

Details of Module

Subject	Chemistry
Course Name	M. Sc. Ist Semester
Paper No.	Core Course III (Organic Chemistry-I)
Module Name/Title	Diazonium coupling
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Date	23/04/2020

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(1) Diazo Compounds

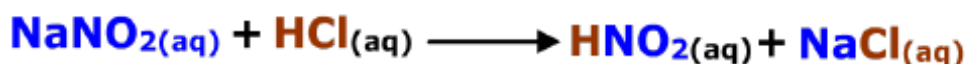
Compounds containing -N=N- group are known as diazo compounds. Their general structure is R-N=N-R' . Here R and R' are preferably arene groups and the azo group is thus stabilised by becoming part of extended delocalised system.

They are prepared by coupling reaction between a **diazonium salt** and a **coupling reagent**.

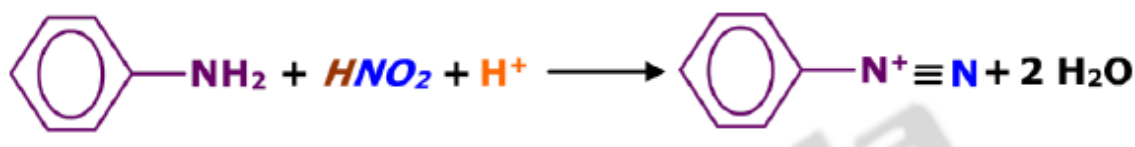
(2) Diazonium Salt

Diazonium salts are prepared by adding cold solution of sodium nitrite (NaNO_2) to arylamine solution in dilute acid below 5°C temperature. This process is called **diazotisation**. The diazonium salts are prepared fresh and used immediately.

(i) The hydrochloric acid reacts with sodium nitrite to form unstable nitrous acid.



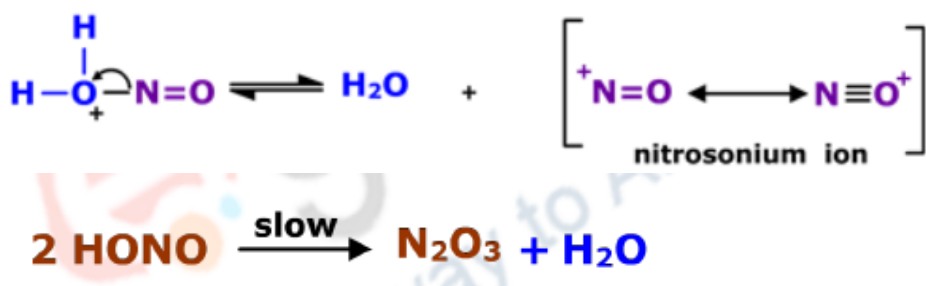
(ii) The nitrous acid formed *in situ* reacts with the arylamine to form diazonium ion.



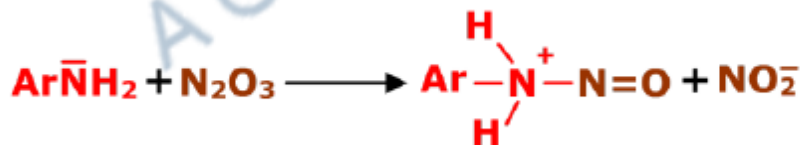
Mechanism of diazotization:

Step 1: Formation or generation of NO^+ (nitrosonium ion) or dinitrogen trioxide:

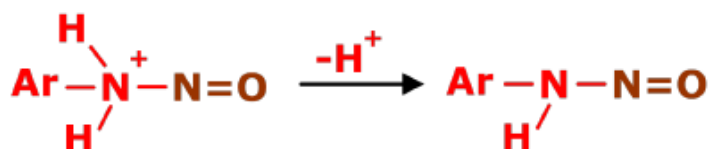
The nitrosonium ion formation takes place as follows where water is removed from nitrous acid.



Step 2: Attack of NO^+ (nitrosonium ion) or N_2O_3 on the amine



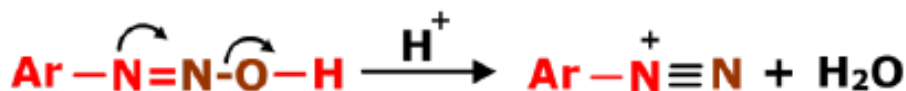
Step 3: Loss of proton



Step 4: Tautomerisation



Step 5: Loss of water and formation or generation of diazonium ion



Stability of diazonium ion:

The aromatic diazonium salts are relatively more stable than aliphatic diazonium salts, as the electron rich benzene ring stabilises the $-\text{N}^+\equiv\text{N}$ group. If the temperature rises above 5°C , the benzenediazonium chloride decomposes to form phenol and nitrogen gas is given off. The aromatic groups present stabilise the diazonium ion through donating electrons via delocalisation in comparison to aliphatic groups.

(3) Coupling Reaction

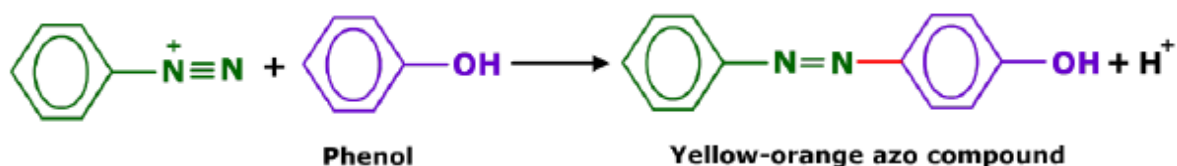
If the benzenediazonium chloride is reacted with another compound containing a benzene ring, called a coupling

agent (such as phenol or aromatic amine), an azo compound is produced. This reaction is known as coupling reaction.

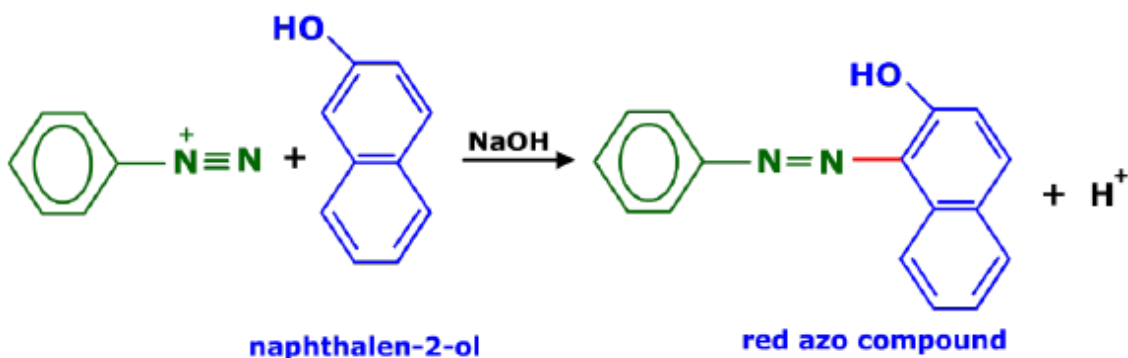
The diazonium salt acts as an electrophile in a coupling reaction. Many of the products of coupling reactions are important dyes. A coloured precipitate of azo compound is formed immediately on reaction of diazonium salt with amines or phenols.

Examples of coupling reactions:

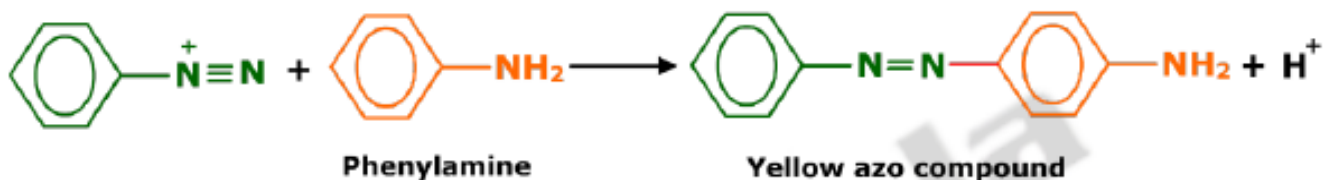
(a) Benzenediazonium salt and alkaline phenol gives a yellow orange azo compound.



(b) Benzenediazonium salt and alkaline naphthalen-2-ol gives a red azo compound.

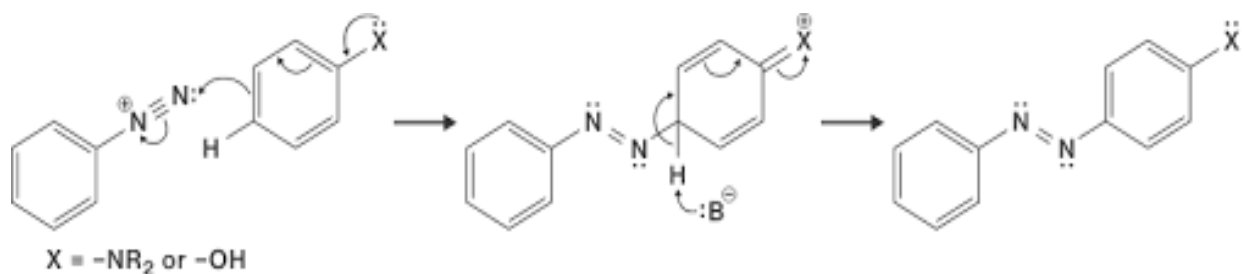


(c) Benzenediazonium salt and phenylamine gives a yellow azo compound.



Mechanism of coupling reaction:

The mechanism involves an initial attack of coupling agent (phenols or anilines) on an electrophilic diazonium ion, followed by loss of a proton. The product is normally a *trans*-diazo compound rather than *cis*



(4) Uses of Diazo Compounds

Diazo compounds are used as pH indicators and dyes.

(i) pH indicators

Methyl yellow, methyl orange, methyl red, congo red and alizarine yellow are some typical azo compounds used as pH indicators.

(ii) Dyes

Aniline Yellow, Orange G, Xylidine, Alizarin Yellow R, Bismark Brown Y and Congo Red are examples of some dyes containing azo linkages, which are synthesized by coupling reaction.