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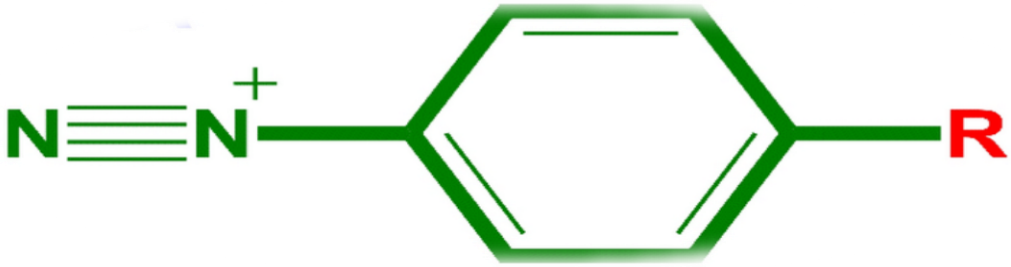
ARYL DIAZONIUM SALT - A REVIEW



BHALGAT SAKSHI, DESHMUKH GAURI, Mr.MAHESH KSHIRSAGR , Dr.NILESH JADHAV

SAJVPM'S College of Pharmaceutical Science and Research Center, Kada (Beed), Maharashtra , India.

ABSTRACT :

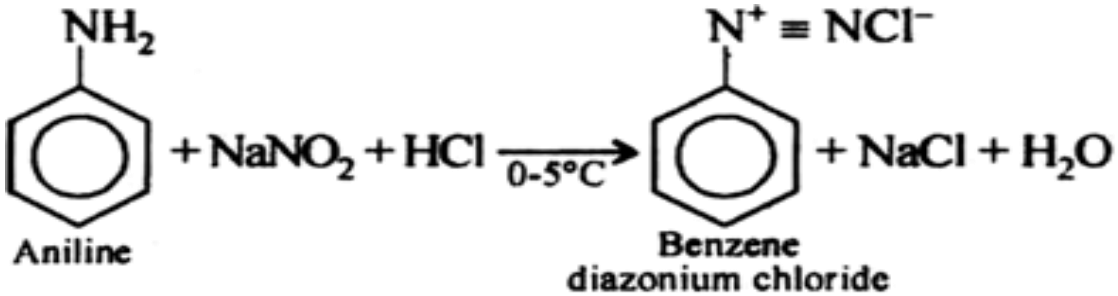
*The diazonium salts (**di** refers to '**two**', **azo** is indicative of '**nitrogen**' and **ium** implies that it is **cationic** in nature), or diazonium compounds are a group of organic compounds that share one common R-NH2+X– group of functions. R is an organic group, in R-NH2+X–. For example, the group alkyl or aryl. If R is an aryl group (like Benzene) it is called aryl diazonium salt . and X is halogens, hydrogen sulphate etc. (chlorine) eg, benzene diazonium chloride . The aryl diazonium salt in chemistry is very useful and exciting.it is a important intermediates. They are colourless , ionic,and crystalline in nature.They mainly used in dye as well as pigment industry.useful in synthesis of large variety of organic compound , mostly aryl derivatives. Aryl diazonium ions is more stable than alkyl diazonium ions because aryl diazonium ions have more resonance due to alternate double bonds.the diazonium salt are popular colouring agent . the overall process involved in the creation of diazonium salt is ,step 1) being with an alkyl or primary arylamine and step 2) in contact with sodium nitrate ,in presence of HCL and form Nitrogen triple bond* and loss of water. The aryl diazonium salt can be used to modify ultrananocrystaline diamond (UNCD). we summarize here all information for fast development area of research.

KEY WORDS: Diazonium salt, Nano diamond, Intermediate, Azo dyes, Diazo group, Colouring agent.

INTRODUCTION:

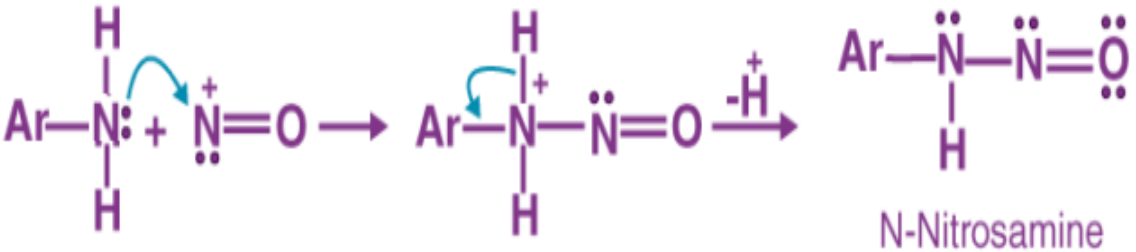
SYNTHESIS OF ARYL DIAZONIUM SALT,

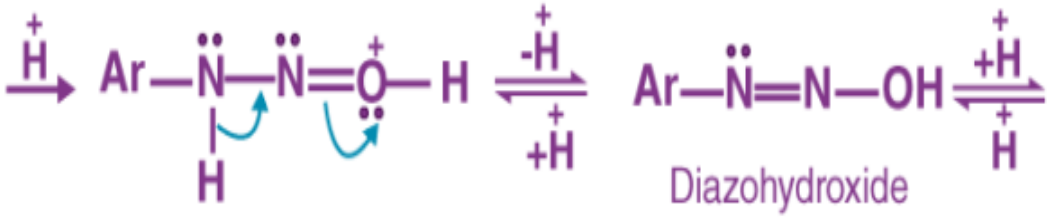
***DIAZOTIZATION :** when primary aromatic amine react with sodium nitrate and hydrochioric acid in presence of ice cold water at 0-5 degree celcious temperature to form diazonium salt is called as

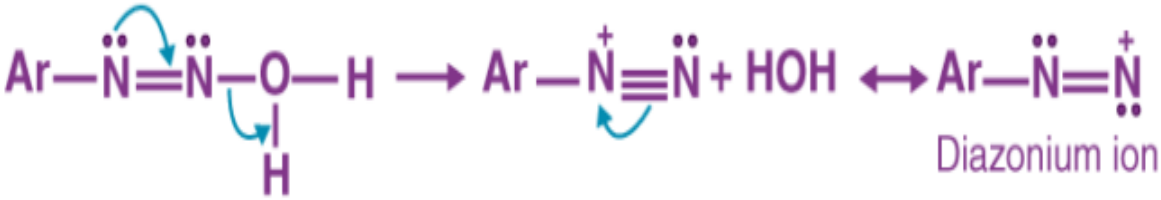


Diazotization.

MECHANISM:

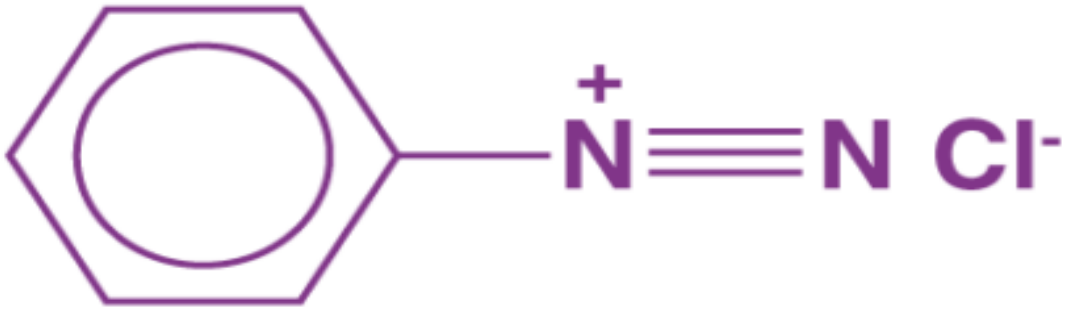






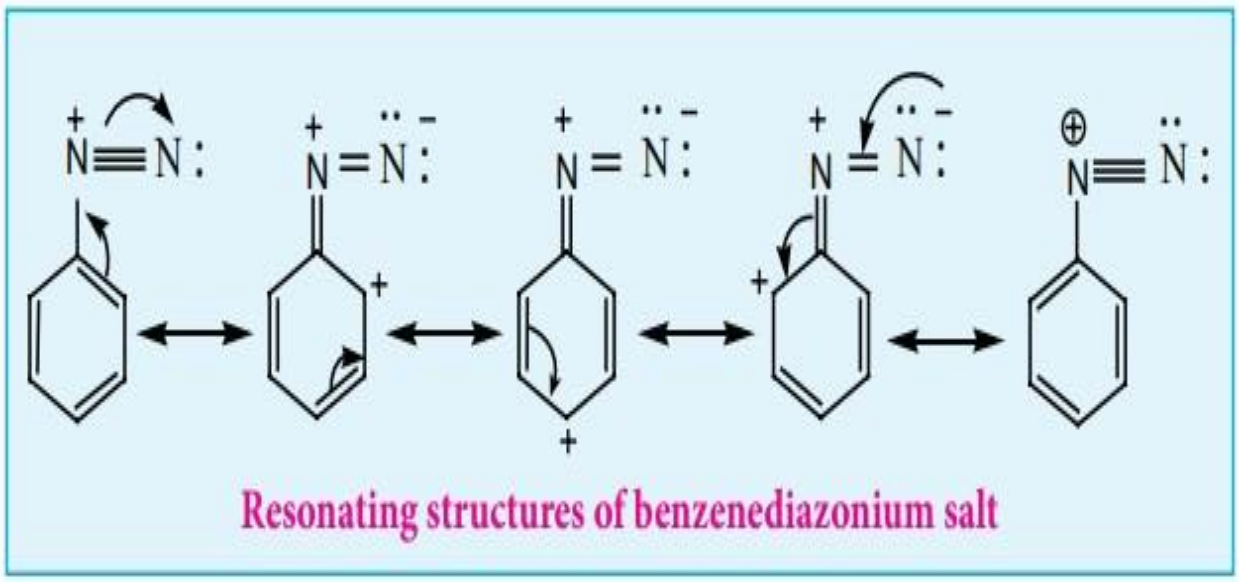
ARYL DIAZNIUM SALT : Diazonium salts are one of the most versatile combinations of organic and inorganic components. Its general way of representation is **$R-N_2^+X^-$**. The R is an organic group, that is an aryl group while X represents ion. Generally, diazonium salts have Cl^-, Br^-, BF_4^-, as X.

For eg: Benzenediazonium chloride.



[Benzenediazonium chloride=(aryl diazonium salt)]

RESONANCE IN ARYL DIAZONIUM SALT: Due to presence of resonance that is delocalization of pi bound aryl diazonium salt is more stable than alkyl diazonium salt.



HISTORY :

Origin of Diazonium Salt : The first predicted the reaction of aryl diazonium salt by scientist 'PETER GRIESS ' in 1858. He also discovered many reactions of this new developed compounds. Most commonly diazonium salt are prepared by treatment of aromatic amines with nitrous acid and addition of otheracid like hydrochloric acid.

(PETER GRIESS-1829 to 1888)

PHYSICAL PROPERTIES OF ARYL DIAZONIUM SALT:

1) Diazonium salts are crystalline in nature.

2) They are colourless but darken when exposed to air.

3) When heated or hit when dry, several diazonium salts of nitrates and perchlorates explode.

4) They are ionic in nature.

5) They are soluble in water.

6) Benzenediazonium chloride is soluble in water but reacts with it only when warmed .

7) Benzenediazonium fluoroborate is not soluble in water.

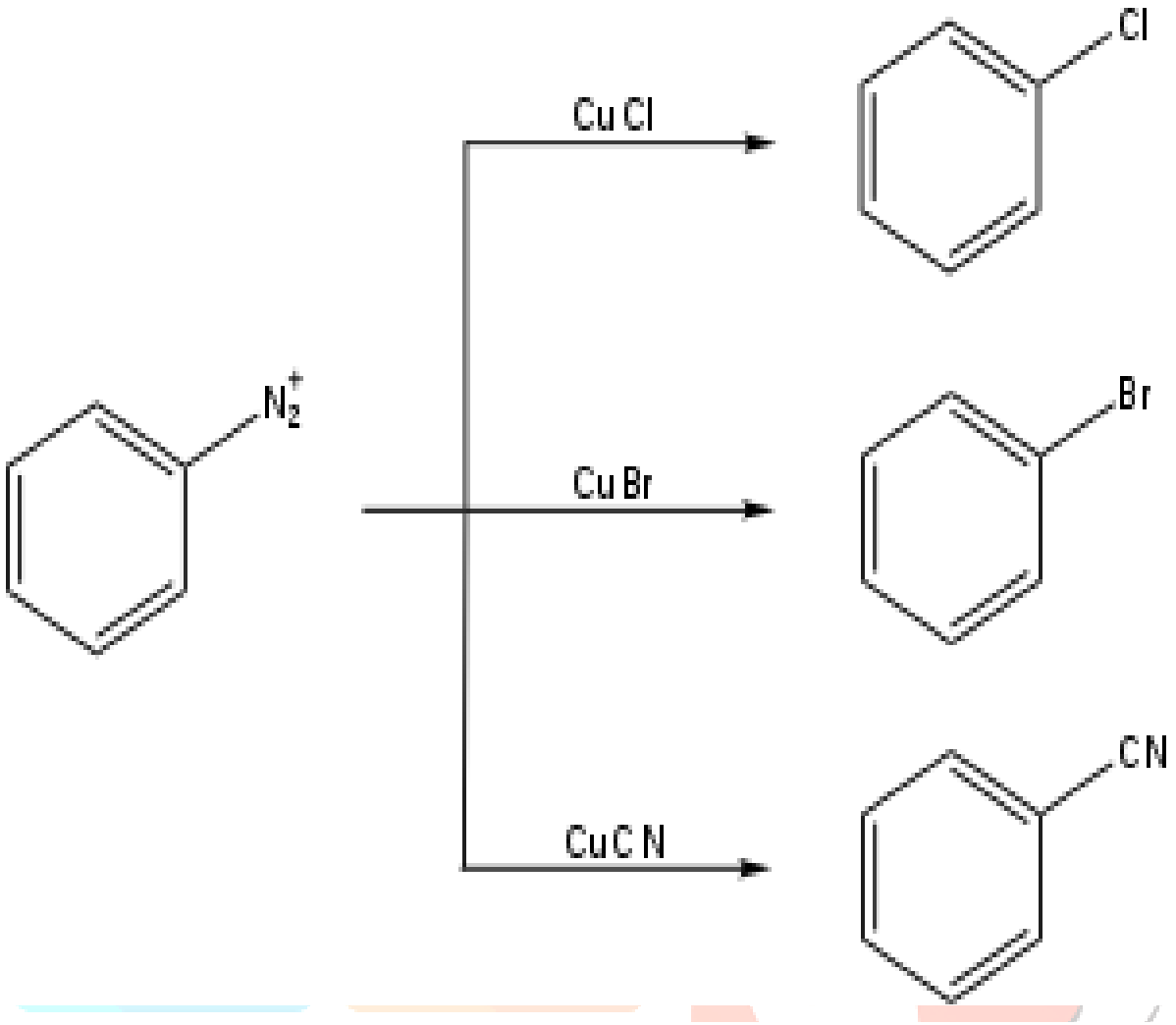
8) It is stable at room temperature.

Synthetic application and Chemical properties of aryl diazonium salt: Aryl diazonium salt reactions are usefull as well as necessary because of their ability to form many bulding block of organic compound. The reactions are as below.

1) sandmeyer reaction: Replacement by halide or cyanide ion:

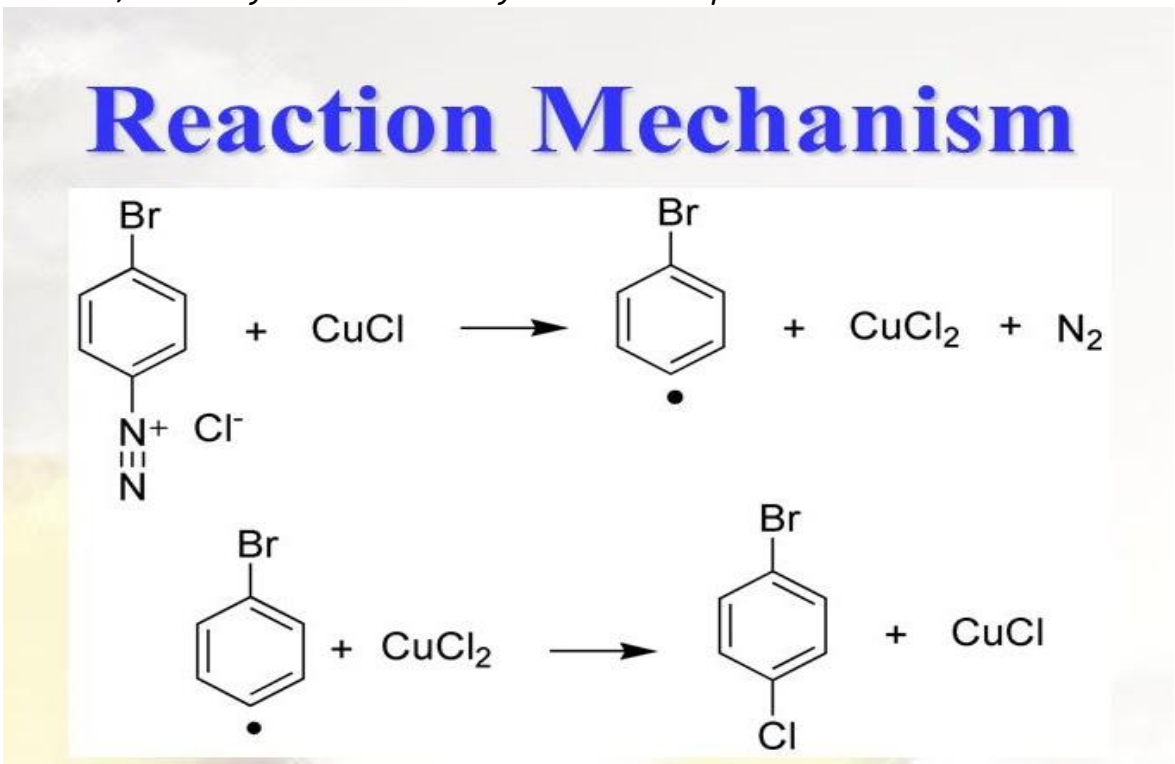
The nucleophiles such as Cl^-, Br^-, CN^- can be easily introduced in the benzene ring in the presence of Cu (I) ion. This reaction is commonly known as the Sandmeyer reaction.or *One way to transform diazonium salts is by treating them with various compounds of copper. These are known as* ***Sandmeyer*** *reactions, after Traugott Sandmeyer who first discovered the reaction in 1884 (with copper acetylide) it is also called as radical-nucleophilic aromatic substitution..*

- *CuCl transforms aryl diazonium salts into aryl chlorides*
- *CuBr transforms aryl diazonium salts into aryl bromides*
- *CuCN transforms aryl diazonium salts into aryl cyanides (nitriles).*

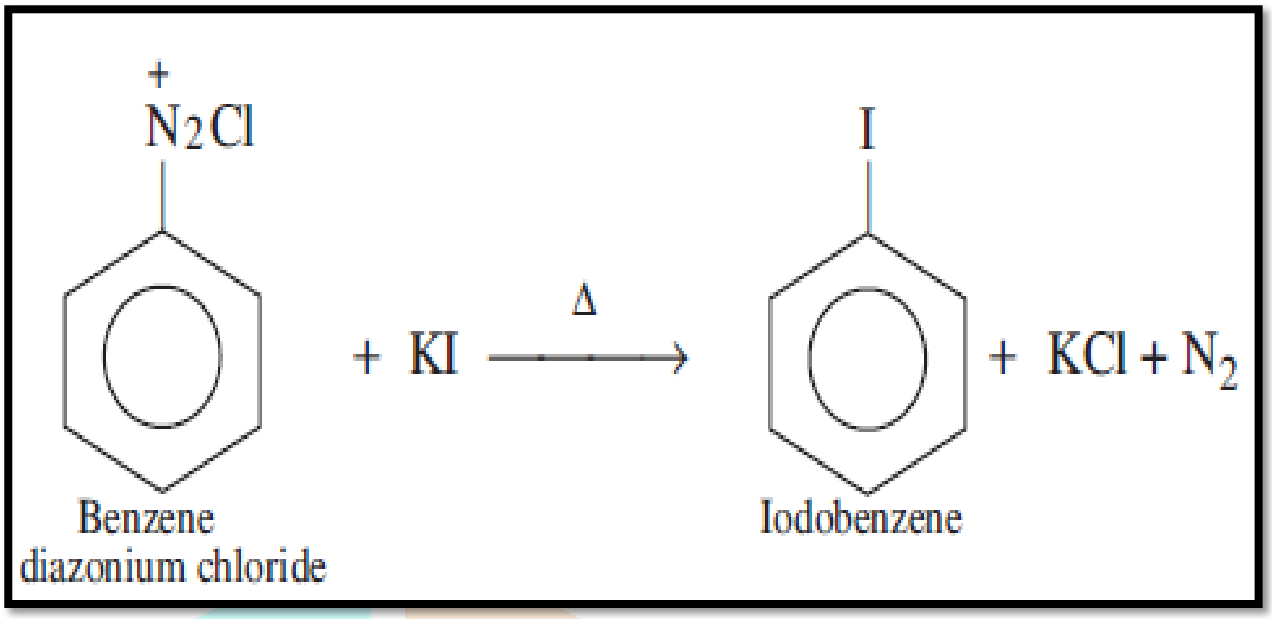


Mechanism:

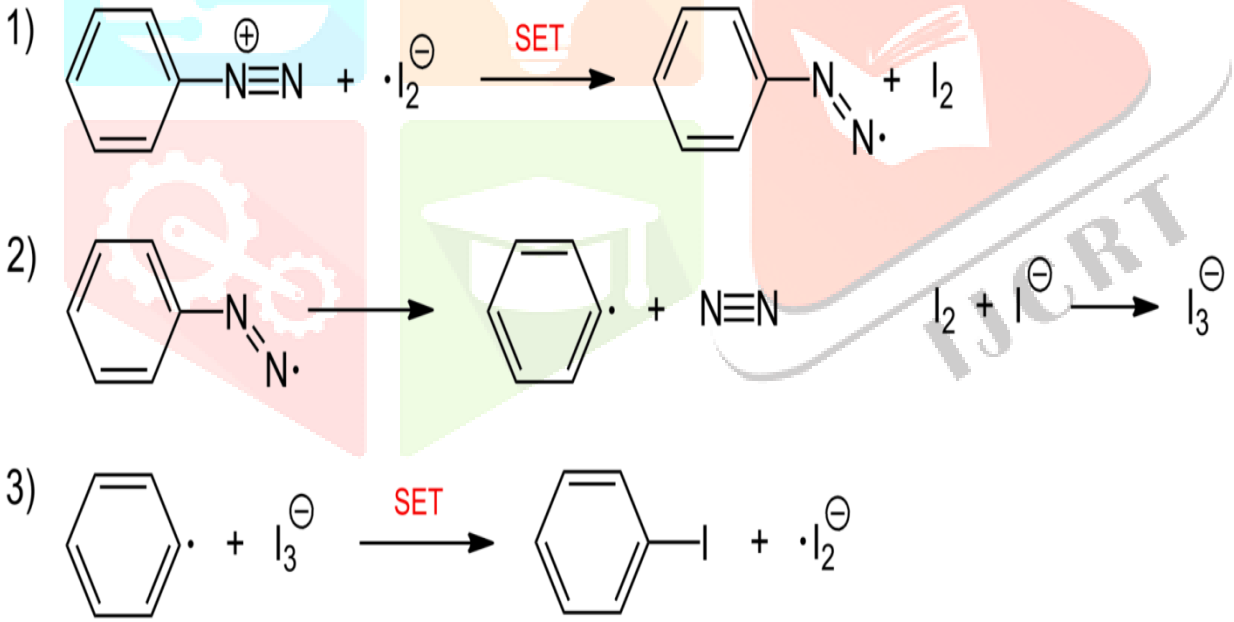
The mechanism involves 2 steps in first step a reduction of diazonium ion by cuprous ion, and form an aryl radical · in second step aryl radical abstracts halogen from cupric chloride, reducing it and resulting in the final product·



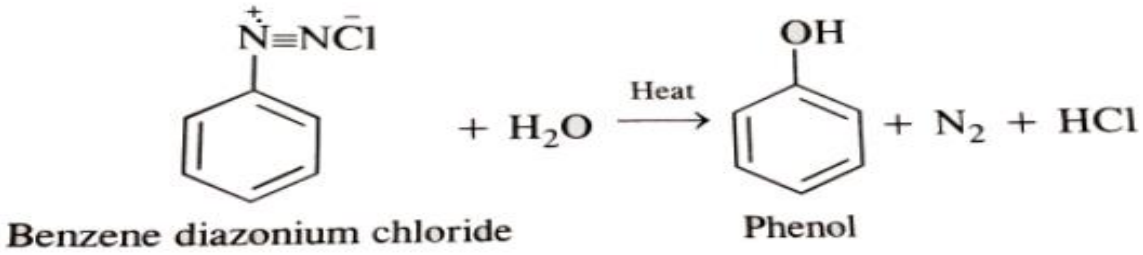
2)Replacement by iodide ion: When aryl diazonium salt is reacted with potassium iodide then iodobenzene is formed.



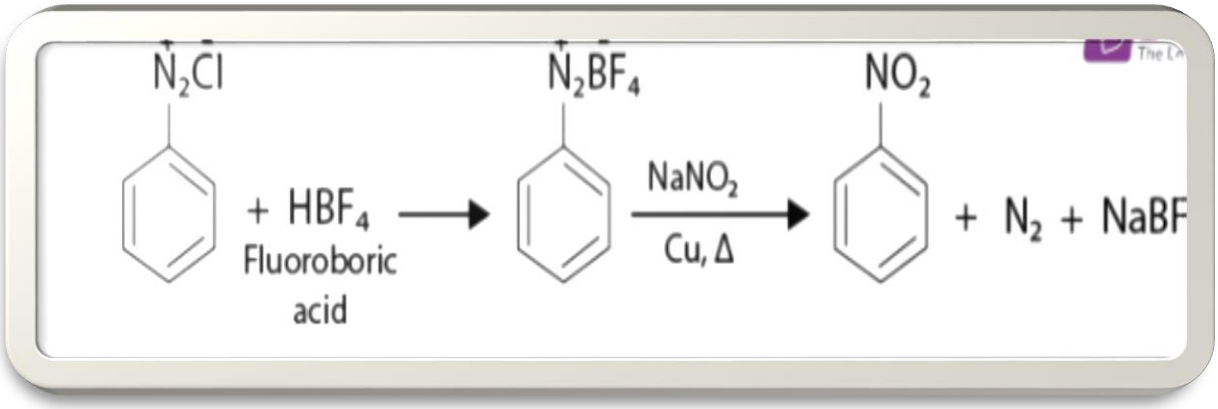
MECHANISM:



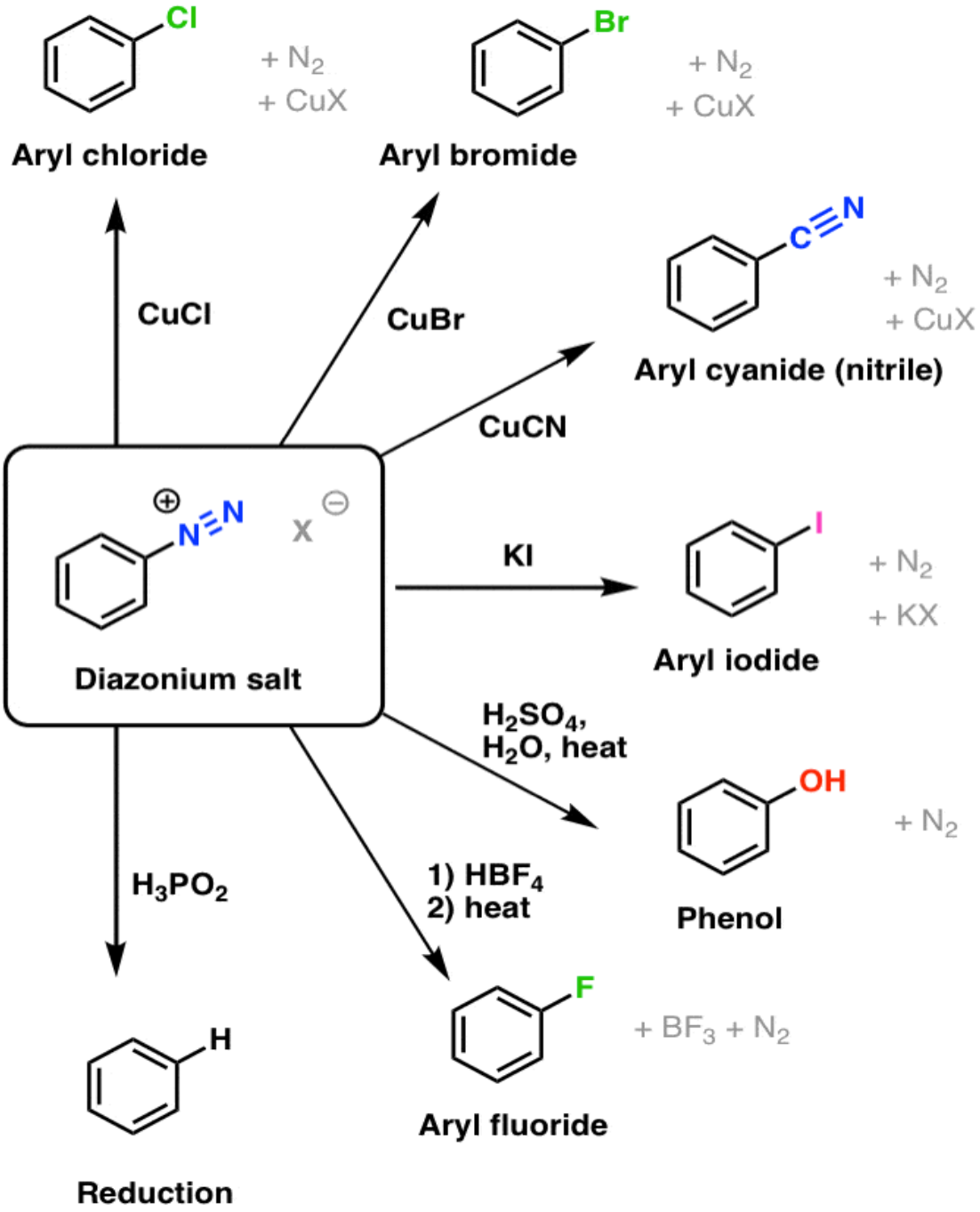
3) Replacement by hydroxyl group: When aryl diazonium salt is hydrolyzed it forms phenol and byproduct is hydrochloric acid.



4)Replacement by –NO2 group: When aryl diazonium salt heated with fluroboric acid the intermediate is diazonium fluroborate and after adding aqueous sodium nitrate solutions,in presence of copper then diazonium group is replaced by nitro group.



5) Some more reactions are:

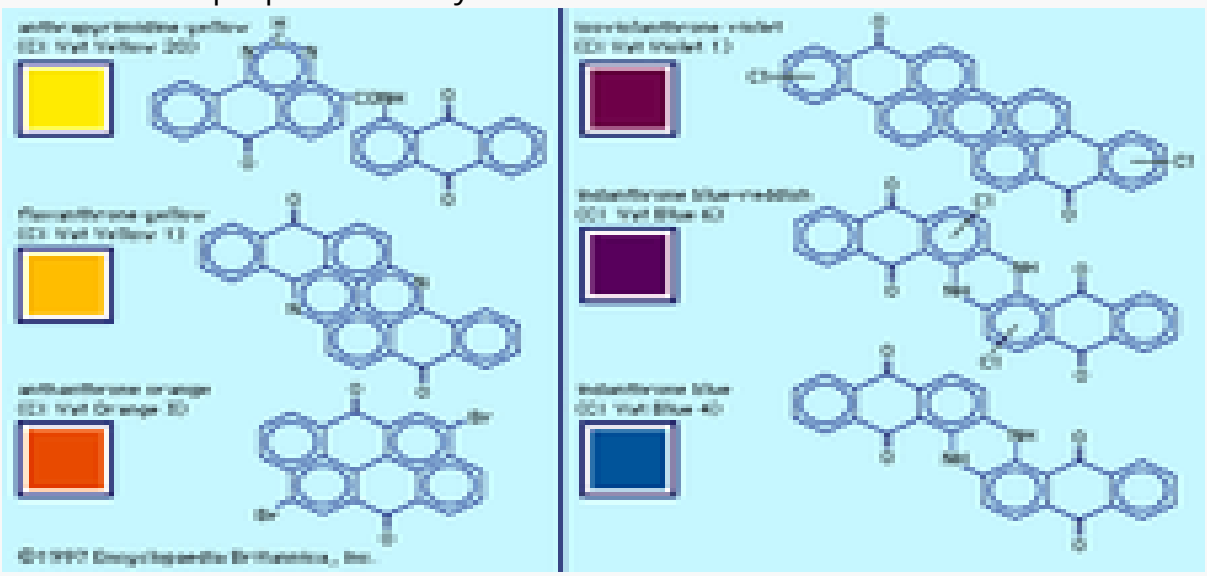


6) AZO Coupling reactions : Aromatic azo compounds tend to be brightly colored due to the extended conjugated systems (means,a system of connected p orbitals with delocalization of electron in molecules.). Many are used as dyes (a colouring agent). Important azo dyes include methyl red and pigment red 170. Azo printing exploits this reaction as well.

An **azo coupling** is an organic reaction between a diazonium compound and another aromatic compound that produces an azo compound. In this electrophilic aromatic substitution reaction, the aryldiazonium cation is the electrophile and the activated arene is a nucleophile. Azo dyes are the most diverse group of synthetic dyes. Azo dyes are prepared in two steps. The diazonium salt is produced in the first step, which then reacts with highly reactive aromatic compounds such as phenol is the second step. Different pathways are followed to obtain the desired color properties of dyes. 'The highly reactive phenols and tertiary aromatic amines react with weak electrophiles such as diazonium ions to form highly colored derivatives known as azo compounds'.

Gernal formula for azo-compounds is R-N=N-R

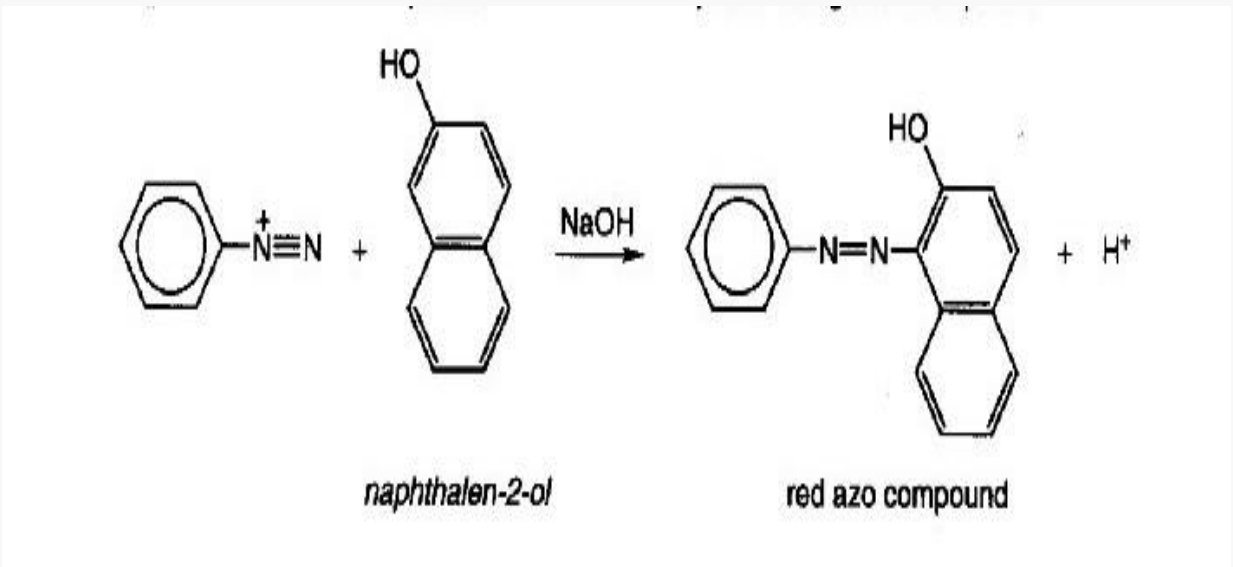
History of dyes : The main dyes were extracted from Indian like red dye. The leaves of the indigo plant were used to produce the blue dye which is still used to dye jeans. The most famous dye 'Tyrian purple' was produced from the mucus of several species of murex snail. It is a reddish-purple natural dye.



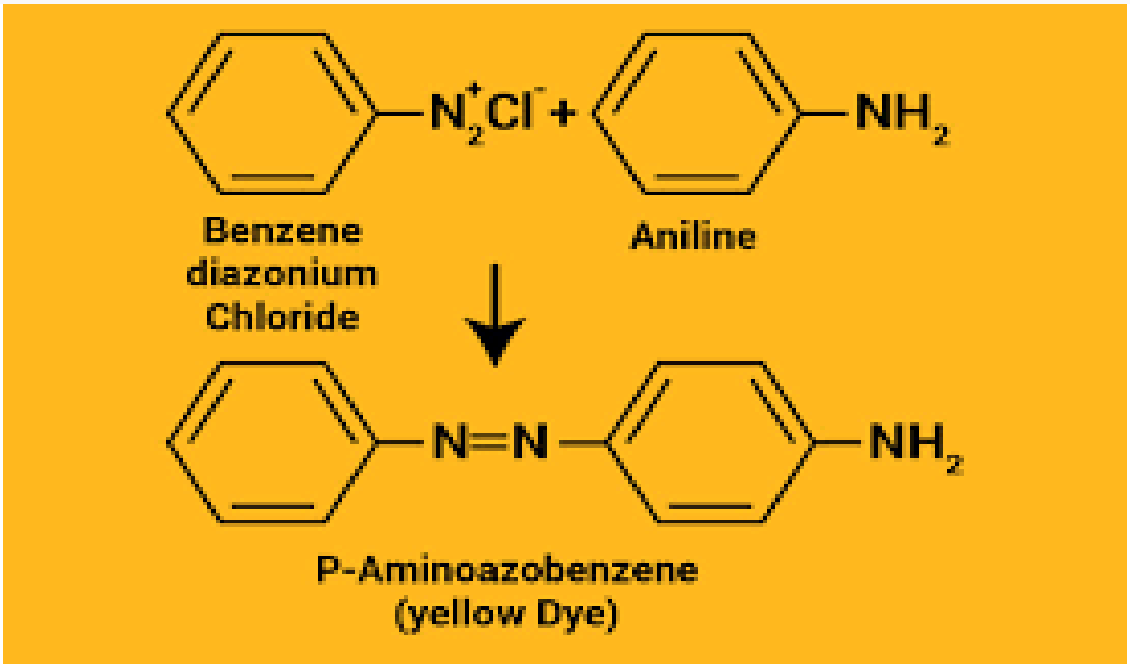
Are the Example of azo dyes.

After synthesis of aryl diazonium salt the dyes are chemically produced ,they are as fallow:

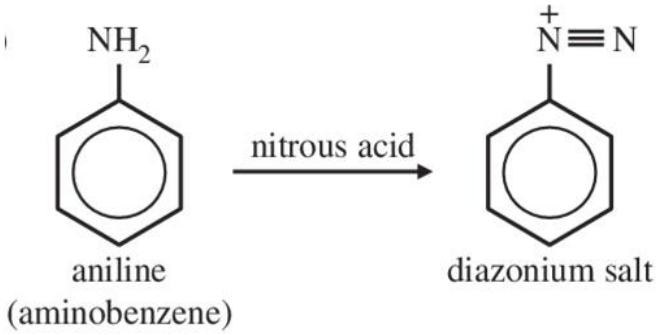
a)Synthesis of phenyl Azo-β-naphthol (Red dye): .

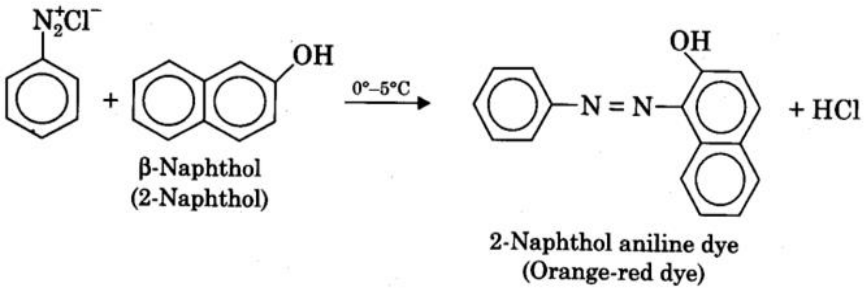


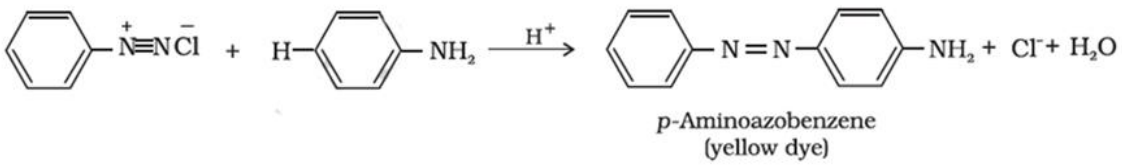
b)Synthesis of paraminoBenzene(yellow dye)



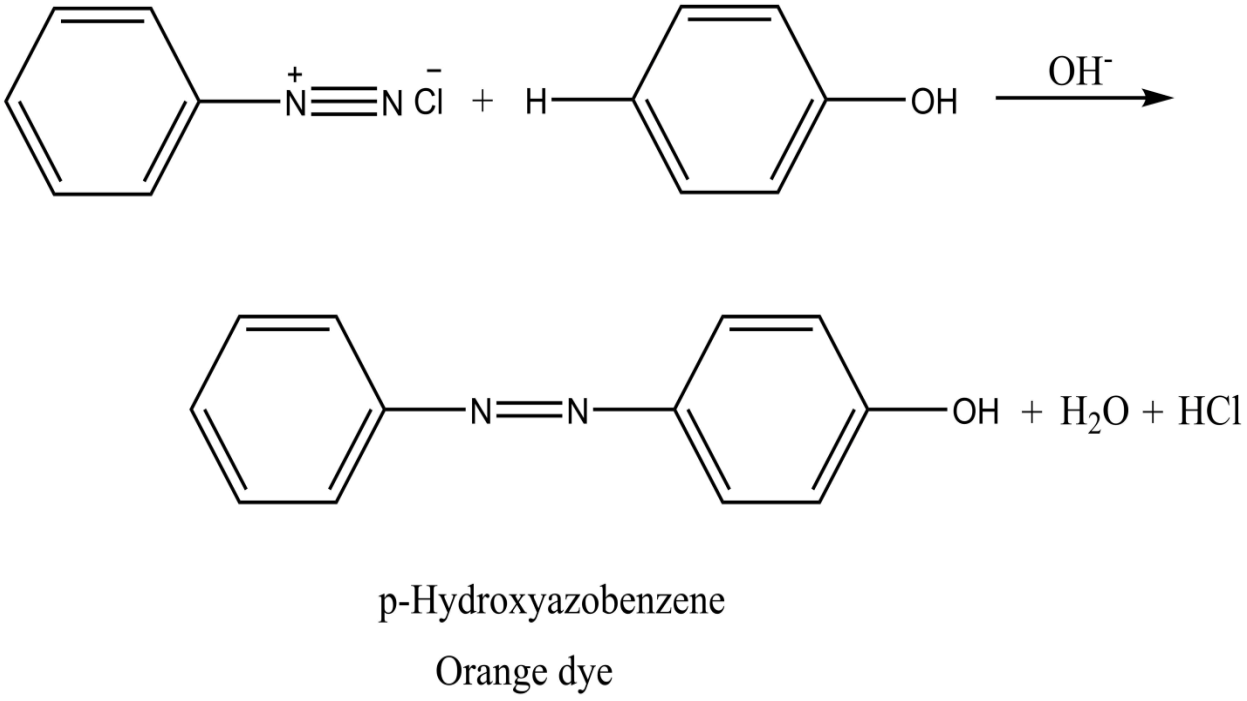
***Mechanism:**







c)Synthesis of parahydroxybenzene(orange dye):



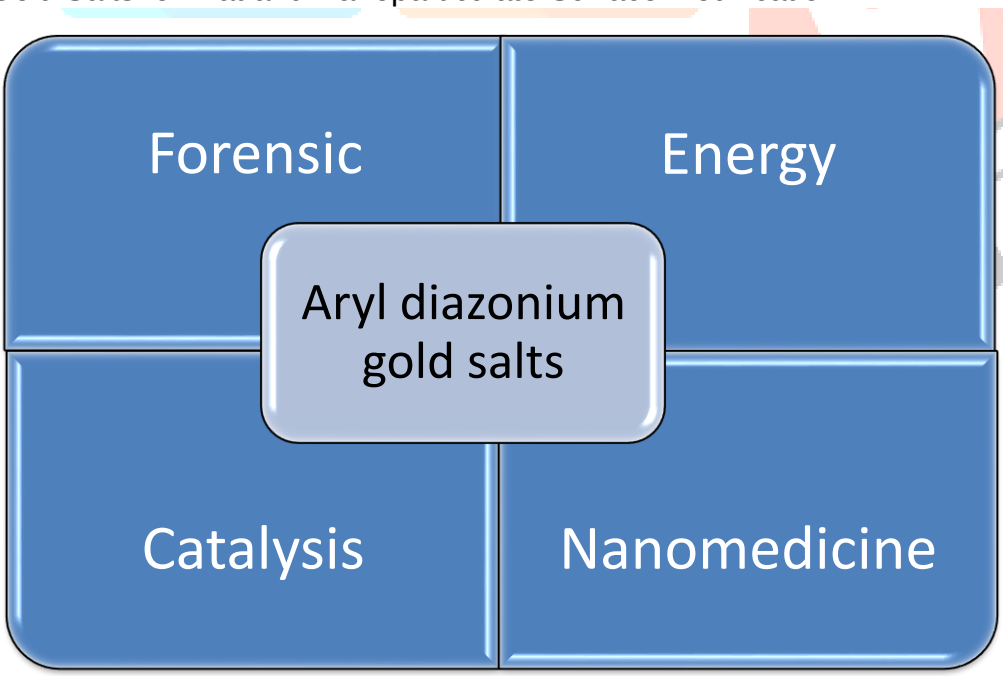
p-Hydroxyazobenzene

Orange dye

7)Reaction of aryl diazonium salt with gold substrates:

1. Preparation of gold nanoparticles from reducing aryldiazonium gold(III) salts..

2. Metal Nanoparticles Modification with Aryls from Aryldiazonium Salts. 3.Aryldiazonium Gold Salts for Flat and Nanoparticulate Surface Modification.



APPLICATION OF ARYL DIAZONIUM SALT:

1) It is used in the dye and pigment industry.

2) It is used in document reproduction as these compounds are light sensitive and break down under UV or violet light.

4) It is used in namotechnology to exfoliate the nanotubes.

Benefits of aryl diazonium salt in Nanotechnology :

1) Diazonium compounds are a key component in the realm of nanotechnology.

2) They are combined with an ionic solvent in a mortar and pestle to exfoliate the nanotubes.

3) Due to significant cohesive forces between the tubes ,diazonium compounds prohibit the tubes from forming intimate bundles , which is a recurring difficulty in nanotube technology.

CONCLUSIONS : The current review article present all about information of aryl diazonium salt ,diazotization reaction it's mechanism synthetic application of aryl diazonium salt ,azo coupling in which many important organic compound are formed by the help of catalysts.

Future aspects: Due to properties of azo coupling of aryl diazonium salt many colouring agent that is indicators will newly formed,which will help in titration process.
When diazonium salts are concentrated ,they have property of shock sensitive so they will used as current flowing material in light wire.

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17. Reaction sequence: silicon surface reaction with ammonium hydrogen fluoride creates hydride layer. An electron is transferred from the silicon surface to the diazonium salt in an open circuit potential reduction leaving a silicon radical cation and a diazonium radical. In the next step a proton and a nitrogen molecule are expelled and the two radical sidues recombine creating a surface silicon to carbon bond.

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