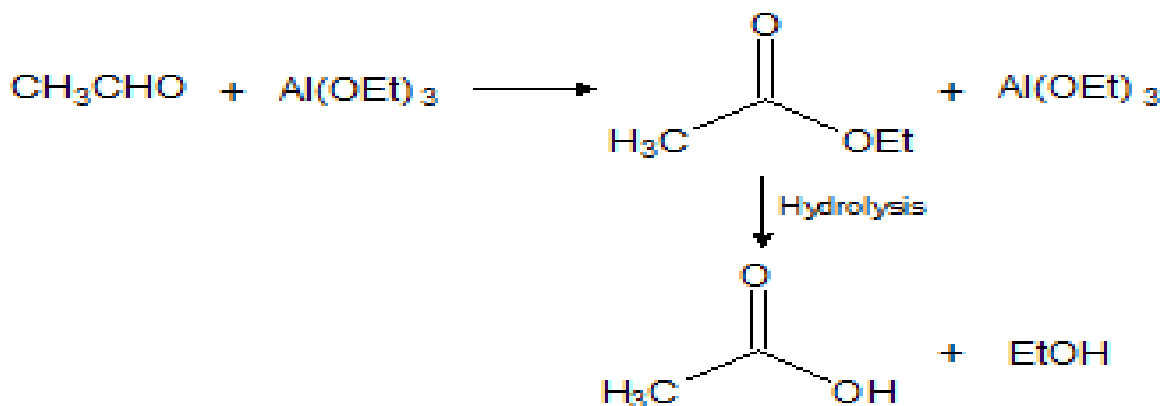


j) Addition of Ammonia:



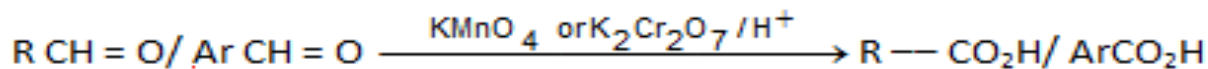
k) Tischenko reaction:

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.



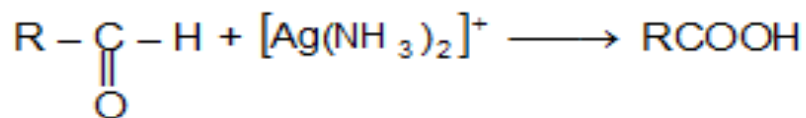
Oxidation of Aldehydes and Ketones

a)



b) Tollen's Reagent

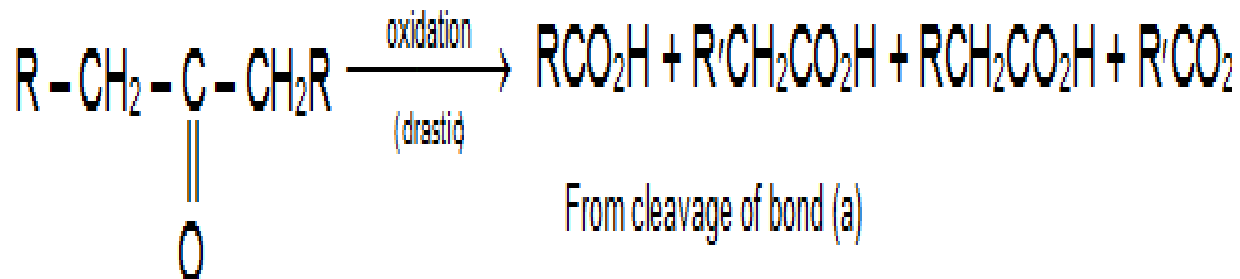
A specific oxidant for RCHO is $[Ag(NH_3)_2]^+$



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

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

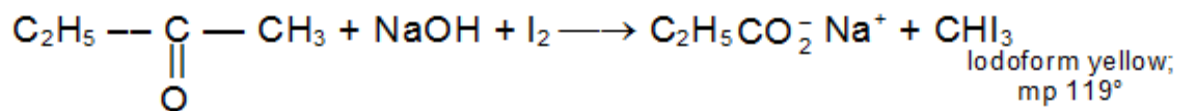
c) Strong Oxidants: Ketones resist mild oxidation, but with strong oxidants at high temperature they undergo cleavage of C - C bonds on either sides of the carbonyl group.



d) Haloform Reaction

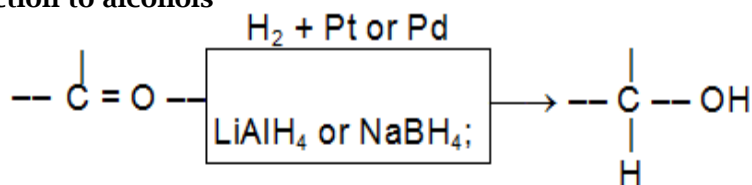
CH_3COR are readily oxidised by NaOI ($NaOH + I_2$) to iodoform, CHI_3 , and RCO_2Na

Example:



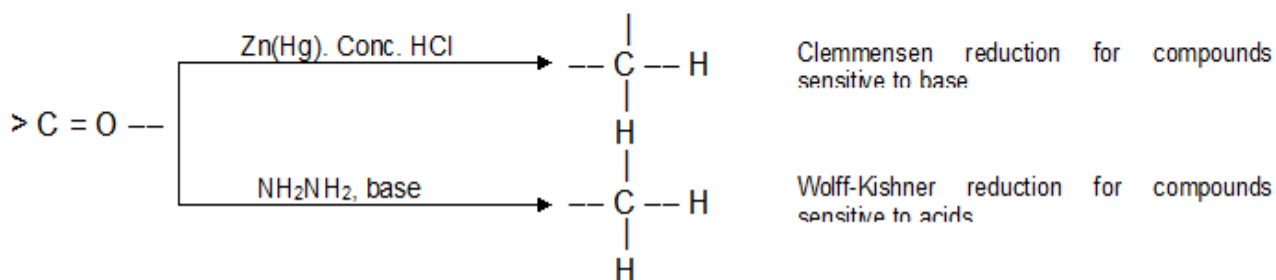
- Reduction

a) Reduction to alcohols



Aldehydes \rightarrow 1° alcohols; Ketones \rightarrow 2° alcohols

b) Reduction to hydrocarbons



Carboxylic Acids:

Carboxylic Acids	Common Names
HCOOH	Formic acid
CH ₃ COOH	Acetic acid
CH ₃ -CH ₂ -COOH	Propionic acid
CH ₃ (CH ₂)COOH	Butyric acid
CH ₃ (CH ₂) ₃ COOH	Valeric acid
CH ₃ (CH ₂) ₁₄ COOH	Palmitic acid
CH ₃ (CH ₂) ₁₆ COOH	Stearic Acid

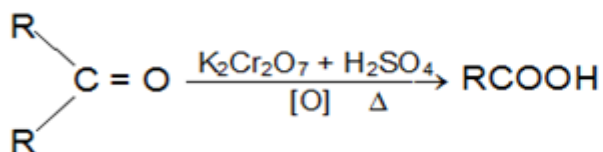
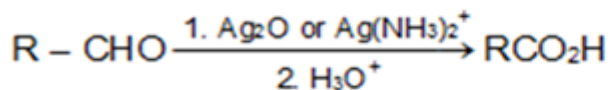
Physical Properties of Carboxylic Acids

- The first three acids are colourless, pungent smelling liquids.
- First four members are miscible in water due 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 a-position increases the acidity, eg. CCl₃COOH > CHCl₂COOH > ClCH₂COOH > CH₃COOH
- Increase in the distance of Halogen from COOH decreases the acidity e.g CH₃ - CH₂ - CH(Cl) - COOH > CH₃ - CH(Cl) - CH₂ - COOH > CH₂ - CH₂ - CH₂ - COOH

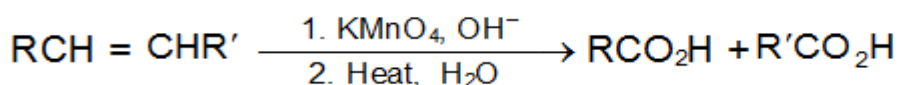
- Increase in the electro negativity of halogen increases the acidity.
FCH₂COOH > BrCH₂COOH > ICH₂COOH

Methods of Preparations of Carboxylic Acids

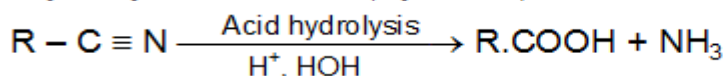
a. Oxidation of Aldehydes & Ketones



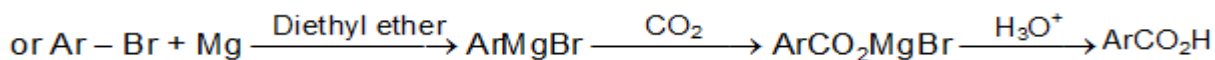
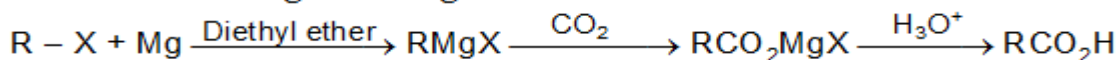
b. Oxidation of Alkanes:



c. Hydrolysis of Nitriles (Cyanides)

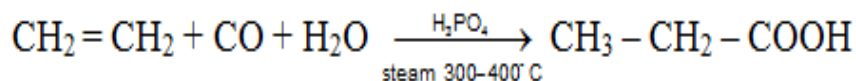


d. Carbonation of Grignard Reagents

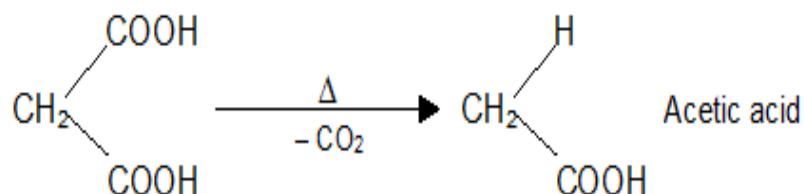


e. Koch Reaction:

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

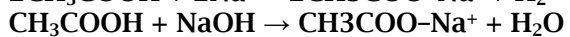
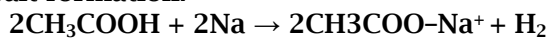


f. Heating Gem Dicarboxylic Acids:

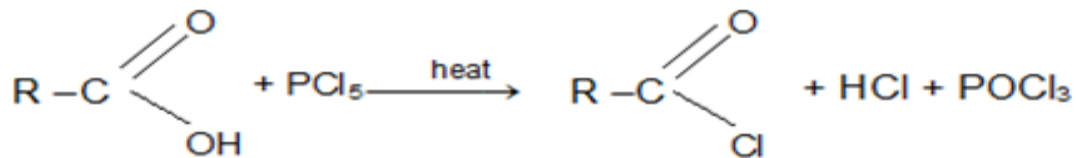
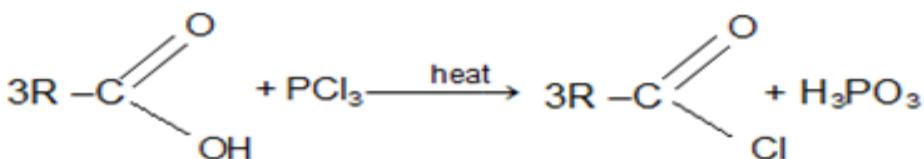
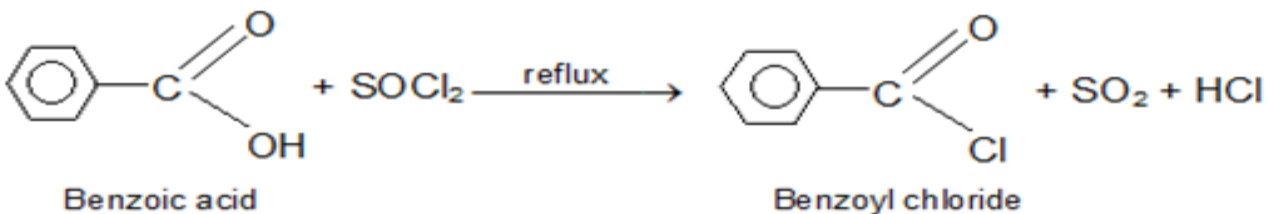


Chemical Reactions of Carboxylic Acids

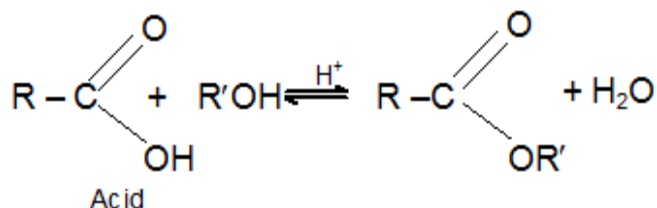
a. Salt formation:



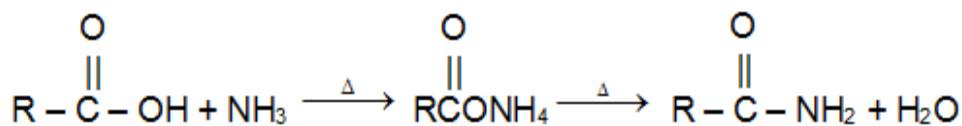
b. Conversion into Acid Chlorides:



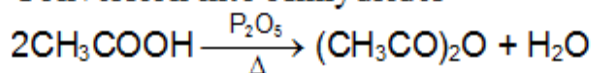
c. Conversion into Esters (Esterification)



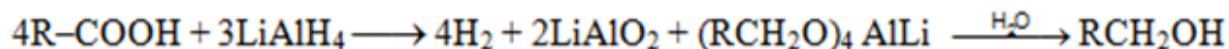
d. Conversion into Amides



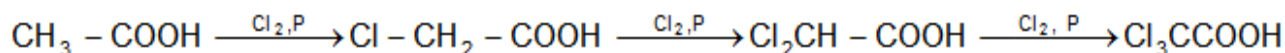
e. Conversion into Anhydrides



f. Reduction:

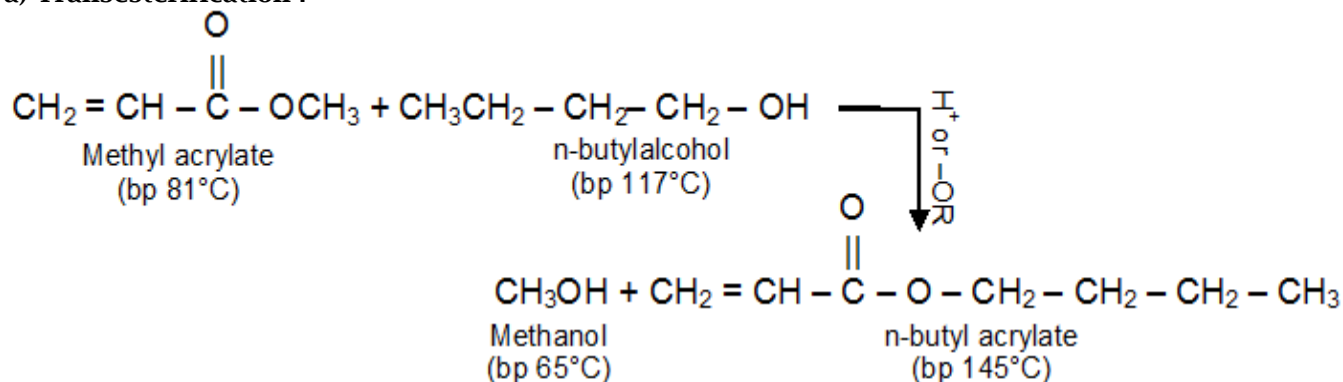


g. Halogenation:

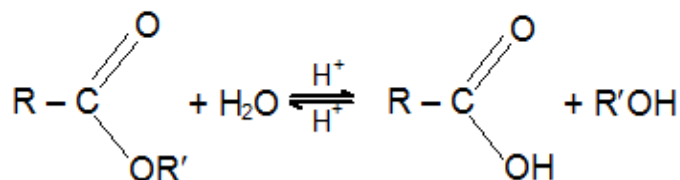


Esters

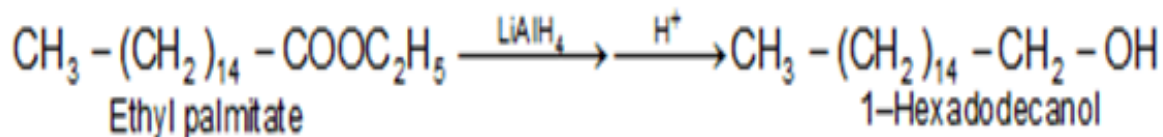
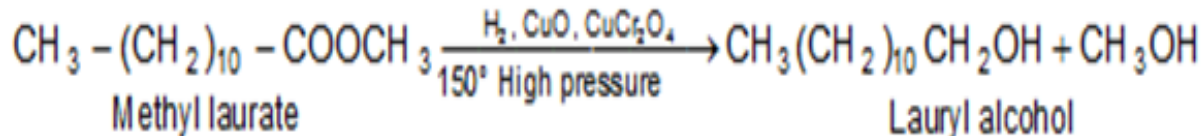
a) Transesterification :



b) Hydrolysis:

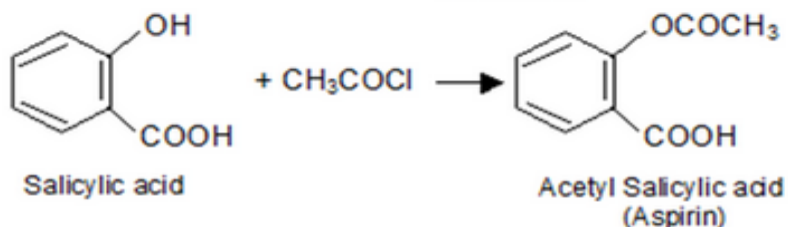
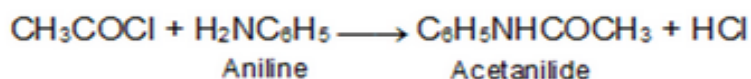
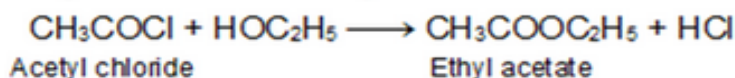


c) Reduction:

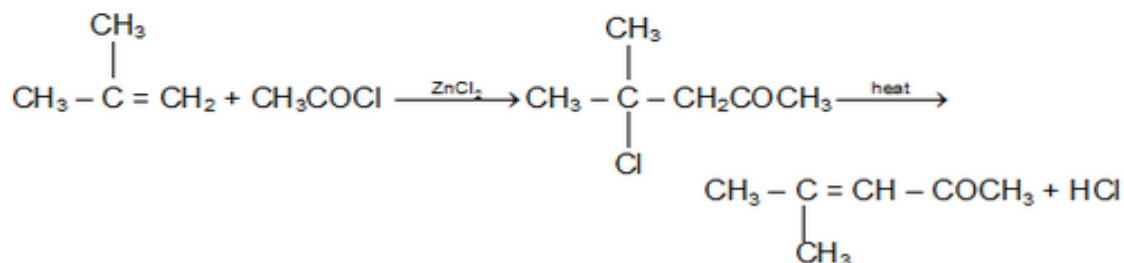


Acid Chlorides:

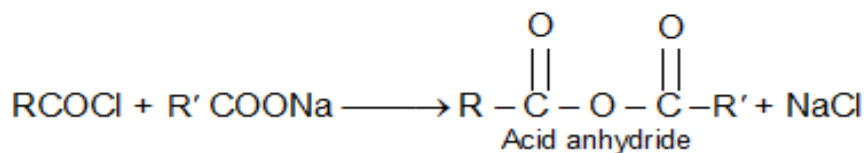
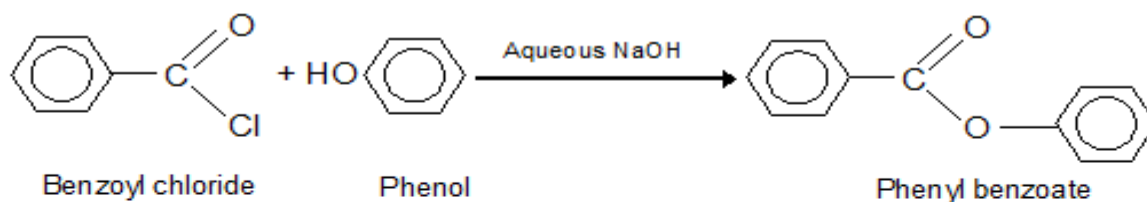
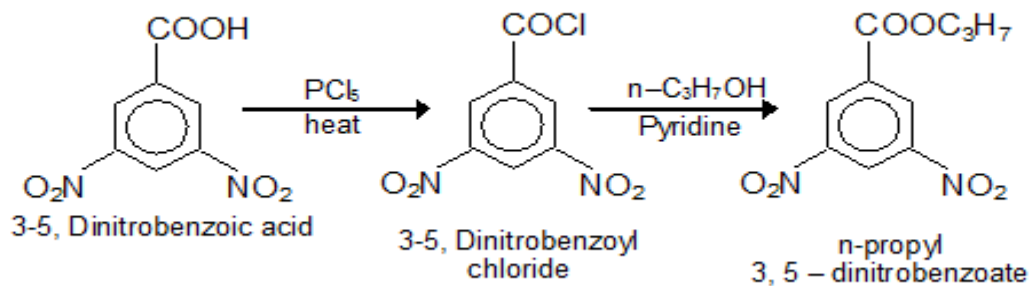
a) Acetylation



b) Reaction with Olefins:

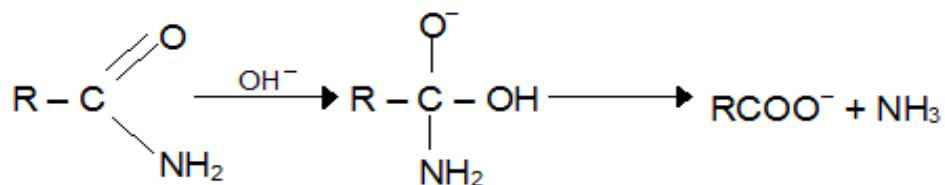
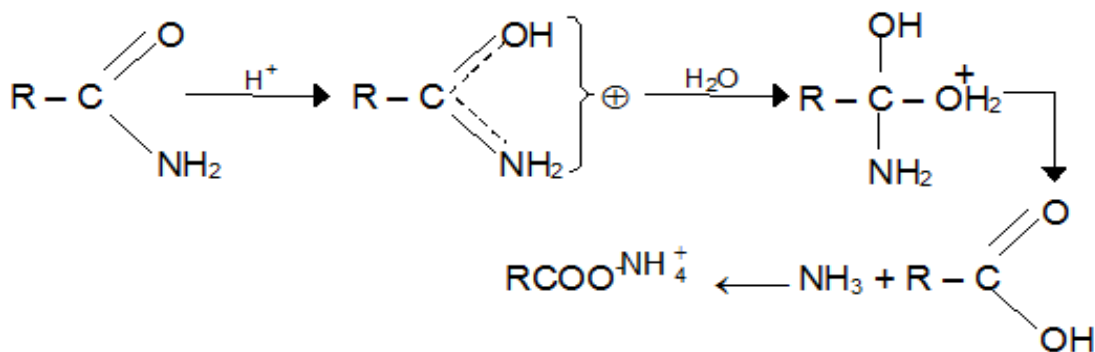


c) Conversion of Acid Chlorides into Acid Derivatives:

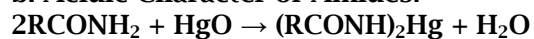


Amides

a. Hydrolysis:

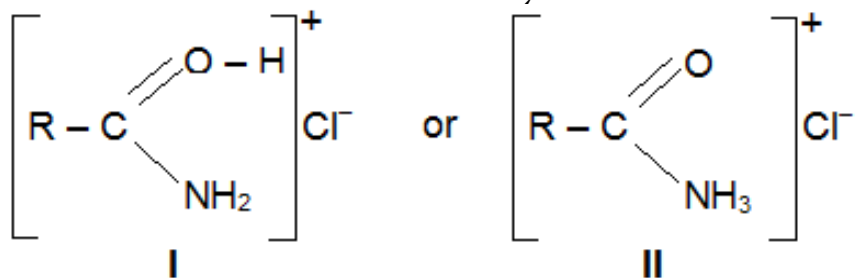


b. Acidic Character of Amides:

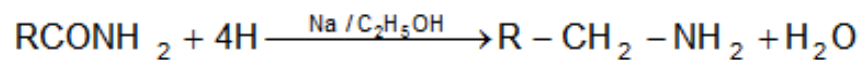


c. Basic Character of Amides:

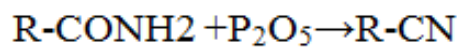
Amides are very feebly basic and form unstable salts with strong inorganic acids. e.g. RCONH_2HCl . The structure of these salts may be I or II



d. Reduction:



e. Reaction with Phosphorus Pentaoxide:



f. Reaction with Nitrous Acid:

