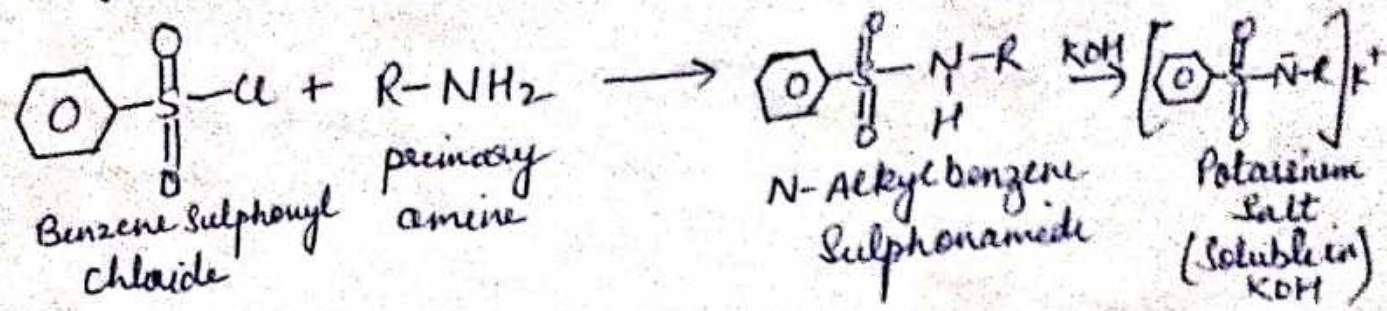
Hinsberg Test :-

It is an excellent method for separating a mixture of primary, secondary and tertiary amine. All amines are treated with benzene sulphonyl Chloride and the resulting reaction mixture was treated with aq. KOH.

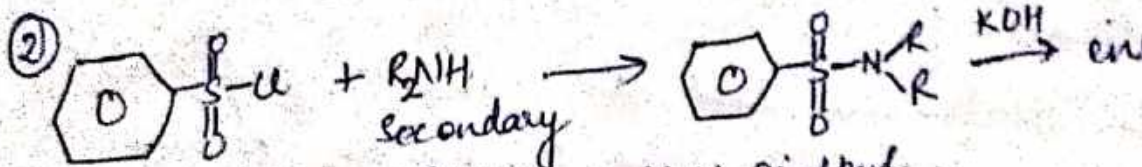
① 

Benzene Sulphonyl Chloride

primary amine

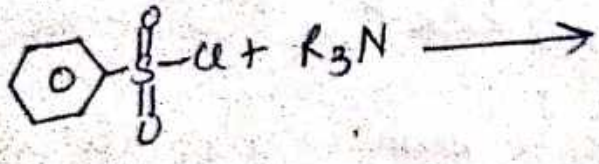
N-Alkyl benzene Sulphonamide

Potassium Salt (Soluble in KOH)

② 

Secondary amine

N, N-Dialkyl Benzene sulphonamide

③ 

{no replaceable hydrogen}

The reaction mixture obtained after treatment with benzenesulphonylchloride in presence of alkali is distilled when tertiary amine distills over. The remaining mixture is filtered and filtrate on acidification gives the sulphonamide of 1° Amine where the Solid residue left on filter paper is Sulphonamide of 2° amine The two sulphonamide thus isolated are hydrolysed separately to regenerate the Corresponding 1° & 2° amines.

Diazonium Salts

General formula $ArN_2^+X^-$

Ar = Aryl group X = Cl^-, Br^-, HSO_4^- etc

Benzenediazonium chloride

p-Chlorobenzene diazonium bromide

Preparation:-

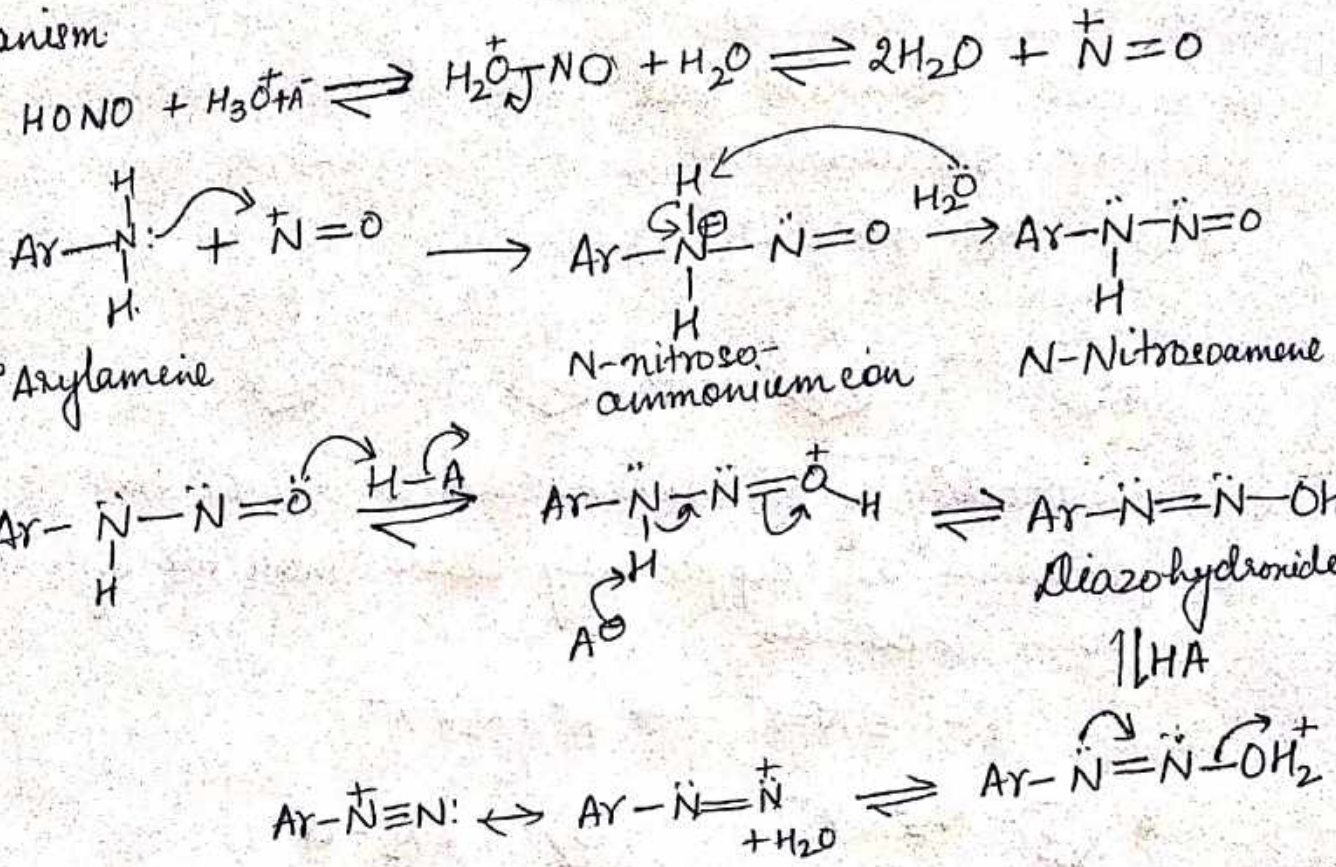
① Diazotisation:-

Aromatic diazonium salts are generally prepared by adding a cold aq. Solution of $NaNO_2$ to the solution of primary aromatic amine in acid at (0-5°C)

$$C_6H_5-NH_2 + NaNO_2 + 2HCl \xrightarrow{0-5^\circ C} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$$

This process of conversion of a primary aromatic amine into its diazonium salt is called diazotisation.

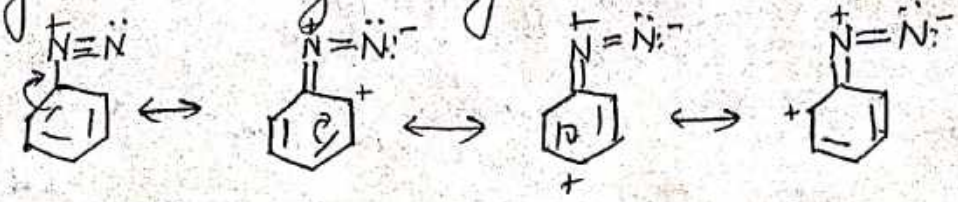
Mechanism:



Diazotisation of a primary amine takes place through a series of steps. In presence of strong acid, nitrous acid dissociates to produce NO^+ ions. These ions then react with the Nitrogen of the amine to form an unstable N-nitrosoammonium ion as an intermediate. This intermediate then loses a proton to form an N-nitrosoamine, which, in turn, tautomerise to a diazohydroxide in a reaction that is similar to keto-enol tautomerisation. Then in the presence of acid the diazohydroxide to form the diazonium ion

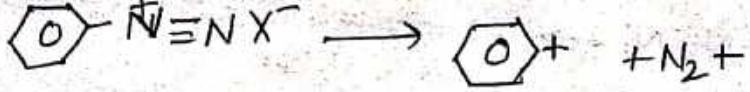
Stability:-

Aromatic diazonium salts are much more stable than aliphatic diazonium salts due to dispersal of positive charge over benzene ring



The instability of diazonium salts is due to their tendency to eleminate an exceptionally stable molecule of nitrogen to form Carbocation

$$R-\overset{+}{N}\equiv N-X^- \longrightarrow R^+ + N_2 + X^-$$



Since phenyl Carbocation is much less stable than alkyl therefore aromatic diazonium salts have lower tendency to eleminate nitrogen than aliphatic diazonium salts. In other words aromatic diazonium salts are much more stable than aliphatic diazonium salts.

Physical Properties

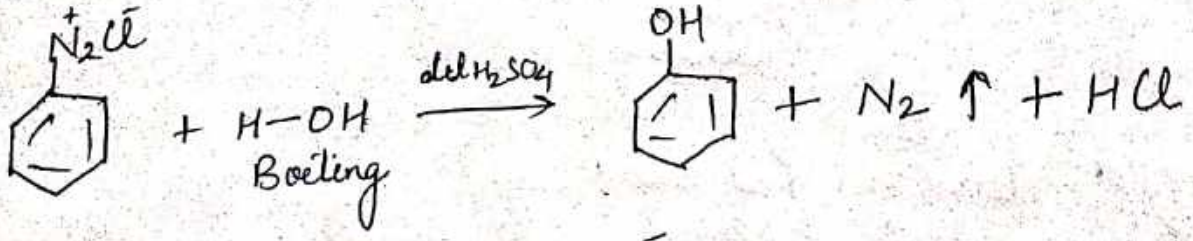
* Generally Colourless Crystalline Solids
* highly Soluble in water
* Many diazonium salts especially nitrites are dangerously explosive in dry state. Therefore they are never isolated but are usually prepared in Situ and used immediately after their preparation.
* Certain diazonium salts such as fluoborates are relatively insoluble in water and are stable enough to be dried and stored

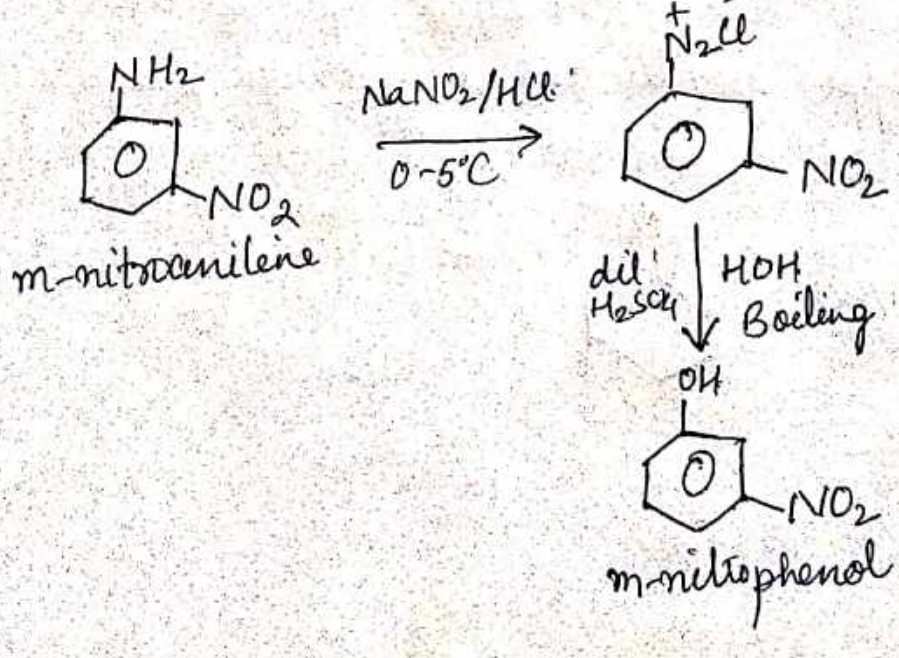
Chemical Properties

Arenediazonium salts are highly reactive Compounds. Their high reactivety arises due to excellent leaving ability of the diazo group as nitrogen gas N_2. They are therefore extremely useful Synthetic reagents in organic chemistry.

Reactions

① Replacement by hydroxyl group :-
diazonium salts react with water in presence of acids to form phenols.



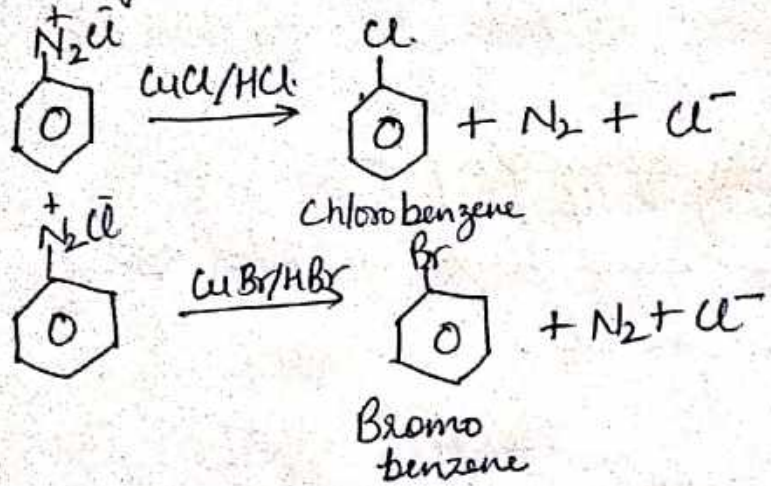


* The acidic Conditions minimize the Side reaction involving the Coupling of phenol with diazonium salts

Replacement by halogens

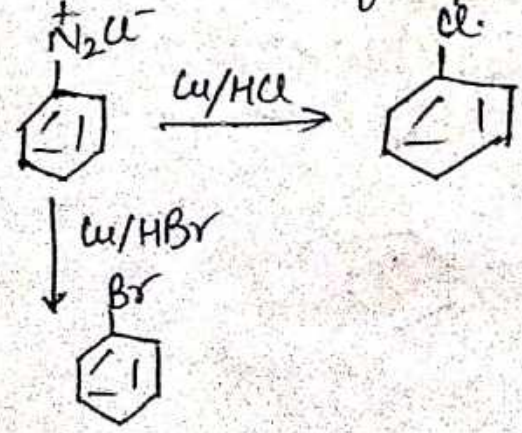
(1) Sandmeyer Reaction :-

In this cold aq solution of an arene diazonium salt is treated with solution of cuprous chloride in HCl or cuprous bromide in HBr to give Aryl chlorides and bromides

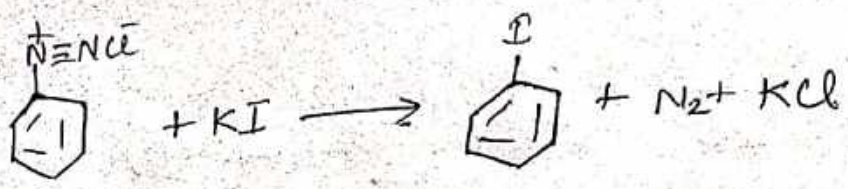


(2) Gattermann Reaction :-

It is a modification of the sandmeyer reaction in which Copper powder and a hydrogen halide are used instead of cuprous halide and hydrogen halide

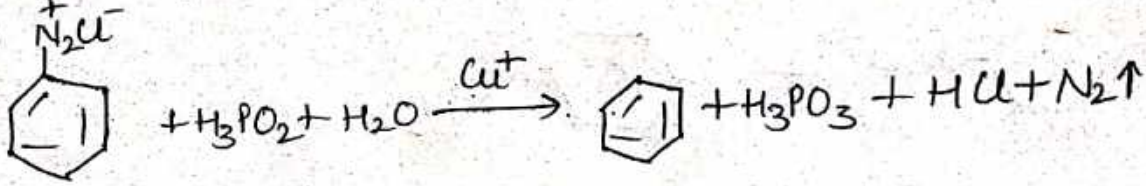


(3) With iodine replacement no catalyst is required. It is simply achieved by treating diazonium salt with KI or a solution of Iodine in KI



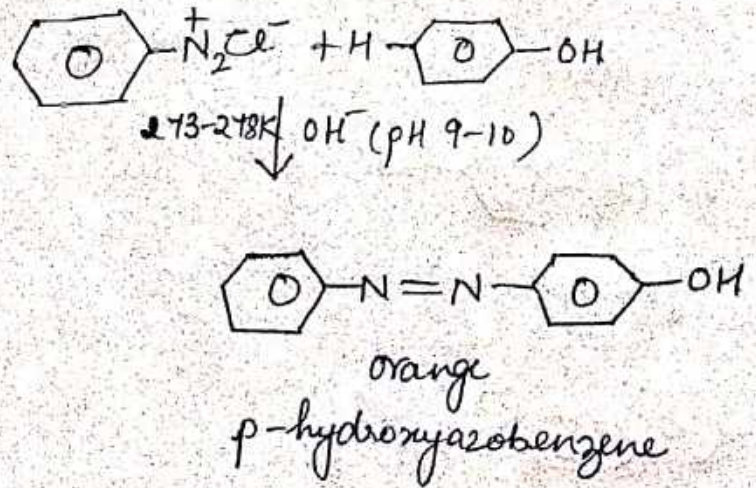
Replacement by hydrogen :- (Deamination)

The replacement of diazonium group by hydrogen to arenes (hydrocarbons) is usually brought about by treating diazonium salts with H_3PO_2 at room temperature in presence of Cu(I) salts as Catalyst



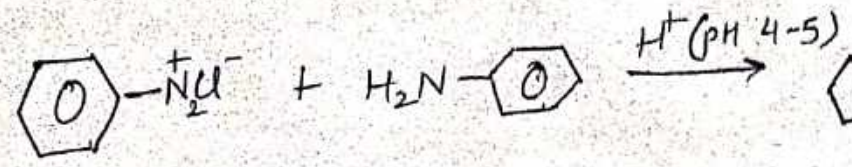
Coupling Reactions :-

Arenediazonium salts react with highly reactive (e^- rich) aromatic compounds such as phenols and amines to form coloured azo compounds. Coupling reaction is an example of electrophilic substitution reaction in which diazonium cation with +ve charge on terminal nitrogen behave as an electrophile while phenols and amines act as nucleophiles



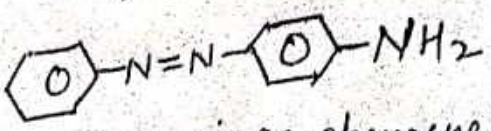
orange

p-hydroxyazobenzene

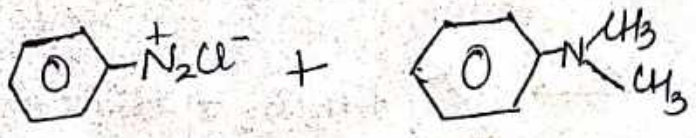


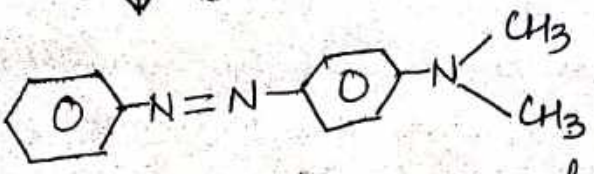
Diazoaminobenzene

rearranges $\downarrow H^+, \Delta$

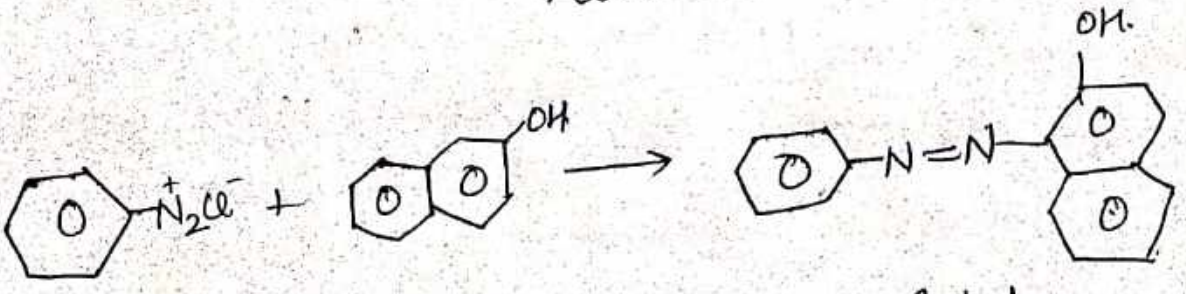


p-aminoazobenzene
(yellow)

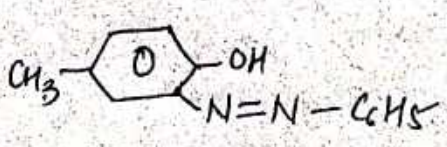




N,N-Dimethyl-p-(phenylazo) aniline
Yellow solid



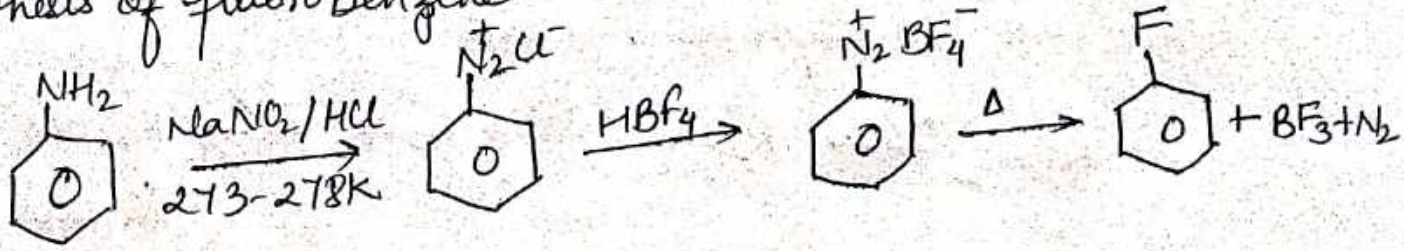
Red dye.



4-methyl 2(phenylazo) phenol

* Coupling usually occurs at p-position with respect to OH or the NH_2 group. If however the p-position is blocked it occurs at o-position.

* Synthesis of fluorobenzene



Hofmann vs Satzeff elemination

Like ammonia, an amine can react with an alkyl halide, the product is an amine. The alkyl halide undergoes nucleophilic substitution, with the basic amine serving as nucleophilic reagent

$$RNH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4\overset{+}{N}X^-$$

Quaternary ammonium salts

* Quaternary ammonium salts are the products of the final stage of alkylation. Quaternary ammonium halides do not have an unshared electron pair on the nitrogen atom and can not act as a base.

When a solution of a quaternary ammonium halide is treated with moist Ag oxide, silver halide precipitates. The mixture is filtered and filtrate is evaporated to dryness and a solid is obtained which is free from halogen. An aq. solution of this substance is strongly alkaline and is comparable to a solution of sodium hydroxide or potassium hydroxide. A compound of this sort is called a quaternary ammonium hydroxide.

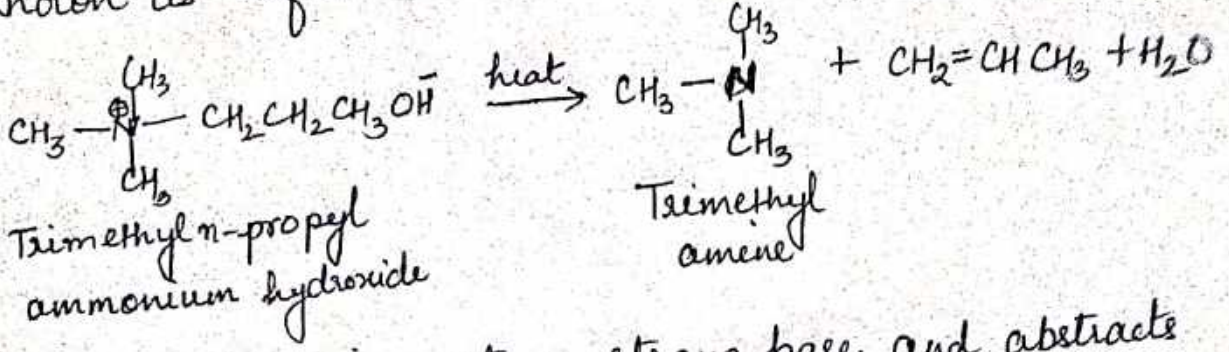
Structure – $R_4\overset{+}{N}OH^-$

Its aqueous solution is basic because solution contain hydroxide ions

$$2R_4\overset{+}{N}X^- \xrightarrow[H_2O]{Ag_2O} 2R_4\overset{+}{N}OH^- + 2AgX$$

insoluble

Pyrolysis of quaternary ammonium hydroxide salts, derived from an amine having alkyl group that is larger than the methyl group, gives an olefin and tertiary amine, water. This type of elemination reaction is known as Hofmann elemination reaction

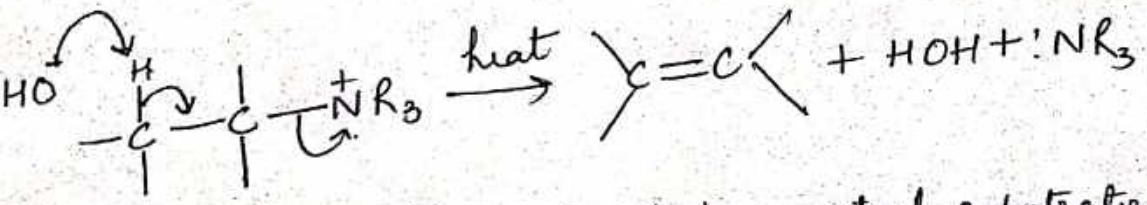


Trimethyl n-propyl ammonium hydroxide

Trimethyl amine

* The hydroxide ion acts a strong base and abstracts β-hydrogen of the alkyl group and π-bond is formed via expulsion of trialkylamine (E_2 elemination)

Hofmann elemination products are generally less substituted alkenes.



Although most elemenations involving neutral substrates tends to follow Saytzeff rule, elemenations with charged substrate tend to follow what is called Hofmann rule and yield mainly least substituted alkene.