SEM IV CHEMISTRY CORE

CHECC 409

UNIT 1: NITROGEN CONTAINING FUNCTIONAL GROUP (BENZENE DIAZONIUM CHLORIDE)

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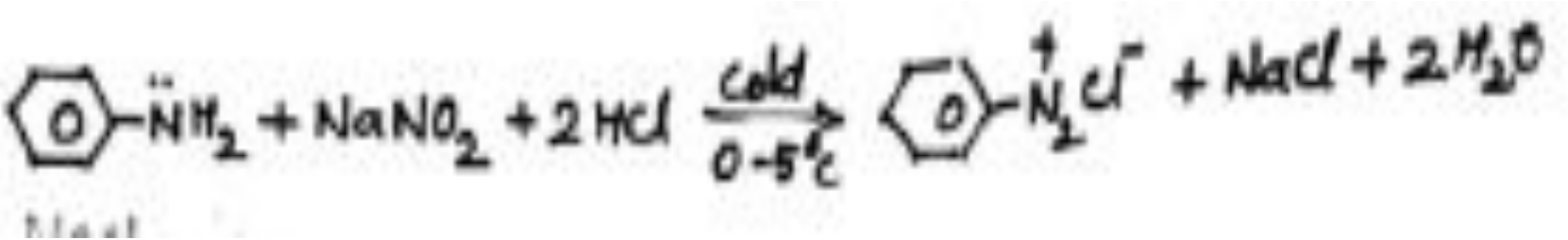
Introduction

- It is prepared by the interaction of primary aromatic amine, sodium nitrite and an acid at 0-5 degree celsius.
- This reaction is called diazotisation(conversion of $-NH_2$ into $N_2^+X^-$
- The reaction was discovered by Griess(1853)



General Procedure for Diazotisation

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- The aromatic amine is dissolved in dilute acid. (Ratio 1:3)
- The solution is cooled to 0-5 degree celsius.
- Cold aqueous solution of sodium nitrite is added to the cold amine solution slowly. (since diazotisation is exothermic)
- Addition of sodium nitrite solution is stopped when a few drops of reaction mixture gives a blue colour to starch -KI paper. This shows unreacted nitrous acid in the reaction mixture.
- Excess of nitrous acid interferes with reaction of diazonium salt so it should be avoided.

General Procedure for Diazotisation

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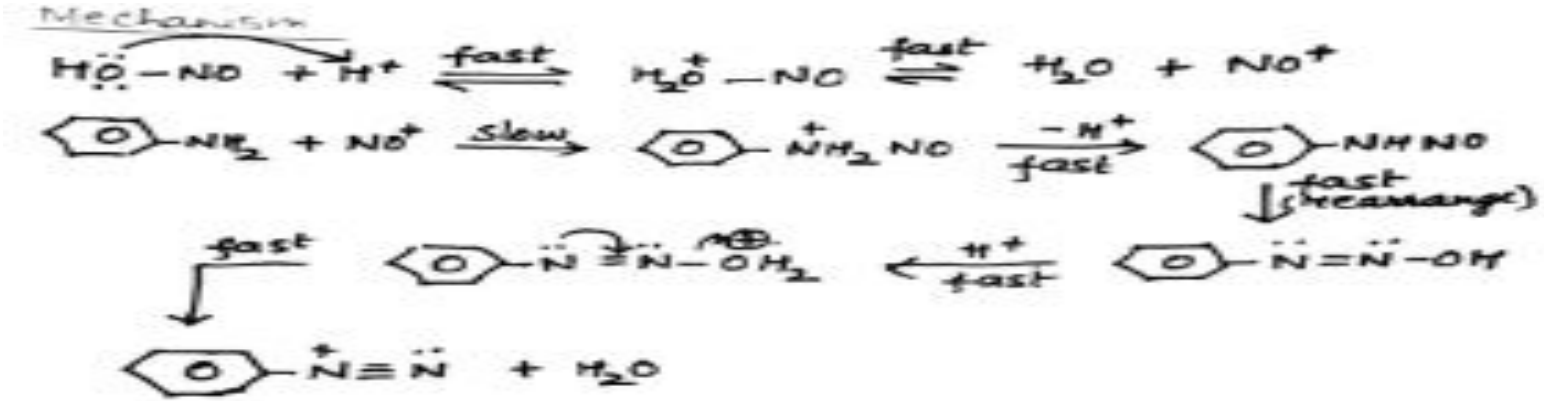
- 3 moles of dilute acid is taken for every mole of amine because:
  - One mole of acid is used to form the salt of amine
  - One mole to liberate Nitrous Acid
  - One mole to keep the reaction mixture acidic to supress undesirable side reaction.

Mechanism of Diazotisation

The mechanism of diazotisation consistent with the kinetic study is:



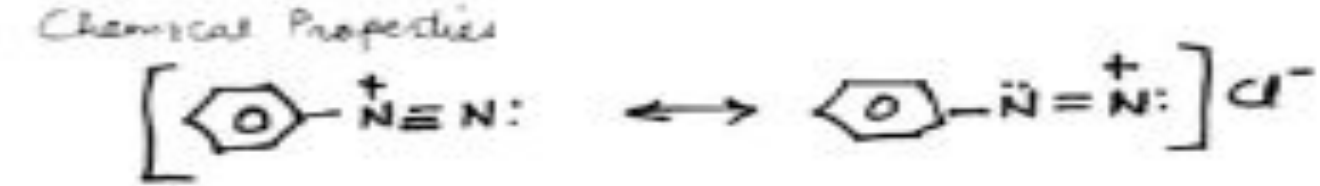
Here the rate determining step is nitrosation of the free amine(to a primary nitrosamine)

Physical Properties

- Diazonium salts are generally colourless, crystalline solids, highly soluble, in water.
- Many especially the nitrates, are explosive in dry state.
- Diazonium salts therefore generally used in solution and their isolation in dry state is avoided.

Chemical Properties

Benzene diazoniumchloride is stable due to resonance. However, this may be represented by



Chemical Properties

- The positive charge is distributed evenly in both nitrogen.Benzene diazonium chloride gives two types of reaction
    - Those in which the - N_2Cl is replaced by another univalent atom or group , with the liberation of $N_{2.}$
    - Those in which the two N atoms are retained.

Replacement Reaction in which N_2 is liberated

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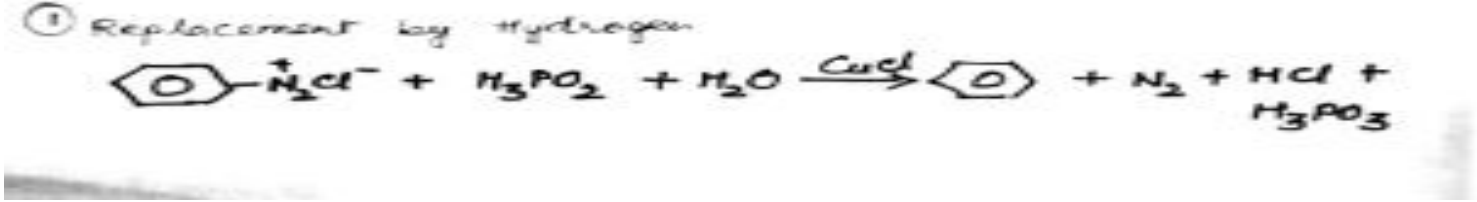
1. **Replacement by Hydrogen**

When benzenediazonium chloride is reduced by hypophosphorus acid(H_3PO_2) in presence of cuprous chloride(Cu^+Cl^-), the product is benzene.

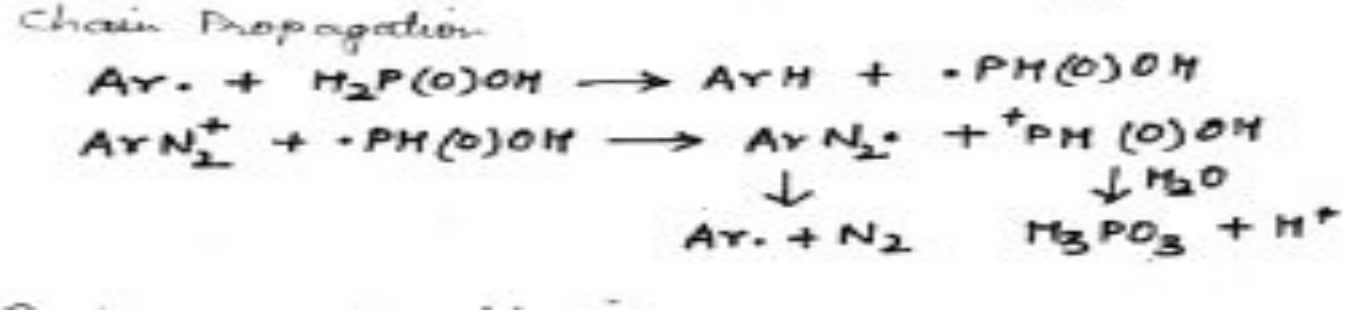


The reaction is supposed to take place via free radical.

Chain initiation:

Replacement Reaction in which N_2 is liberated ---

Chain Propogation:



Replacement Reaction in which N_2 is liberated

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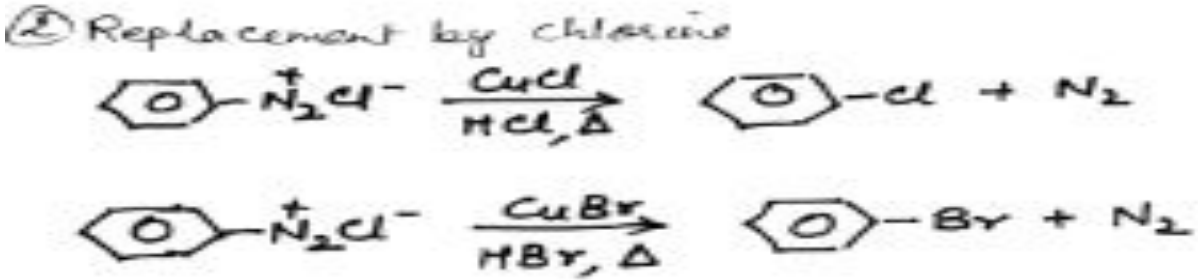
2. Replacement By Chlorine(or Bromine)

A. Sandmeyer Reaction(1884)

When a diazonium salt solution is treated with a solution of cuprous halide dissolved in corresponding halogen acid, the diazo group is replaced by a halogen atom. e.g.



Replacement Reaction in which N_2 is liberated

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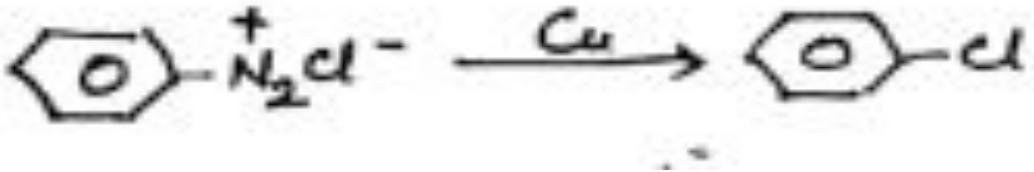
The same can be achieved through Gattermann reaction (1890). But yield is low.

B. Gattermann Reaction

The reaction is carried out by warming the diazonium salt solution in presence of copper powder.



Iodo and Fluro compounds cannot be prepared by the above two methods.

Replacement Reaction in which N_2 is liberated

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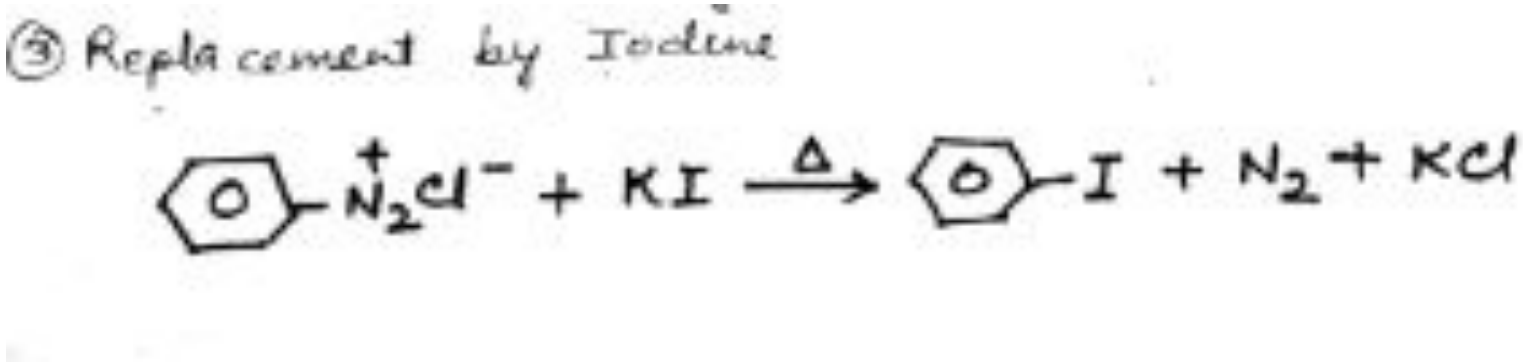
3. **Replacement by Iodine**

- When an aqueous solution of benzene diazonium chloride is heated with potassium iodide the diazonium group is replaced by iodine.
- This is the best method for introducing iodine into the benzene ring.



Replacement Reaction in which N_2 is liberated

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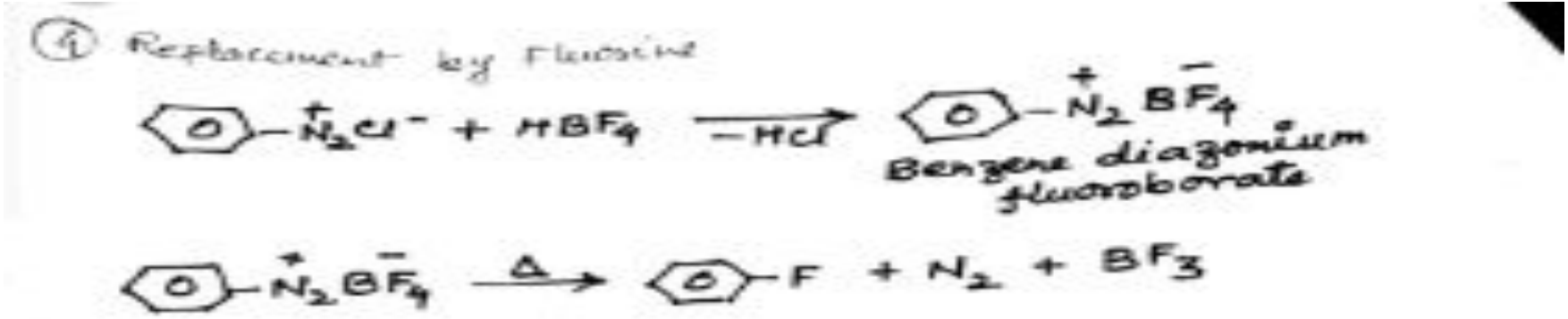
4. Replacement by Fluorine:

- When benzene diazonium chloride solution is added to fluoroboric acid, HBF_4, benzene diazonium fluroborate precipitates out. This is washed and dried. When heated it decomposes into nitrogen, boron trifluoride, and fluorobenzene (Schiemann Reaction ,1927)



Replacement Reaction in which N_2 is liberated

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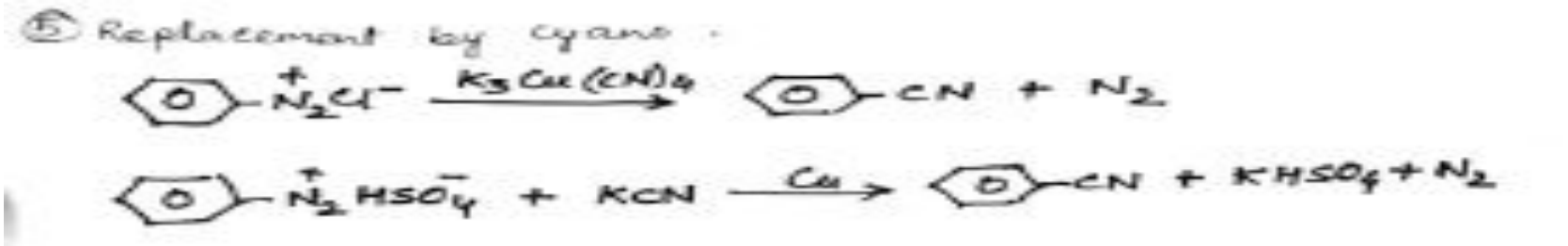
5. Replacement by Cyano Group

- This is a special case of Sandmeyer and Gattermann reactions.
- It is carried out treating benzene diazonium chloride solution with cuprous cyanide dissolved in aqueous KCN (CuCN + KCN -----> $K_3Cu(CN)_4$ or with aqueous KCN in presence of Cu powder.



- This reaction finds use in the preparation of benzoic acid since -CN group can be hydrolysed to -COOH group

Replacement Reaction in which N_2 is liberated

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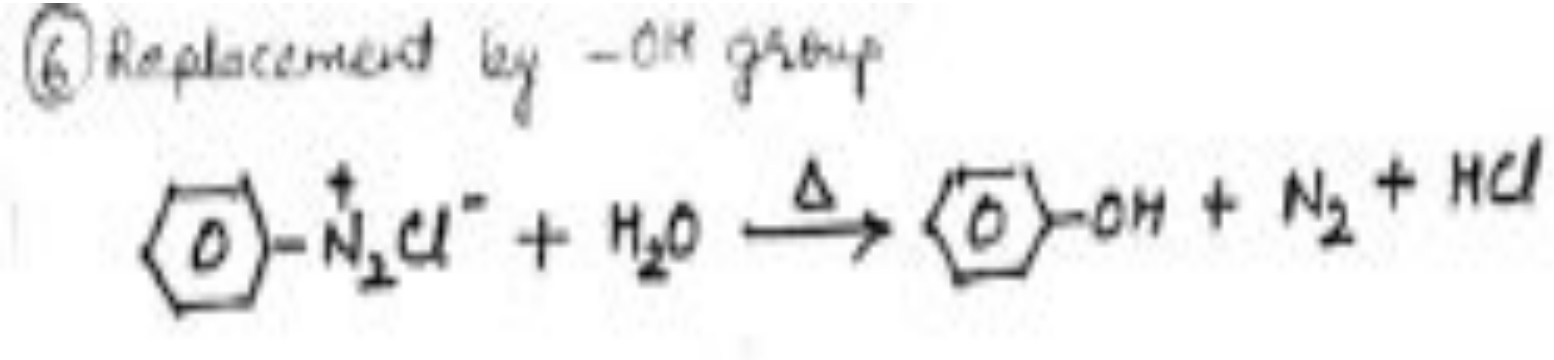
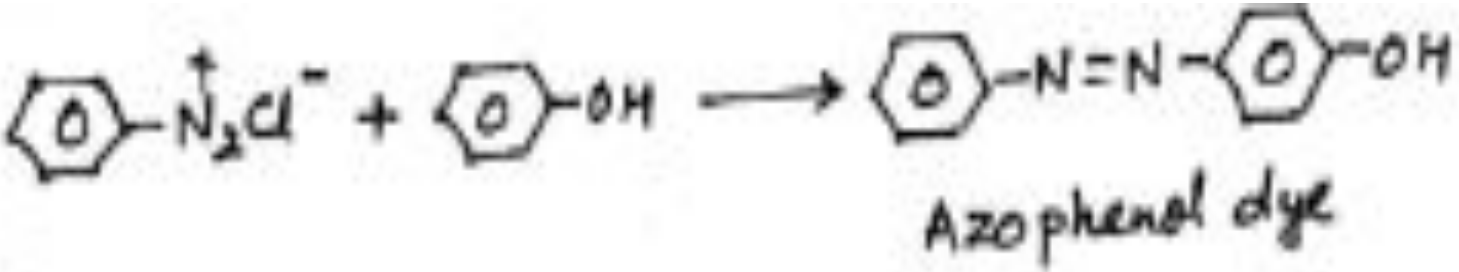
6. Replacement by -OH group

When an aqueous solution of benzene diazonium chloride is heated the diazonium group is replaced by -OH group, forming phenol.



Replacement Reaction in which N_2 is liberated ---

This reaction is usually conducted in an acid medium to prevent the coupling of phenol with the unreacted diazonium salts.



Replacement Reaction in which N_2 is liberated

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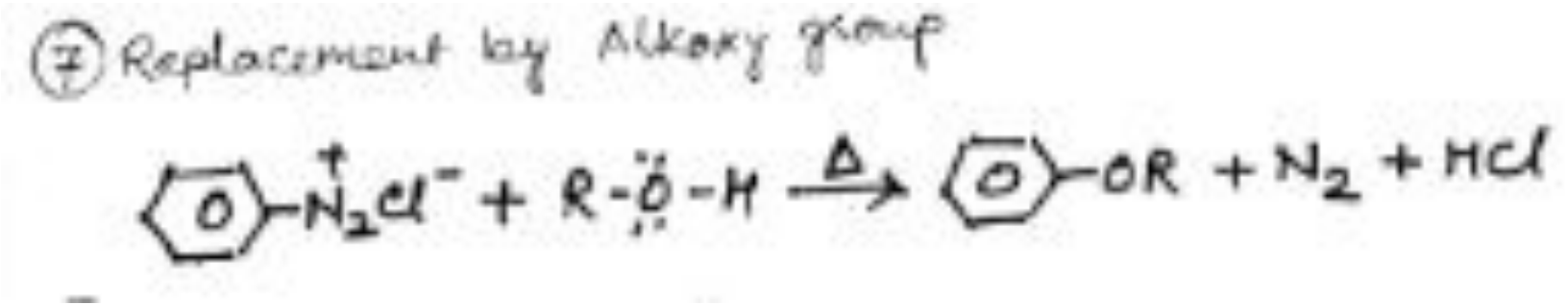
7. Replacement by Alkoxy group

When aqueous solution of benzene diazonium chloride is heated in presence of an excess of alcohol, the diazonium group is replaced by the alkoxy group (-OR group) forming alkyl aryl ether.



Replacement Reaction in which N_2 is liberated

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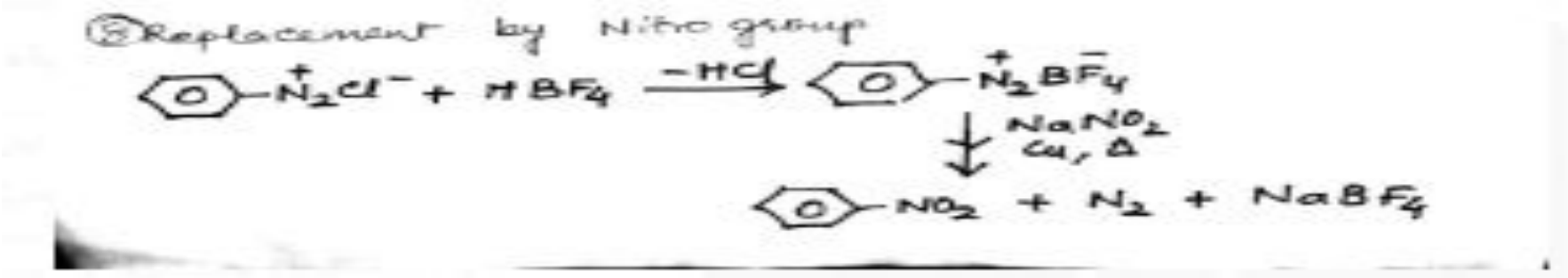
8. Replacement reaction by Nitro group

When benzene diazonium chloride is heated with fluroboric acid, it forms benzene diazonium fluoroborate.

When these are heated with aqueous $NaNO_2$ the diazonium group is replaced by $-NO_2$ group.



Replacement Reaction in which N_2 is liberated

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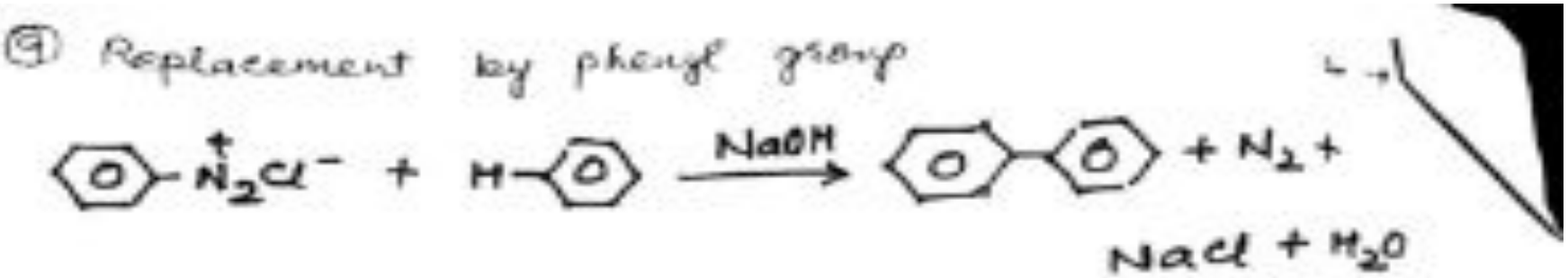
9. Replacement by phenyl group

When benzene diazonium chloride is heated with an aromatic hydrocarbon in presence of NaOH, diphenyl is formed (Gomberg Reaction)



Replacement Reaction in which N_2 is liberated

Also, benzene diazonium hydrogen sulphate may be treated with ethanol and copper powder.(Special case of Gattermann Reaction)

REACTION IN WHICH N ATOMS ARE RETAINED

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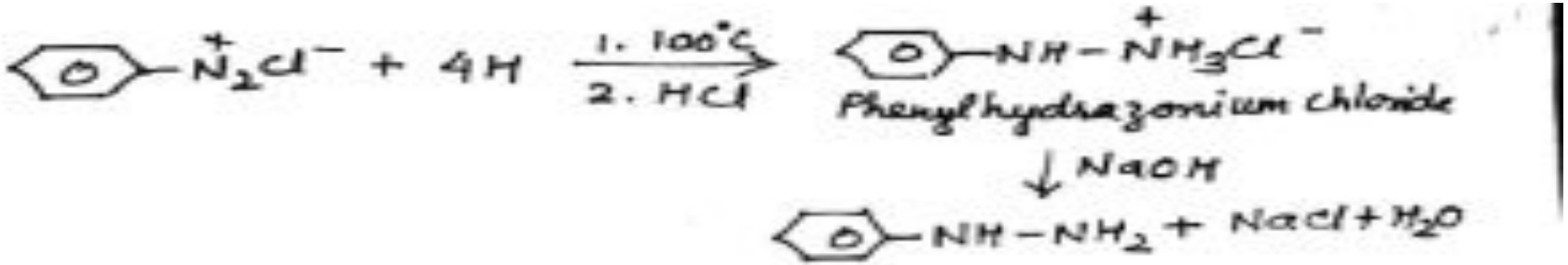
1. **<u>Reduction to Phenyl Hydrazine</u>**

- Benzene diazonium chloride when treated with sodium sulphite is reduced to give phenylhydrazine.
- The process is carried out in three steps:
    - Addition of a solution of benzene diazonium chloride to a warm solution of sodium sulphite heated to 100 degree celsius.
    - This is followed by acidification with HCl when phenylhydrazonium chloride is produced.
    - The resulting solution when treated with alkali forms phenylhydrazine.
        - $Na_2SO_3 + H_2O$----------> $Na_2SO_4 + 4H$

REACTION IN WHICH N ATOMS ARE RETAINED



- The reduction can also be carried out with stannous chloride and hydrocholric acid
- If vigorous reducing agent are used (eg Zn and HCl), the product is an aromatic amine.

REACTION IN WHICH N ATOMS ARE RETAINED

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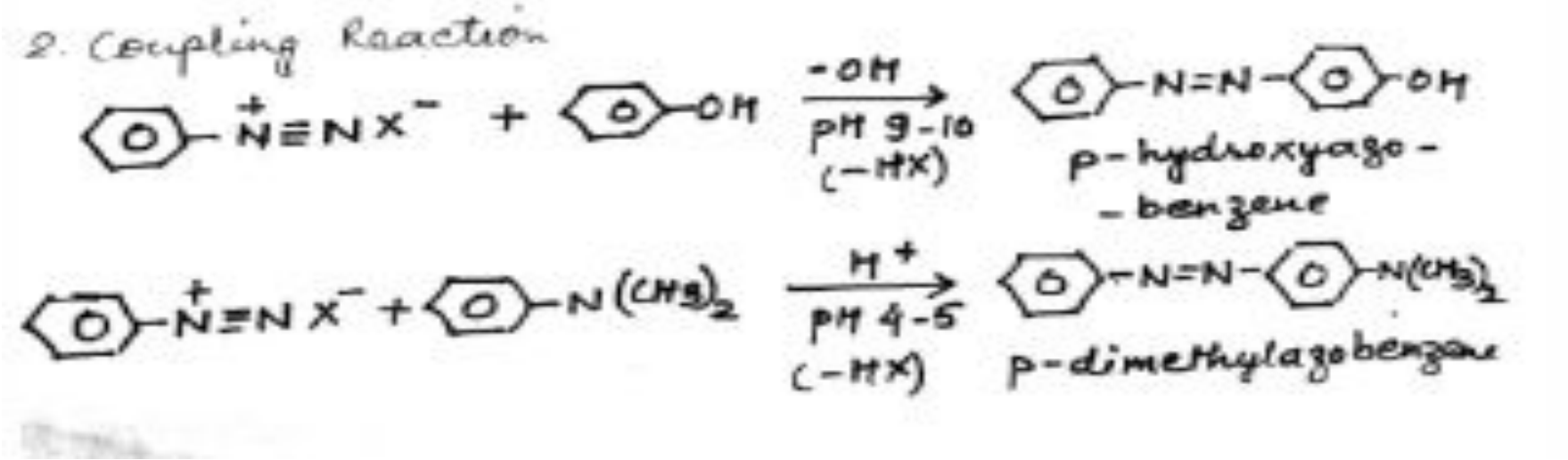
2. Coupling Reaction

- Benzene diazonium chloride reacts with phenols, aromatic amine etc. to form highly coloured azo compound ArN=N-Ar’ (Ar’ - may be phenol or aromatic amine).
- This reaction is called coupling reaction and it forms the basis of azo-dye industry.
- Coupling occurs in para position, preferentially due to steric hinderance at ortho position. If both ortho and para position are blocked then coupling either does not occur or a substitution at para position is displaced followed by coupling in the vacated position.

REACTION IN WHICH N ATOMS ARE RETAINED

Phenol coupling takes place in weakly alkaline medium and amine coupling in weakly acidic medium.



REACTION IN WHICH N ATOMS ARE RETAINED

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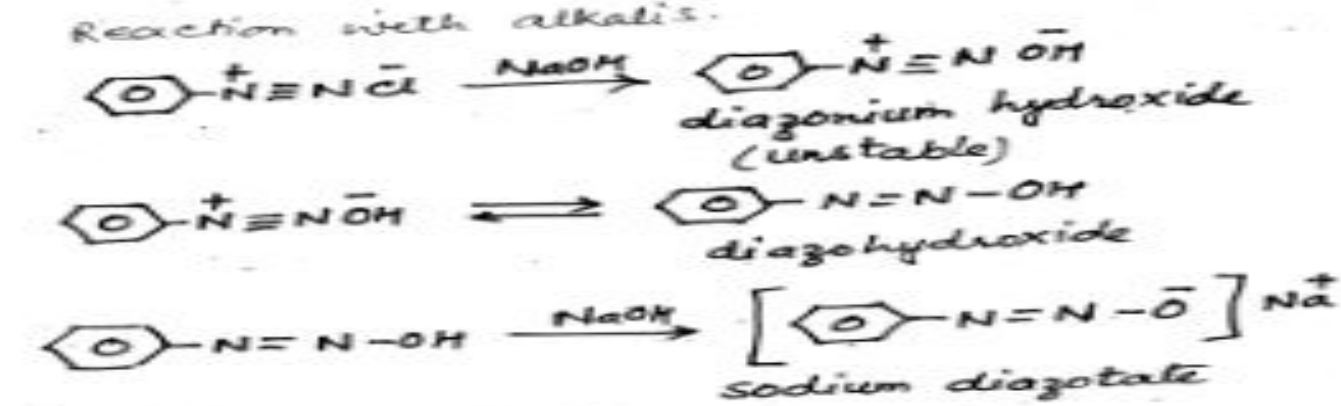
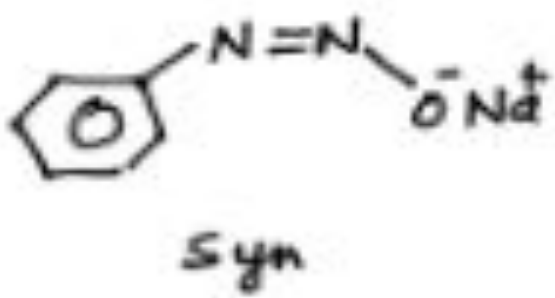
3. Reaction with Alkali

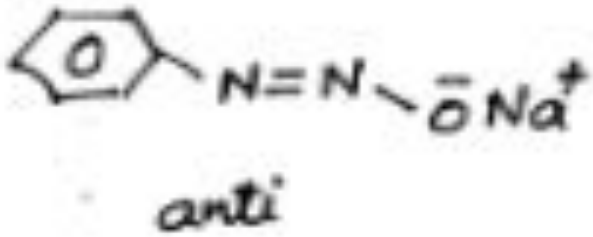
Benzene diazonium chloride reacts with NaOH to form diazonium hydroxide which being unstable rapidly changes to diazohydroxide. This reacts with alkali to form diazotates(salts).



REACTION IN WHICH N ATOMS ARE RETAINED

Diazotates exist in two geometrical isomeric forms : the syn(cis) and anti(trans)





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