

Maa Omwati Degree Collage Hassanpur

NOTES

Subject: - Organic Chemistry

B.Sc. Sem: - 4th

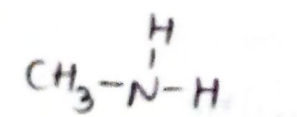
Seesion: 2020-21

Prepared By:

Mr. Devender

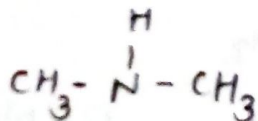
Amines:-

The nitrogenous compounds which may be regarded as derivatives of ammonia in which one or more hydrogen atoms have been replaced by alkyl or aryl groups.



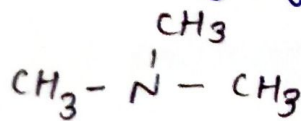
Methylamine

(1°) primary



Dimethylamine

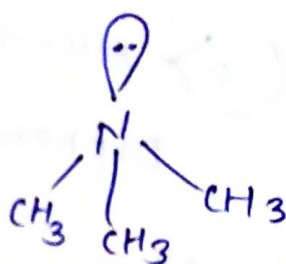
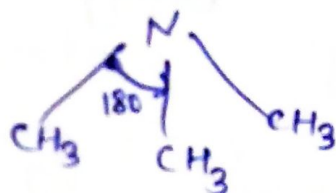
(2°) Secondary



Trimethylamine.

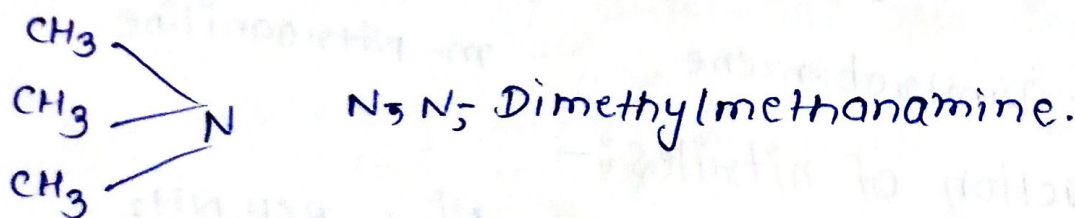
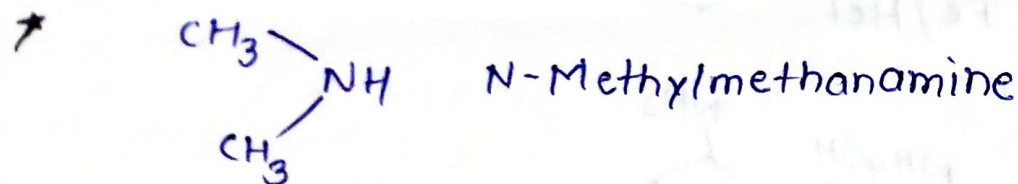
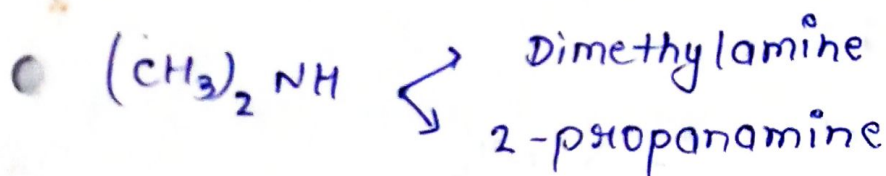
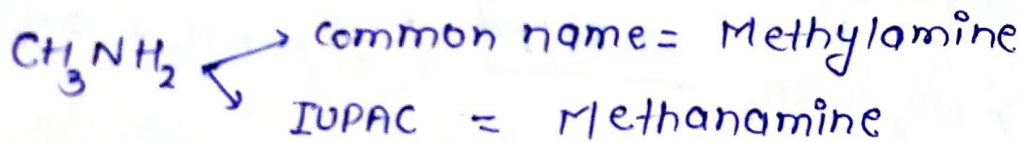
(3°) Tertiary

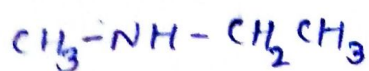
Structure of Amines:-



sp^3 hybridised
(pyramidal shape)

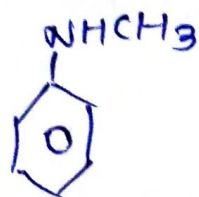
Nomenclature of Amines:-





N-Methylethanamine

Aromatic Amine:-



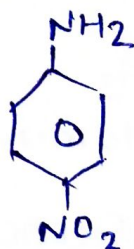
N-Methylaniline

N-Methylbenzenamine



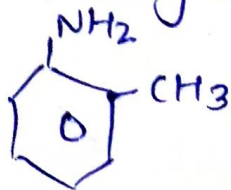
Aniline

Benzenamine

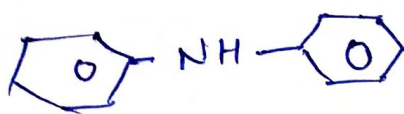


p-Nitroaniline

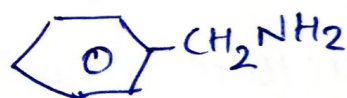
4-Nitrobenzenamine



2-Methylaniline



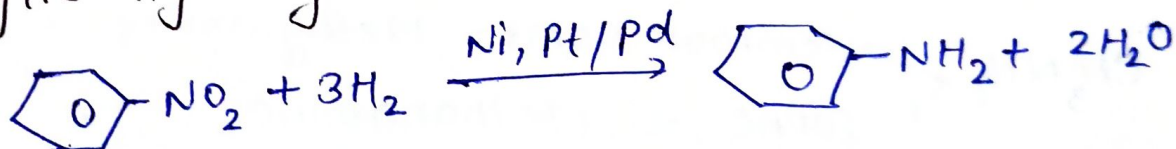
Diphenylamine



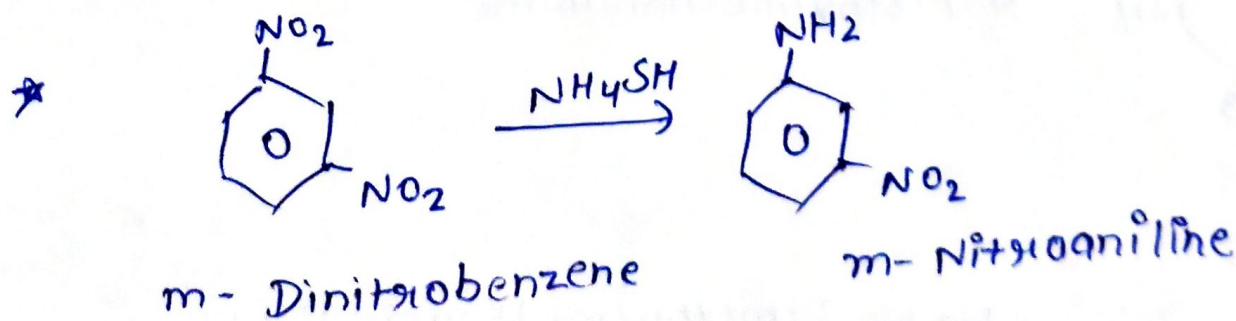
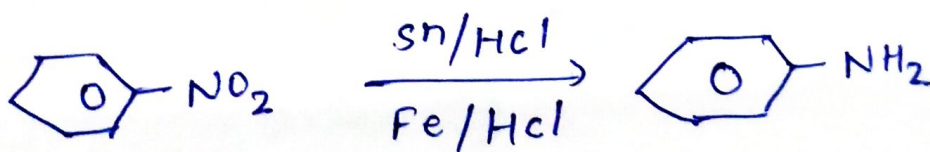
Benzylamine

Preparation of Amines:-

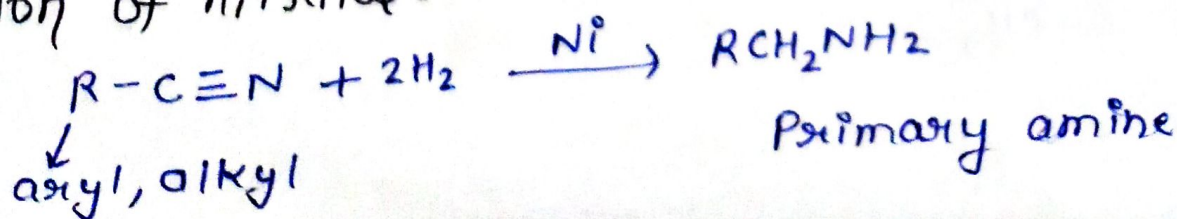
(i) Catalytic hydrogenation:-

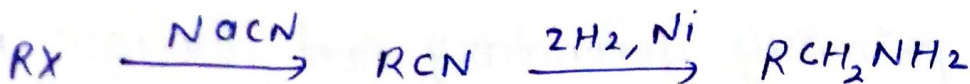


(ii) chemical reduction:-

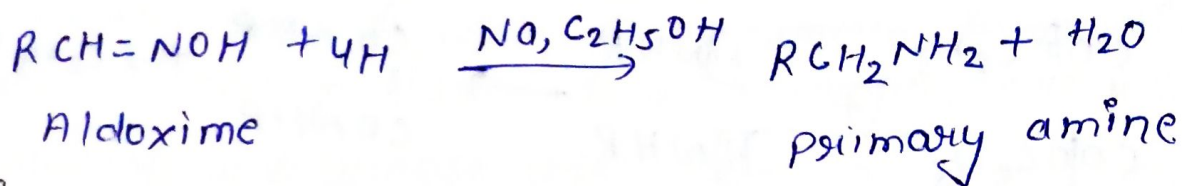


(iii) Reduction of nitriles:-

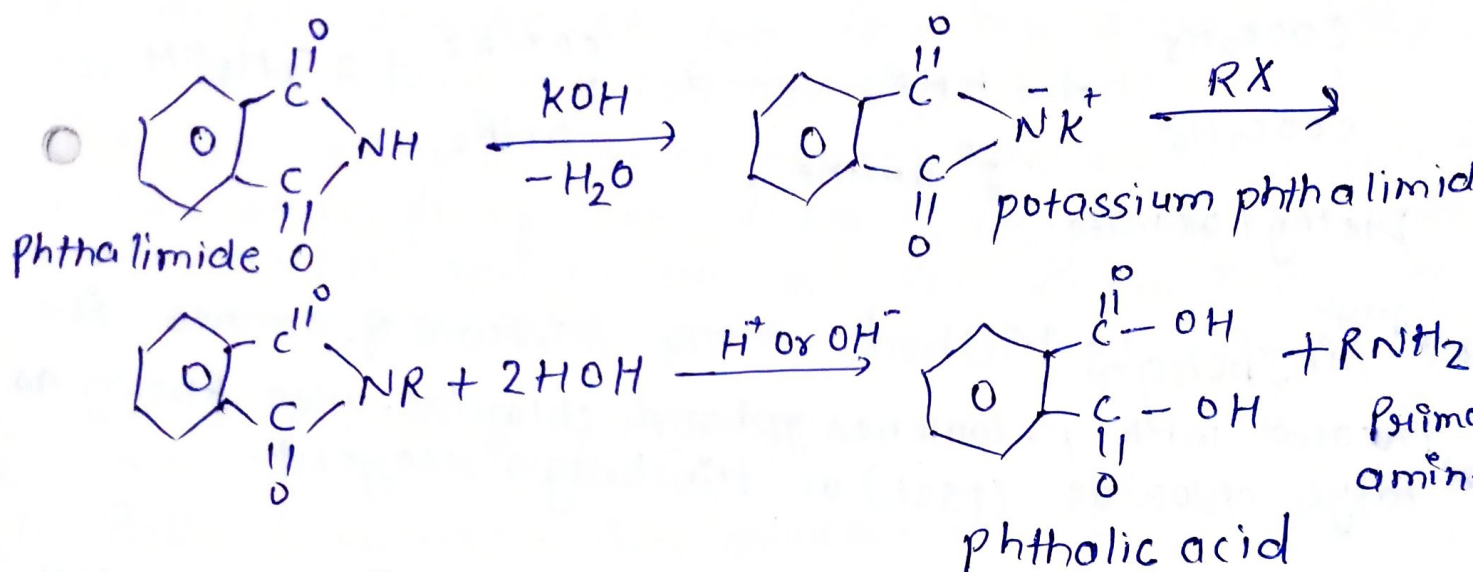




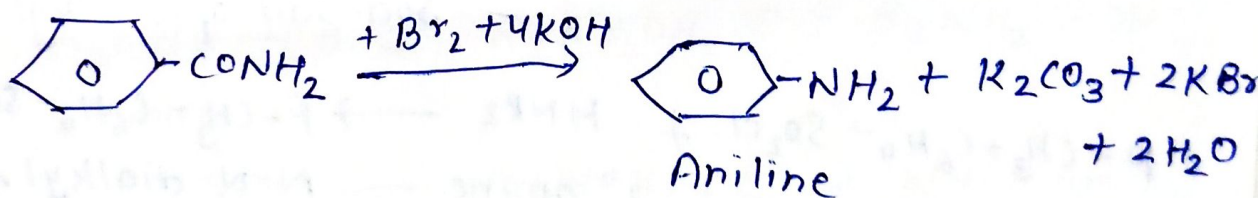
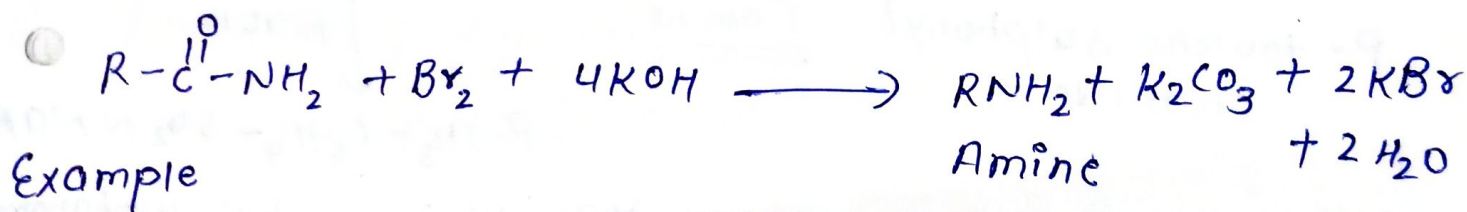
③ Reduction of oximes and amides: -



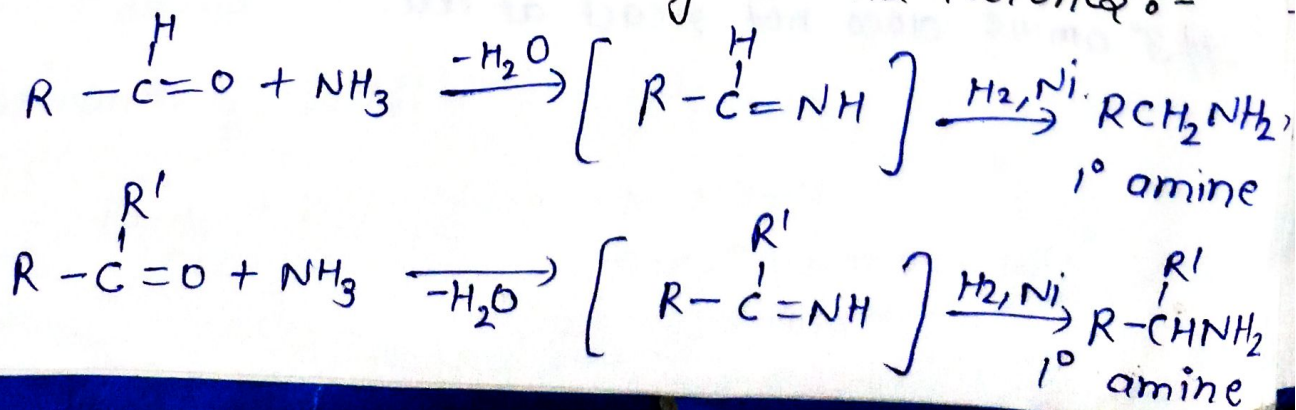
(4) Gabriel Phthalimide Rxn:-



⑤ Hofmann Bromamide Reaction:-

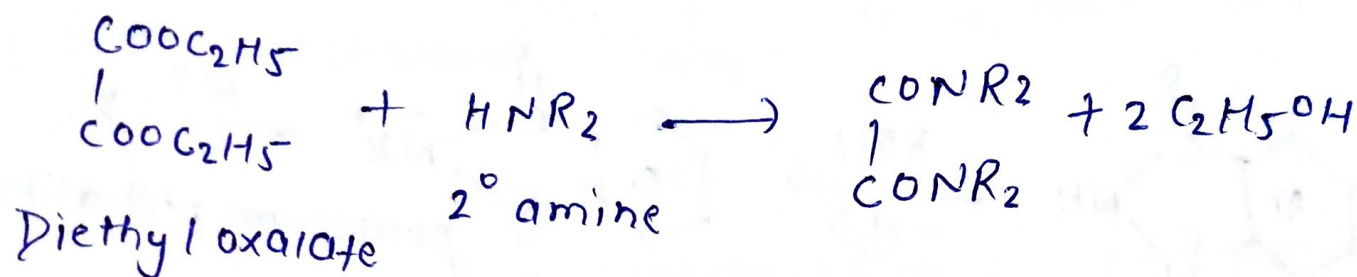
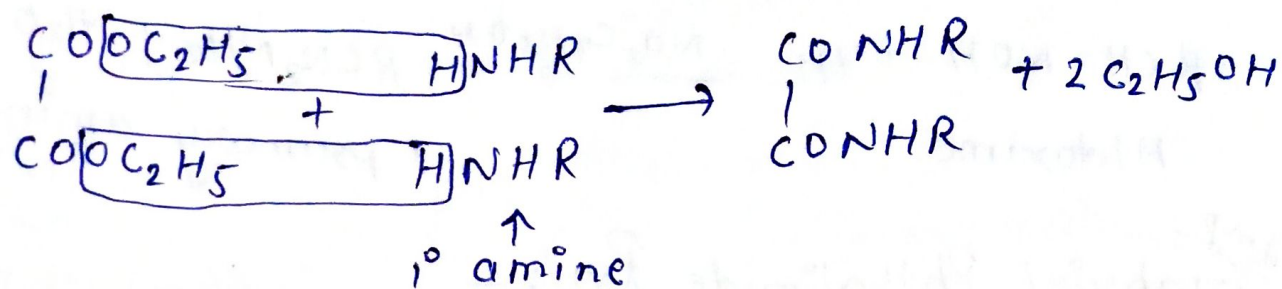


⑥ Reductive amination of aldehydes and ketones:-

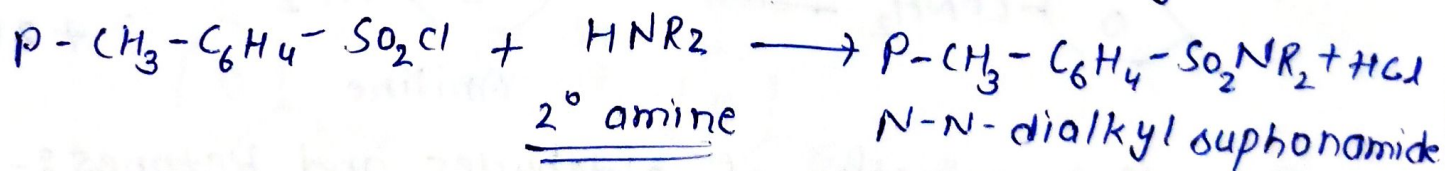
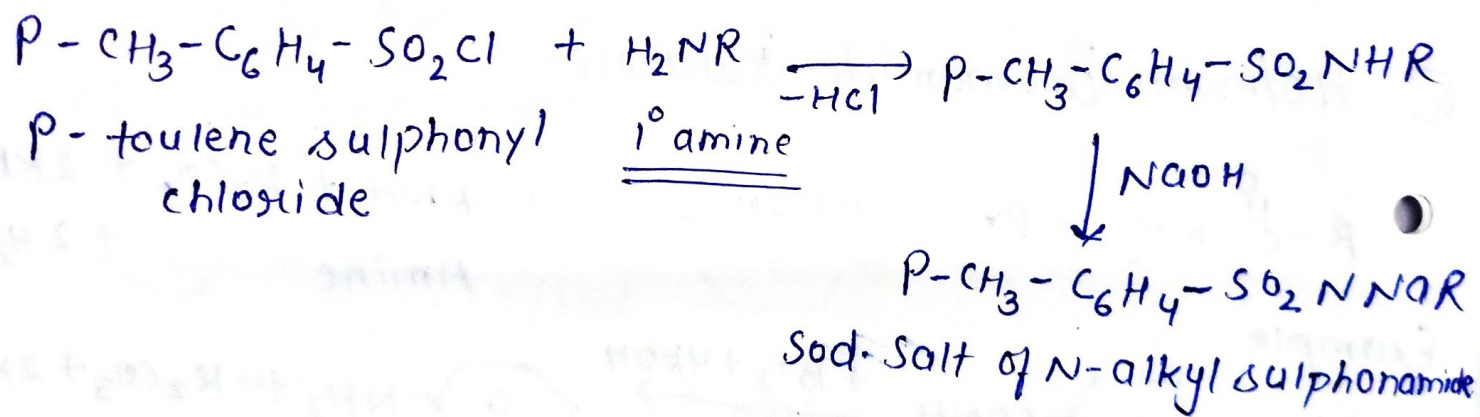


* Separation of primary, Secondary And Tertiary amine

1) Hofmann's Method:-



2) ^{gmp} Hinsberg's Method:- The mixture of amines is treated with p-toulenesulphonyl chloride. Also known as tosyl chloride (TsCl) or Hinsberg's reagent.



3° amine does not react at all.

3. PHYSICAL PROPERTIES of Amines:-

The lower members of aliphatic amines are gases having ammonia like odour while the higher amines are mostly liquid with fishy smells. Aromatic amines are either liquid having unpleasant odours. Pure amines are almost colourless.

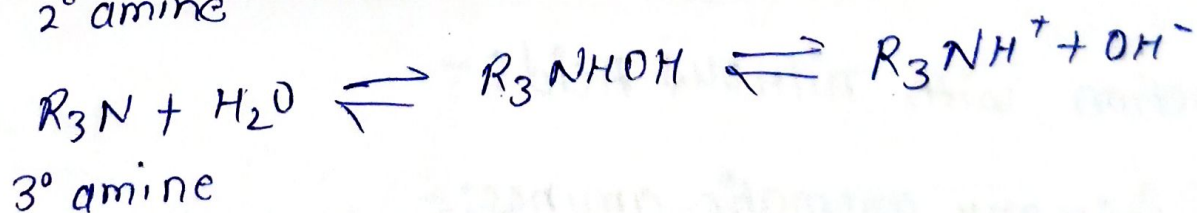
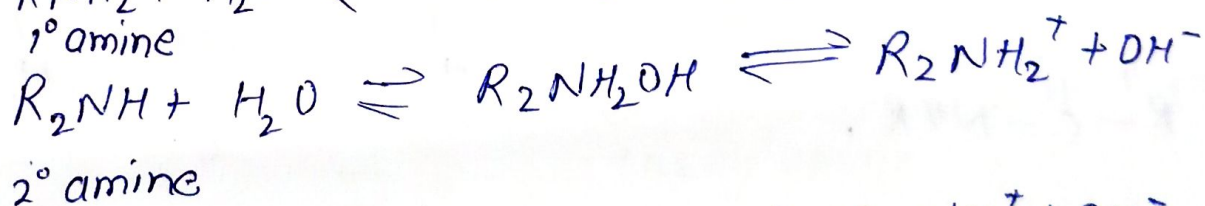
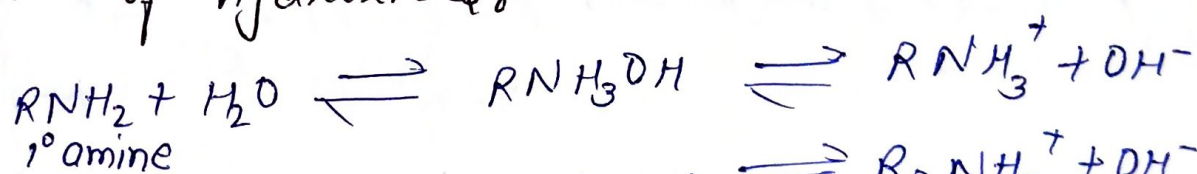
2) Melting and boiling Points:- Amines are polar compounds and except for tertiary amines they can form intermolecular hydrogen bonds.

The lower amines of all classes are quite soluble in water since all of them form hydrogen bonds with water. Higher amines are insoluble due to ↑ size of non-polar hydrocarbon part.

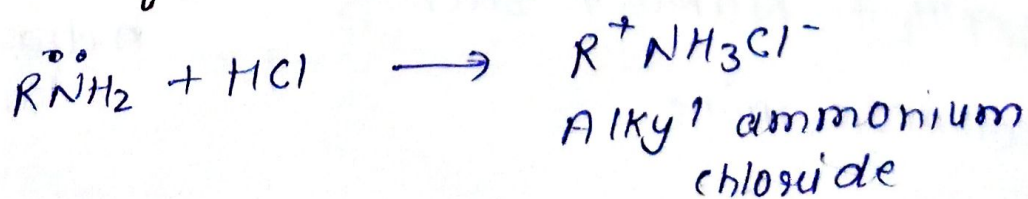
Chemical Properties of Amines:-

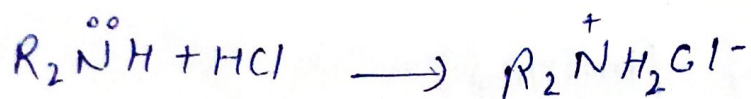
(i) Basic character:- Like ammonia, all the classes of amines have a lone pair of electron on the nitrogen atom.

(i) formation of hydroxides:-

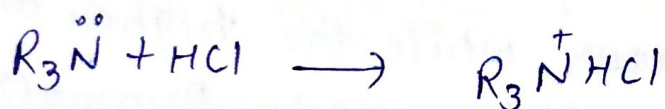


(ii) formation of Salts:-



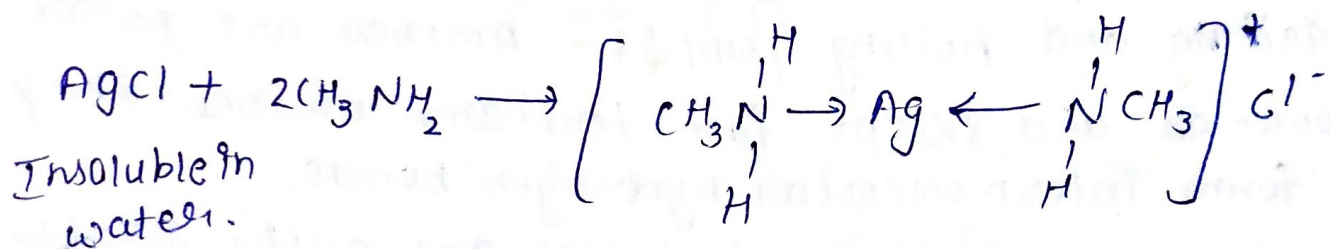


Dialkyl ammonium chloride.



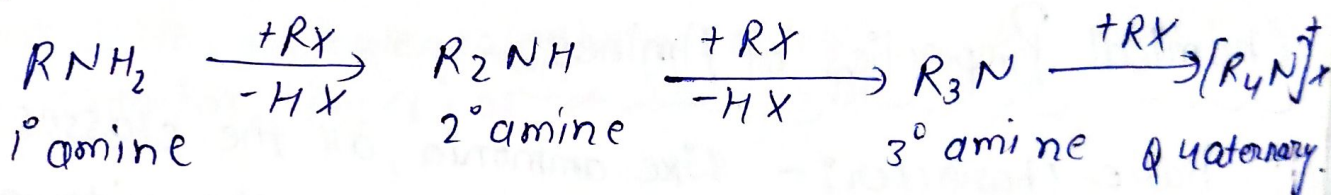
Trialkylammonium chloride.

★ Reaction with metal ions:-

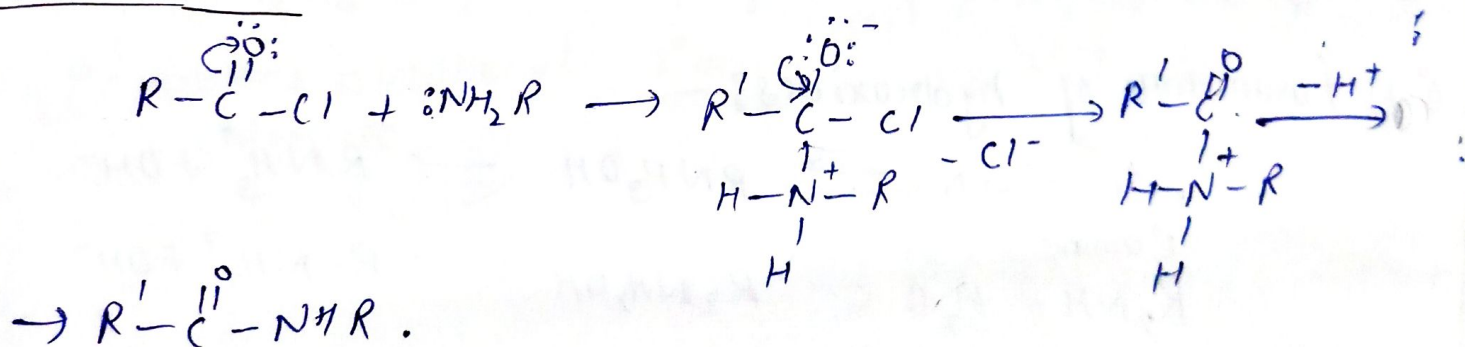


Bis (methylamine) silver(I) chloride (soluble)

③ Alkylation:-

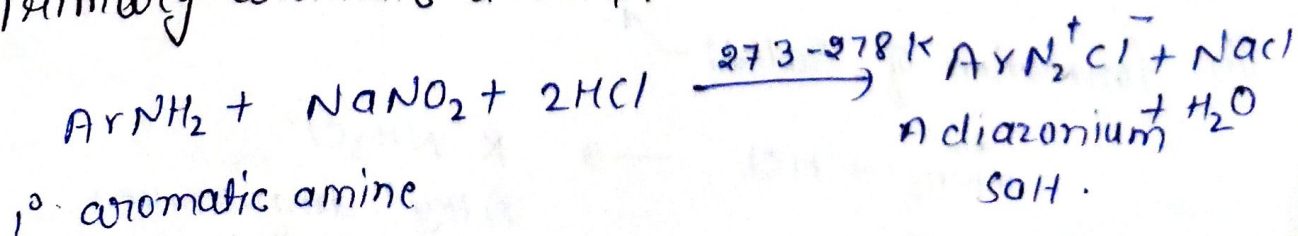


Mechanism:-

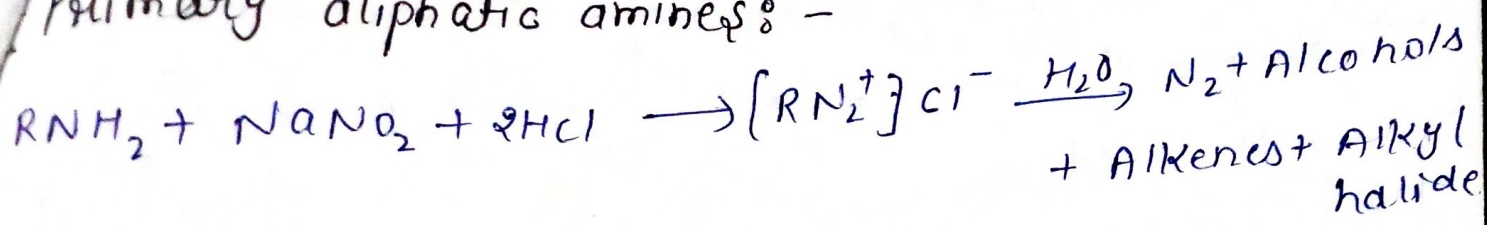


Reaction with nitrous acids:-

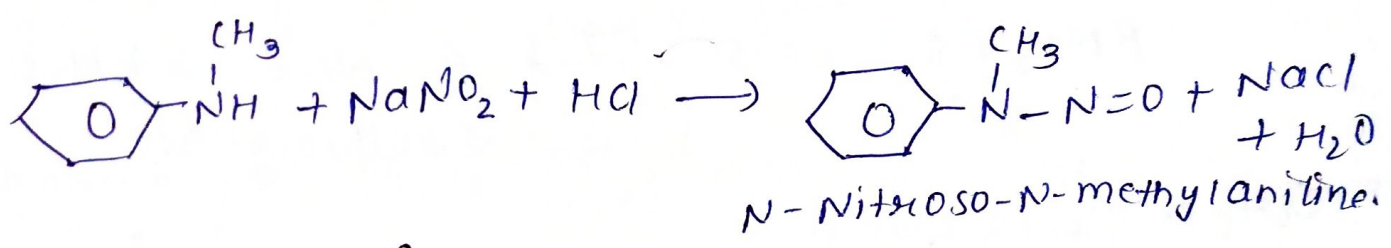
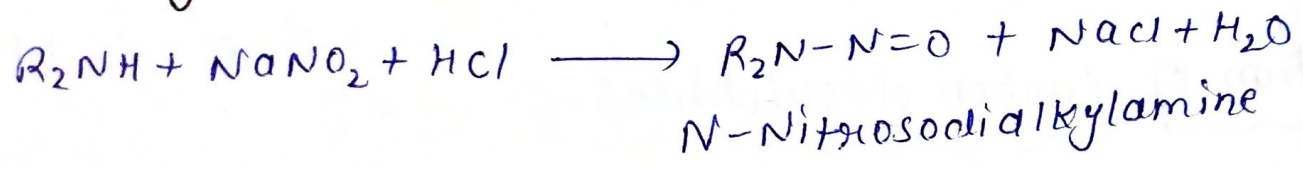
① Primary aromatic amines:-



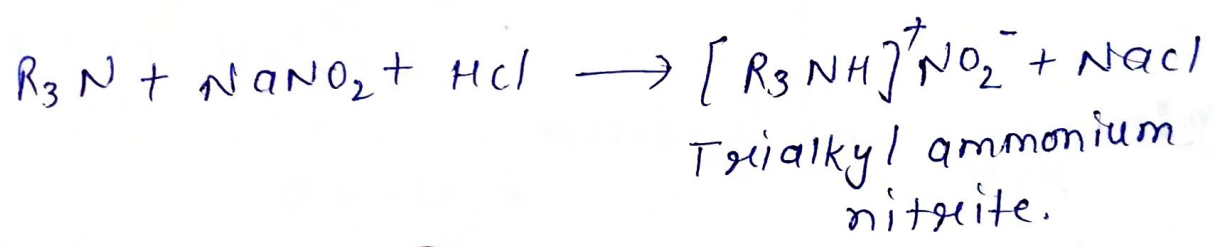
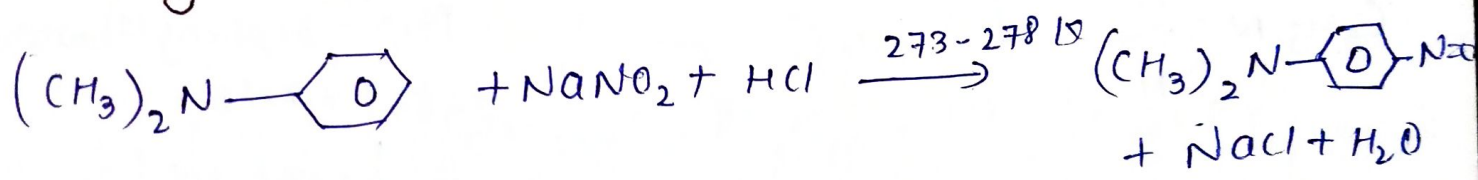
Primary aliphatic amines:-



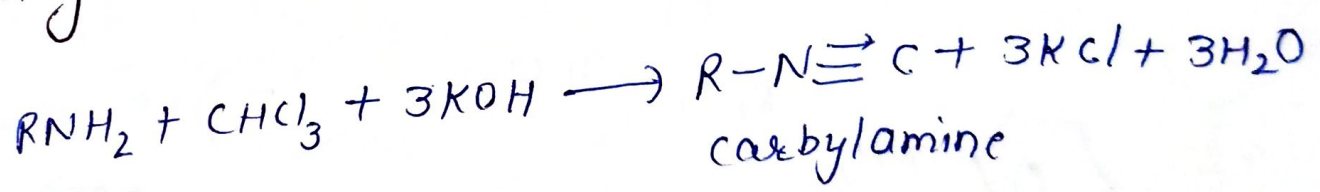
② Secondary Amines:-



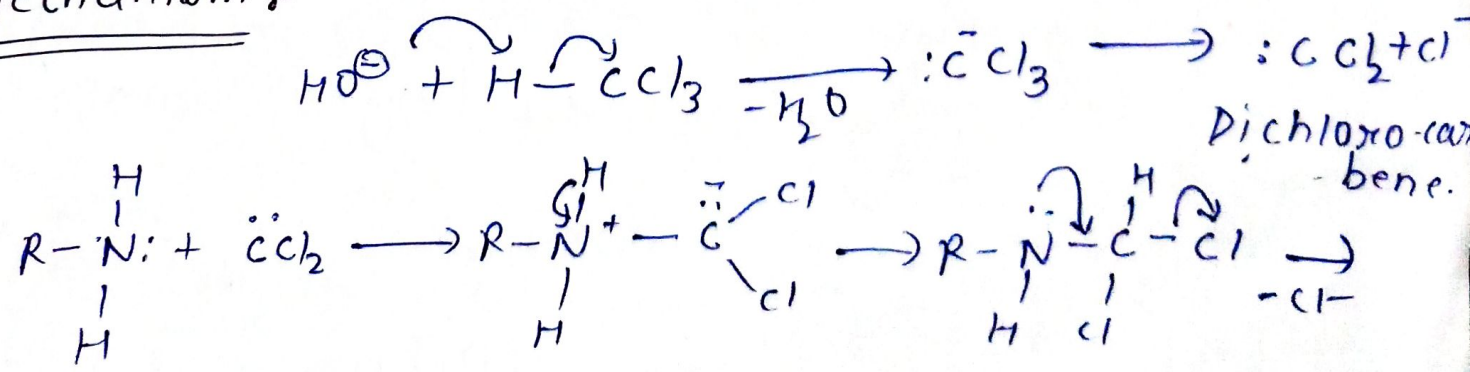
Tertiary aromatic amines:-

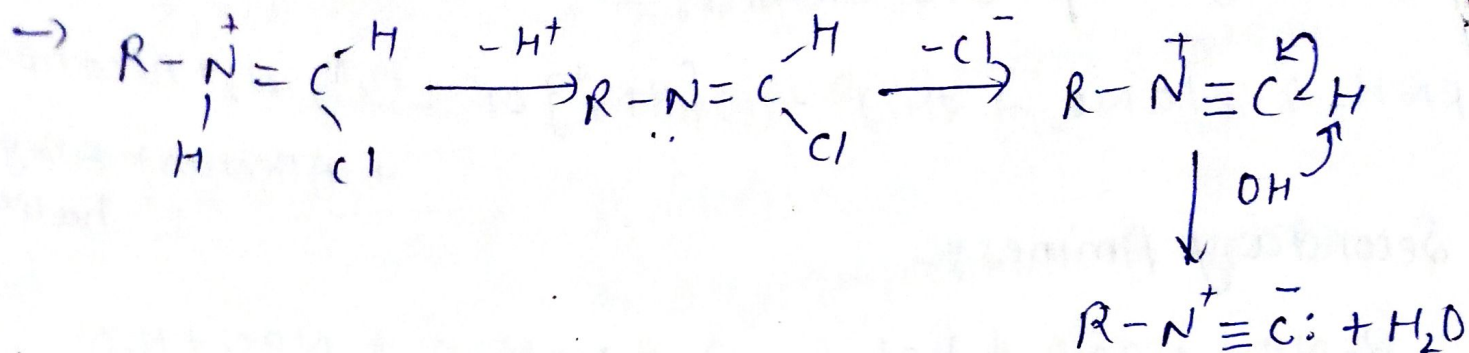


Carbylamine Reaction:-

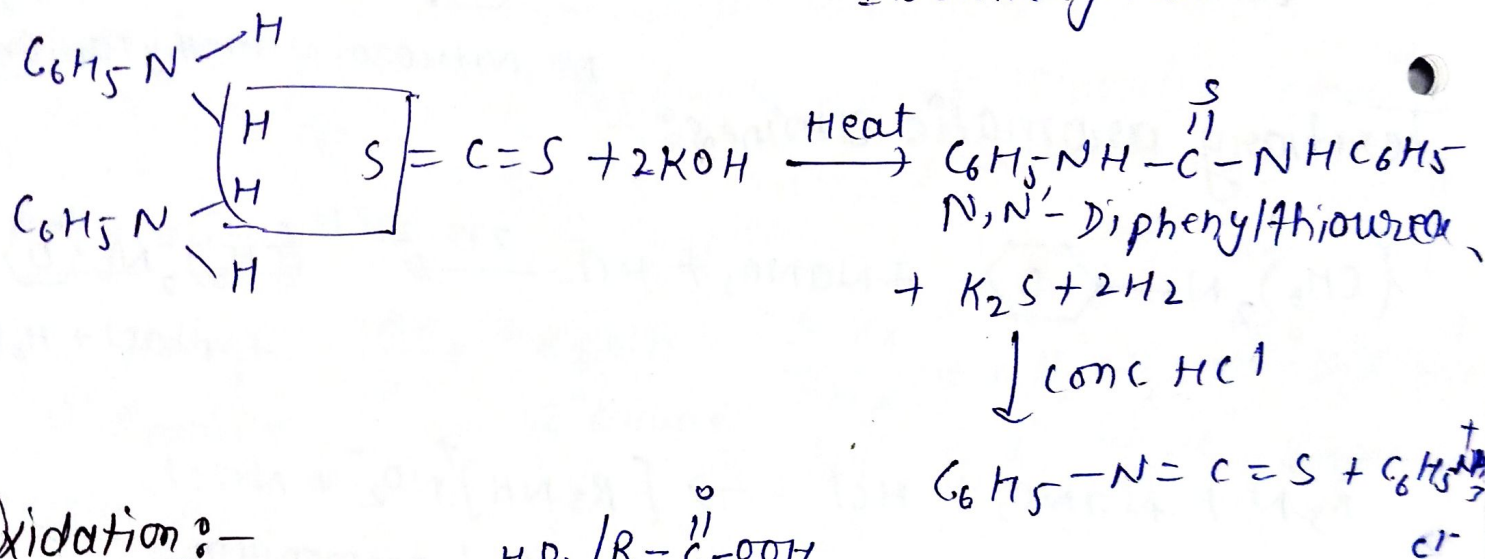
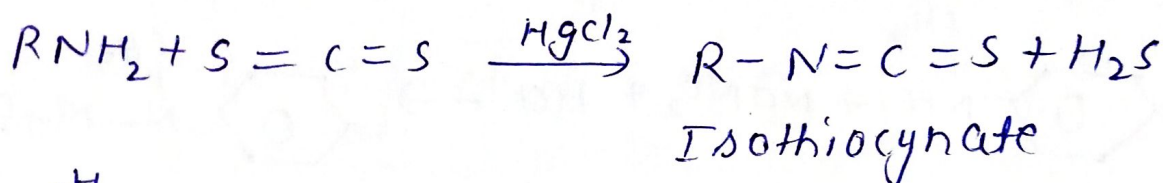


Mechanism:-

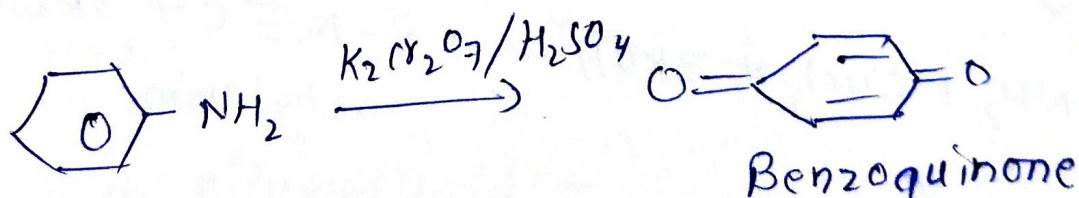
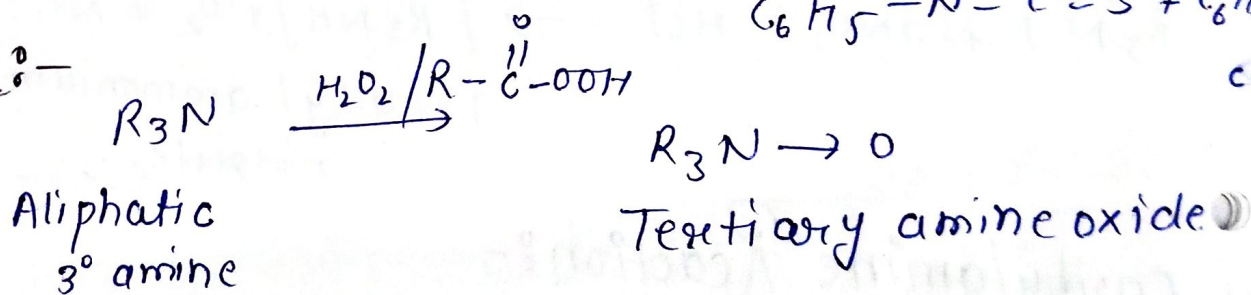




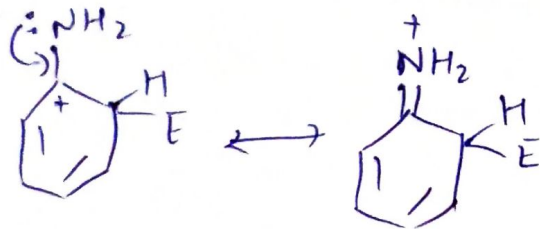
Action of carbon disulphide:-



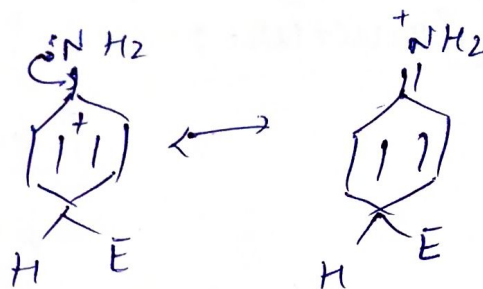
Oxidation:-



Electrophilic aromatic substitution in aryl amines: - 5.

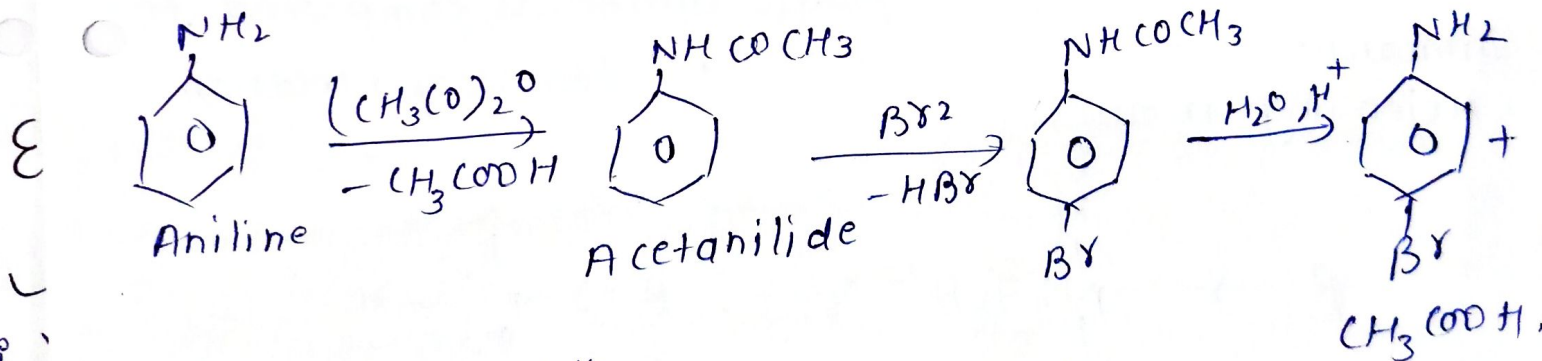
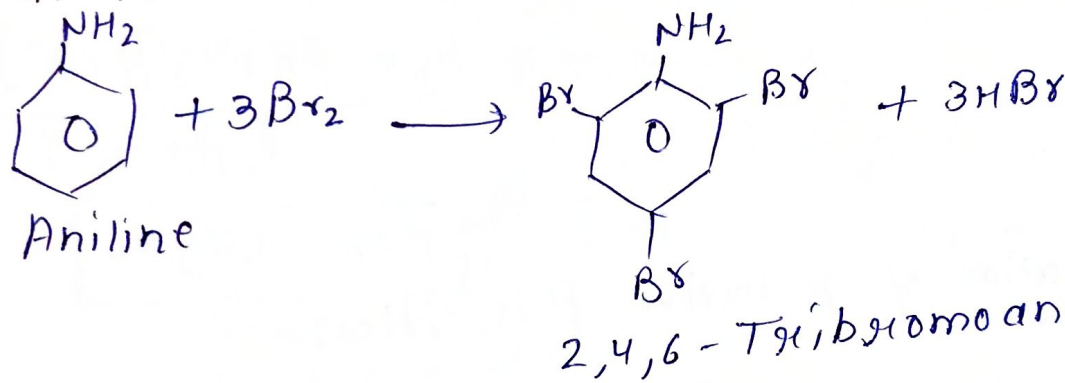


attack ortho position.

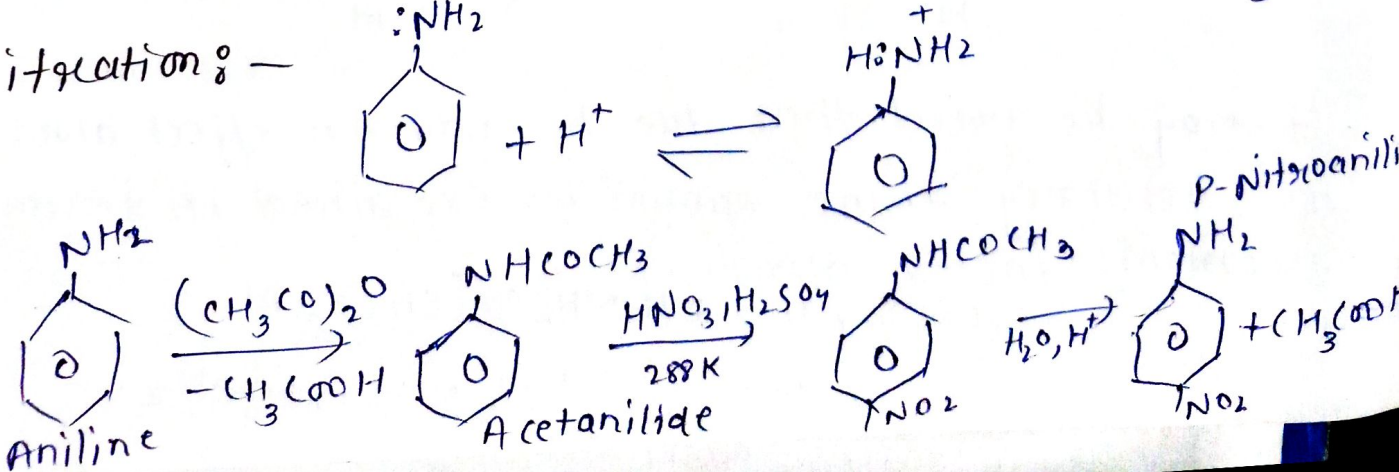


attack at para position.

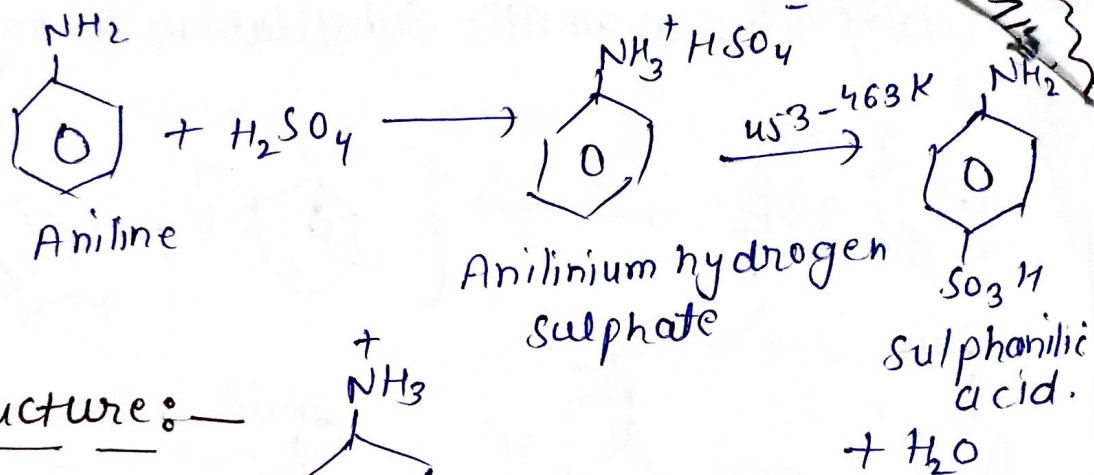
Halogenation: -



Nitration: -



Sulphonation:-



Zwitter ion Structure:-



Basicities of Amines:-

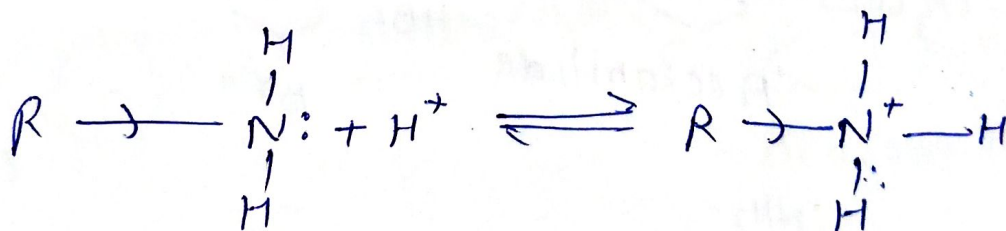


$$K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]}$$

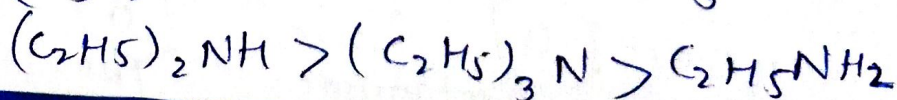
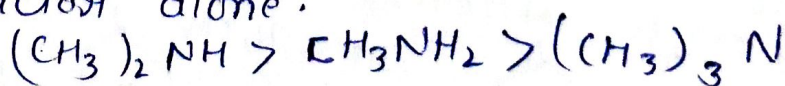
$$\boxed{\text{p}K_b = -\log K_b}$$

Explanation of Relative Basicities:-

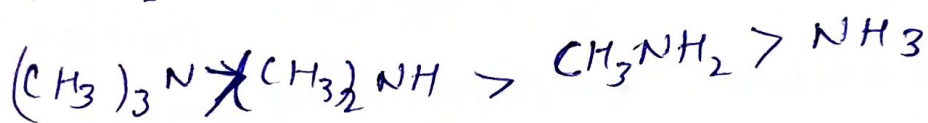
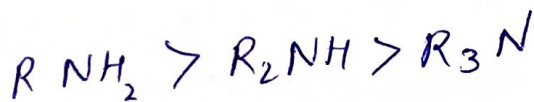
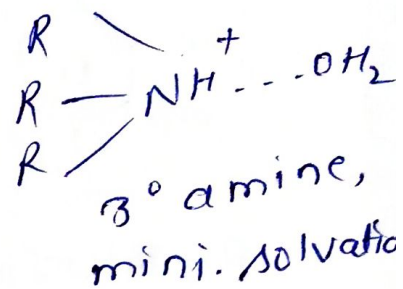
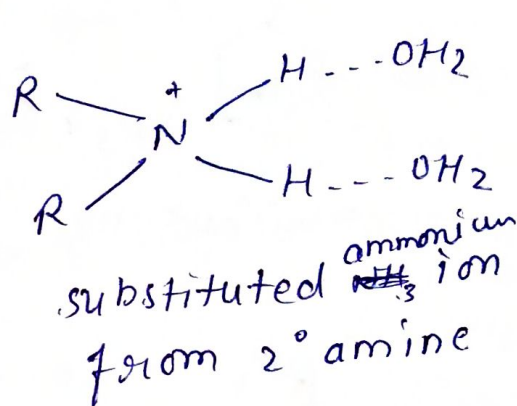
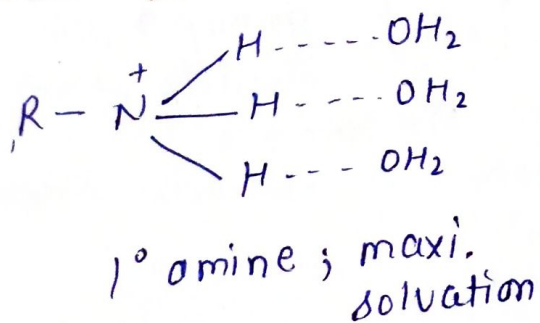
Greater basicity of aliphatic amines as compared to ammonia can be explained in terms of electron releasing inductive effect.



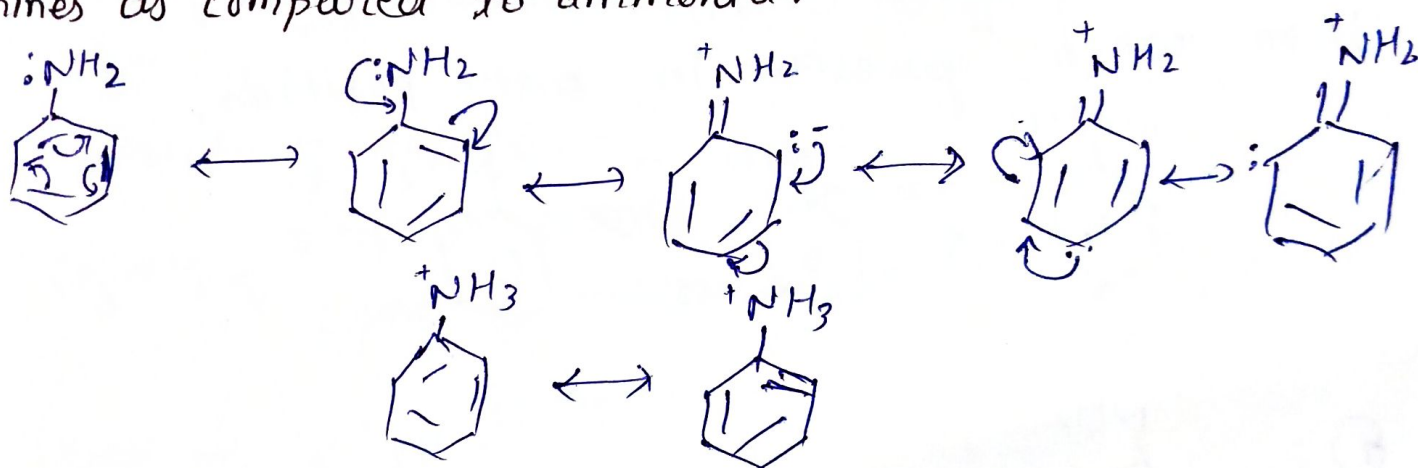
It may be noted that due to inductive effect alone, a tertiary amine cannot be explained in terms of electronic factor alone.



Solvation effect:-



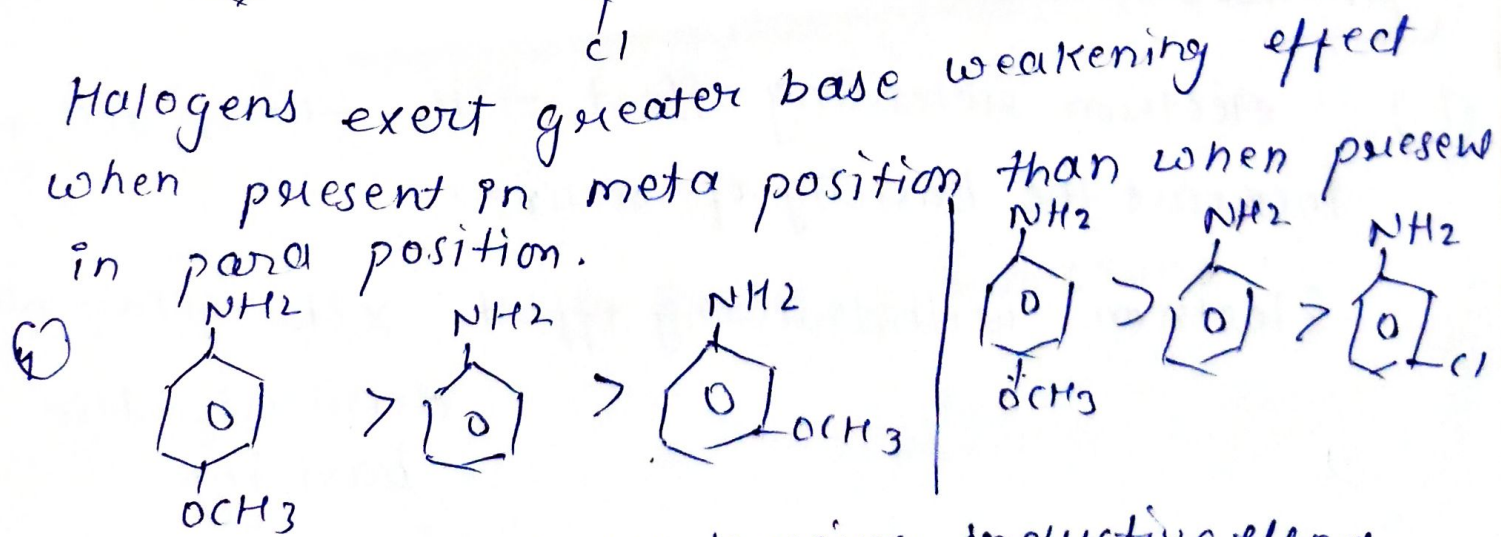
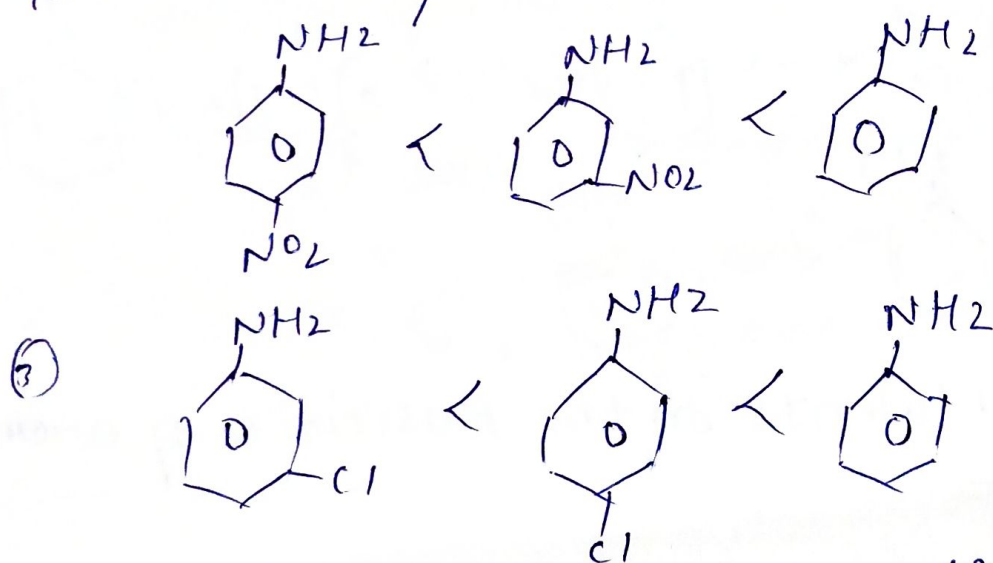
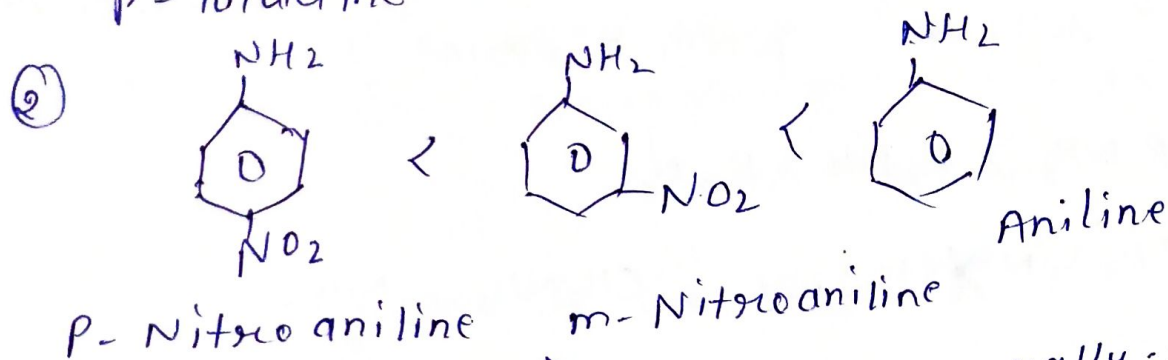
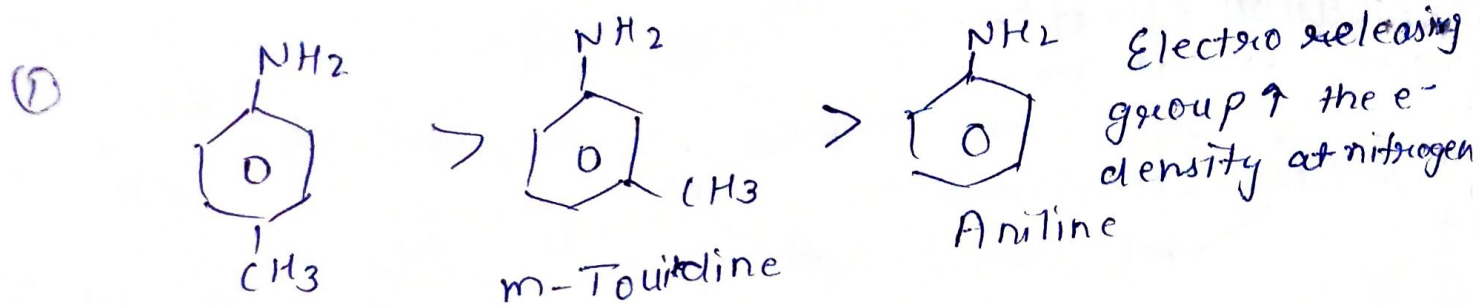
Aromatic amines:- weaker basic character of aromatic amines as compared to ammonia.



Effect of substituents on the Basicities of aromatic Amines:-

(i) electron-releasing effect - CH_3 , $-\text{OCH}_3$, and $-\text{NH}$ increase the basicity of aniline.

Electron-withdrawing effect $\times$ (halogens) - NO_2 decrease the basicity.

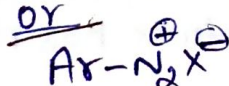
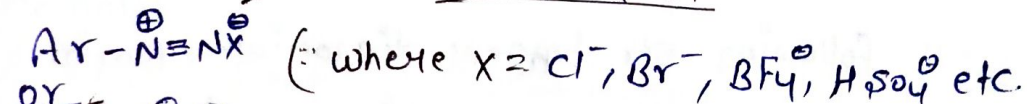


$O-CH_3$ or (OH) has e^- withdrawing inductive effect, an e^- releasing resonance effect (+R).

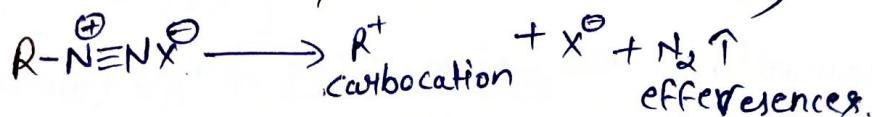
Diazonium Salts

* diazonium salts :- The class of compounds containing diazonium Ion ($-N \equiv N^+$) directly linked to aryl group are known as arene diazonium salt

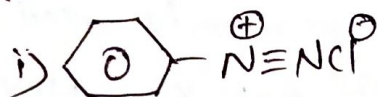
General Formula :-



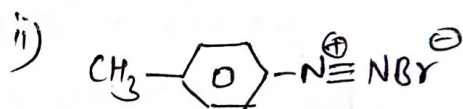
Aliphatic diazonium salt :- $R-N \equiv N^+ X^-$ (where $R = \text{alkyl}$)



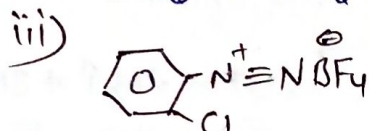
Nomenclature :-



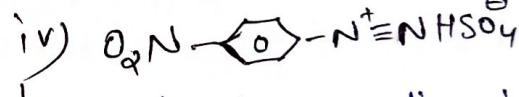
Benzene diazonium chloride



p-toluene diazonium bromide



o-chlorobenzene diazonium tetrafluoroborate



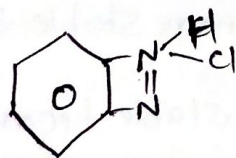
p-Nitrobenzene diazonium Hydrogen sulphate.

* Structure of Benzene Diazonium chloride

1) molecular Formula : gt molecular formula $C_6H_5N_2Cl$

2) Earlier Formula

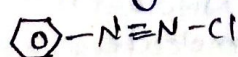
3) Weyss Structure :- The earliest structural formula for benzene-diazonium chloride was suggested its discoverer "Peter Weyss." In this formula the two nitrogen atom were directly attached to benzene nucleus.



This formula was immediately rejected it could not account for following properties of benzene diazonium chlorides.

- i) gt salt-like character
- ii) Its reduction to phenylhydrazine which contains only one nitrogen directly attached to benzene nucleus.
- iii) The formation of azo compound in coupling rxn.
- iv) The displacement N_2Cl group whole in most of reaction.

b) Kekule Formula :- Kekule proposed the following str. only one nitrogen directly attached to benzene ring.

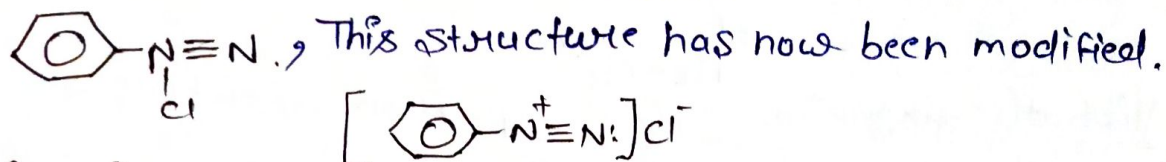


This Formula could explain most of reaction of benzene-diazonium chloride Failed account.

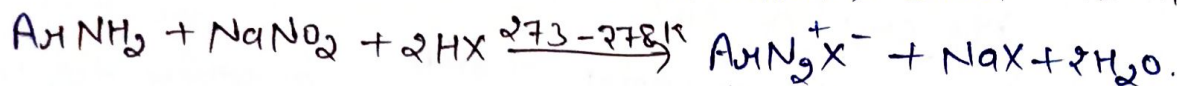
- i) Salt-like behaviour of benzene diazonium chloride.
- ii) Instability of benzene diazonium chloride as compared to azo compound since both contain "N=N" linkage.

c) Blomstrand Formula and its modified Form :-

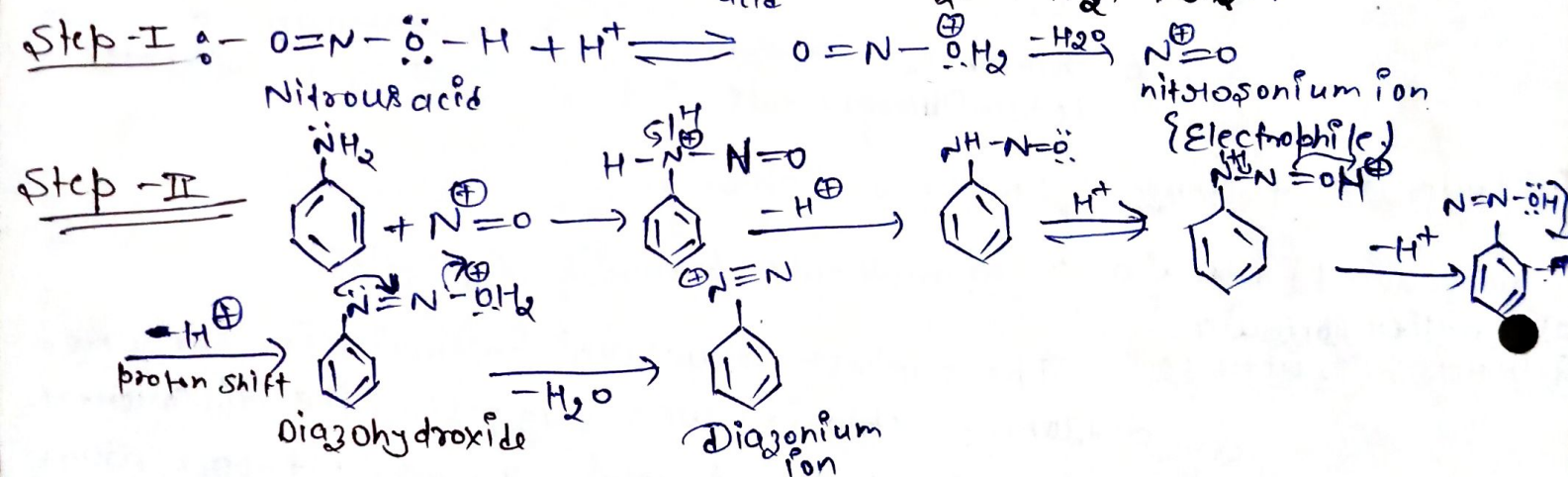
following str. benzene diazonium chloride Blomstrand suggested



* Preparation of Diazonium salts :- Diazonium salts are usually prepared by reaction b/w aromatic primary amine and nitrous acid at 273-278K. the reaction is called diazotisation and



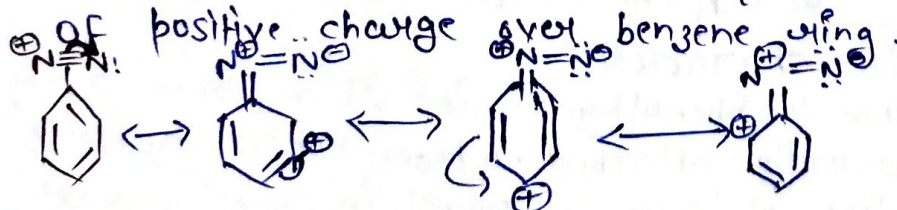
Mechanism of diazotisation :- $\text{NH}_2\text{CONH}_2 + \text{HNO}_2 \rightarrow \text{C}_6\text{H}_5\text{N}_2^+ + 2\text{N}_2\uparrow + 3\text{H}_2\text{O}$



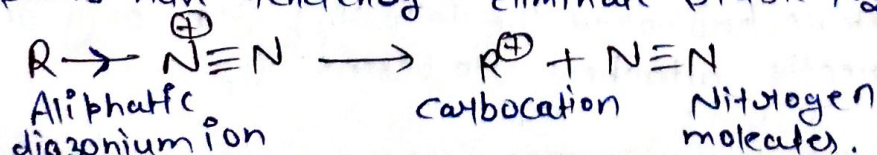
* Stability of Diazonium salts

Aromatic diazonium salt are much more stable than aliphatic diazonium salts.

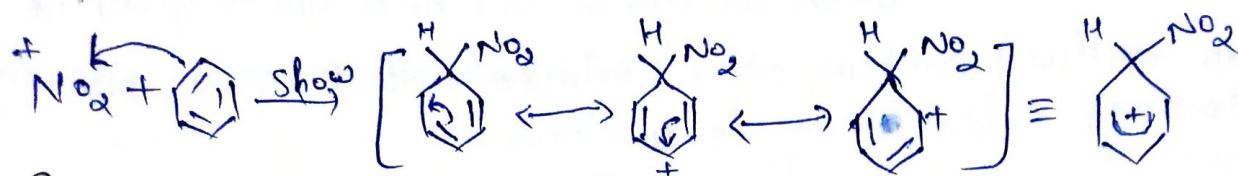
Ans The arene diazonium salts are quite stable because of dispersal of positive charge over benzene ring.



on the otherhand due to effect of alkyl group aliphatic diazonium salts have tendency to eliminate stable N_2 molecule form carbocation



Formation of carbocation ion.



ii) Proton transfer from the carbocation to yield the final product.



PHYSICAL Properties of Nitro compound.

i) Physical state $\rightarrow$ Nitroalkanes are colourless oil liquids when

pure. They have pleasant smell and sparingly soluble in water.

$\rightarrow$ Nitrobenzene are yellow oily liquids other aromatic nitro compound are yellow crystalline solids. Nitro, Nitrobenzene has an odor of bitter almonds inorganic compound.

2) Solubility $\rightarrow$ Nitroalkanes are sparingly soluble in water while nitroarenes are insoluble in water. However nitroalkanes and nitroarenes are readily soluble in organic solvent such as benzene, ethanol etc.

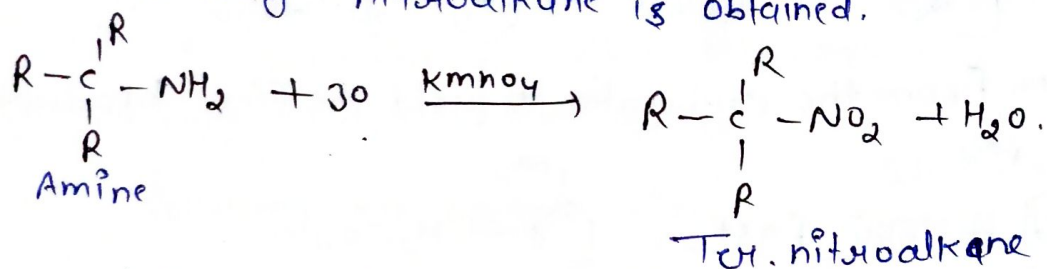
3) Stability : Nitroalkanes are sparingly soluble in water while nitroarenes are not. When poly nitro compound heated strongly they decompose with explosive violence.

4) Density : - All the nitroalkanes and nitro-arenes are heavier than water.

5) Melting and boiling points $\rightarrow$ Nitro compounds are polar in nature. So, nitro compound have strong dipole-dipole interaction of comparable molecular masses.

Nitro Compounds	B.Pt	M.Pt
1. Nitrobenzene	210°C	—
2. o-Dinitrobenzene	239°C	118°C
3. o-Nitrotoluene	221°C	—
4. m-Nitrotoluene	231°C	—
5. p-Nitrotoluene	239°C	—
6. m-Dinitrobenzene	—	90°C
7. p-Dinitrobenzene	—	173°C

3) Oxidation of amines :- When an amine in which amino group is attached to tertiary carbon atom oxidised with potassium permanganate a tertiary nitroalkane is obtained.



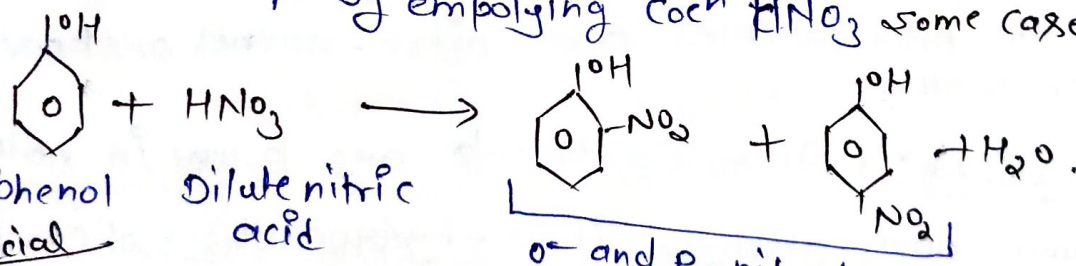
* Preparation of nitroarenes :- Nitroarenes are almost prepared by direct nitration of arenes. The nitrating agents,

- i) concentrated or fuming nitric acid
- ii) mixture of concentrated or fuming nitric acid and concⁿ sulphuric acid. This mixture most commonly used nitrating agent
- iii) Mixture of concentrated nitric acid and acetic anhydride or boron trifluoride

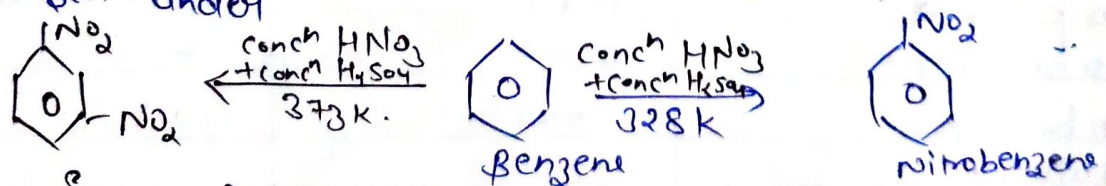
iv) Acetyl nitrate ($\text{CH}_3\text{CO}\cdot\text{ONO}_2$) obtained nitrating agent used for nitration compound depend upon following two factors,

- i) Nature of compound to be nitrated.
- ii) Number of nitro group to be introduced.

The nitration of aromatic compound containing electron releasing or activating group. NH_2 , OH and CH_3 this reaction readily at room temp. by employing concⁿ HNO_3 some case even dil HNO_3 .

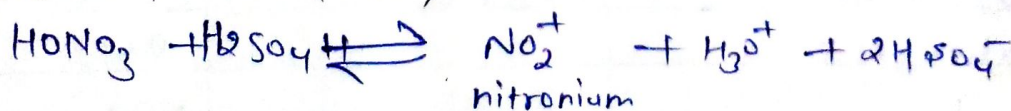


nitrobenzene and m-dinitrobenzene for instance, can be obtained from benzene under



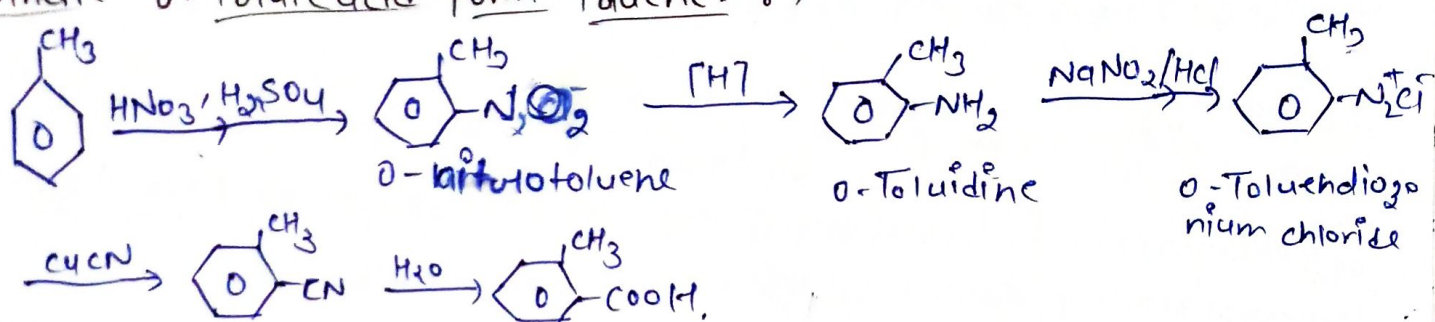
Mechanism of nitration :- Nitro

i) Generation of electrophile,

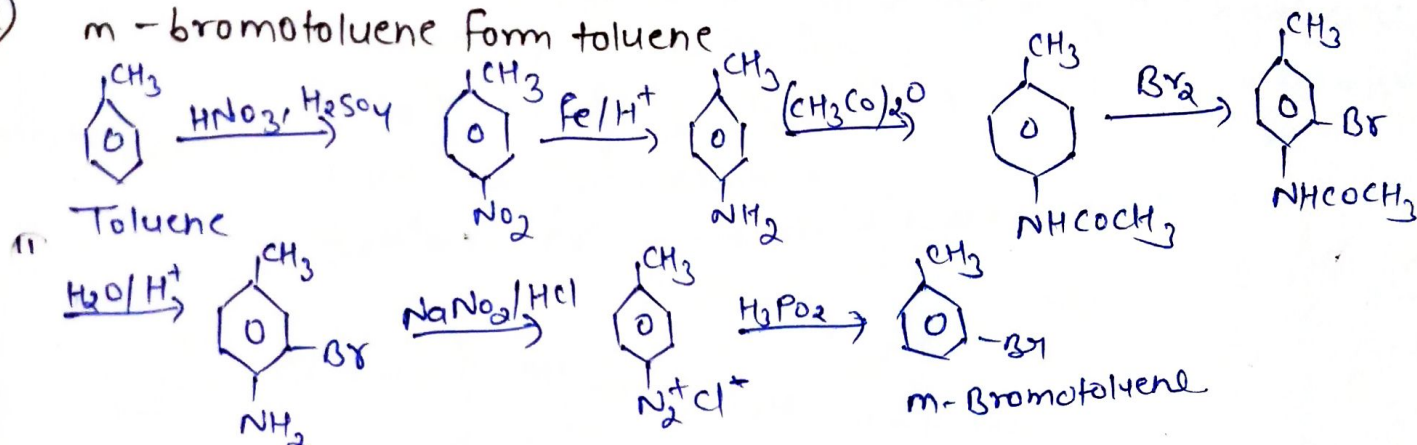


Synthetic Application of Diazonium Salt's :-

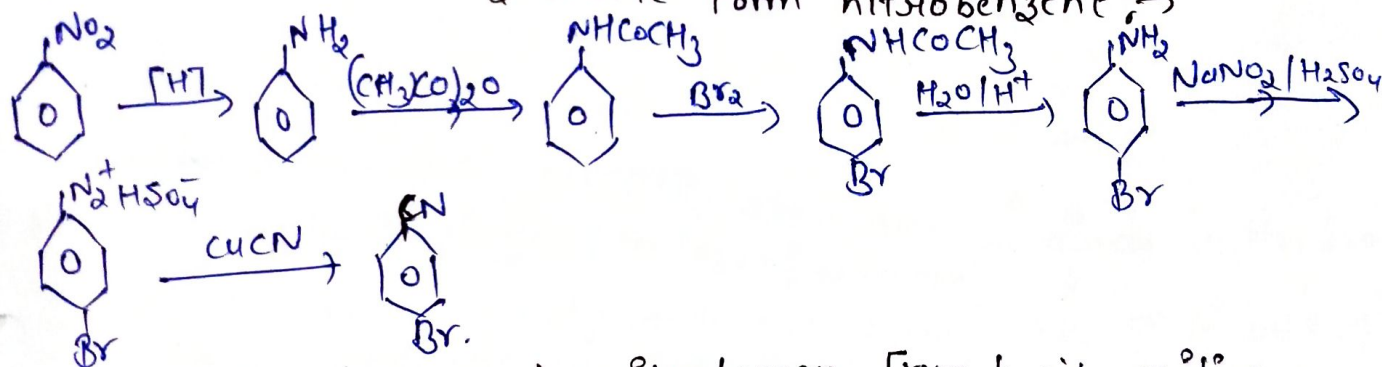
Synthetic o-Toluic acid Form Toluene. :-



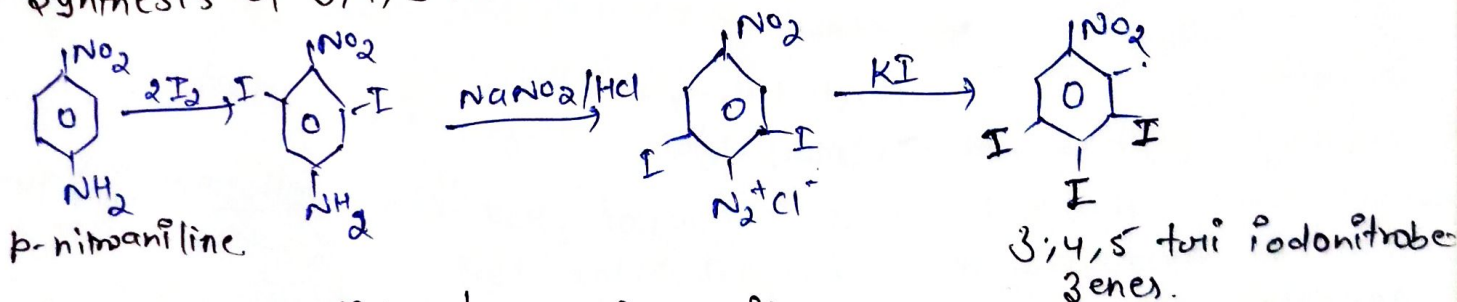
2) m-bromotoluene Form toluene



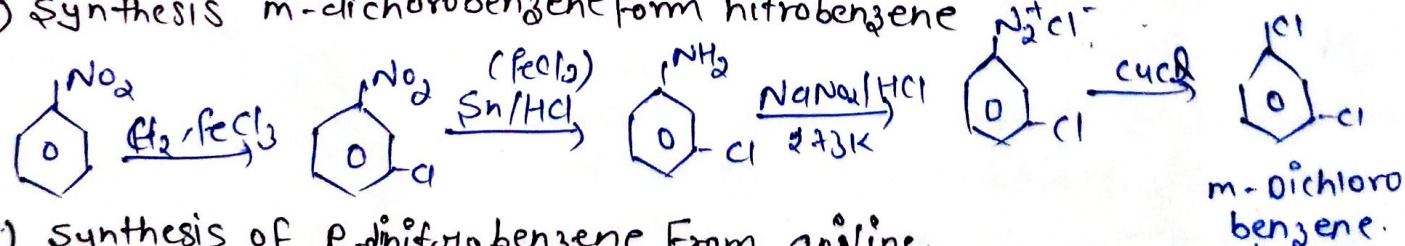
2) Synthesis of p-bromobenzamide Form nitrobenzene :-



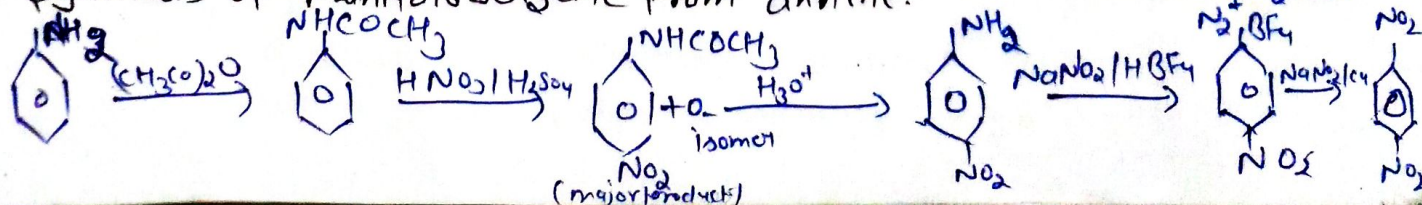
3) Synthesis of 3,4,5 tri-iodonitrobenzen From p-nitroaniline.



4) Synthesis m-dichlorobenzene form nitrobenzene

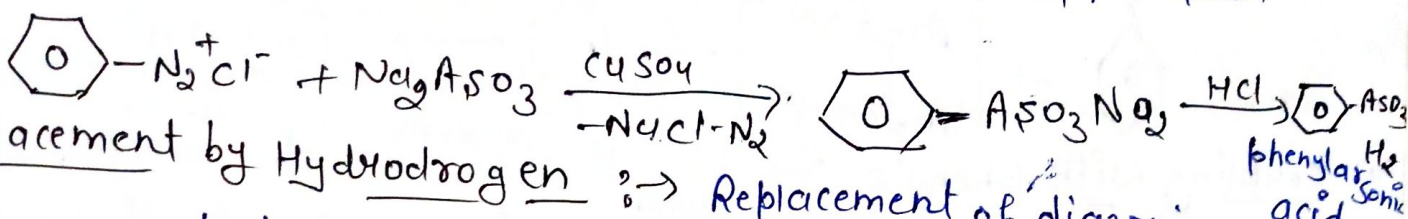


5) Synthesis of p-dinitrobenzene From aniline.

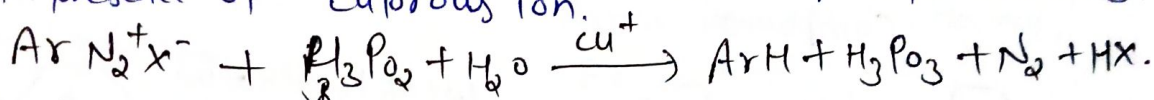


Replacement by arsonic acid group, AsO_3H (Bart Reaction)

This is carried out by decomposing a diazonium salt with sodium arsenite in the presence of copper salt



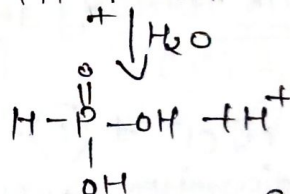
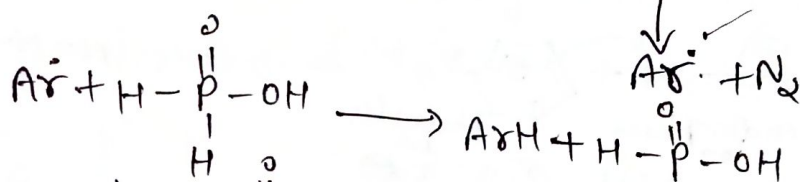
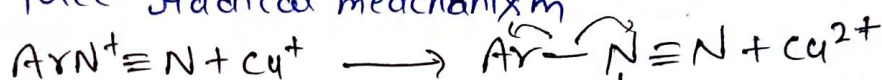
8) Replacement by Hydrogen $\rightarrow$ Replacement of diazonium group by hydrogen best carried out by allowing the diazonium solution stand contact with hypophosphorous acid in presence of cuprous ion.



Mechanism:-

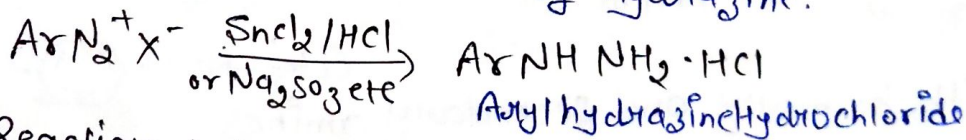
Free radical mechanism

ii



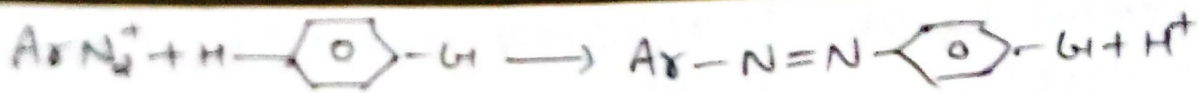
b) Reactions in which nitrogen atom are retained in the product

a) Reduction by hydrazines : (No loss of Nitrogen) on reduction with reduction agent such stannous chloride and hydrochloric acid sodium bisulphite or sodium sulphite diazonium salt reduced by hydrazine.

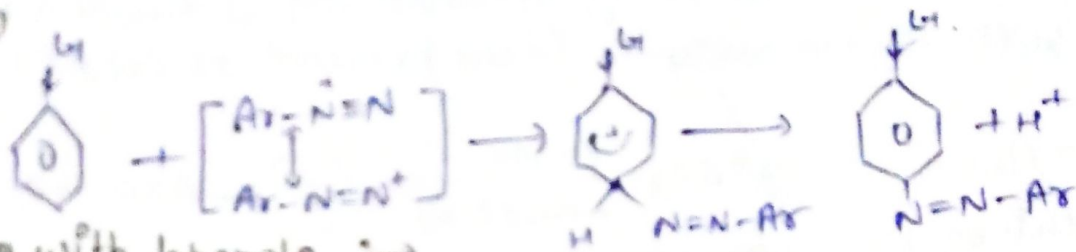


Coupling Reaction : $\rightarrow$ very important group of Reaction of diazonium salt involves the reaction of diazonium ion the with aromatic compound containing powerful electron releasing substituent $-\text{OH}$, $-\text{NH}_2$, $-\text{NHR}$ and $-\text{NR}_2$ etc known as coupling leads to the formation of compound called azo compound.

$\text{Ar}-\text{N}=\text{N}-\langle\text{O}\rangle-\text{G}$, where $\text{G} = -\text{OH}$, $-\text{NHR}$, $-\text{NH}_2$, $-\text{NR}_2$ azo compound strongly coloured compounds with constitute a group of dyes known as azo dyes.

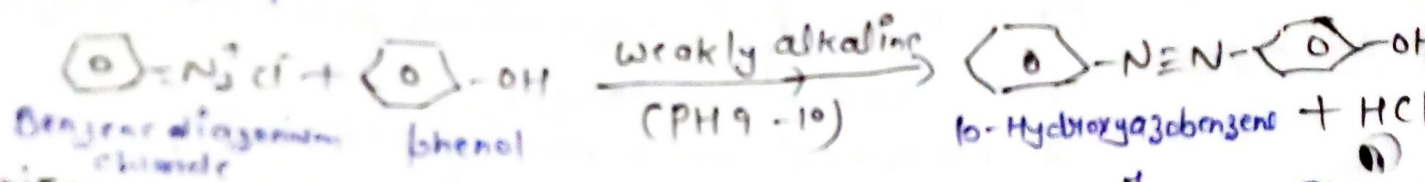


Mechanism

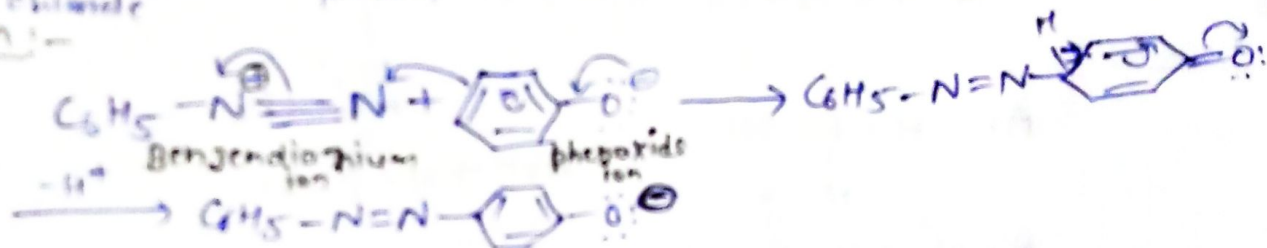


10) Coupling with phenols :-

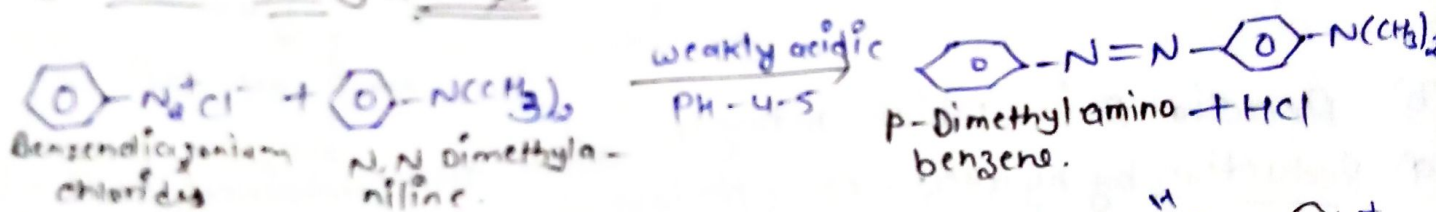
When treated with phenol in weakly alkaline solution diazonium salt undergo coupling to form hydroxyazo compound.



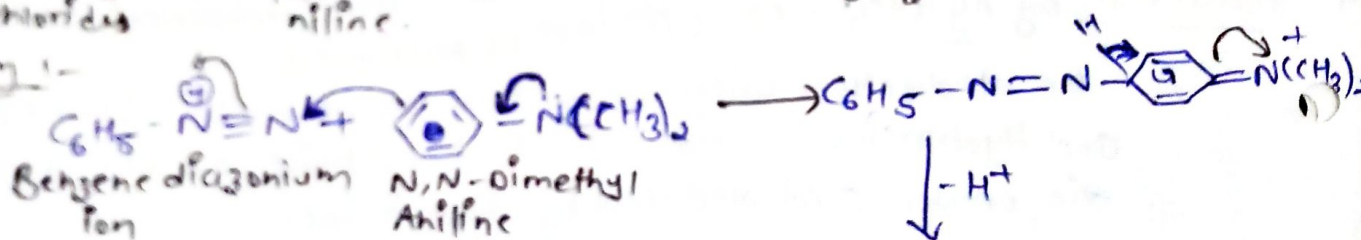
Mechanism :-



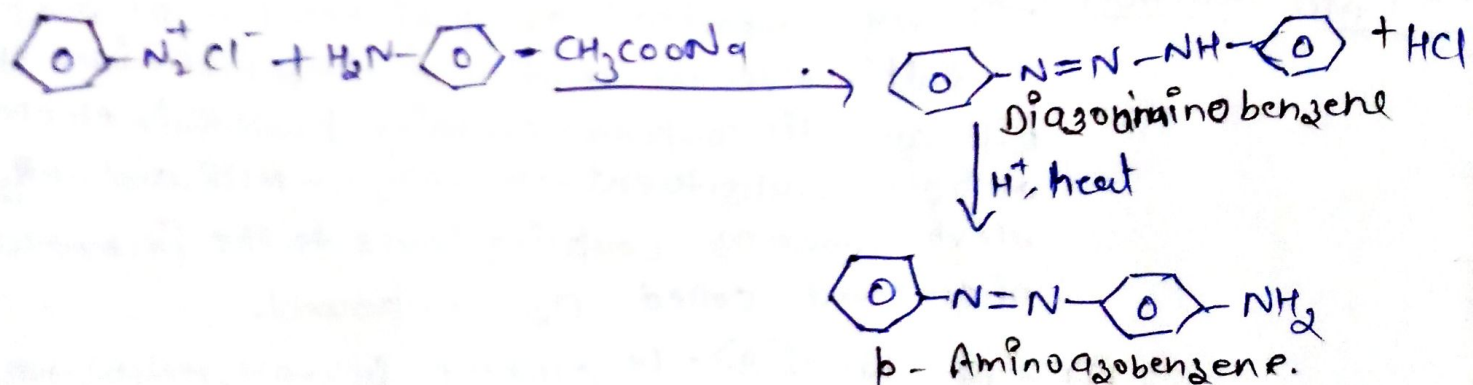
11) Coupling with tertiary amines



Mechanism :-



12) Reaction with primary and secondary amines.



CHAPTER - 4

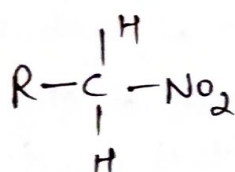
Nitro Compound

Organic compound containing into $[-\text{NO}_2 \text{ or } -\text{N}^+ \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} \text{ or } -\text{N} \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}]$ group is called nitro compound.

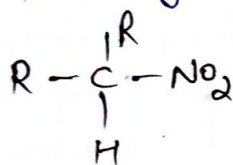
i) $\text{R}-\text{NO}_2$
Aliphatic nitro comp.
 R - Alkyl group

ii) $\text{Ar}-\text{NO}_2$
Aromatic nitro compound.
 Ar - Aryl group.

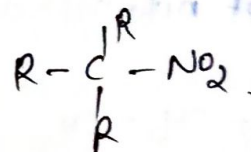
* Classification of nitroalkanes $\Rightarrow$ nitroalkanes are further classified primary secondary and tertiary depend upon the nitro group attached to primary, secondary and tertiary carbon atom.



(1°) primary nitroalkane

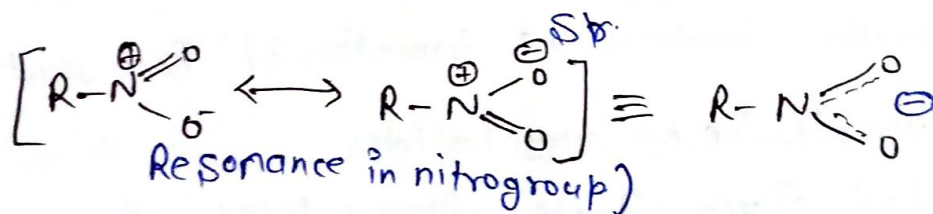


(2°) secondary nitroalkane



(3°) tertiary nitroalkane.

* Structure of Nitro group $\Rightarrow$ Nitro group regarded as resonance hybrid of two equivalent contributors.



* Nomenclature

i) CH_3NO_2
nitromethane

ii) $\text{CH}_3\text{CH}_2-\text{NO}_2$
Nitroethane

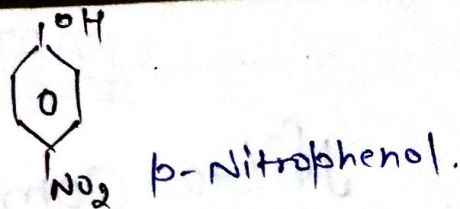
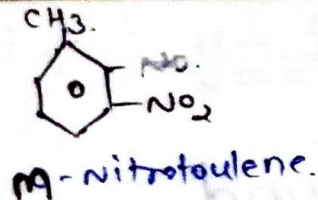
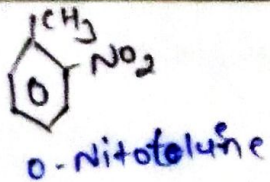
iii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$
Nitropropane.

ii) $\begin{array}{c} \text{H}_3\text{C}-\text{CH}-\text{CH}_3 \\ | \\ \text{NO}_2 \end{array}$
2-Nitropropane

iv) $\begin{array}{c} \text{H}_3\text{C}-\text{CH}-\text{CH}-\text{CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{NO}_2 \end{array}$
2-Nitro-3-methyl butane

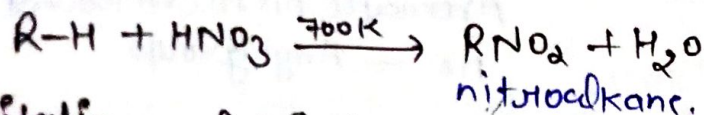
v) $\begin{array}{c} \text{H}_3\text{C}-\text{C}-\text{NO}_2 \\ | \\ \text{CH}_3 \end{array}$
2-Methyl-2-nitropropane.

vi) 
Nitrobenzene.



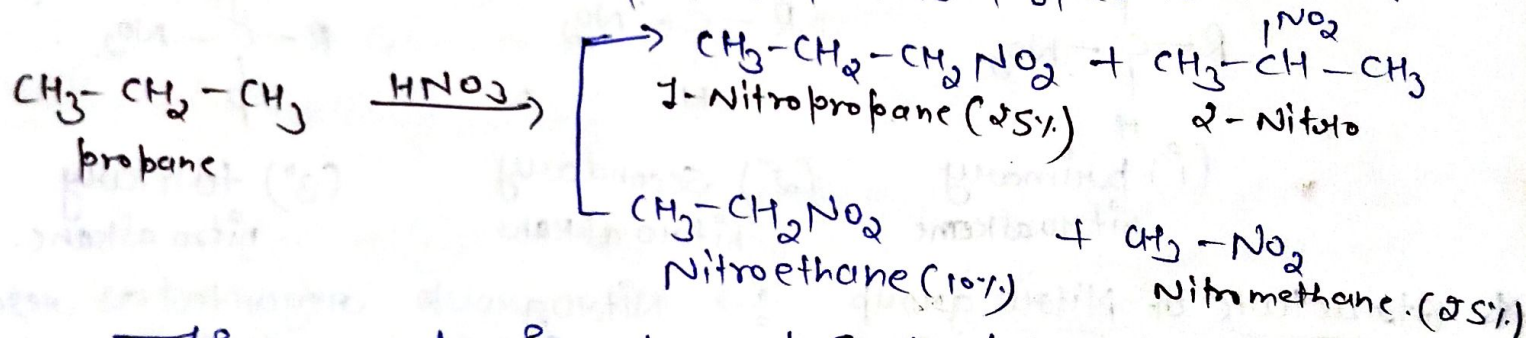
* Preparation of nitro compound.

1) Vapour phase nitration of alkanes $\Rightarrow$ This reaction involve the substitution of hydrogen atom alkane by nitro group. it is carried out vapour state by heating the alkane with nitric acid at 700K



Limitations of this process

During nitration of higher alkane, all possible isomeric nitro product are formed more rupture of carbon-carbon bond takes place leading to formation of nitroalkanes contained lesser number of carbon atom.

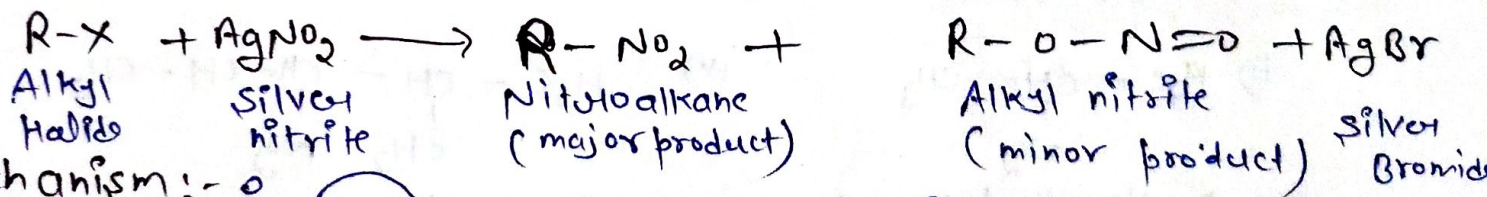


This method is not used for the laboratory preparation

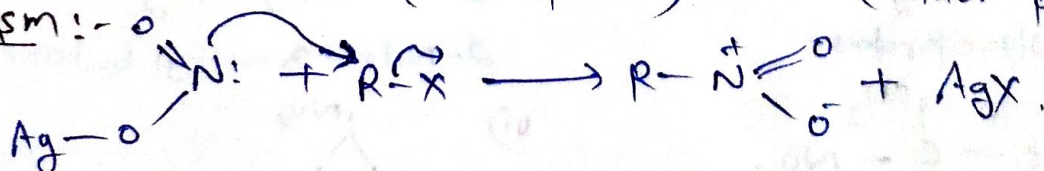
Mechanism:- reaction involved the formation of "Free radicals"

2) Action of silver nitrite on alkyl halides

When we heated silver nitrate, alkyl halides undergoes nucleophilic substitution to form nitroalkanes. alongwith heated small quantity alkyl nitrites ($R-O-N=O$). this is because NO_2^- is an ambident nucleophile



Mechanism:-



Physical properties

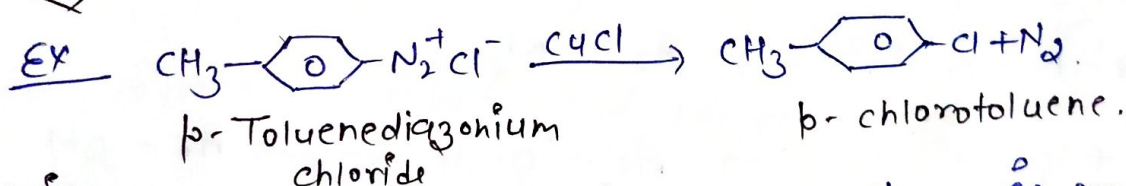
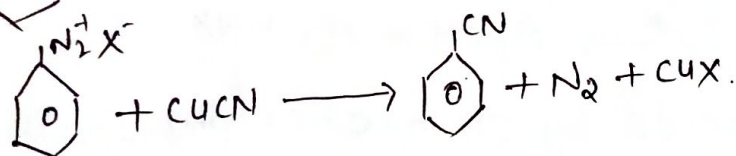
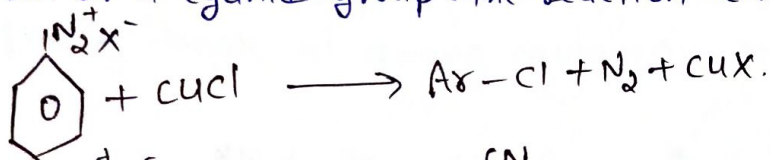
- i) Diazonium salts are generally colourless solid freely soluble in water.
- ii) They are seldom isolated because of their instability and explosive nature.
- iii) with certain metallic salts such as zinc chloride diazonium salt form double salt $(ArN_2^+)ZnCl_4^{2-}$ are quite stable.

Chemical properties

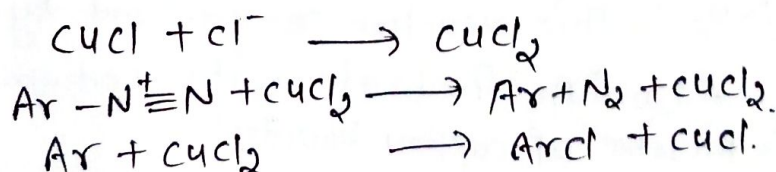
- a) Reaction in which N-atoms are lost as the diazo group is replaced by some monovalent atom/group.
- b) Reaction in which nitrogen atom are retained in the product is coupling reaction.

i) Replacement by Cl, Br or CN:- (Sandmeyer reaction)

In which the diazonium group is replaced by chloride or Bromine atom or a cyano group. the reaction is carried out by treating solution of freshly prepared diazonium salts with cuprous chloride, cuprous bromide or a cyanide group. the reaction carried



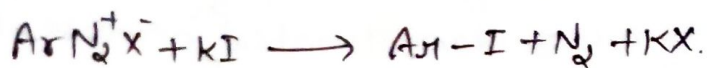
Mechanism:- mechanism Sandmeyer reaction. ~~not~~ radical free.



Wattmann reaction:- In Wattmann reaction replacement Cl, Br and CN is carried out using copper powder and halogen acid, or potassium cyanide is place cuprous.



2) Replacement by iodine $\rightarrow$ Replacement of diazonium group by iodine can be brought about merely by warming of diazonium salt solution with potassium iodine soln.



Mechanism :- The rxn proceeds by S_N^1 mechanism, and constitutes the best method introducing iodine onto aromatic ring



3) Replacement by Fluorine :- (Balz-Schiemann Reaction) :-

Replacing the diazonium group Fluorine the diazonium salt solution is treated with Fluoboric acid HBF_4 , when diazonium fluoroborate $\text{ArN}_2^+\text{BF}_4^-$ get precipitate is filtered.



Mechanism :- reaction proceeds S_N^1 mechanism

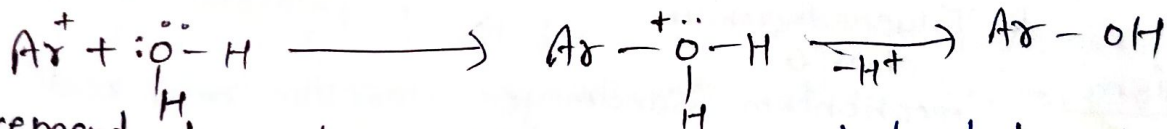
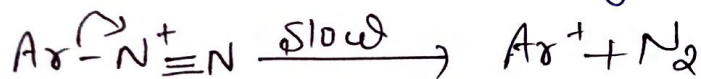


4) Replacement by -OH :- on warming an aqueous soln of diazonium salt, the diazonium group is readily replaced by OH.

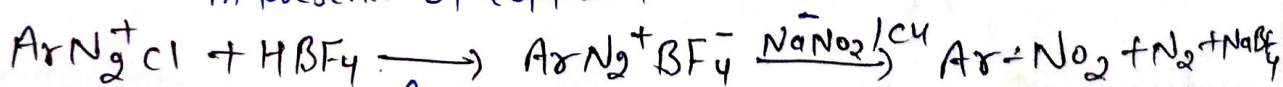


Mechanism

reaction proceeds by S_N^1 mechanism

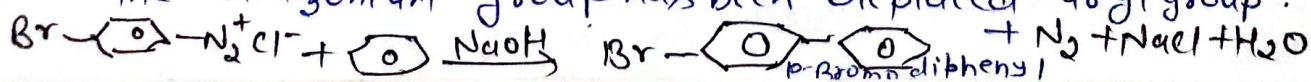


5) Replacement by -NO₂ :- This reaction carried out by decomposition diazonium fluoroborate with sodium nitrite soln in presence of copper powder.



6) Replacement by aryl group :- (Gomberg-Bachmann reaction)

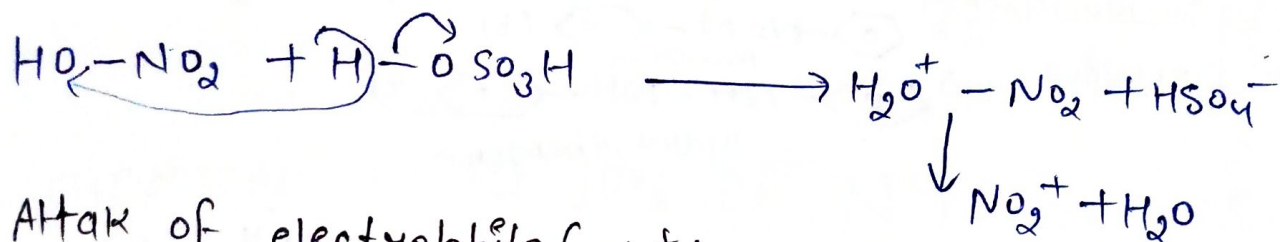
many diazonium salt react with other aromatic compound in alkaline soln to furnish compound in which the diazonium group has been replaced aryl group.



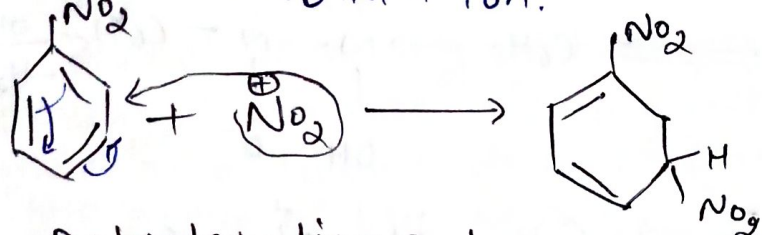
Mechanism :-

mechanism involves following steps:-

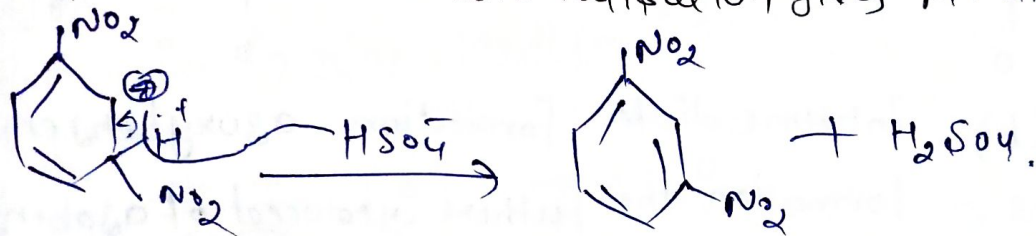
i) Formation of nitronium ion.



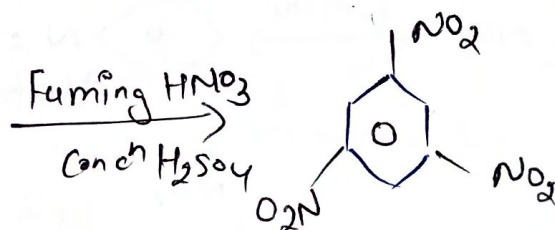
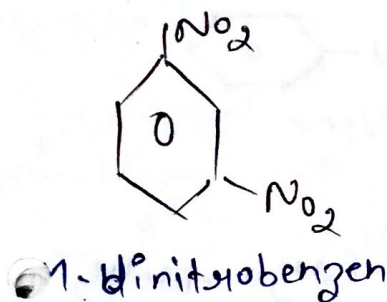
ii) Attack of electrophile (NO_2^+) on benzene ring, m-position



iii) Deprotonation and aromatisation gives m-dinitrobenzene.



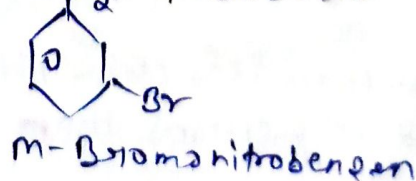
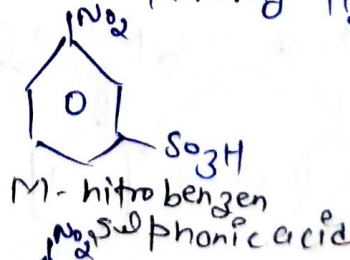
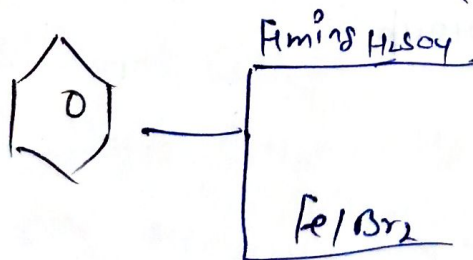
m-dinitrobenzene



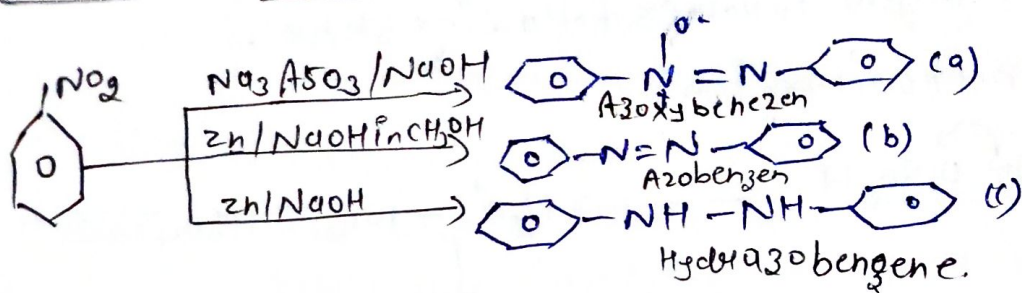
1,3,5-trinitrobenzene

Similar nitrobenzene Fe/Br_2

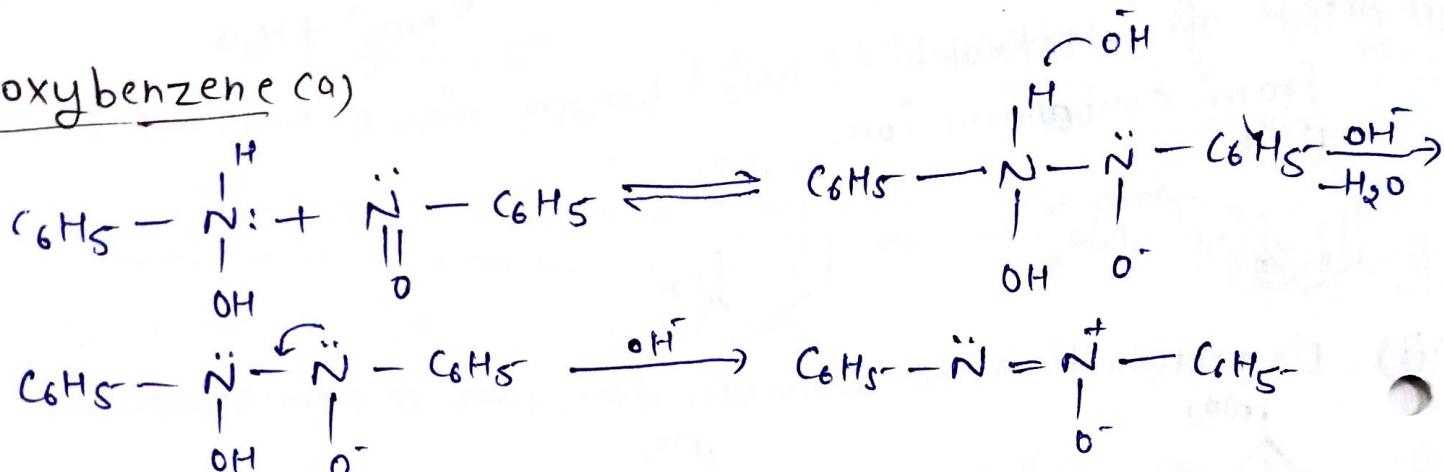
and Fuming H_2SO_4



v) Reduction in alkaline medium $\rightarrow$



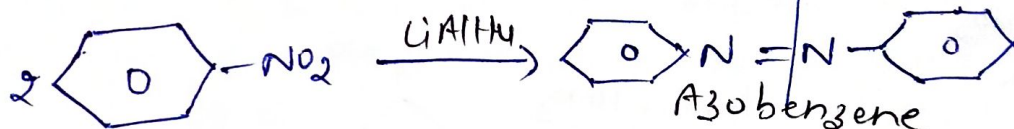
Azoxybenzene (a)



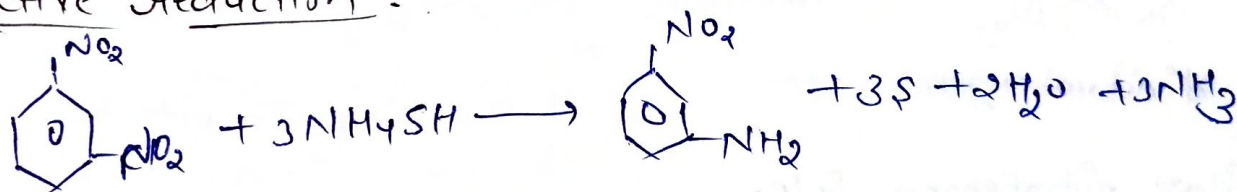
b) azobenzene (b). Intermediate formation azoxybenzene

c) Hydrazobenzene: - Formation the further reduced of azobenzene.

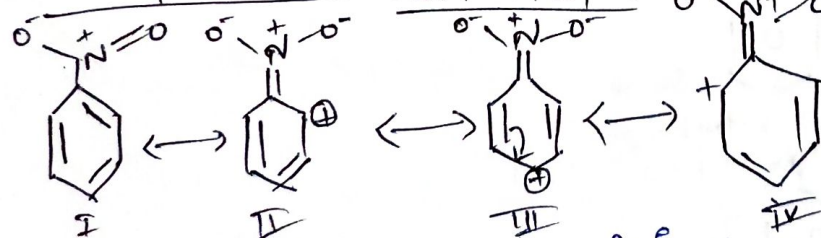
v) Reduction with LiAlH_4



vi) Selective reduction :-

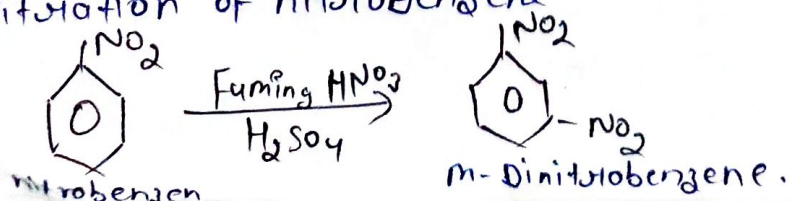


Electrophilic substitution :- Nitro group

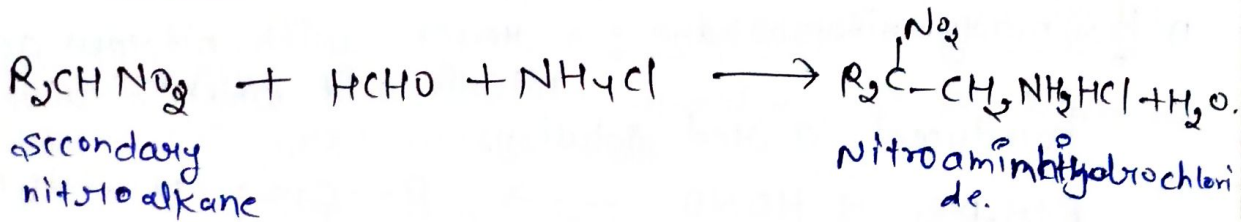


From resonating structure it is clear nitro group reduced electron density more o- and p- positions than m position.

nitration of nitrobenzene



8) Mannich Reaction : $\rightarrow$

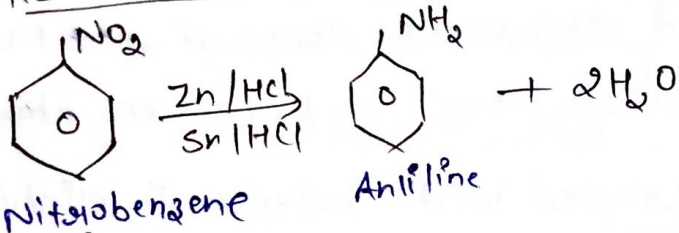


~~S~~ CHEMICAL REACTION OF NIROARENES

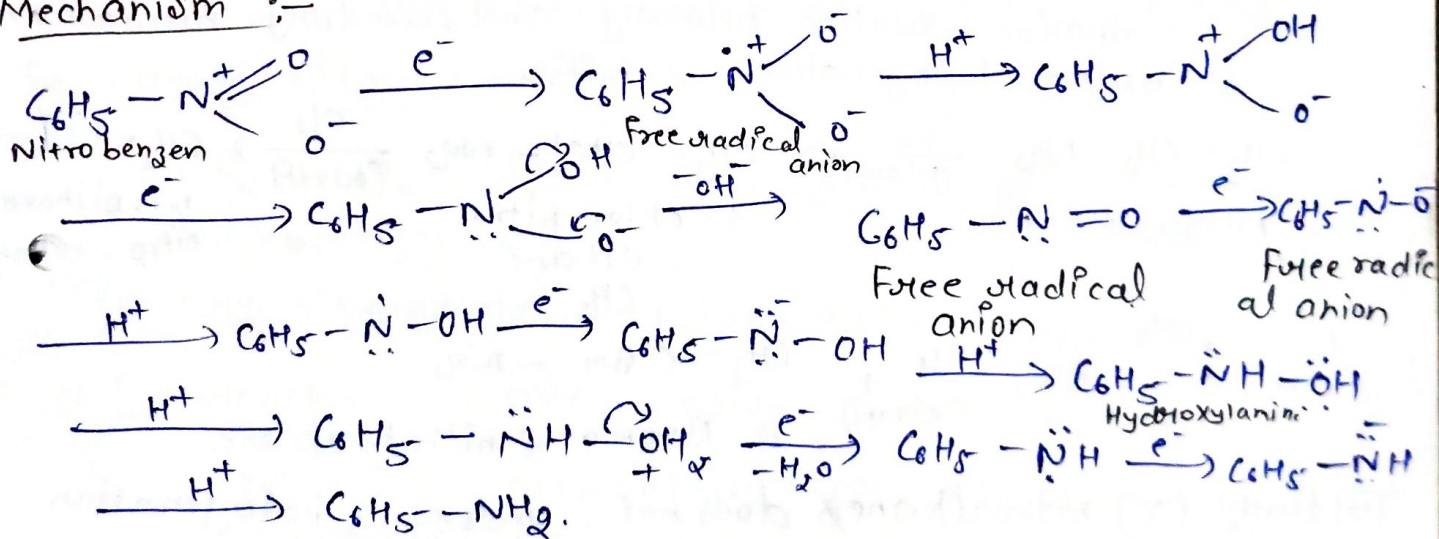
i) Acidic nature $\rightarrow$ Unlike primary and secondary nitroalkanes do not have any α -hydrogen atoms. Nitro group compound having two or more nitro group attached to benzene ring is acidic in nature (final product depends on strong electron withdrawing effect of nitro group of benzene ring).

Reduction :-

Reduction in acidic Medium $\rightarrow$

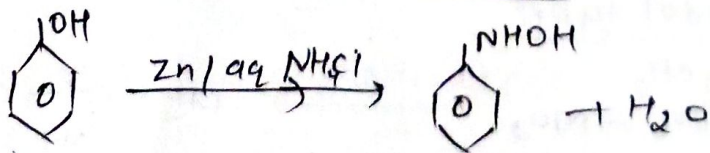


Mechanism :-



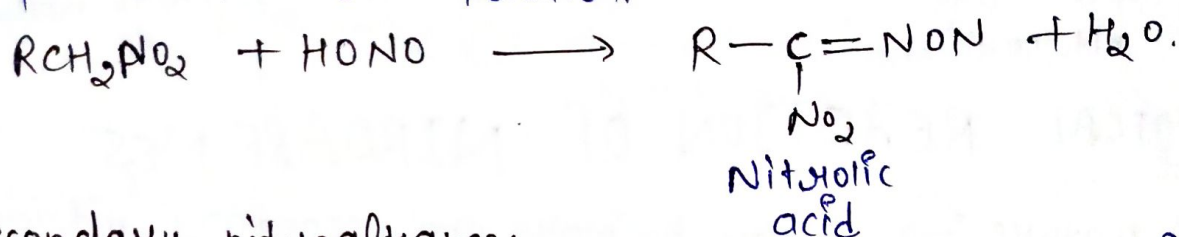
ii) Catalytic reduction ^{Aniline.} $\rightarrow$ Reduction of nitrobenzene with H_2 in presence of Ni or Pt catalyst also leads to the formation of aniline.

iii) Reduction in neutral medium $\rightarrow$ on reduction alkaline.



5) Action with nitrous acid $\therefore \rightarrow$

i) Primary nitroalkane $\therefore \rightarrow$ React with nitrous acid to form nitrolic acid. which dissolve. NaOH. to produced a med solution.

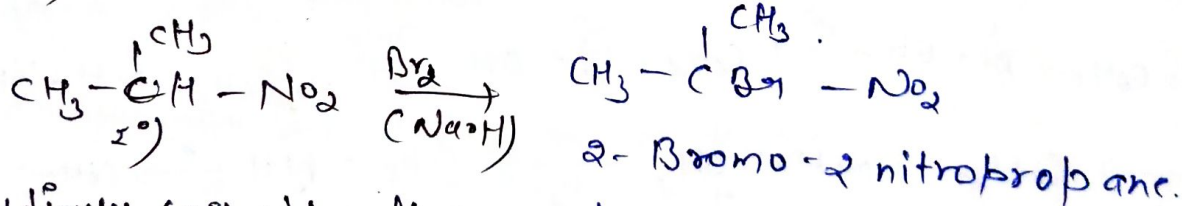
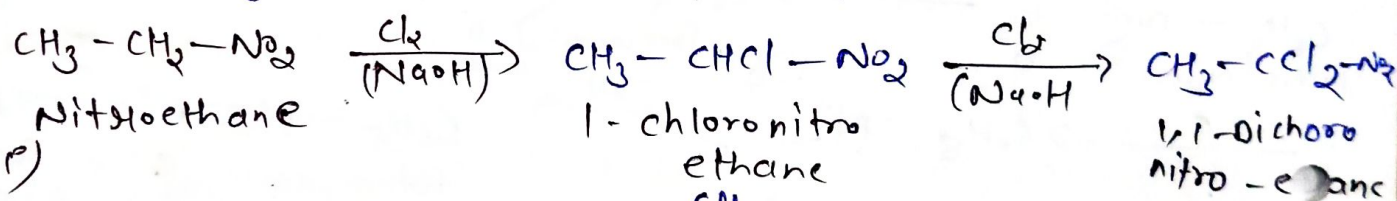


ii) Secondary nitroalkanes:- React with nitrous acid to form pseudonitroles. which have blue colour but donot dissolved NaOH.



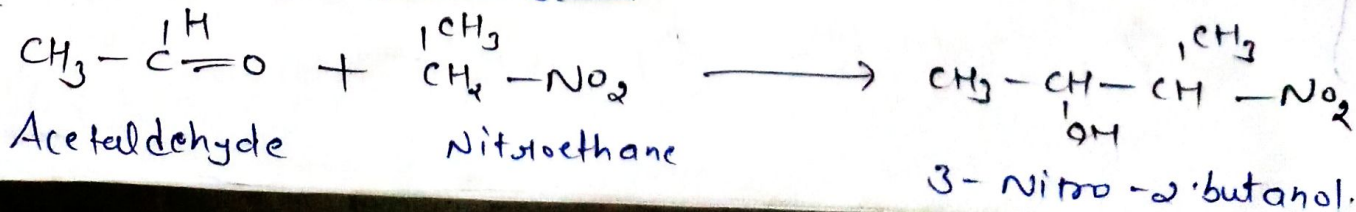
iii) Tertiary nitroalkanes and nitroarenes does not react with nitrous acid donot contain any α -hydrogen. atom.

6) Halogenation:- When treated with halogen in slightly alkaline solution primary and secondary nitroalkanes undergo halogenation α -position.



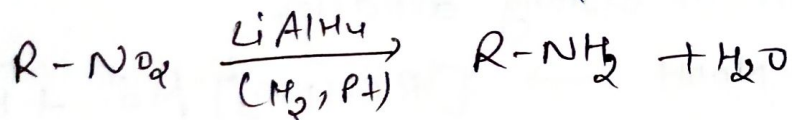
Tertiary (3°) nitroalkanes does not undergoes halogenation because they do not have α -Hydrogen

7) Condensation with aldehydes $\therefore \rightarrow$ Due to the presence of active α -Hydrogen atoms primary and (2°) nitroalkanes undergo aldol type.

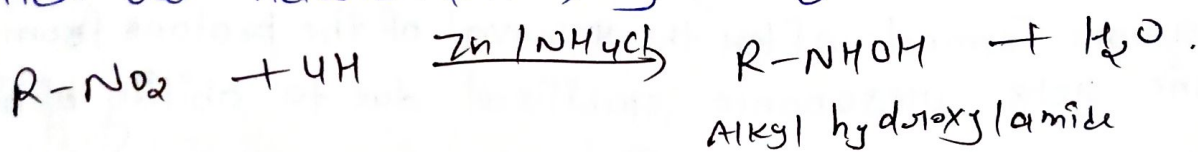


i) Catalytic reduction with LiAlH_4 :-

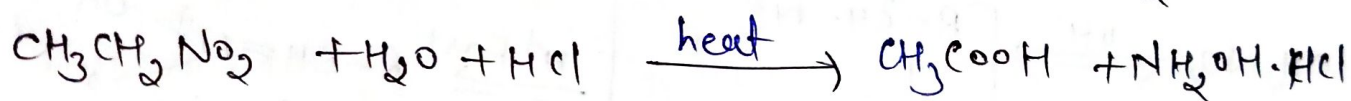
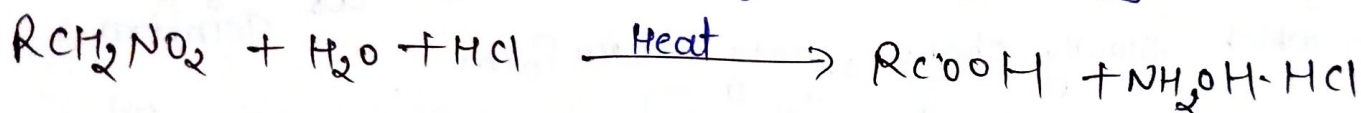
or H_2 in the presence of nickel, palladium or platinum or platinum catalyst also yield same.



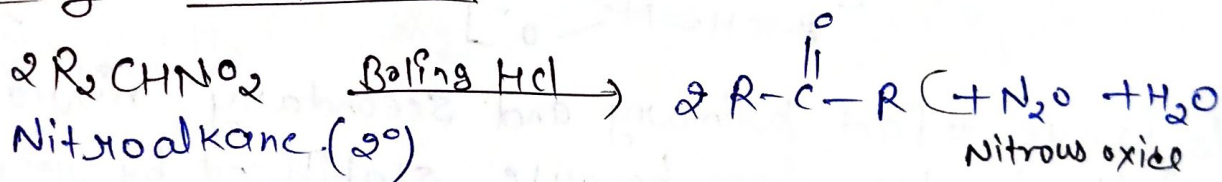
ii) Reduction in neutral medium :- If the reduction is carried out neutral solⁿ, hydroxylamine derivative



3) Hydrolysis :- When boiled with concⁿ HCl or H_2SO_4 primary nitro alkanes undergo hydrolysis form Carboxylic acid and corresponding salt hydroxylamine.



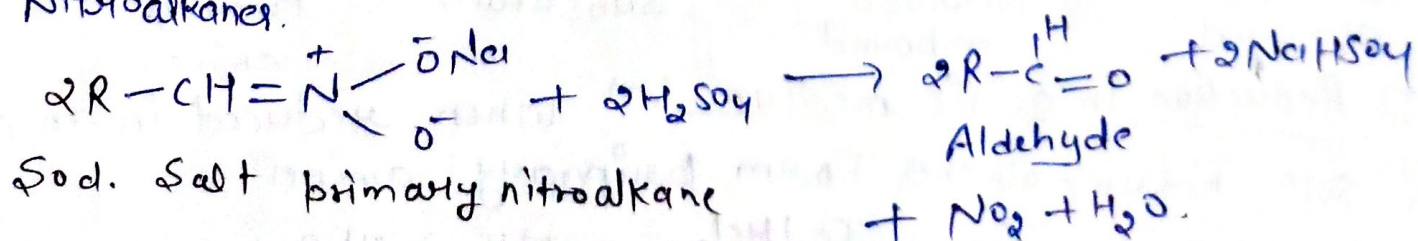
ii) Secondary nitroalkanes :-



iii) Tertiary nitroalkanes . $\rightarrow$ does not hydrolysed by acids

iv) NeF- reaction :- When sodium salts of primary and secondary nitroalkanes are hydrolysed boiling

The reaction proceeds through the aci-nitro form of Nitroalkanes.



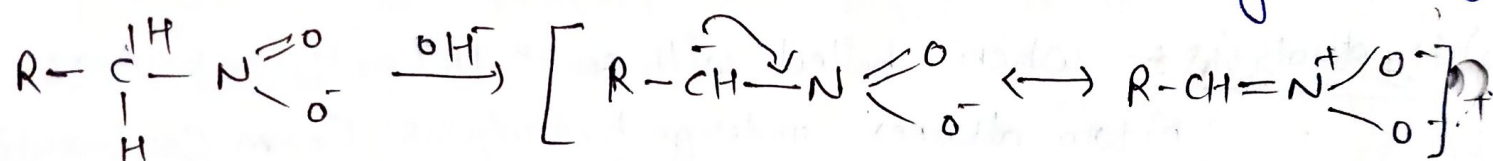
CHEMICAL REACTIONS OF NITROALKANES

1) Acidic nature - Tautomerism :- Primary and secondary nitroalkanes exhibit acidic behaviour and form salts in the presence of strong alkalies

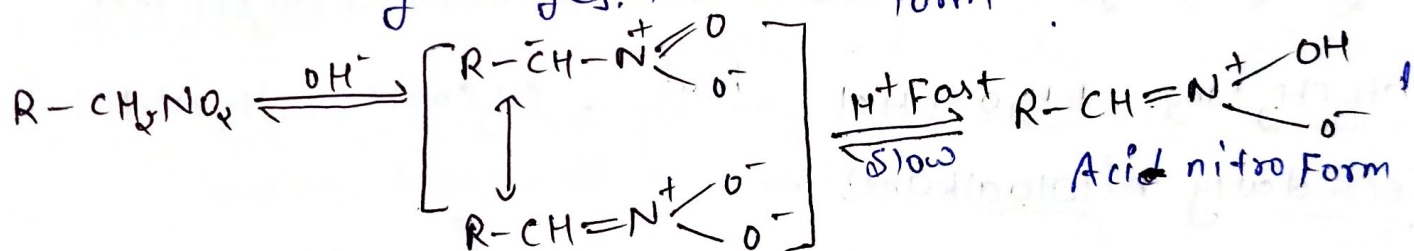


The acidity can be attributed to the fact that

- i) Nitro group has strong electron withdrawing inductive effect atoms (-I effect)
- ii) The anion formed after the removal of the protons from nitroalkane gets resonance stabilised due to ability of nitro-group



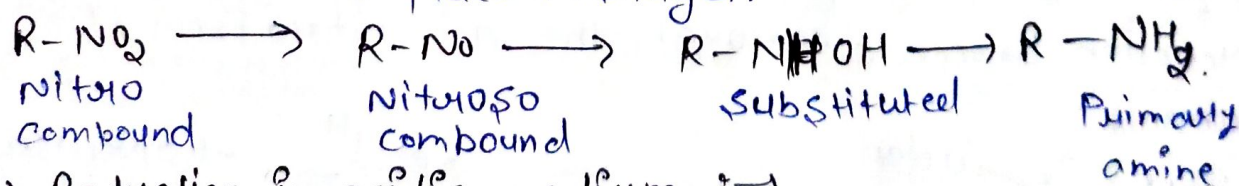
We get another form of nitroalkane known as ^{+ H₂O} acinitro form which slowly changes into nitro form



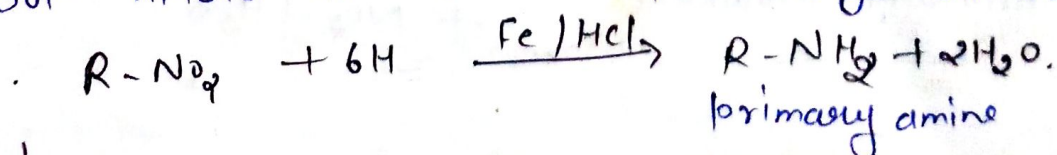
This is due to fact primary and secondary nitroalkanes exhibit tautomerism because stabilised by resonance of nitro-group.

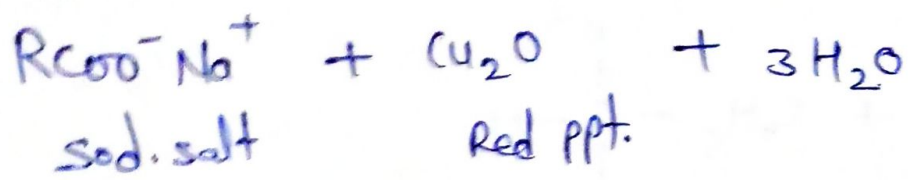
2) Reduction of nitroalkanes :- Reduction of nitro compounds

and is one their most important reaction the reduction of nitro takes place in stages.

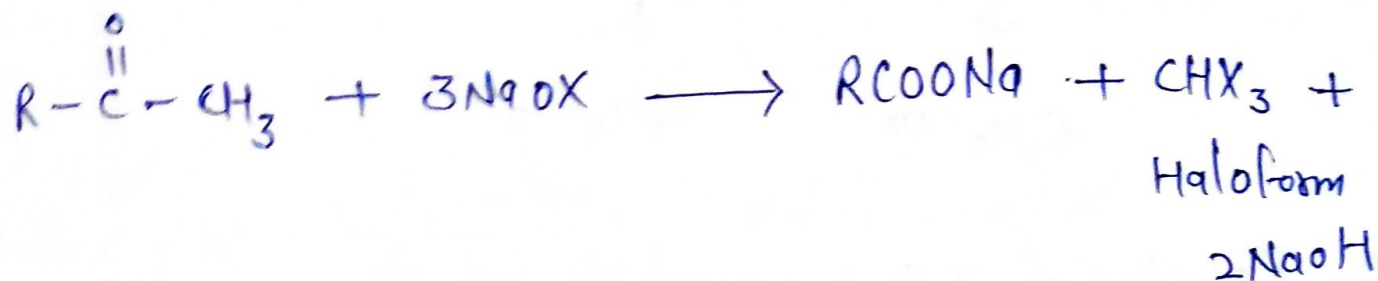


i) Reduction in acidic medium :- when reduced in an acidic soln nitro-alkanes form primary amines.

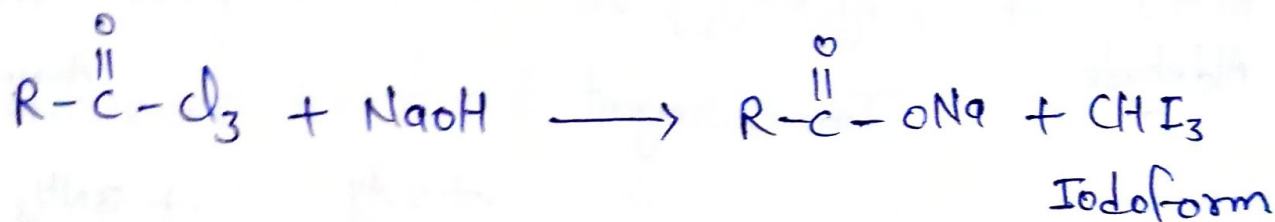




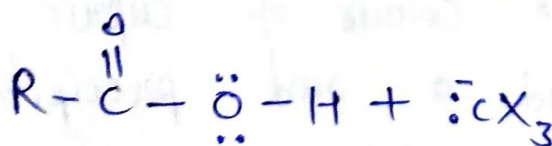
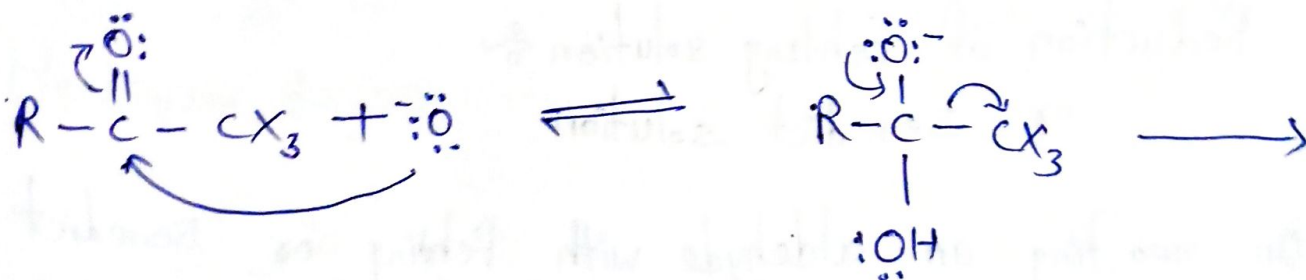
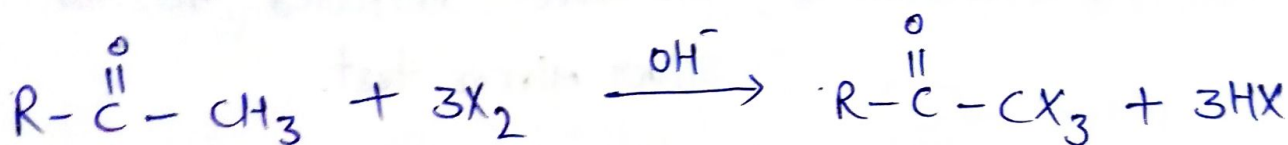
Haloform reaction :-



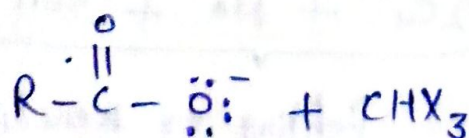
The reaction is termed as Iodoform test (or) -

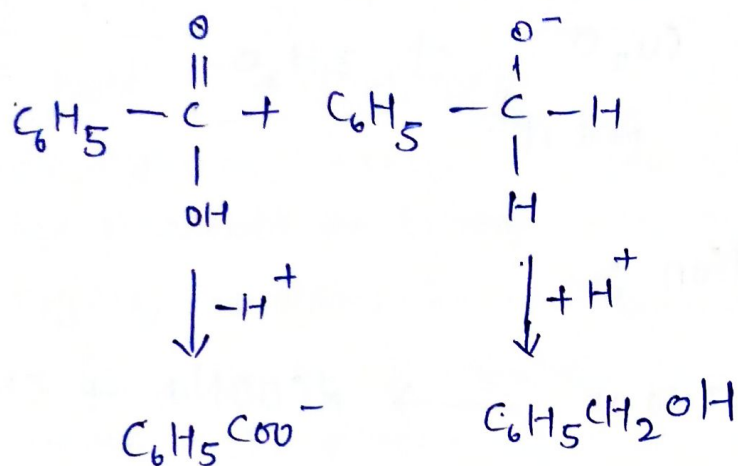


Mechanism :-

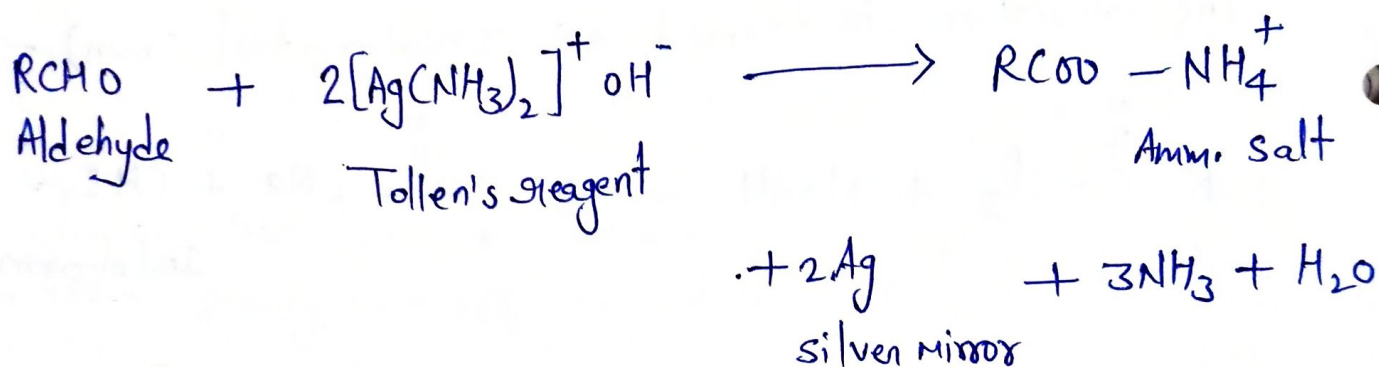


↑ Proton transfer





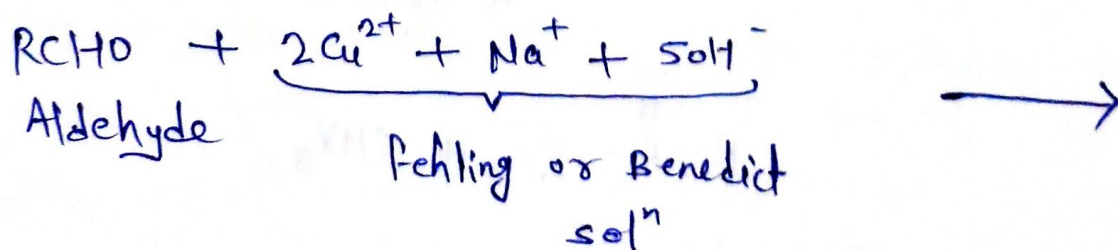
Reduction of Tollen's reagent ~

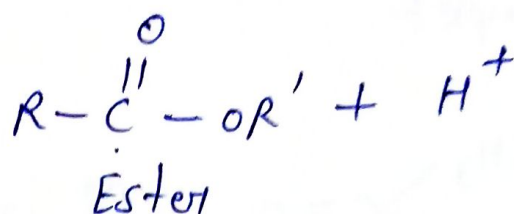
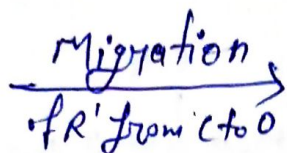
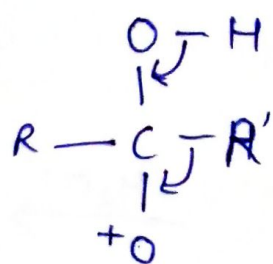
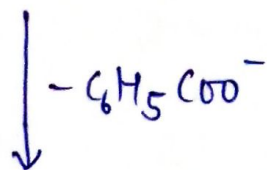
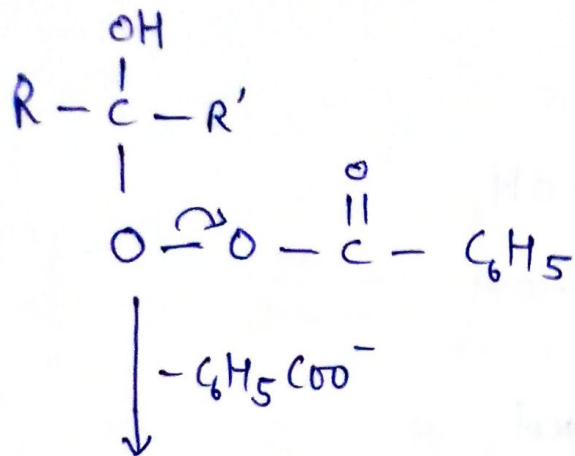


The reaction is, therefore, referred to as silver mirror test.

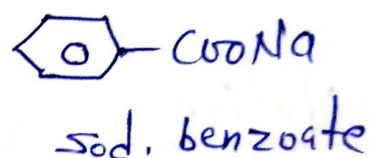
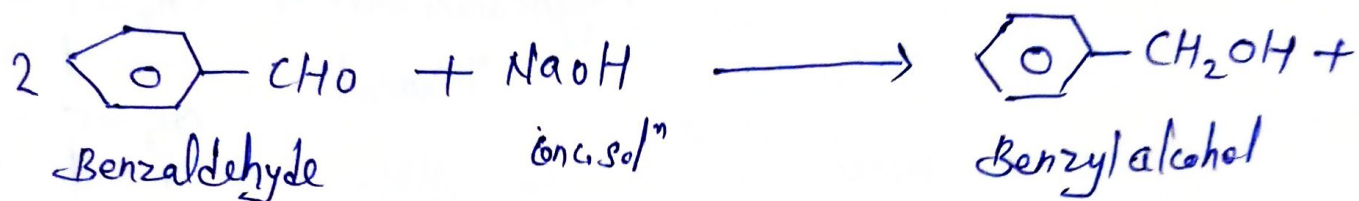
Reduction of Fehling solution ~
or Benedict solution

On reacting an aldehyde with Fehling or Benedict solⁿ, the blue colour of cupric ion is discharged and a red precipitate of cuprous oxide is formed. The rxn may be —

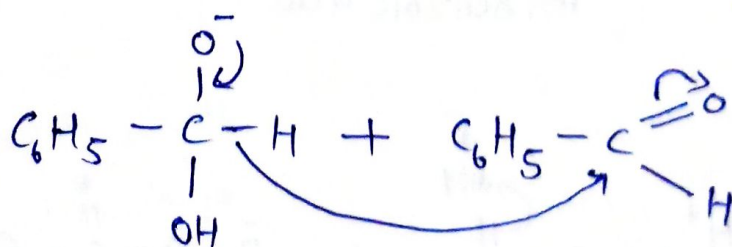
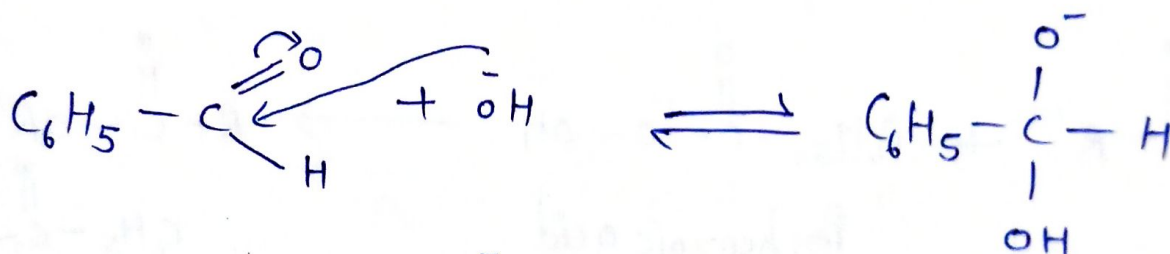




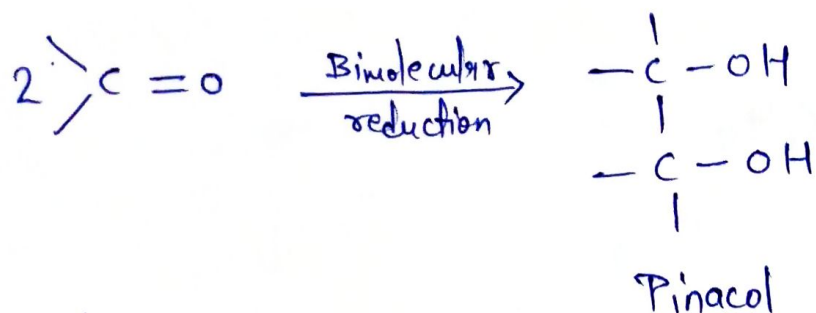
* Cannizzaro reaction :-



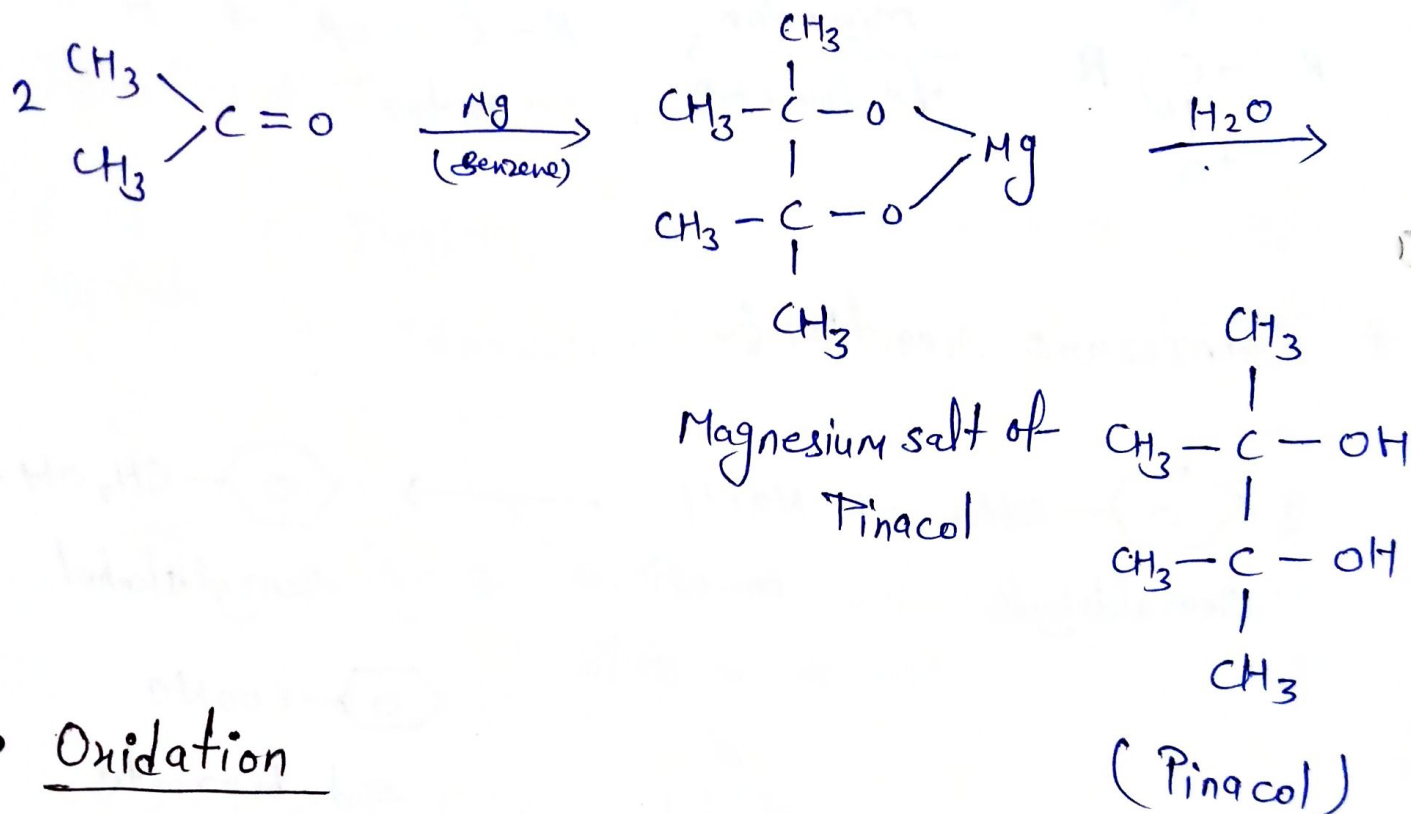
• Mechanism :-



* Bimolecular reduction :-

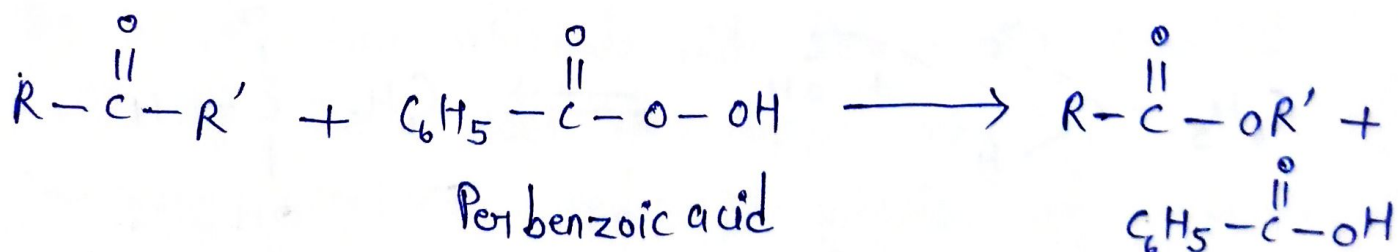


Example :-

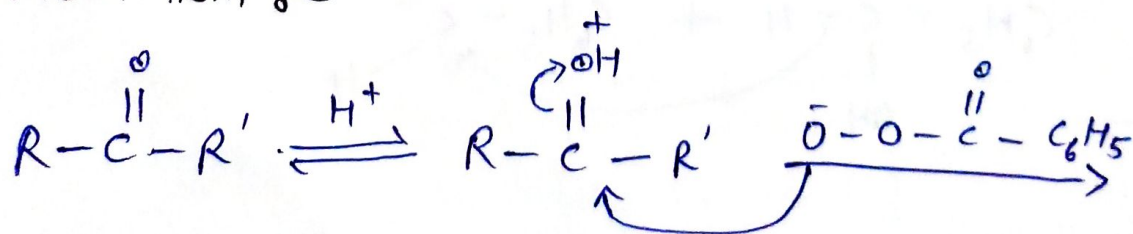


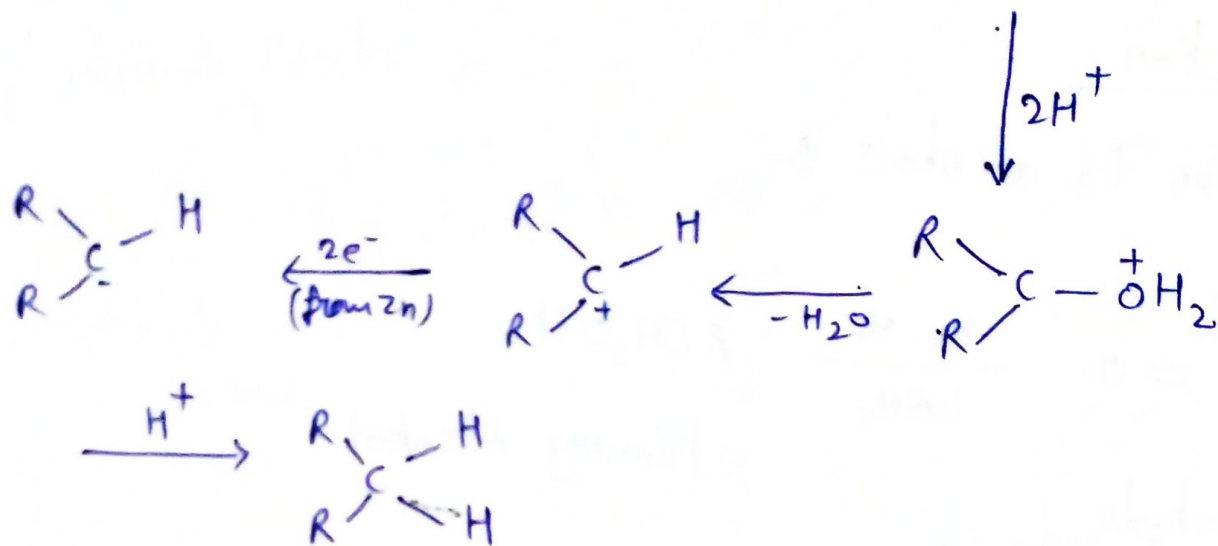
• Oxidation

Baeyer-Villiger oxidation :-

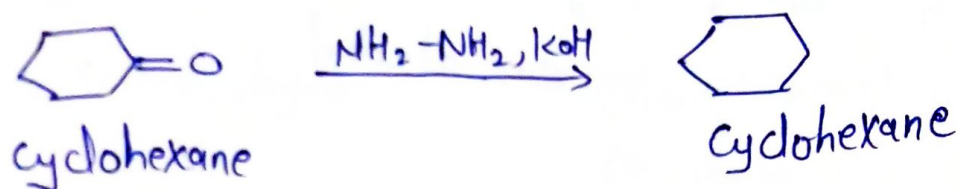


Mechanism :-

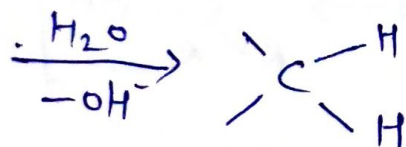
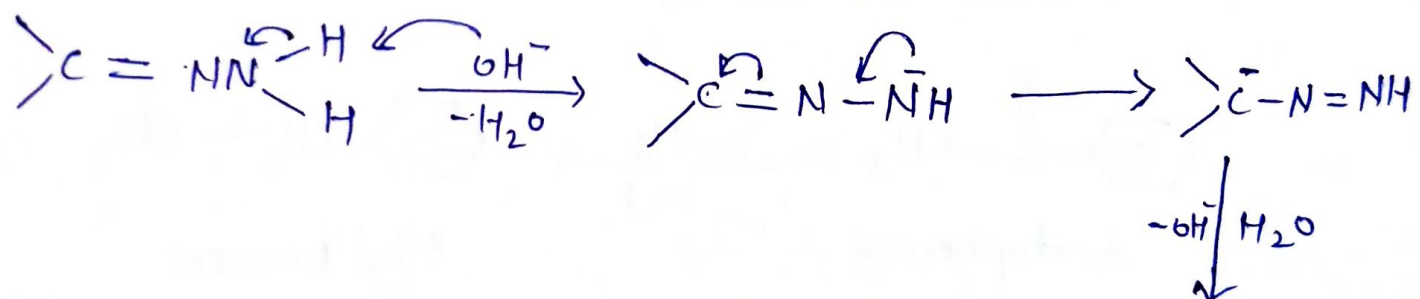




* Wolff-Kishner reduction :-

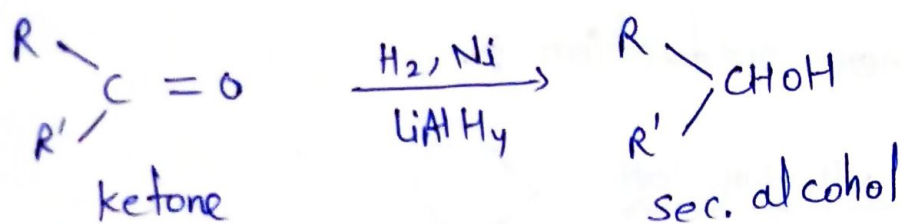
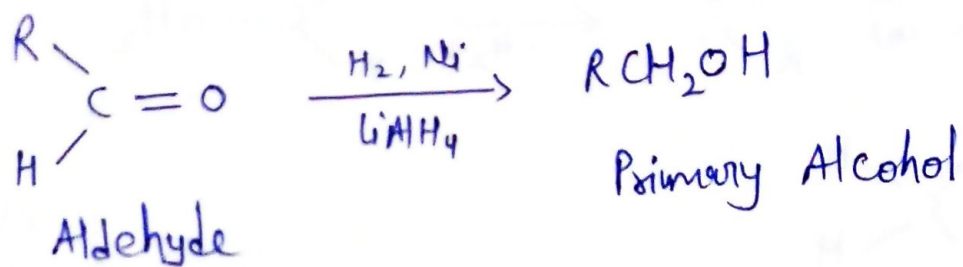


Mechanism :-

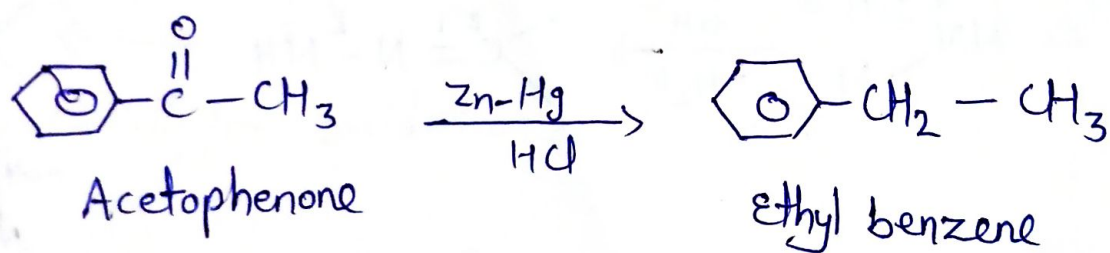


* Reduction

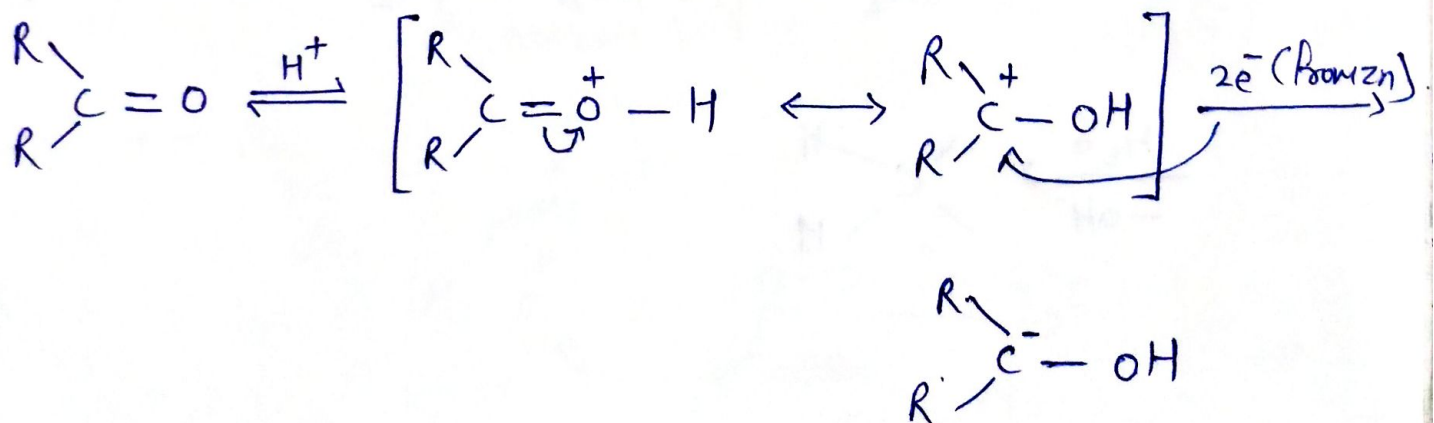
Reduction to alcohols ~

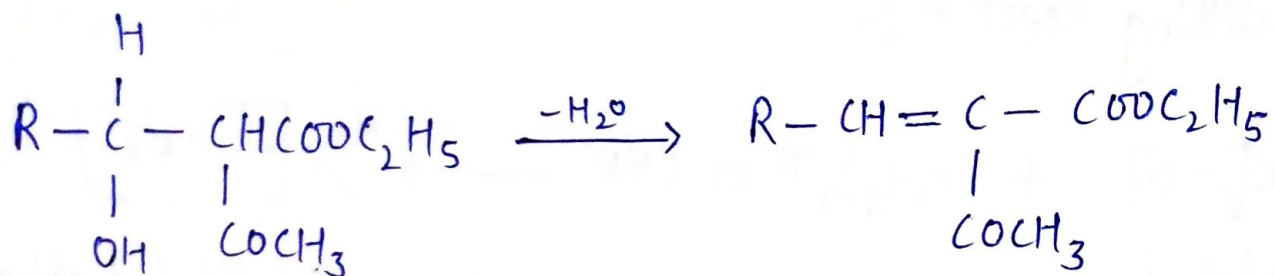


* Clemmensen reduction ~

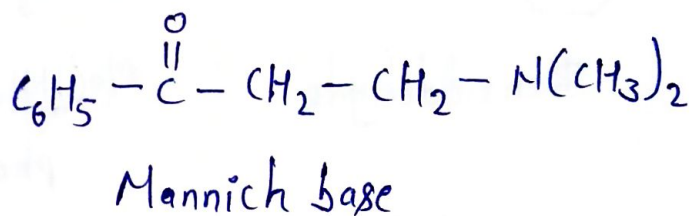
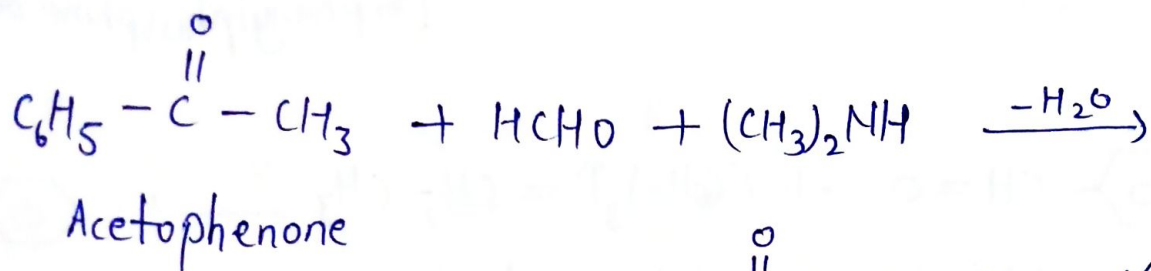


Mechanism ~

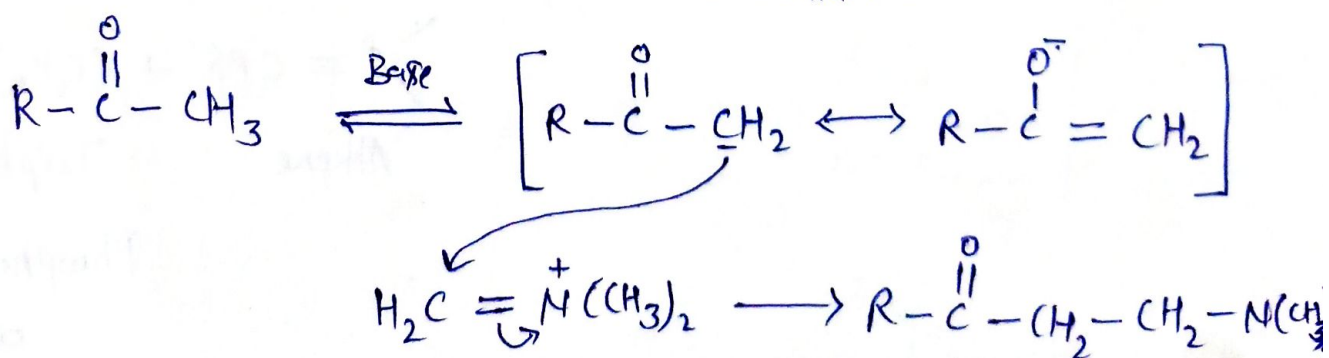
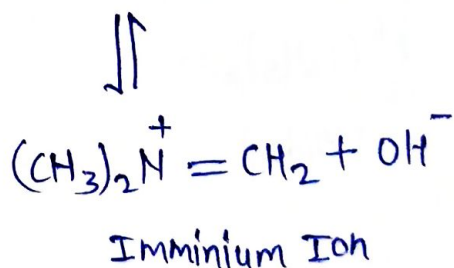
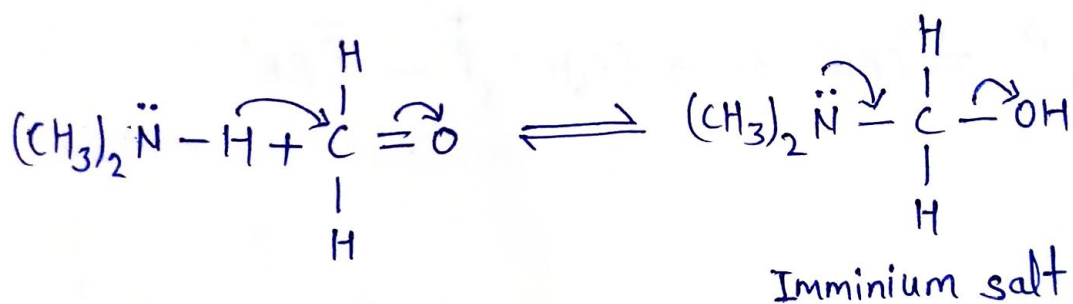




* Mannich Reaction :-



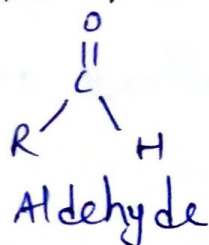
Mechanism :-



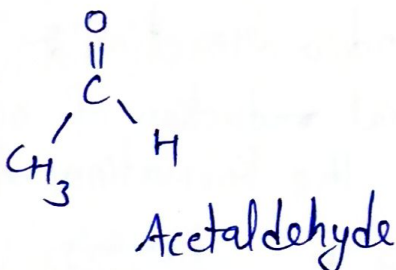
Aldehydes and Ketones

- Both aldehydes and ketones contain a carbonyl group ($>C=O$) and hence they are collectively known as carbonyl compounds. They may be represented by the general formula $C_nH_{2n}O$.

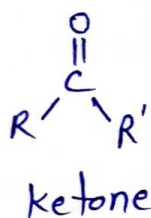
- In case of aldehydes :-



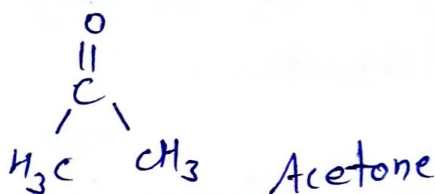
examples:-



- In case of ketones :-



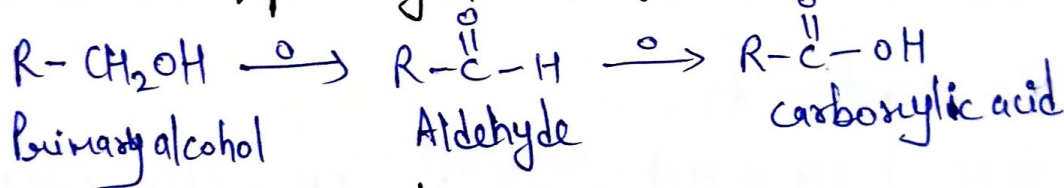
Examples:-



- Preparation of ALDEHYDES AND KETONS...

⇒ Preparation of aldehydes is

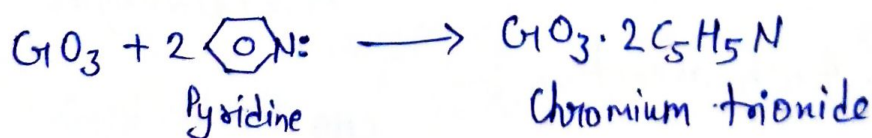
- 1) Oxidation of primary alcohols is That is:



- special oxidising agents :-

- i) Sarett's reagent or Collins's reagent is

It consists of a complex formed by careful addition of CrO_3 to excess of Pyridine ($\text{C}_5\text{H}_5\text{N}$).



- ii) Corey's reagent is

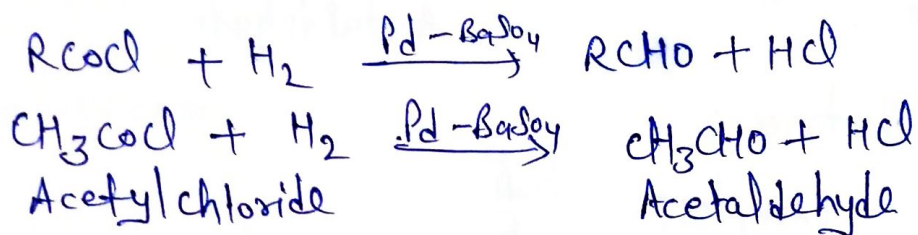
It consists of Pyridinium chlorochromate (PCC), $\text{C}_5\text{H}_5\text{NH}^+\text{CrO}_3\text{Cl}^-$ and HCl .

It is also used in methylene dichloride solvent to convert alcohols into aldehydes.

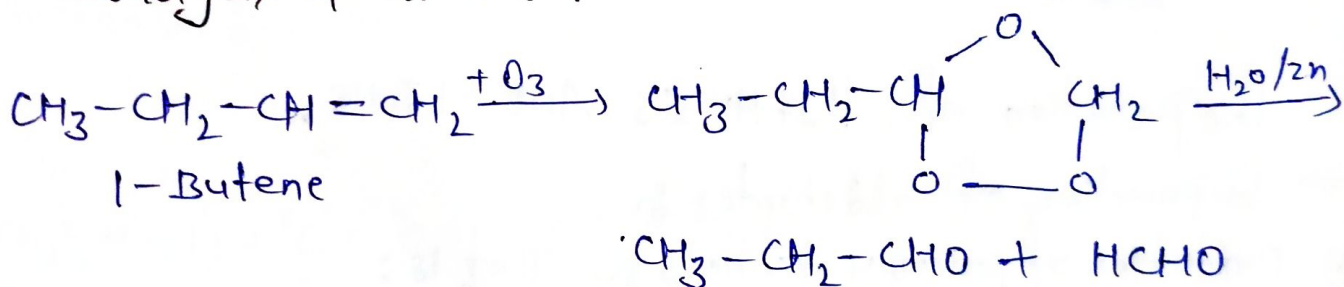
iii.) Pyridinium dichromate (PDC), $(C_5H_5NH^+)_2 Cr_2O_7^{2-}$. It is obtained by mixing pyridine - potassium dichromate and HCl in CH_2Cl_2 .

• (2.) Rosenmund's reaction :-

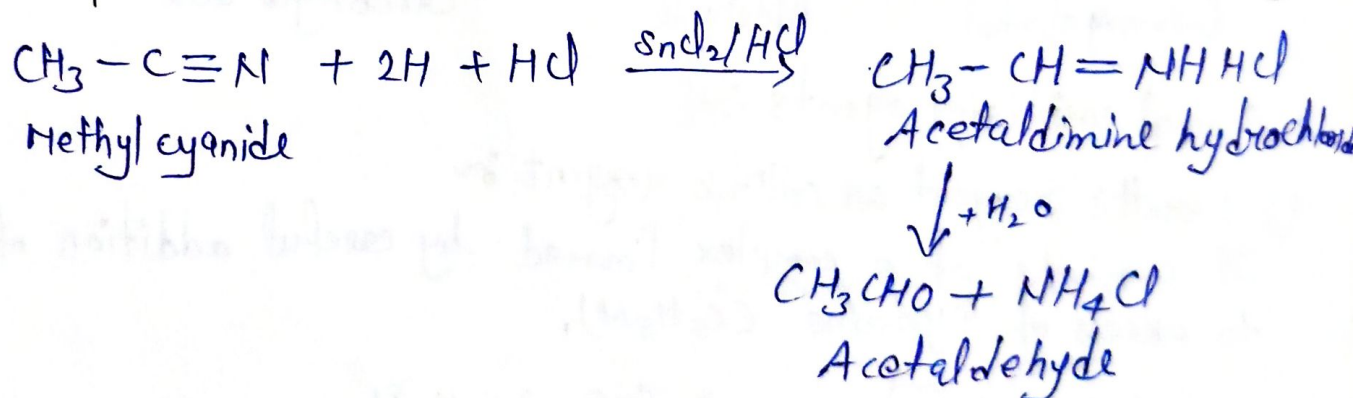
The partial reduction of acid chlorides affords another method for the formation of aldehydes.



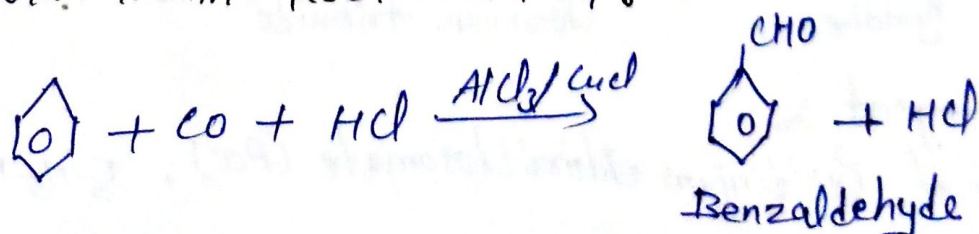
3.) Ozonolysis of alkenes :-



4.) Stephen's reaction :-

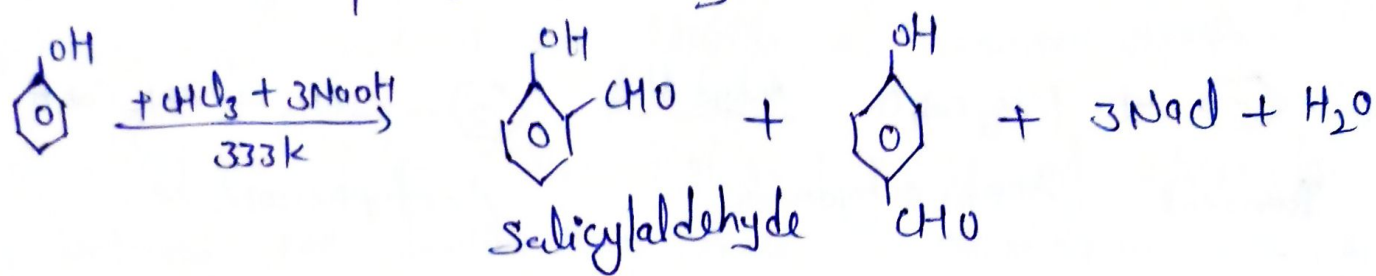


5.) Gattermann-Koch reaction :-



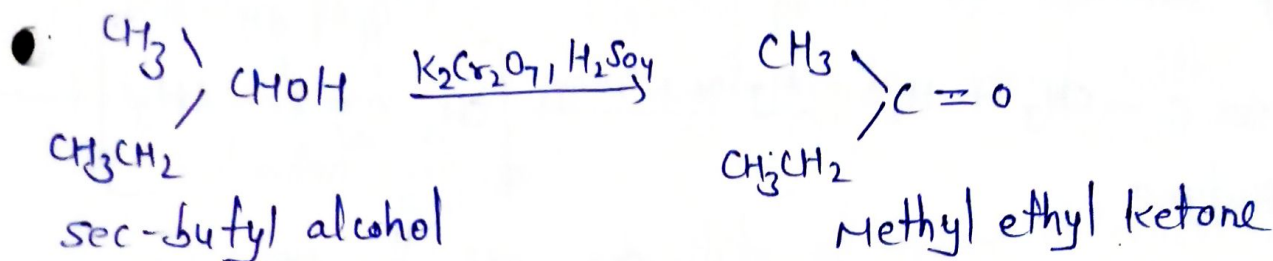
6.) Reimer - Tiemann reaction :-

The reaction is carried out by treating a phenol with chloroform and aqueous sodium hydroxide solution.



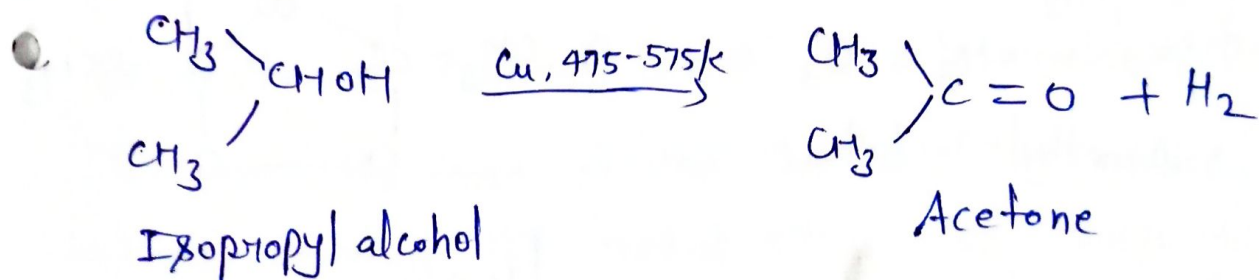
Preparation of ketones :-

1.) Oxidation of secondary alcohols =

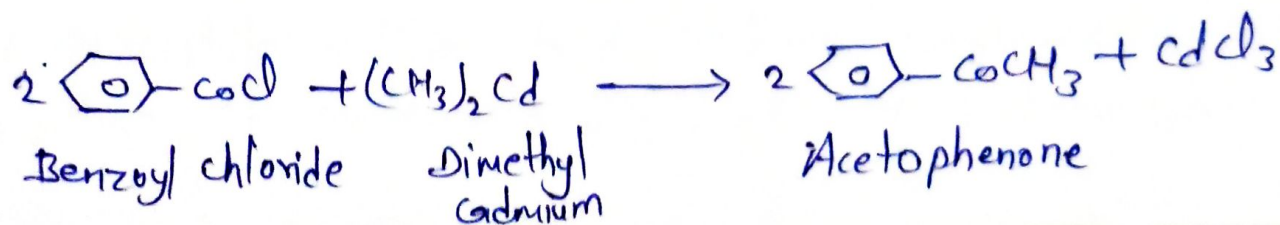
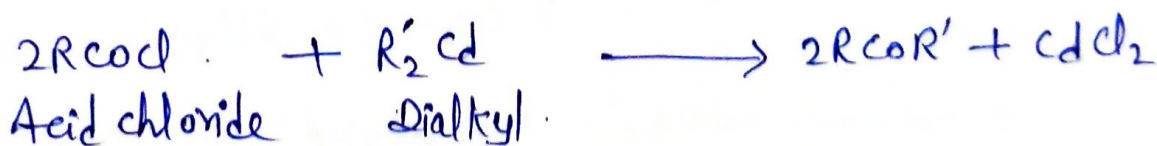


There is no risk of further oxidation of ketones taking place as ketones are not easily oxidised.

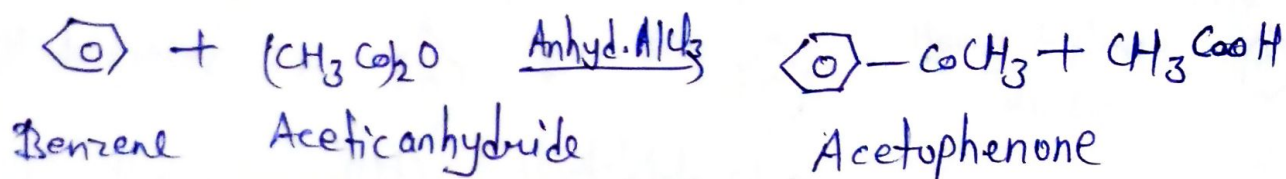
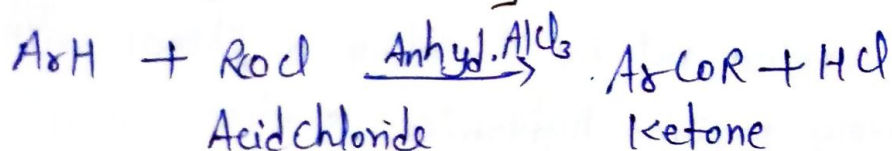
2.) Catalytic dehydration of secondary alcohols :-



3.) Reaction of acid chlorides with organocadmium compounds :-

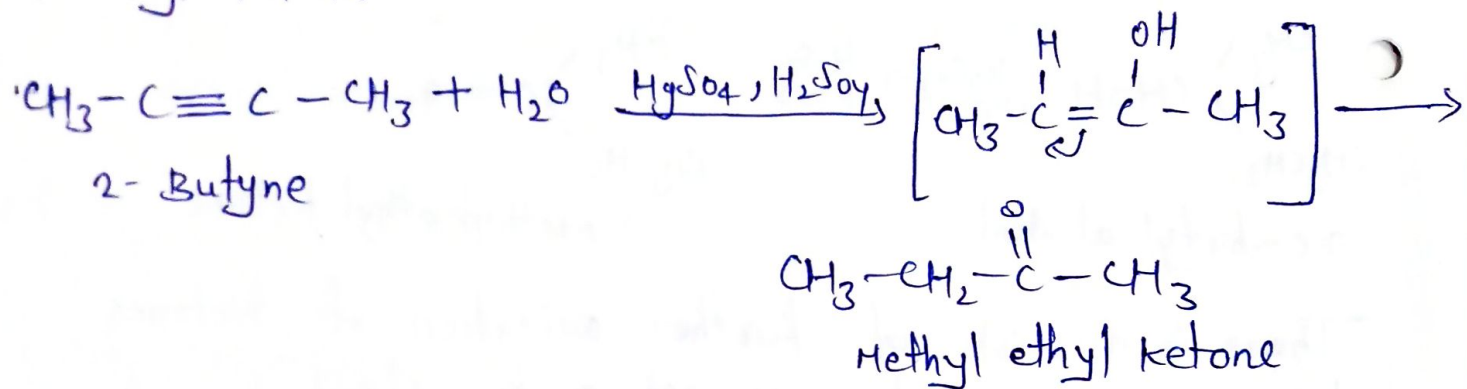


4.) Friedel - Crafts acylation :-

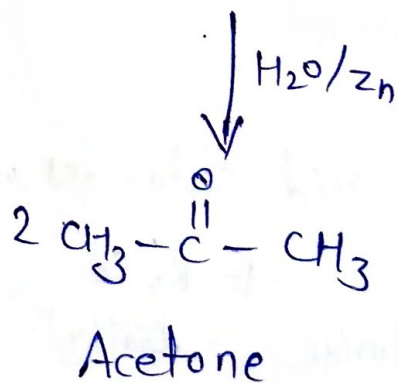
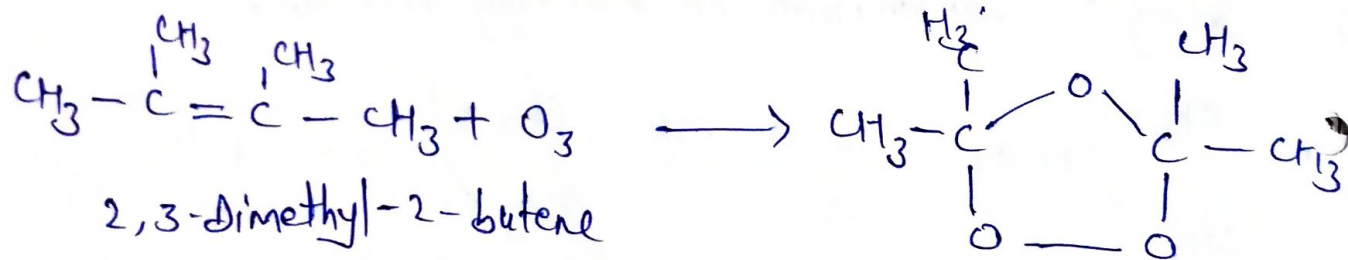


5.) Hydration of alkynes :-

Hydration of homologues of acetylene leads to the formation of methyl ketones.



6.) Ozonolysis of alkenes :-



Physical Properties of Aldehydes and Ketones :-

- 1.) Physical state :- With the exception of formaldehyde which is a gas at a room temp, most of the common aldehydes and ketones are liquids at ordinary temp.
- 2.) Boiling points :- The Boiling points of aldehydes or ketones are lower than those of alcohols or carboxylic acids. There are no hydrogen bonds b/w aldehyde or ketone molecules. Al boiling points is higher.
- 3.) Melting points :- Melting points of aldehyde and ketones do not show any regular trend with increase in molecular weights.
- 4.) Solubility :- The solubility of lower aldehydes and ketones in water is due to the formation of intermolecular hydrogen bonds involving the carbonyl group as shown ahead.

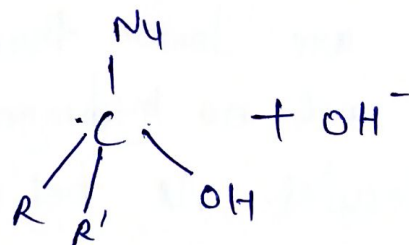
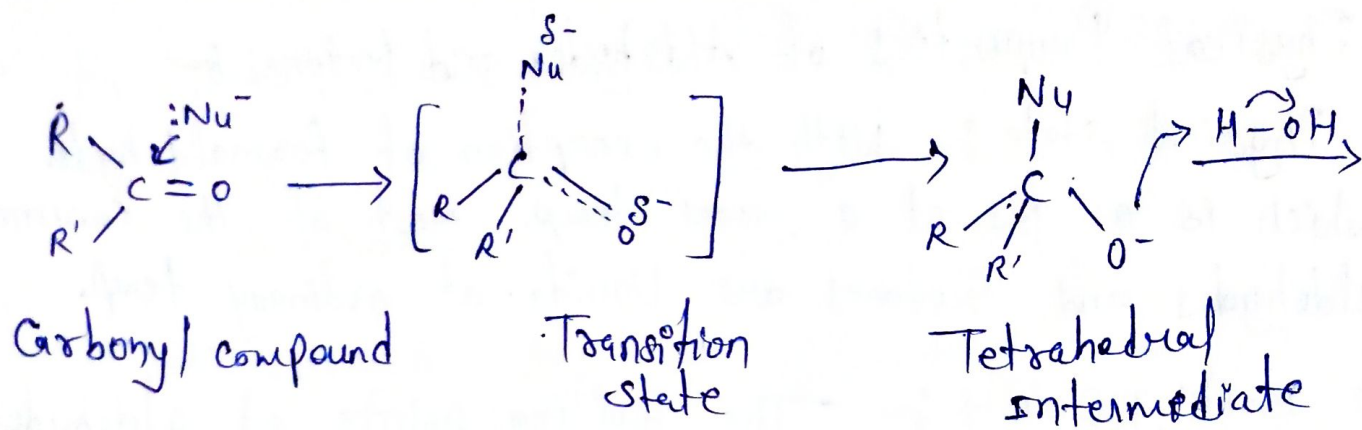
Chemical properties of Aldehydes or Ketones :-

• Reactivity of carbonyl group Towards Nucleophilic ~~Acid~~ Attack

Therefore, the most of the reactions of Aldehydes or ketones involve the initial attack of nucleophilic reagent on the relatively less stable electron deficient carbonyl carbon and ultimately lead to the formation of addition products.

Mechanism of Nucleophilic Addition Reaction :-

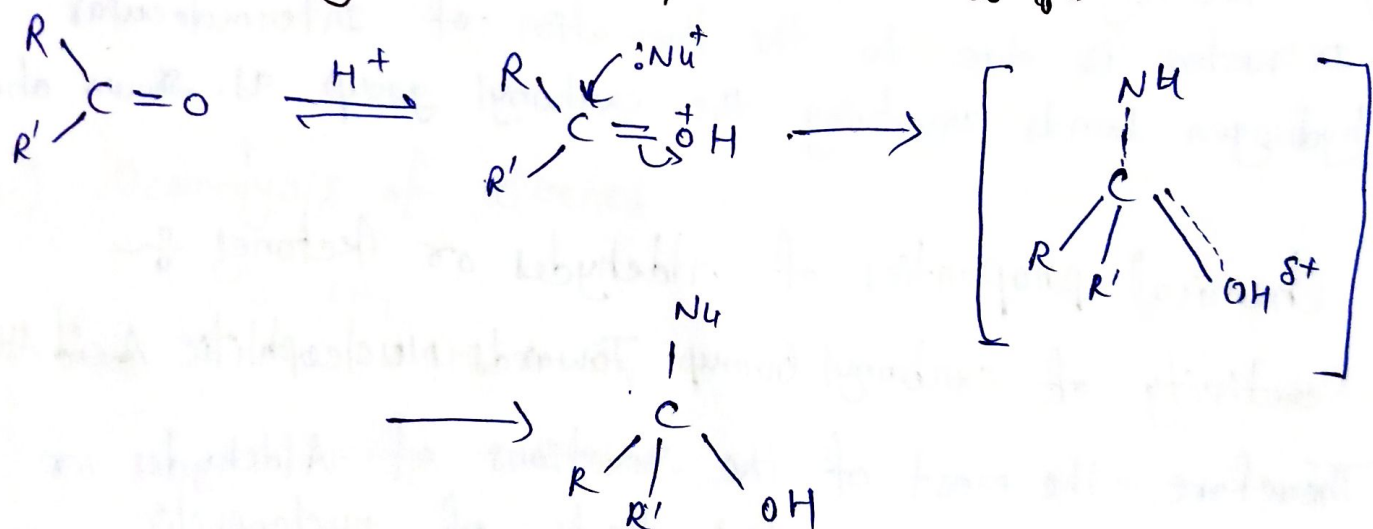
The nucleophilic addition to a carbonyl compound is initiated by attack of nucleophile (:Nu^-) on the carbonyl carbon.



Addition product

The attacking nucleophilic reagent can be either a negatively charged ion and or a neutral molecule.

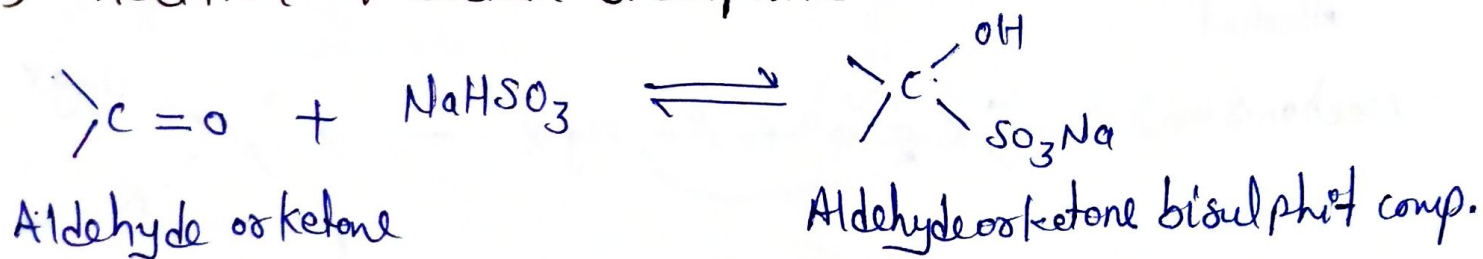
Acid Catalysis in Nucleophilic Reactions



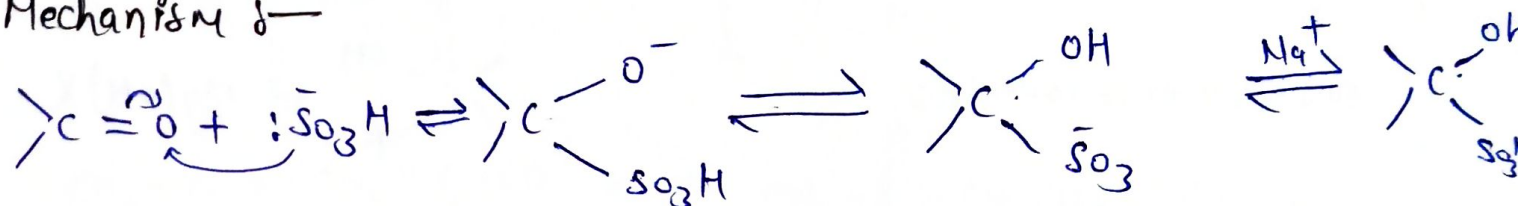
The addition of powerful nucleophiles does not require any acid catalysis at all, it is only the weak nucleophiles such as alcohols and ammonia derivatives which need the assistance of a little acid catalysis.

* Nucleophilic's Addition Reactions:-

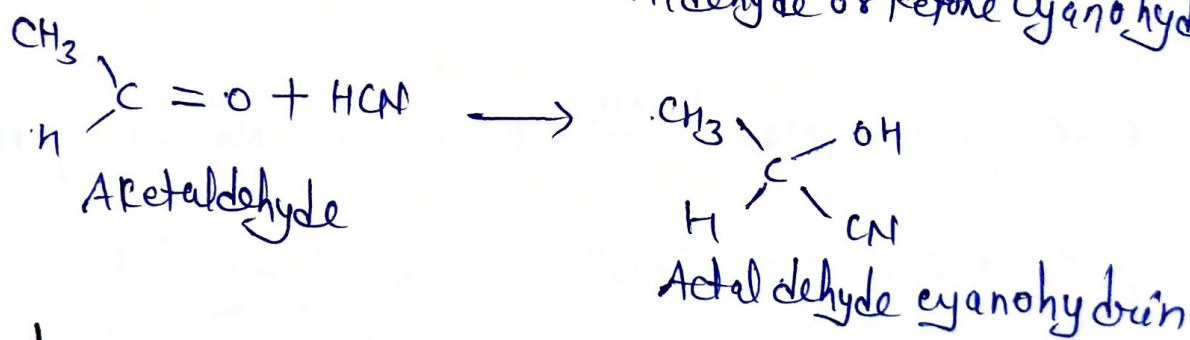
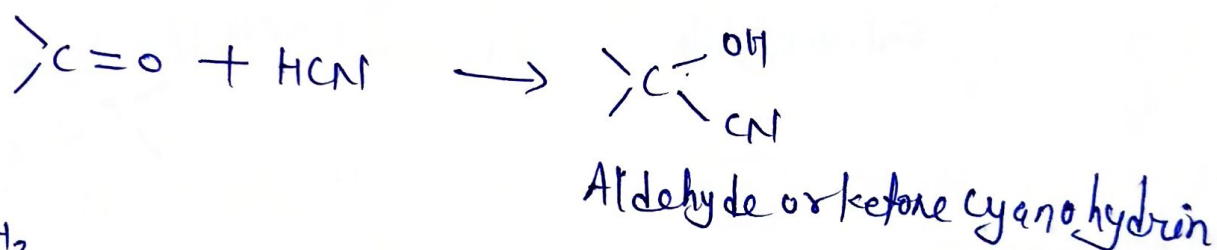
1.) Addition of sodium bisulphite :-



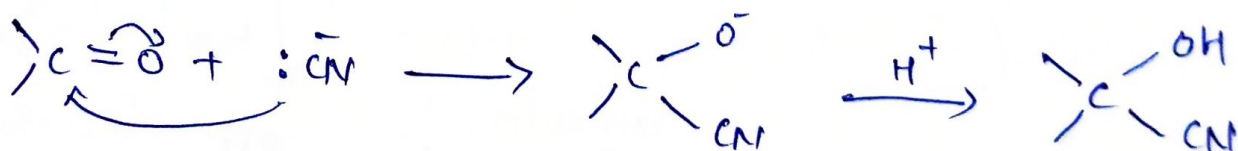
Mechanism :-



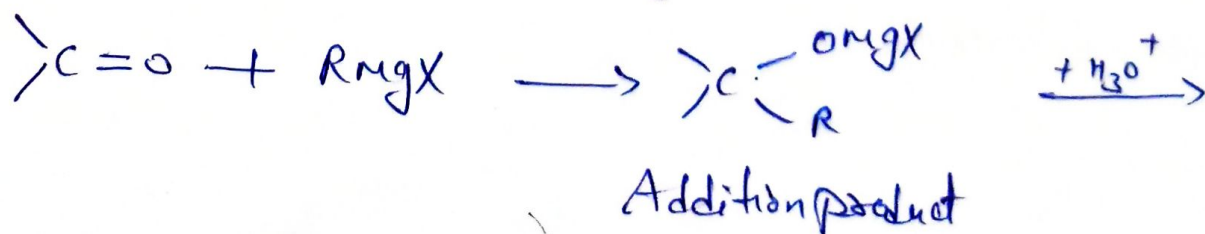
2.) Addition of hydrogen cyanide :-

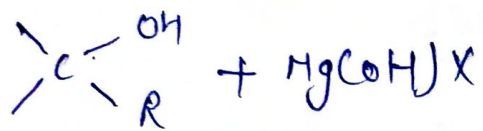


Mechanism :-

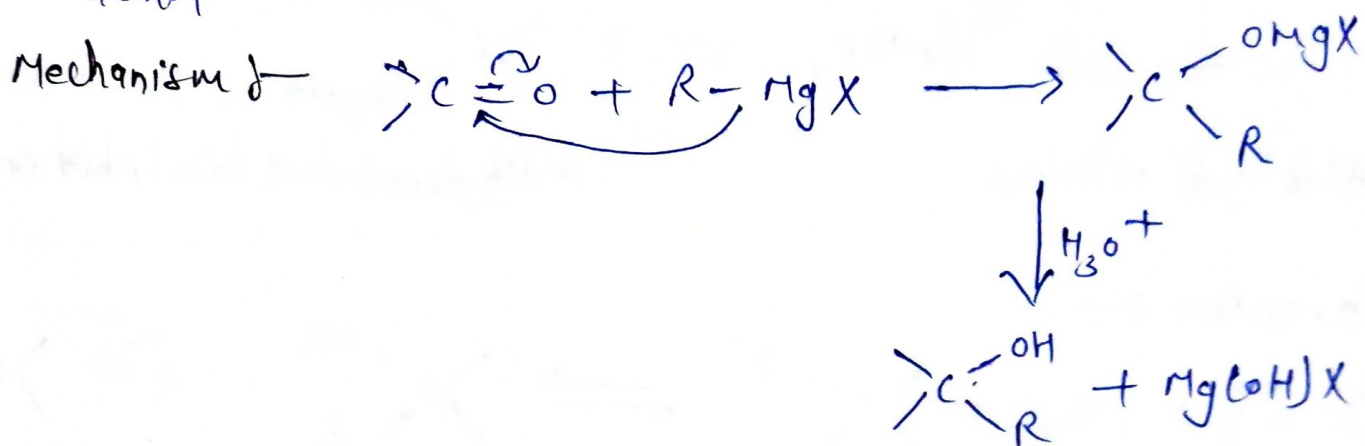


3.) Addition of Grignard reagents :-

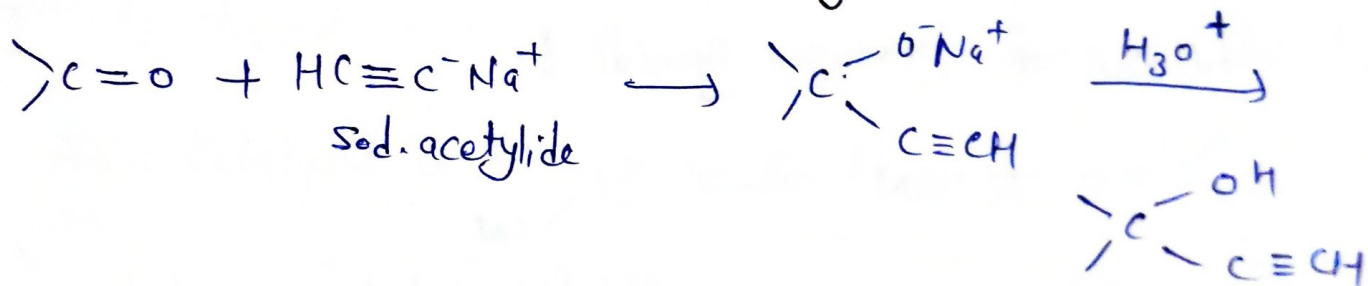




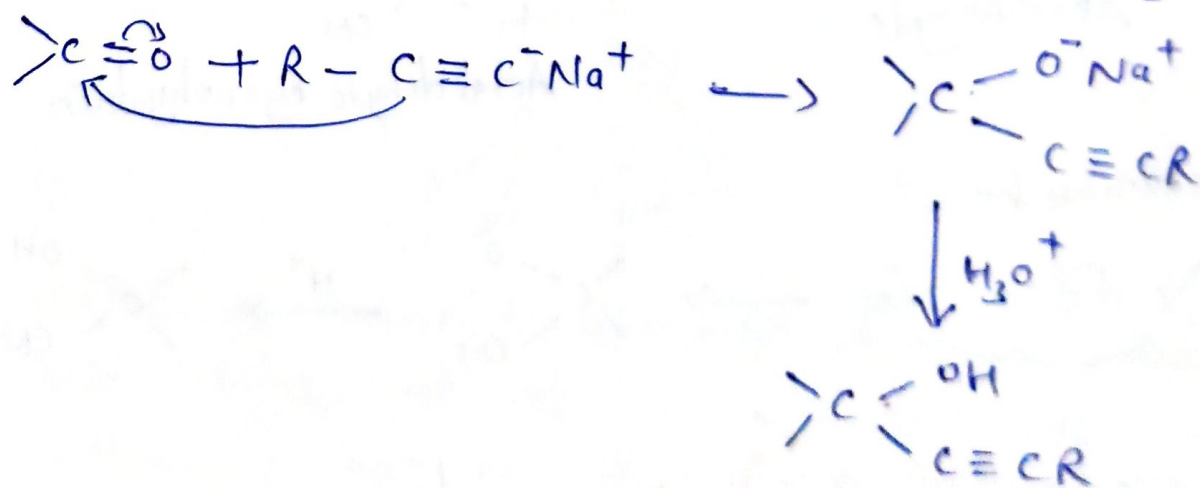
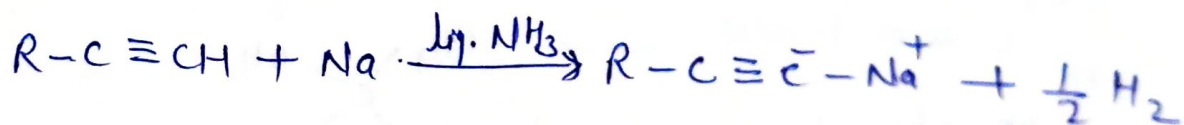
Alcohol



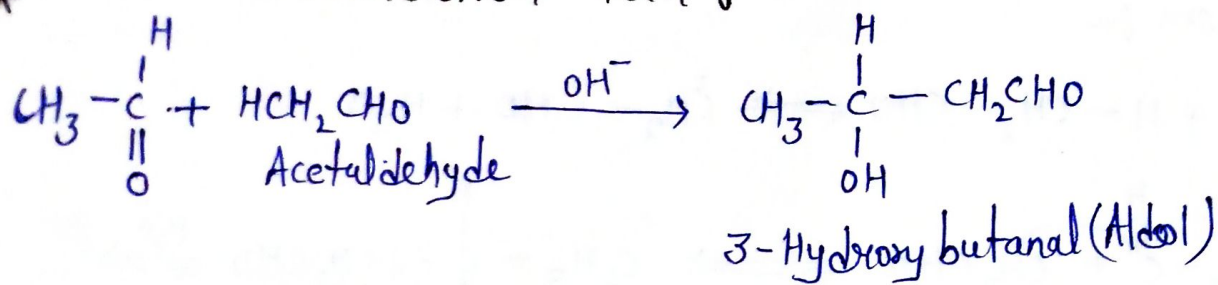
4.) Addition of salts of terminal alkynes :-



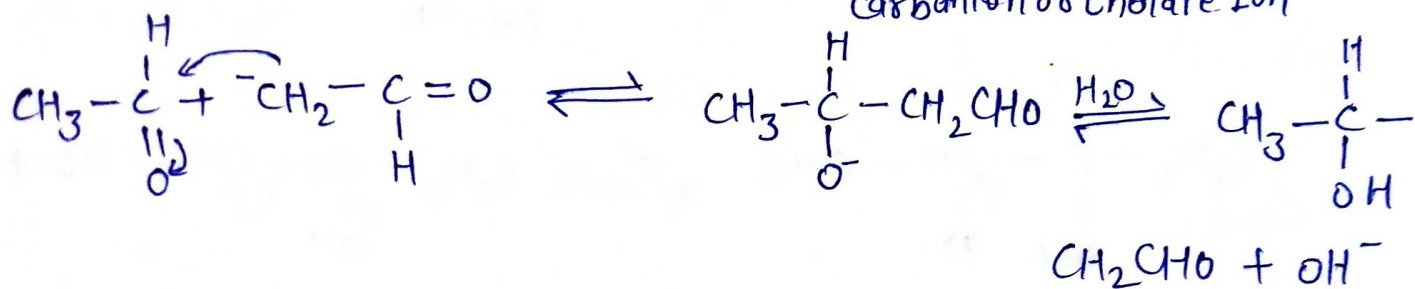
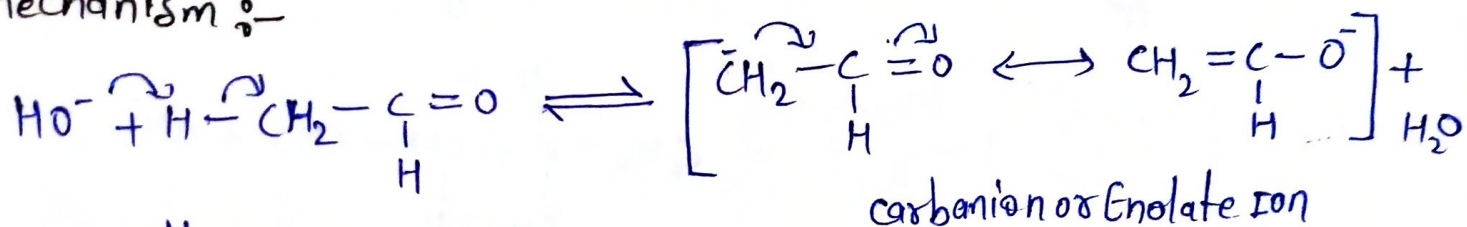
Mechanism :-



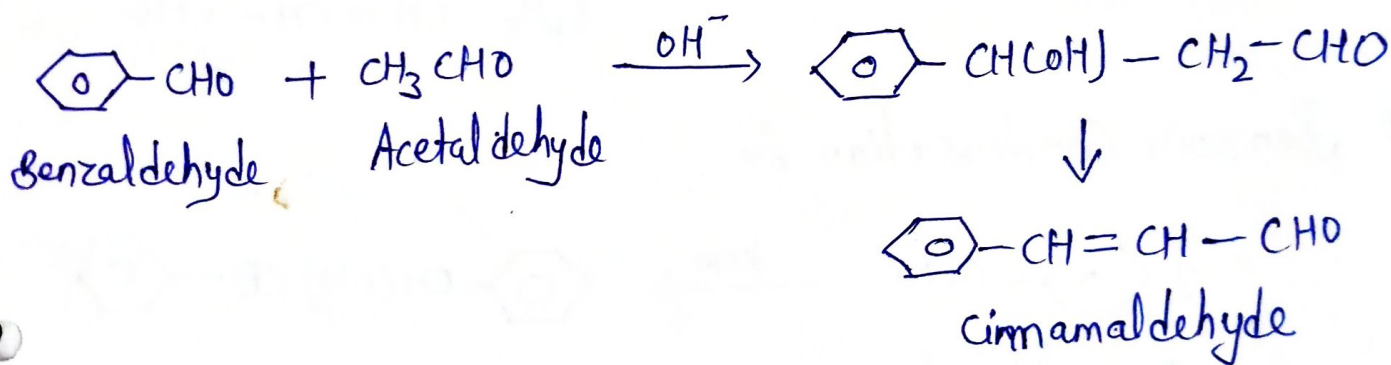
* Aldol condensation Reaction :-



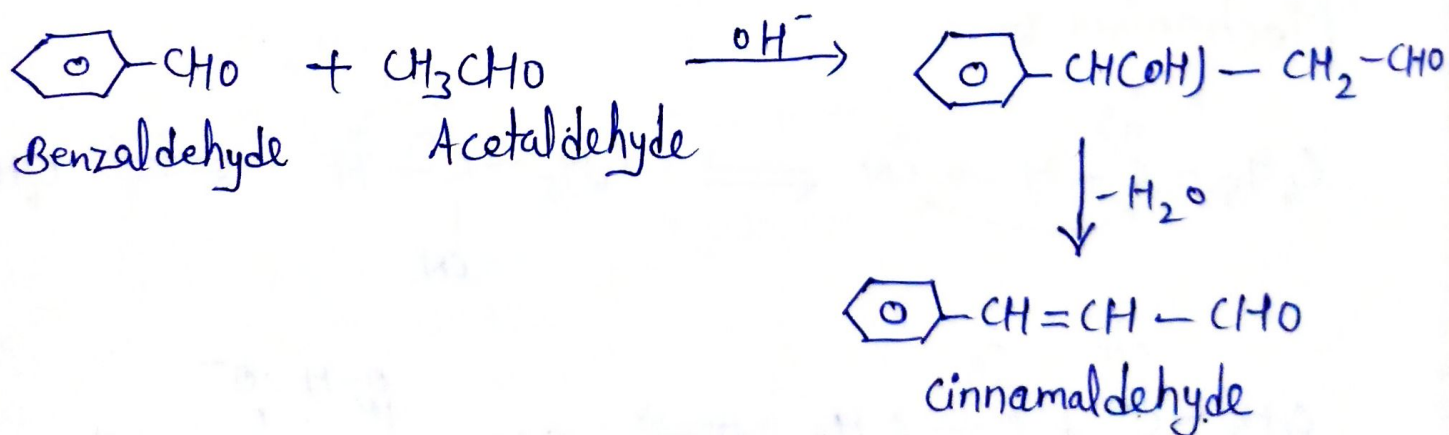
Mechanism :-



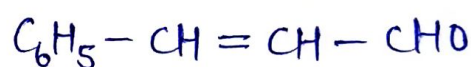
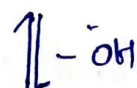
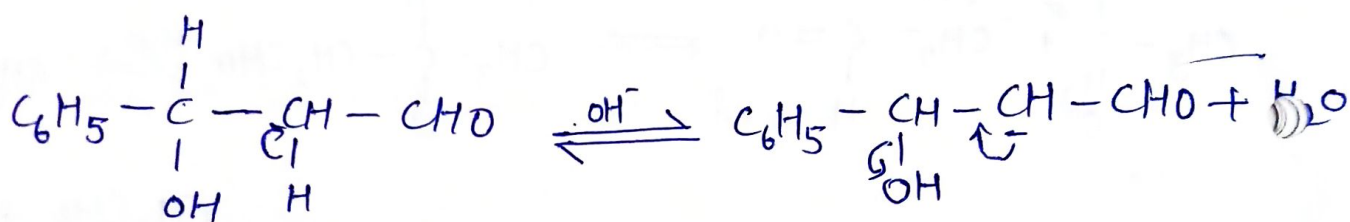
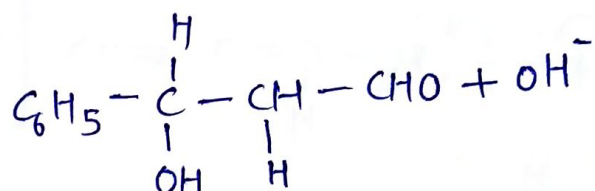
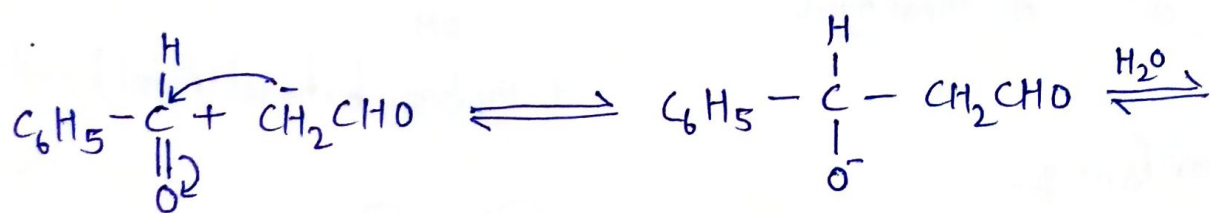
* Crossed aldol condensation :-



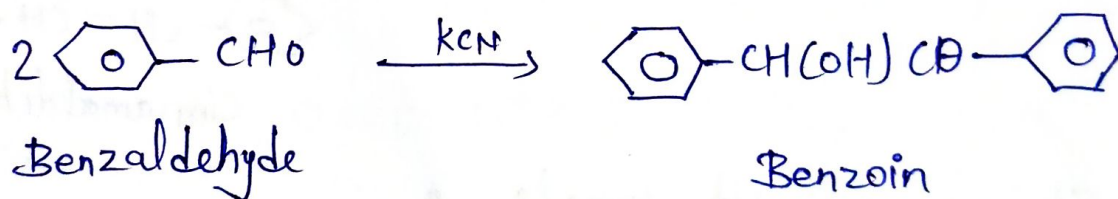
* Claisen-Schmidt reaction :-



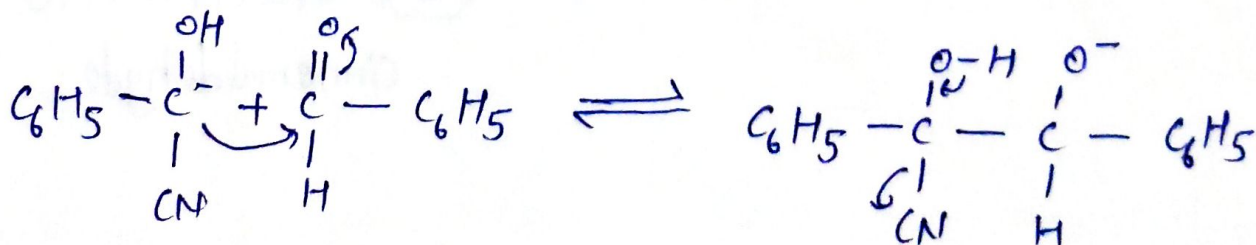
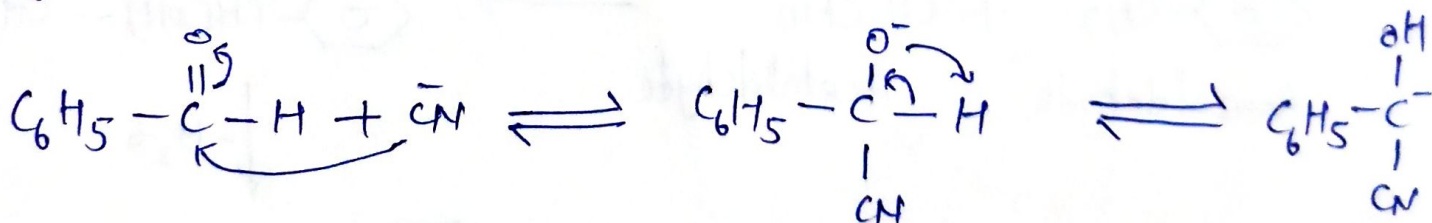
Mechanism :-

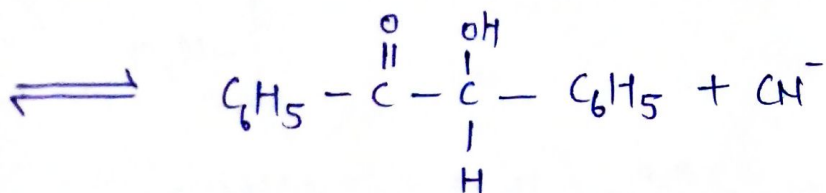


* Benzoin Condensation :-

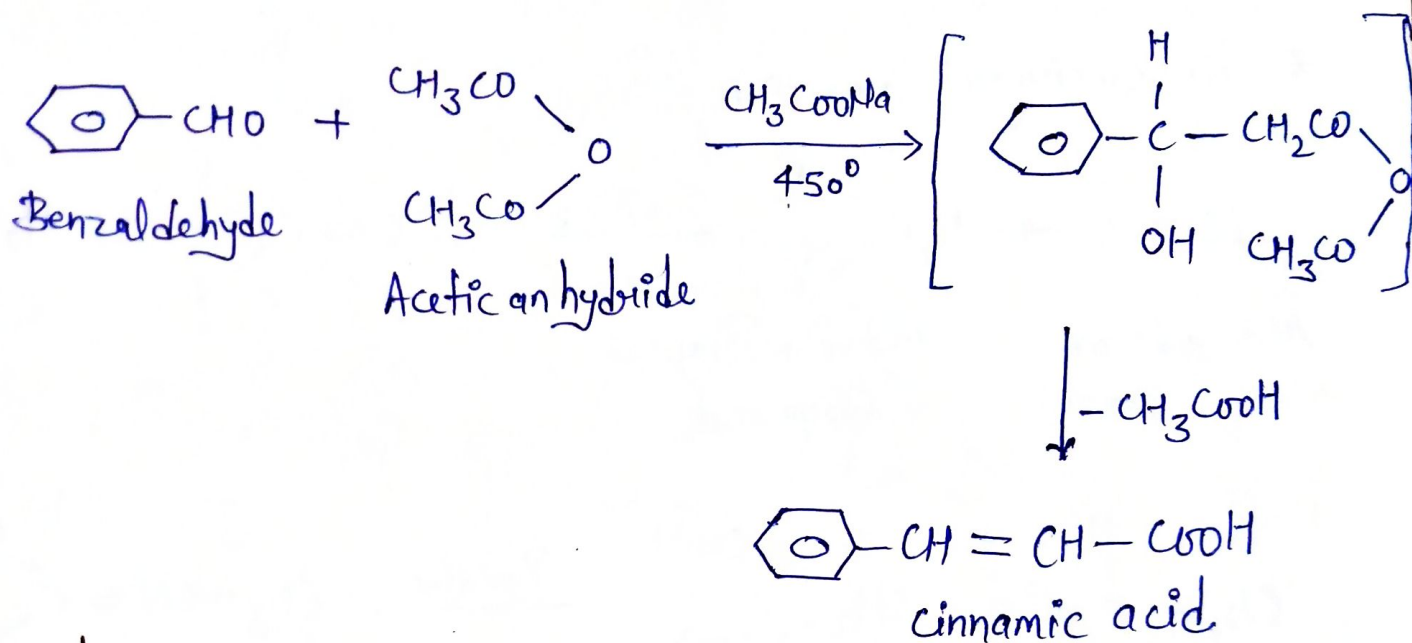


Mechanism :-

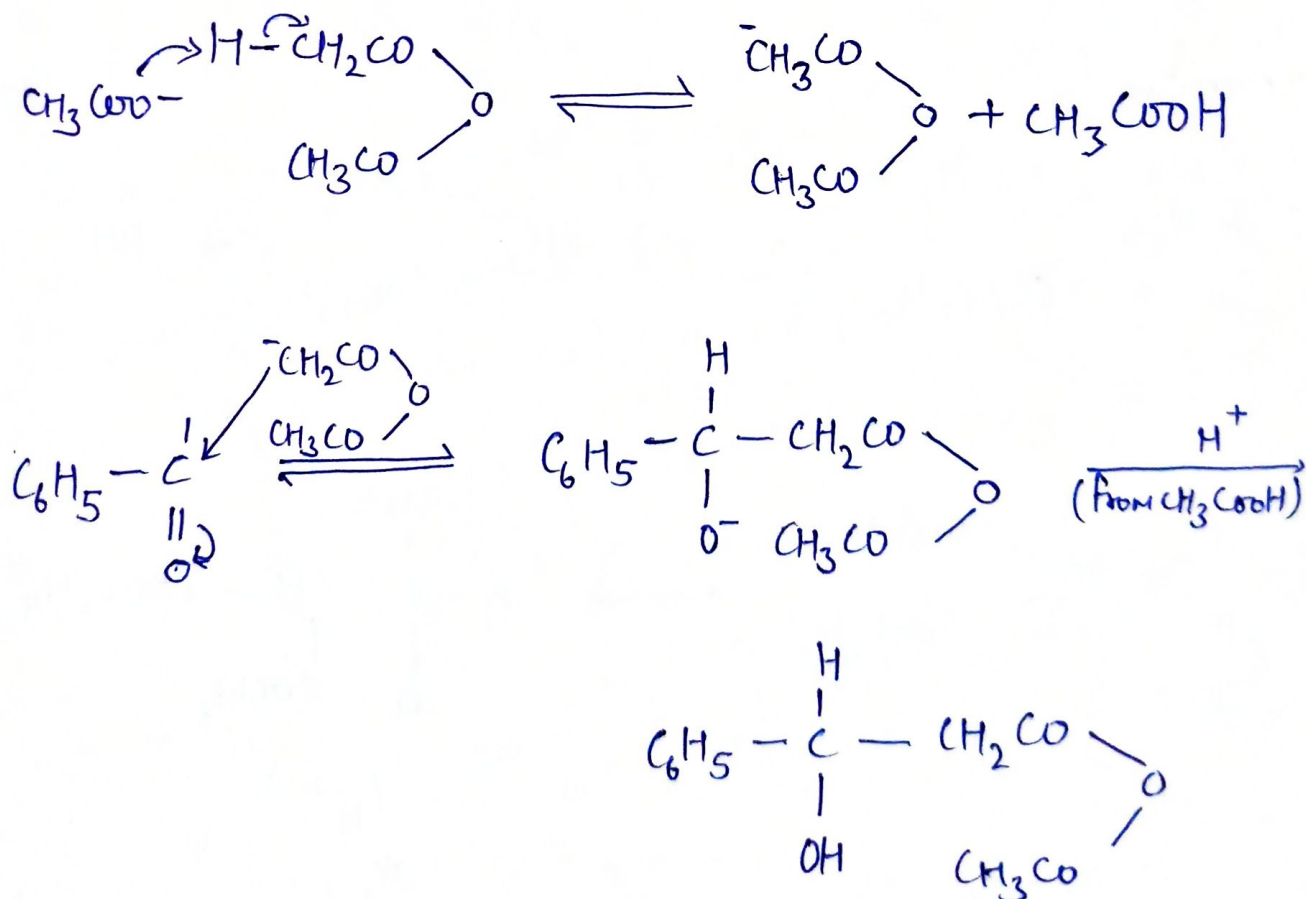


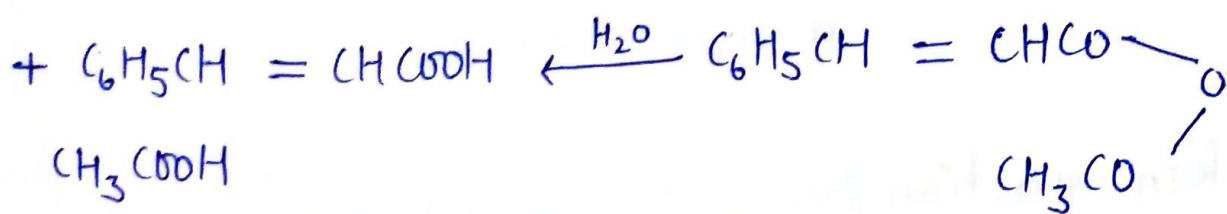


* Perkin reaction :-



Mechanism :-




$$\begin{array}{ccc} \diagup \text{C} = \text{O} + \text{H}_2\text{C} \begin{array}{l} \diagup \text{X} \\ \diagdown \text{Y} \end{array} & \xrightarrow{:\text{B}} & \diagup \text{C} = \text{C} \begin{array}{l} \diagup \text{X} \\ \diagdown \text{Y} \end{array} + \text{H}_2\text{O} \\ \text{Aldehyde or ketone} & & \text{Active methylene compound} \end{array}$$
