Name Reaction

Topic : Halogen Derivatives of Alkanes

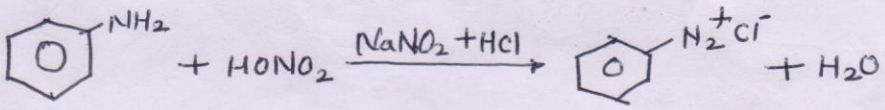
1. Sandmeyer's reaction

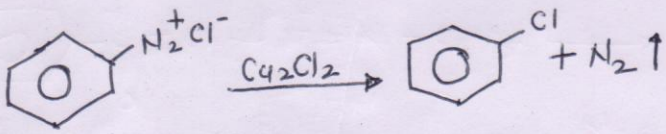
Replacement of diazonium group by chloride or bromide using cuprous salt is called Snadmeyer's reaction.

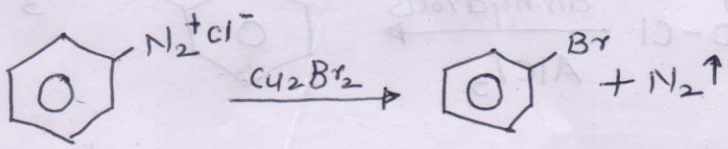
nium : nitrogen carries +ve charge.

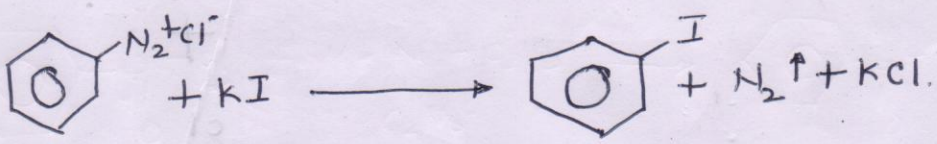
Carbonium : Carbon carries +ve charge

(1) Primary amine reacts with HNO3 to give diazonium cation.

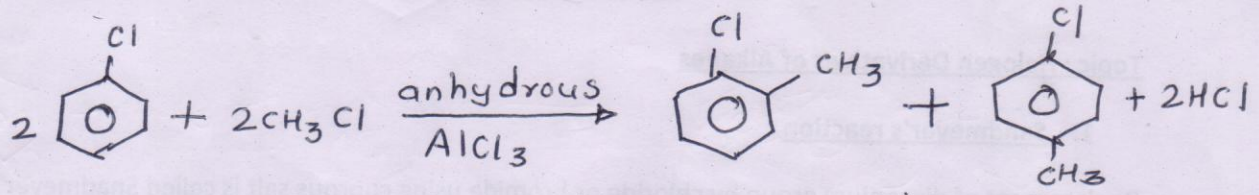








2. Frields Craft's alkylation.

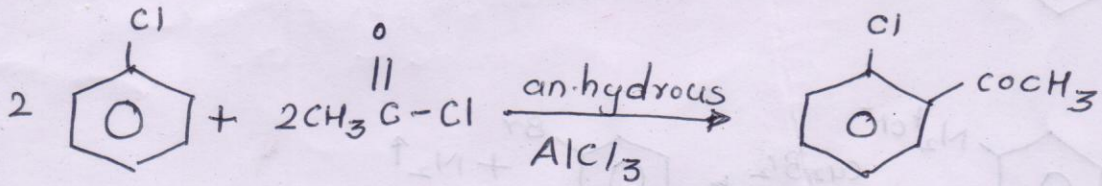


1-chloro-2-methyl benzene
Minor

1-chloro-4methyl benzene

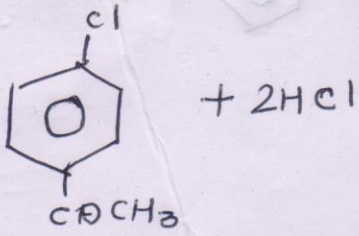
Introduction of alkyl/acyl groups in benzenering.

3. Friedl's craft's acetylation.



2-chloroacetophenone

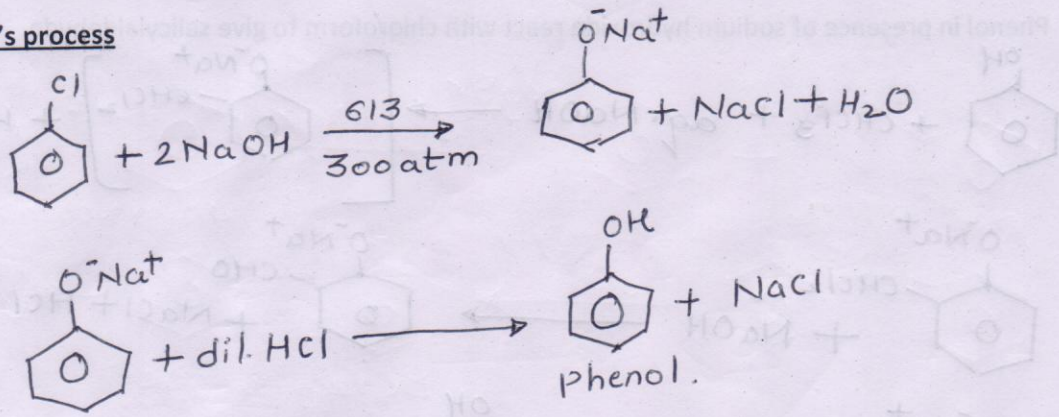
+



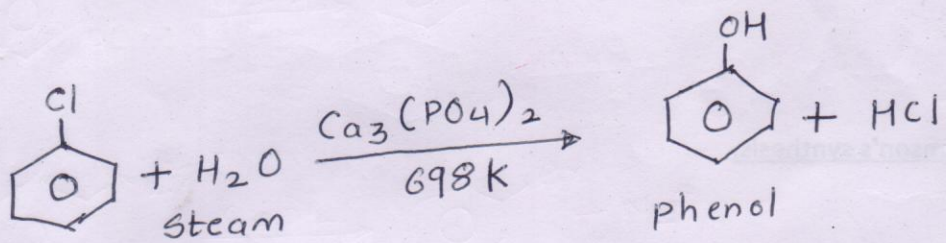
4-chloroacetophenone (minor)

Topic : Alcohols, Phenols and ethers.

1. **Dow's process**



2. **Rasching Reaction.**

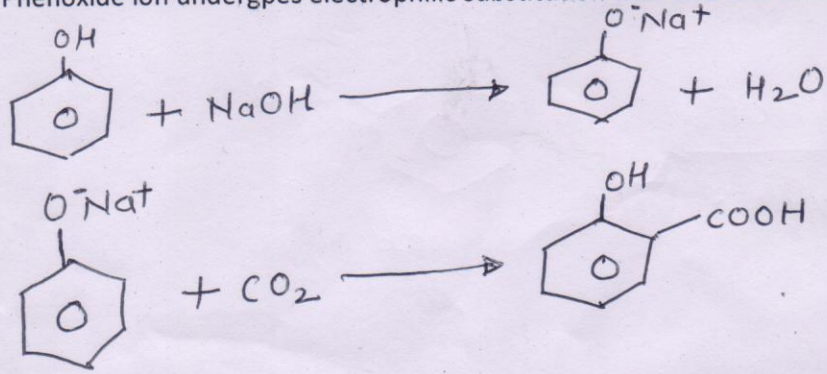


chlorobenzene.

3. **Kolbe's reaction.**

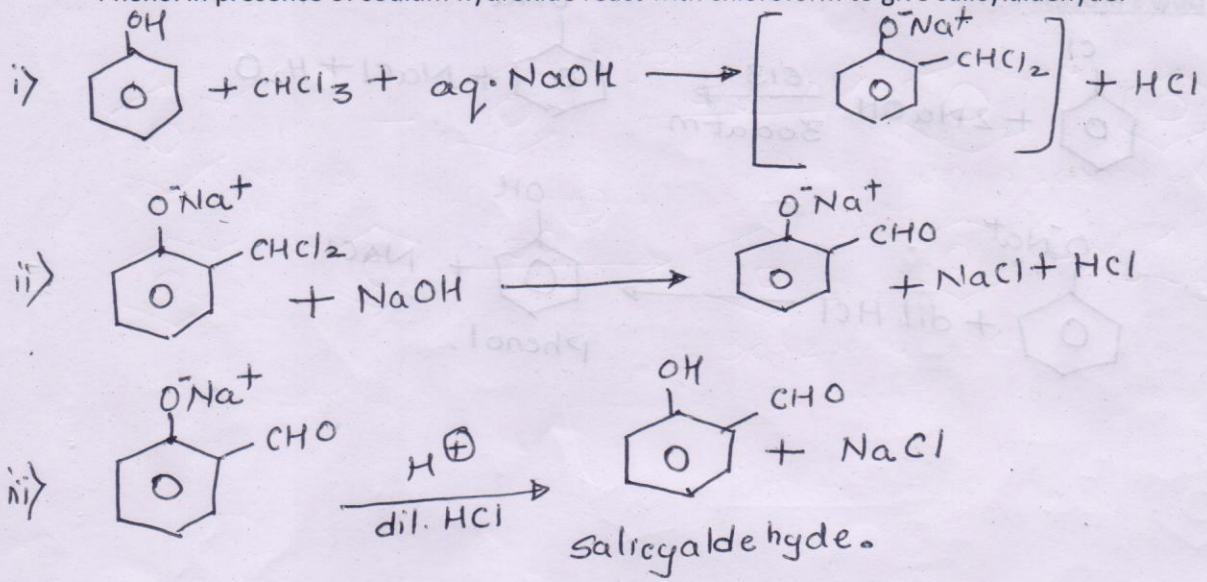
Phenol react with sodium hydroxide to give sodium phenoxide.

Phenoxide ion undergpes electrophilic substitution with CO2 and form salicylic acid.

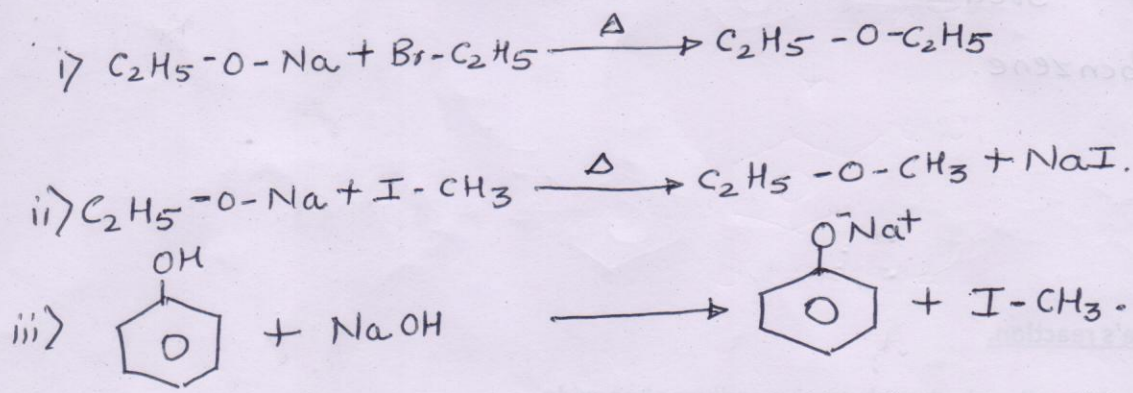


4. Reimwr-Tiemann Reaction

Phenol in presence of sodium hydroxide react with chloroform to give salicylaldehyde.



5. Williamson's synthesis.



Topic : Aldehyse, Ketones and Ethers

1. **Stephen's reaction**

It is useful to prepare aldehyde .

Nitriles are reduced by imine hydrochloride by SnCl2 + HCl which on hydrolysis gives aldehyde.

i) $R-C\equiv N + 2[H] \xrightarrow{SnCl_2 + dil.\ HCl} R-CH=NH\cdot HCl$

imine.

ii) $R-CH=NH\cdot HCl \xrightarrow{H_2O} R-\overset{H}{\underset{|}{C}}=O + NH_4Cl.$

Nitriles are selectively reduced by diisobutylaluminuium hydride (DIBAL-H) to imine followed by acid hydrolysis to aldehyde.

i) $H_3C-CH=CH-CH_2-C\equiv N \xrightarrow{DIABLH} H_3C-CH=CH-CH_2-CH=NH.$

imine.

ii) $H_3C-CH=CH-CH_2-CH=NH \xrightarrow{H_3O^{\oplus}}$

$$H_3C-CH=CH-CH_2-\overset{H}{\underset{|}{C}}=O + NH_3$$

pent-3-enal.

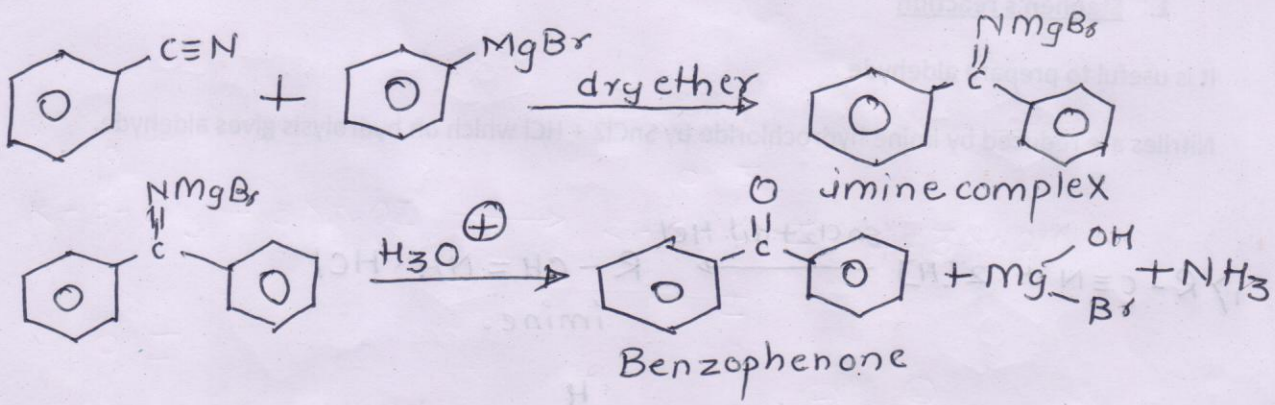
Esters are patially reduced to aldehyde with DIABL-H.

It is carried out at 195 K to avoid further eaction to alcohol.

$$CH_3-[CH_2]_{10}-\overset{O}{\overset{||}{C}}-OCH_3 \xrightarrow[H_3O^{\oplus}]{DIBALH\ in\ toluene} CH_3-[CH_2]_{10}-\overset{O}{\overset{||}{C}}-H$$

Dodecanal

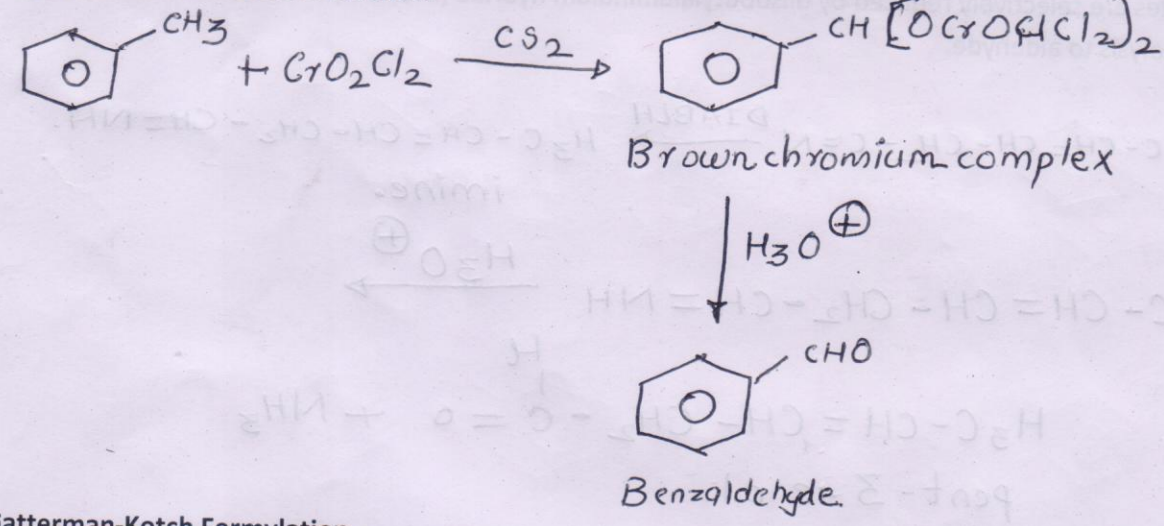
Nitrile react with Grignard Reagent in presence of Dry ether to give imine complex which on acid hydrolysis gives ketone.



Etard reaction

Chromyl chloride convert methyl group to chromium complex which on hydrolysis gives corresponding aldehyde.

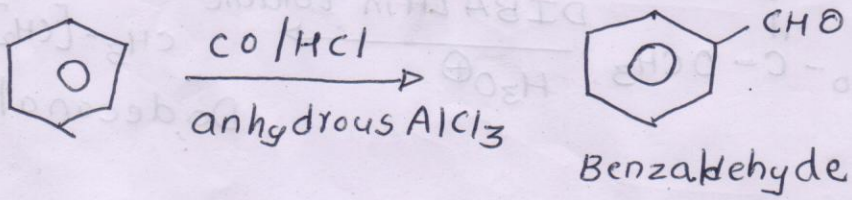
This reaction is called Etard reaction.



Gatterman-Kotch Formylation.

Formyaltion is carried out when benzene or its derivative is treated under high pressure with CO and HCl in presence of anhydrous $AlCl_3$ and Cuprous Chloride Cu_2Cl_2 and it gives benzaldehyde.

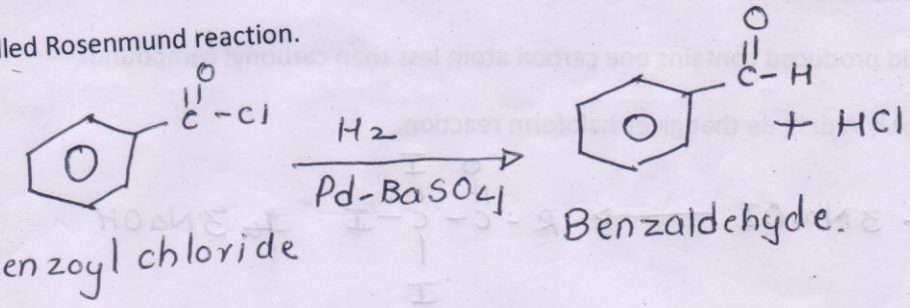
It is widely used to synthesize aryl aldehyde.



Rosenmunde Reaction

An acyl chloride is hydrogenated over catalysy Pd/BaSO4 to give aldehyde.

This is called Rosenmund reaction.

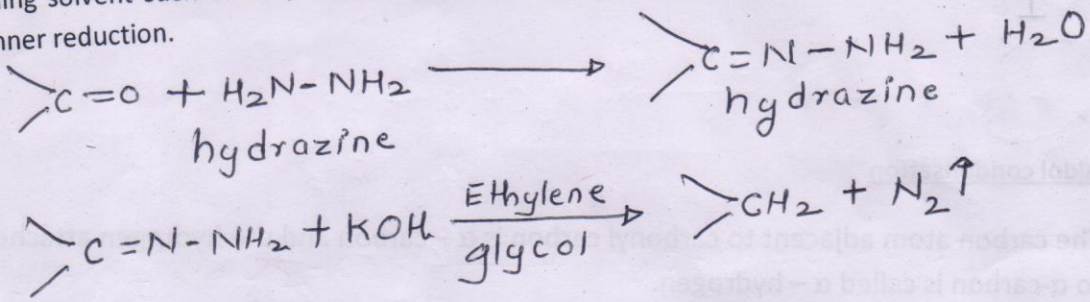


Benzoyl chloride

Benzaldehyde.

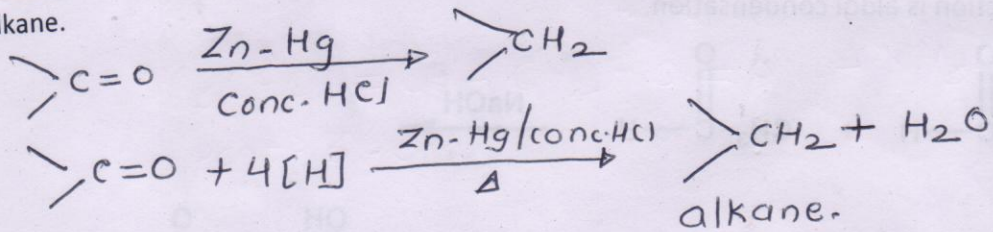
Wolf-Kishner reduction.

Aldehyde and Ketone when heated with hydrazine and KOH or potassium tert-butoxide in high boiling solvent such as ethylene glycol/diethylene glycol give alkane. This reduction is called wolf-kishner reduction.



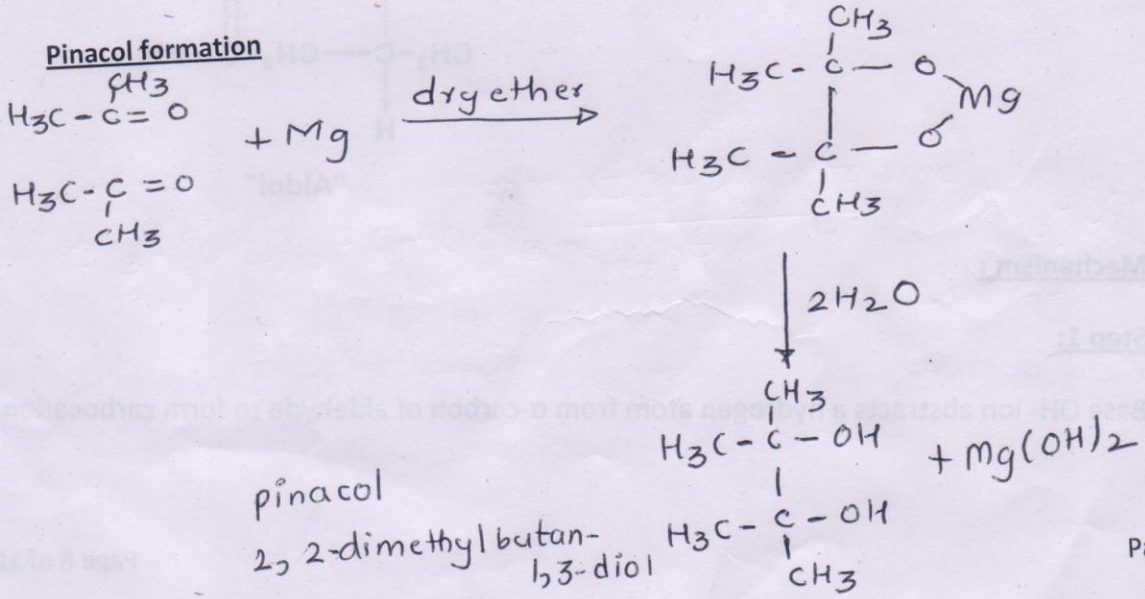
Clemmensen reduction

Aldehyde and ketone which are not sensitive to acids when heated with Zn-Hg and conc. HCl give alkane.



alkane.

Pinacol formation



pinacol

2, 2-dimethyl butan-
1, 3-diol

Haloform reaction.

A ketone having a methyl group attached to Carbonyl carbon is oxidized by NaOI to give sodium salt of carbonyl acid and haloform.

The carboxylic acid produced contains one carbon atom less than carbonyl compound.

Acetaldehyde is only Aldehyde that gives haloform reaction.

i) $R-\overset{O}{\overset{\|}{C}}-CH_3 + 3NaOI \longrightarrow R-\overset{O}{\overset{\|}{C}}-\overset{I}{\underset{I}{\overset{|}{\underset{|}{C}}}}-I + 3NaOH$

ii) $R-\overset{O}{\overset{\|}{C}}-\overset{I}{\underset{I}{\overset{|}{\underset{|}{C}}}}-I + NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^{\ominus}Na^{\oplus} + CHI_3$

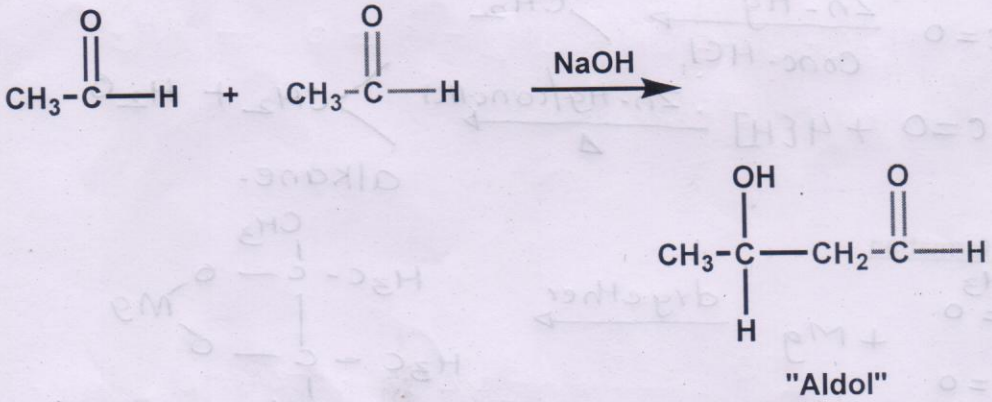
Iodoform.

Aldol condensation

The carbon atom adjacent to carbonyl carbon is α – carbon and the hydrogen attached to α-carbon is called α – hydrogen.

In presence of dilute base like NaOH,KOH or Na_2CO_3 two molecules of an aldehyde or acetone having α –hydrogen add together to give hydroxyl aldehyde or aldol.

This reaction is aldol condensation.

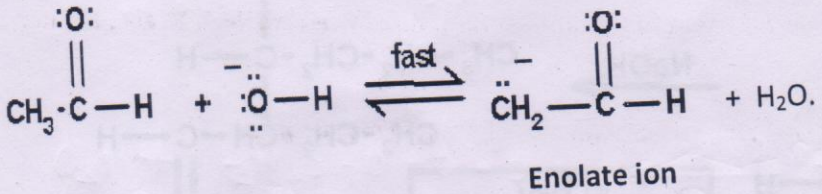


"Aldol"

Mechanism :

Step 1:

Base OH- ion abstracts a hydrogen atom from α-carbon of aldehyde to form carbocation.

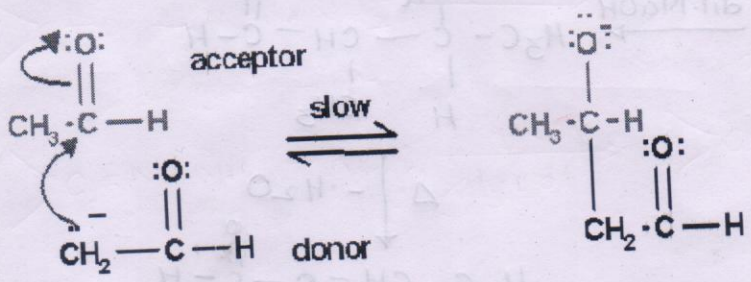


Enolate ion

Step 2 :

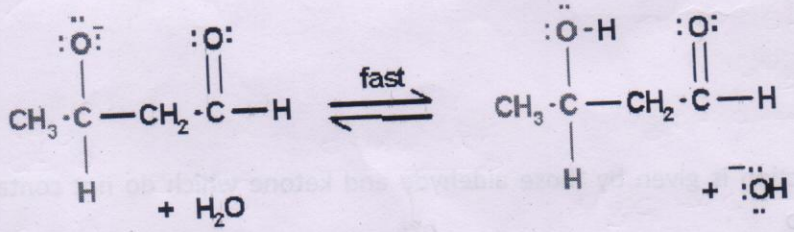
The nucleophilic carbanion or enolate ion attacks electrophilic carbonyl carbon of second aldehyde molecule to form intermediate an alkoxide ion.

A new C-C bond is formed.



Step 3:

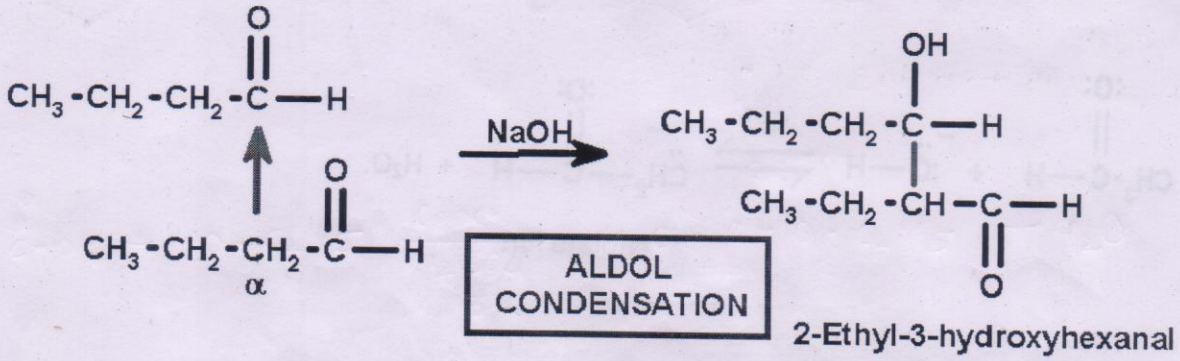
Alkoxide ion abstracts a ion from water to form β-hydroxy aldehyde.Base OH- ion is regenerated.



The carbonyl group plays two roles in this reaction:

1. It provides a site for nucleophilic attack by the enolate ion.

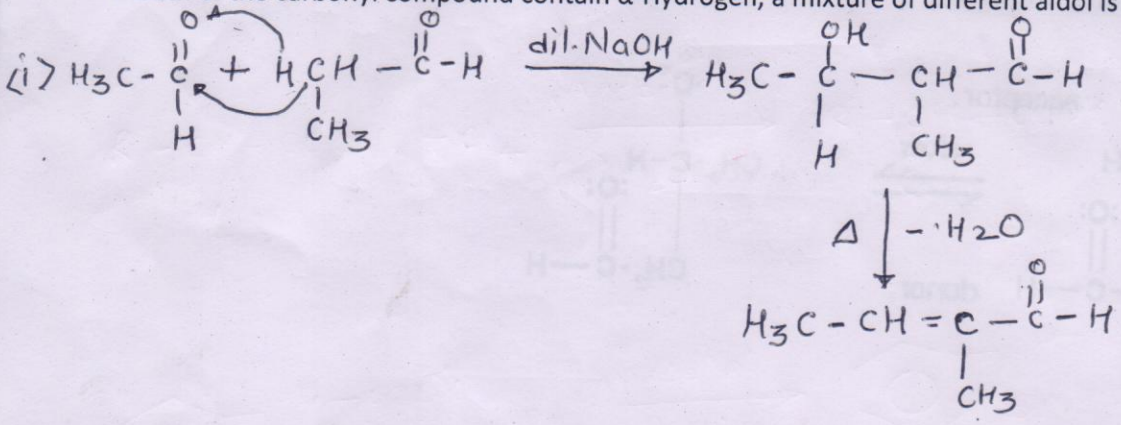
2. It makes the a-hydrogens sufficiently acidic to enable the formation of reasonable concentrations of enolate ion.



Crossed Aldol Condensation.

An aldol condensation between two different carbonyl compound is called crossed or mixed aldol condensation.

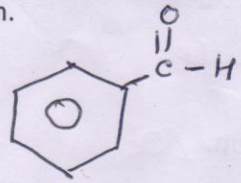
If both of the carbonyl compound contain α-Hydrogen, a mixture of different aldol is obtained.



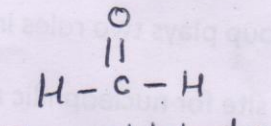
2-methyl-but-2-enal.

Cannizzaros reaction

Type of reactant : The reaction is given by those aldehyde and ketone which do not contain α-hydrogen atom.



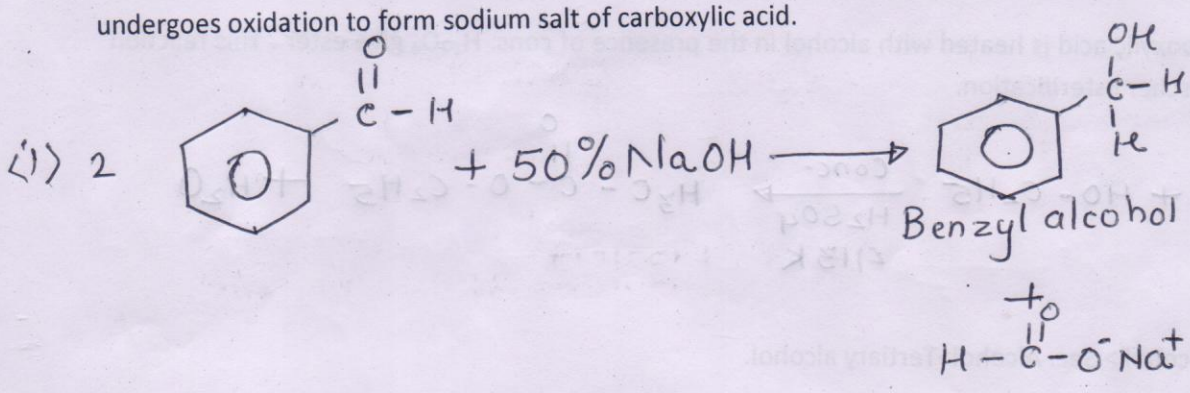
Benzaldehyde

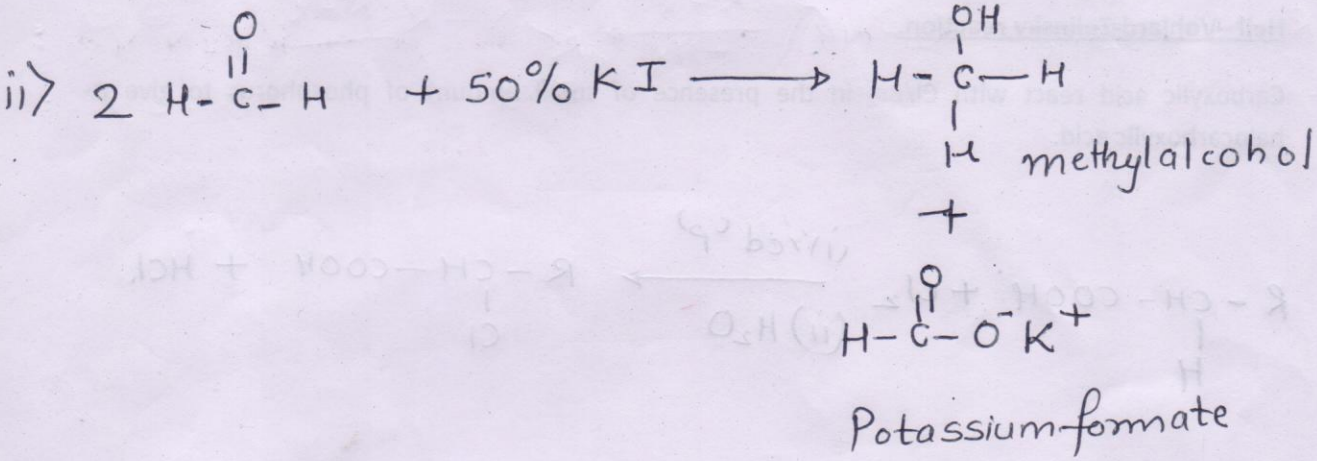


Formaldehyde

Conc. NaOH/KOH/50% NaOH.

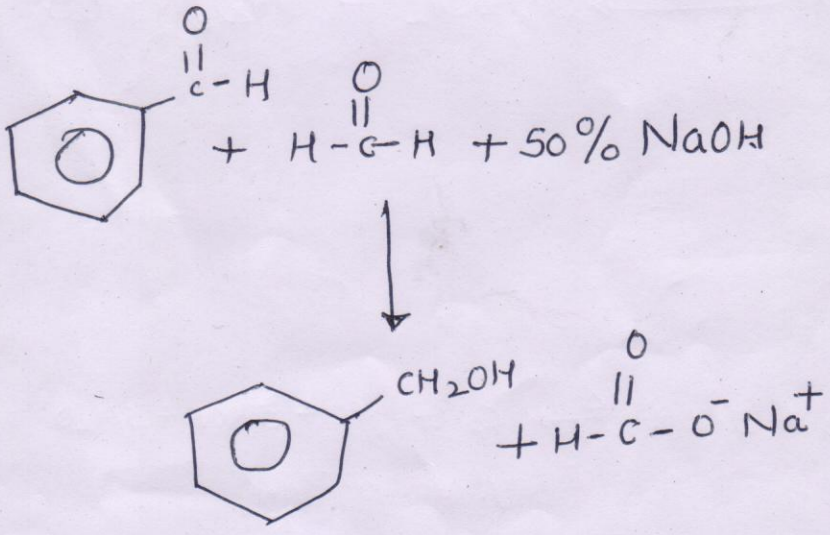
It is self redox reaction in which 1 molecule undergoes reductionto form alcohol and other molecule undergoes oxidation to form sodium salt of carboxylic acid.





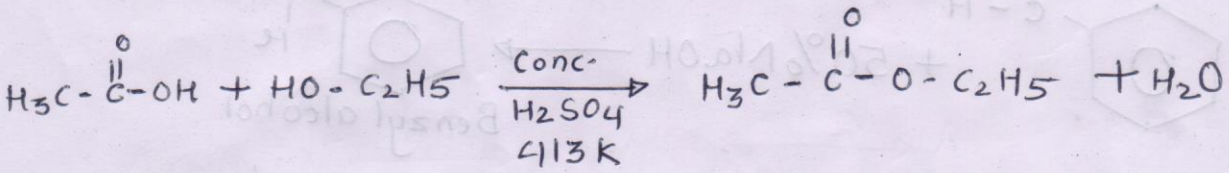
Crossed Cannizaroo's reaction.

Two different Aldehyde not having α-hydrogen undergoes disproportation in presence of conc. NaOH to give 4 product.



Fischer esterification .

When carboxylic acid is heated with alcohol in the presence of conc. H_2SO_4 give ester . This reaction is called Fischer esterification.

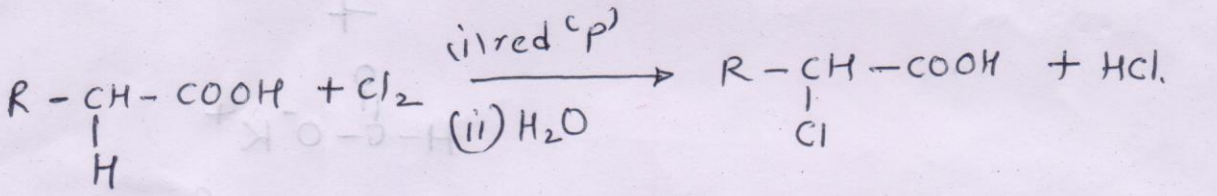


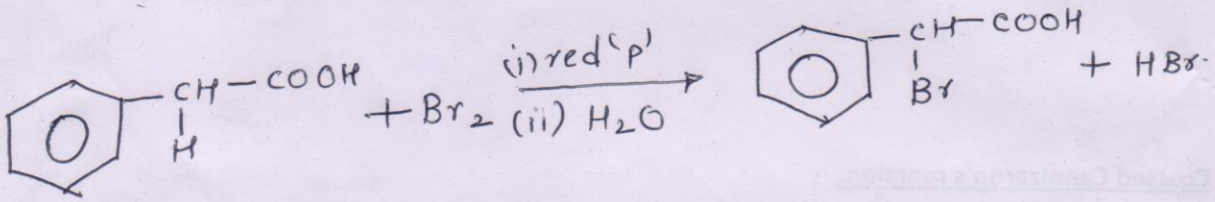
Primary alcohol > Sec. Alcohol>Tertiary alcohol.

HCOOH > CH_3COOH > RCH_2COOH > $R_2CHCOOH$ > R_3CCOOH.

Hell –Vohlard-Zelinsky reaction.

Carboxylic acid react with Cl/Br_2 in the presence of small amount of phosphorus to give α-halocarboxylic acid.

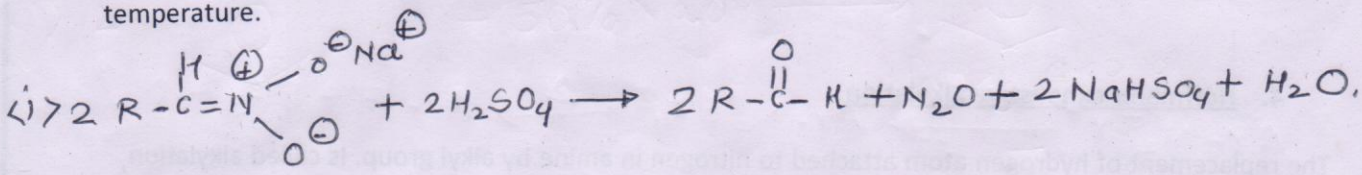




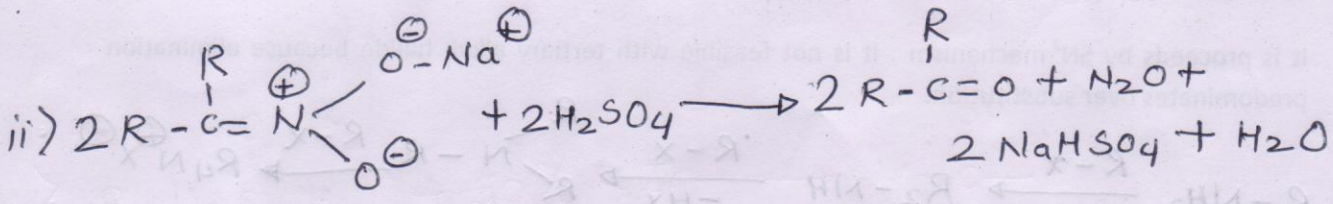
Nitrogen Containing Compounds.

1. **Nef-carbonyl synthesis.**

When the solution of sodium salt of acid /nitronic acid is acidifed with 50% H_2SO_4at room temperature.



i) $2\,R-CH=N(O^{\ominus})-O^{\ominus}\,Na^{\oplus} + 2H_2SO_4 \longrightarrow 2\,R-C(=O)-H + N_2O + 2NaHSO_4 + H_2O$



ii) $2\,R-C(R)=N(O^{\ominus})-O^{\ominus}\,Na^{\oplus} + 2H_2SO_4 \longrightarrow 2\,R-C(R)=O + N_2O + 2NaHSO_4 + H_2O$

2. **Gabriel phthalimide synthesis.**

Phthalimide react with ethenolic potassium hydroxide to give potassium salt of phthalimde.

In this step N-H protons is removed to give imide ion.

It is then heated with alkyl halide to give N-alkylphthlimide which on alcoholic hydrolysis gives primary amine.

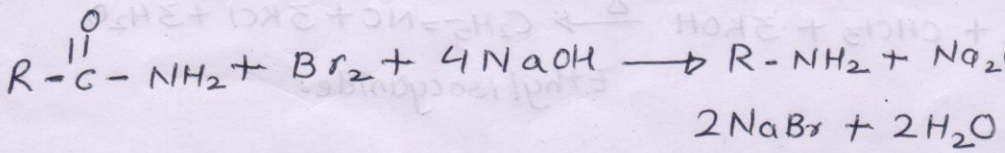
Limitation : Aromatic primary amine cannot cannot prepared because aryl halide don't undergoes nucleophilic substitution with the anion formed by phthalimide.

3. **Hoffmann bromaide degradation**

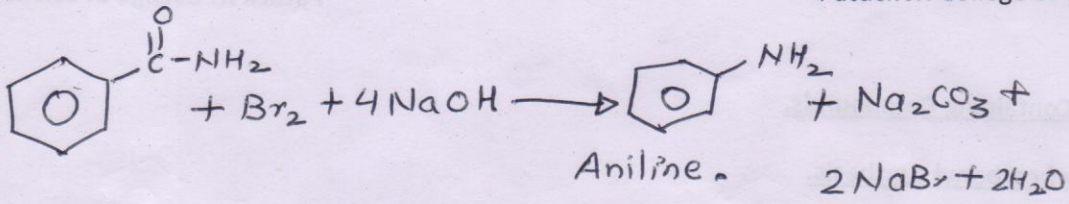
When amide is treated with bromine and aqueous /alcoholic NaOH it gives primary amine.

Thnis reaction is useful for decreasing the length of carbon chain by one carbon atom.

It is an example of intermaolecular arrangement and involeves the migration of alkyl/aryl from carbonyl carbon to the adjacent nitrogen atom.



$R-C(=O)-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

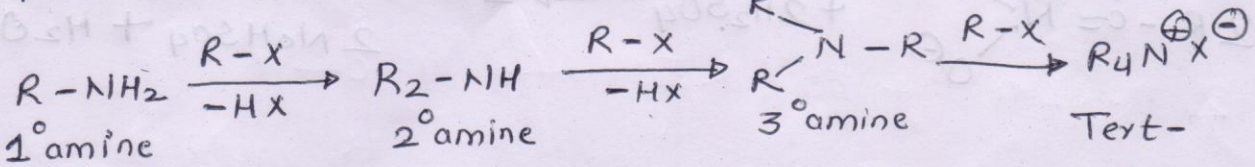


Aniline.

4. Hoffmann-exhaustive alkylation.

The replacement of hydrogen atom attached to nitrogen in amine by alkyl group. Is called alkylation of amine.

It is proceeds by SN^2 mechanism . It is not feasible with tertiary alkyl; halide because elimination predominates over substitution.

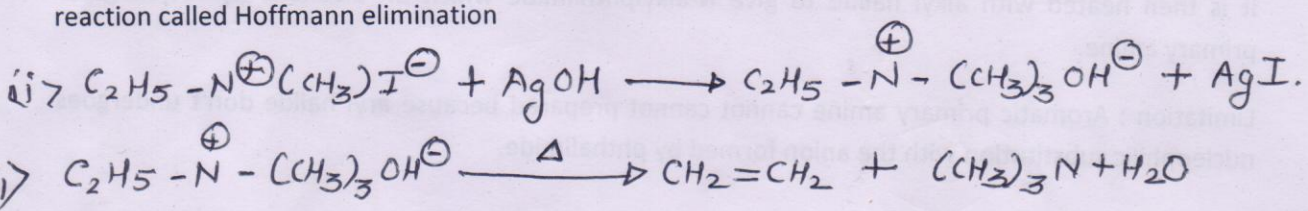


1° amine 2° amine 3° amine Tert-ammonium halide.

5. Hoffmann elimination.

When tetralkyl ammonium halide is heated with moist AgOH, it gives quaternary ammonium hydroxide it gives quaternary ammonium hydroxide which deliquescent crystalline solid which are strongly basic NaOH/KOH.

Quaternary ammonium hydroxide on strong heating undergoes elimination to give alkenbe the reaction called Hoffmann elimination

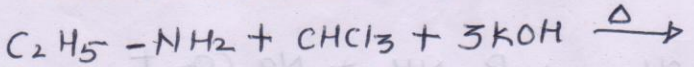


6. Hoffmann's carbylamines test.

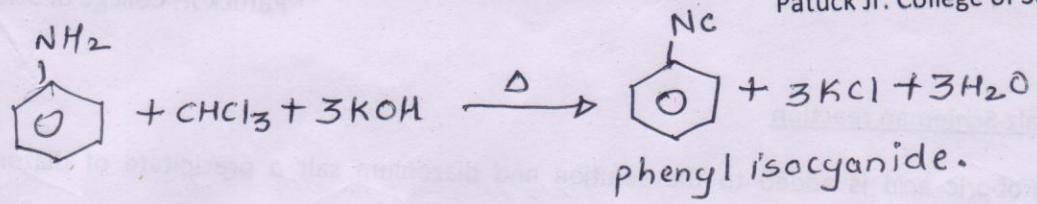
Isocyanide test.

Aliphatic/aromatic amine on heating wioth chloroform and alcoholic KOH gives foul smelling alkyl isocyanide or carbylamine.

Secondary/tertiary amines do not gives this reaction.



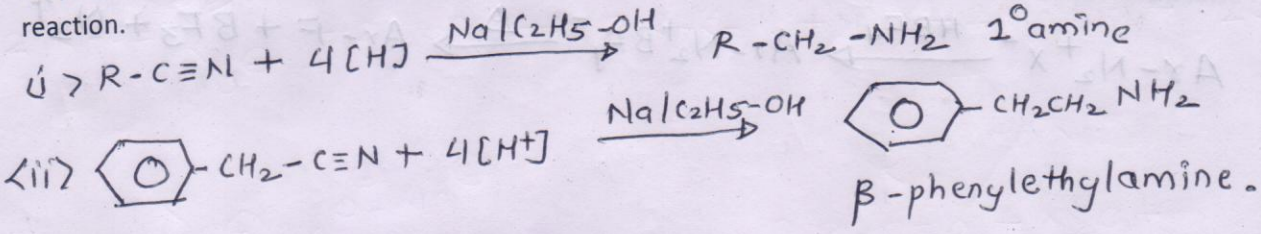
Ethyl isocyanide.



phenyl isocyanide.

7. Mendius reaction

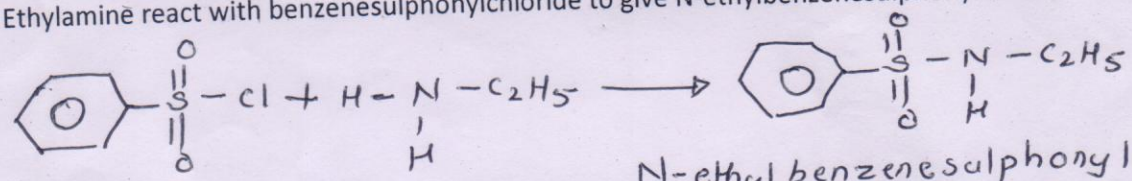
Alkyl cyanide on reduction by Na/Ethyl alcohol gives primary amine. This reaction is called mendius reaction.



β-phenylethylamine.

8. Hinsberg's Test.

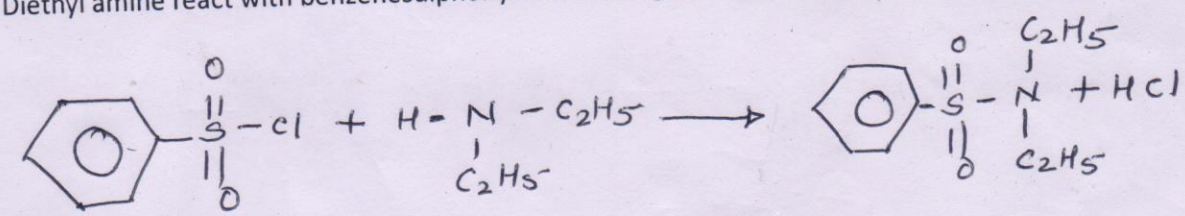
Ethylamine react with benzenesulphonylchloride to give N-ethylbenzenesulphonylamide.



N-ethyl benzenesulphonyl amide + HCl.

The hydrogen attached to nitrogen in sulphonanmide is strongly acidic due to the presence of strong electron withdrawing sulphenyl group. It dissolves in aqueous KOH to gives clear solution which on acification regenerates insoluble amide.

Diethyl amine react with benzenesulphonylchloride to give N,N diethylbenzene sulphonyl amide.



Which does not conatain any hydrogen attached to nitrogen . Hence it is not acidic and does not dissolve in aqueous KOH.

Triethyl amine does not contain H- attached to nitrogen. Hence it does not react with benzene sulphonyl chloride.

9. Balz-Schieman reaction

When fluroboric acid is added to the solution and diazonium salt a precipitate of diazonium fluroborate is obatained.

Dry dizazonium fluroborate on heating decomposes to give aryl Fluoride. This reaction is called Balz-Schiemann reaction.