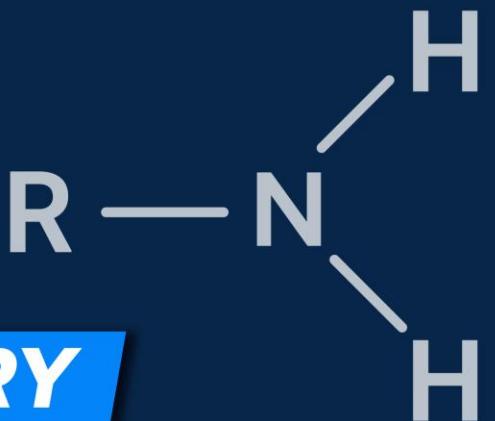




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NEET

STUDENTS' SURVEY



LINK IN
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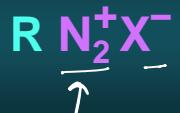
Diazonium Salts

$\text{Z}^- \text{N}^+ \text{cation}^-$

Diazonium Salts

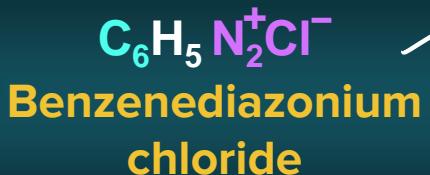
Alkyl diazonium salts can not be isolated

General formula



- R stands for an **aryl** group
- X^- ion may be Cl^- , Br^- , BF_4^- etc.

Example



Diazonium Salts

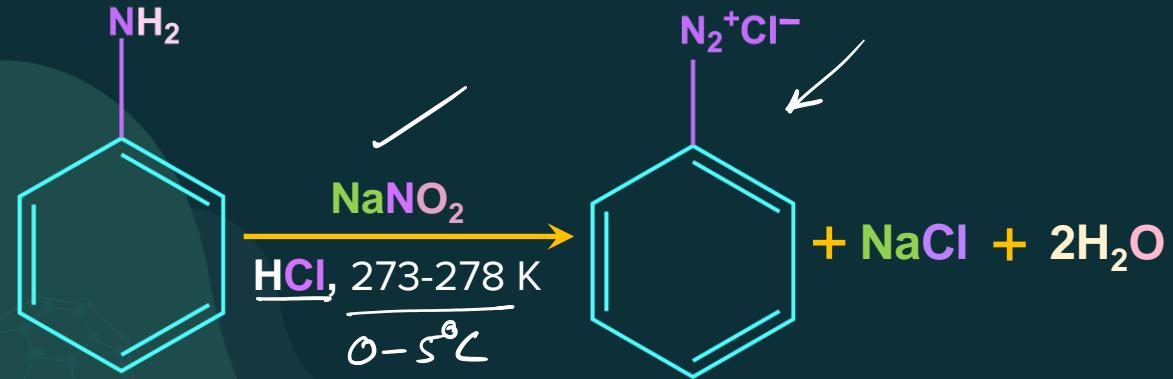


Primary aliphatic amines react with nitrous acid to form **diazonium salts**. However, the aliphatic diazonium salts being unstable, decompose to yield a mixture of alcohols, nitrogen gas, and byproducts.

major

Primary arylamines react with **nitrous acid** to give **arenediazonium salts**.

Preparation of Diazonium Salts



*nitrous acid
is generated in
reaction mixture itself*

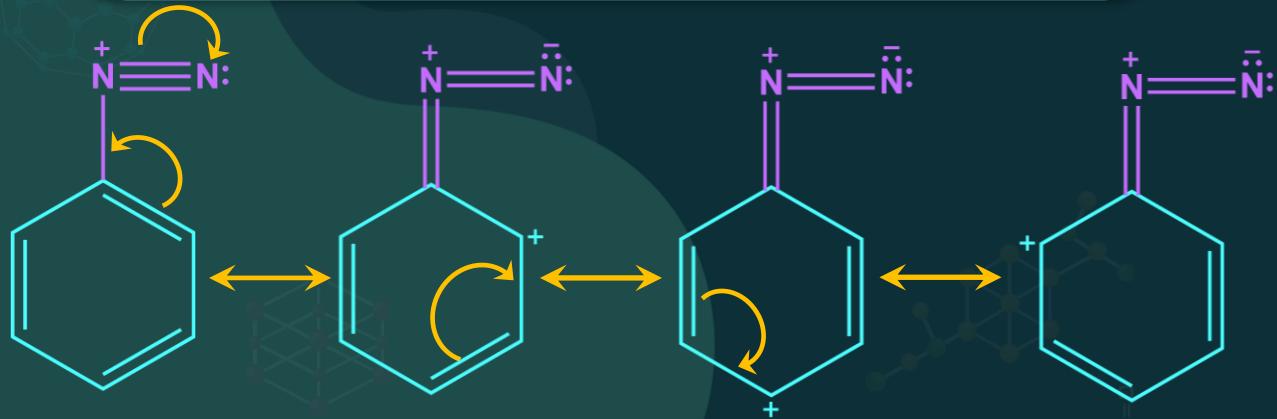
Diazonium Salts



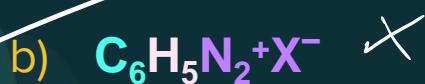
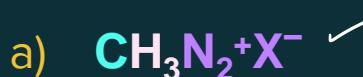
conjugation stabilized

Even though arenediazonium salts are **unstable**, they are still far more stable than aliphatic diazonium salts.

They **do not decompose** at an appreciable rate in solution when the temperature of the reaction mixture is kept **below 5°C**.



Which of the following will be **most stable** diazonium salt RN_2^+X^- ?



NEET 2014

a, c, d \rightarrow alkyl diazonium salts.
so are highly unstable.



Physical Properties

Benzenediazonium Chloride



It is a **colorless crystalline solid.**

It is **readily soluble in water.**

It is **stable in cold** but reacts with water when warmed.

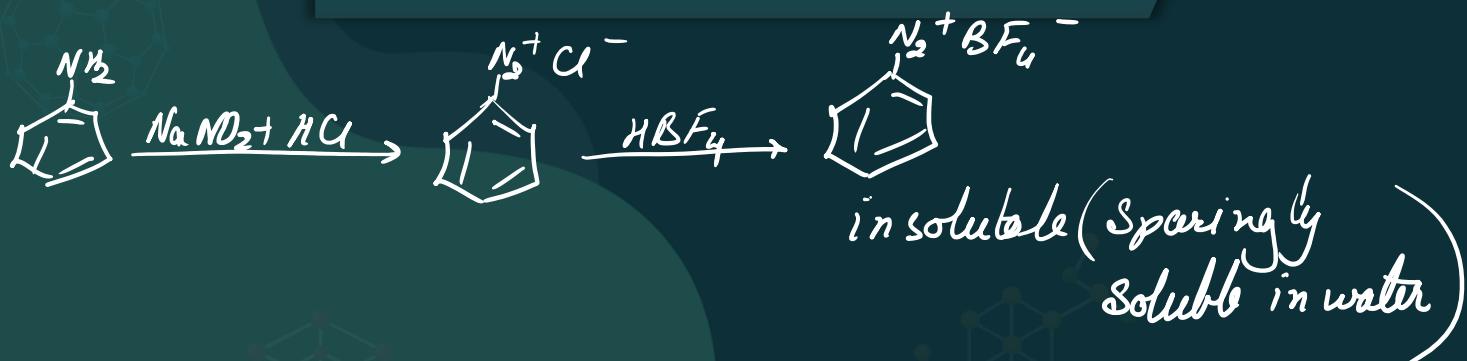
It **decomposes** easily in the **dry state.**

Benzenediazonium Fluoroborate



It is **water insoluble**.

It is **stable at room temperature**.





Chemical Reactions of Benzene Diazonium Chloride

Chemical Reactions

Reactions involving displacement of nitrogen

Reactions involving retention of diazo group

electrophile



nucleophile



Reactions Involving Displacement of Nitrogen

Replacement by $-CN$

Replacement by $-X$

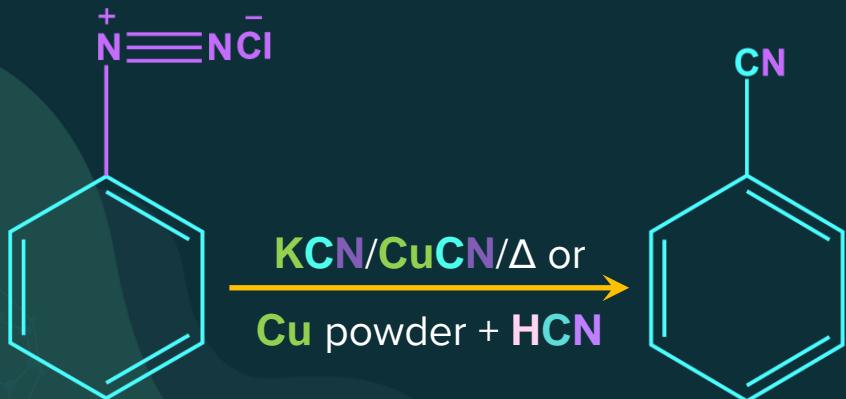
Replacement by $-H$

Replacement by $-OH$

Replacement by $-NO_2$

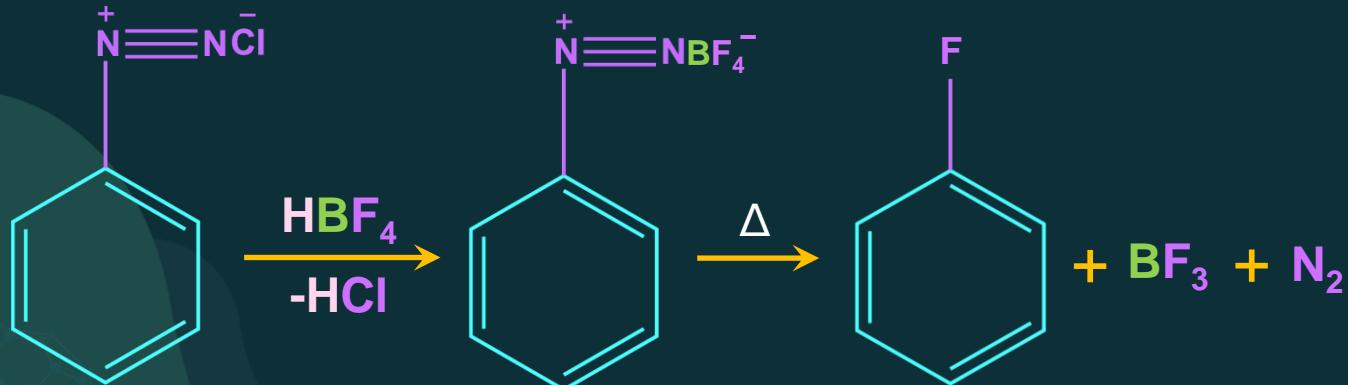


Replacement by $-\text{CN}$



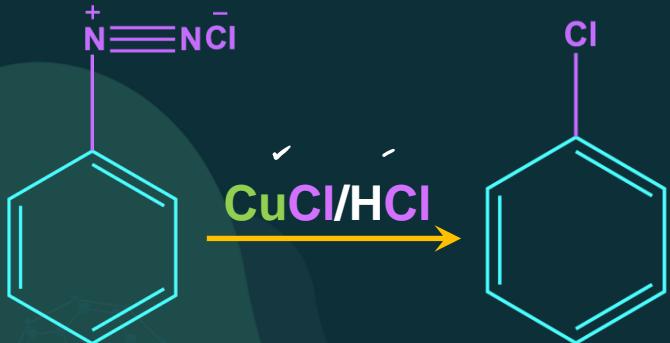
Replacement by $-F$

Only practical method of preparation of fluoro benzene .



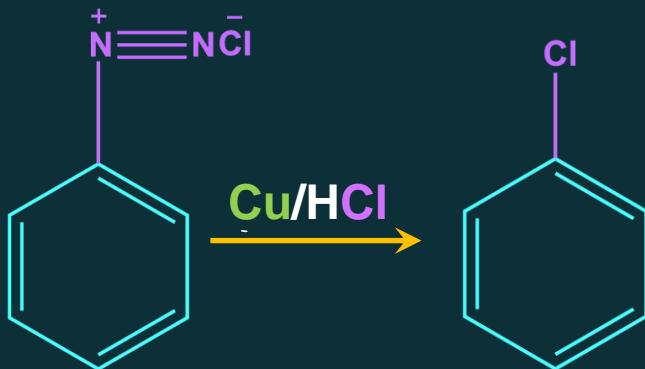
✓
Balz-Schiemann reaction

Replacement by $-Cl$



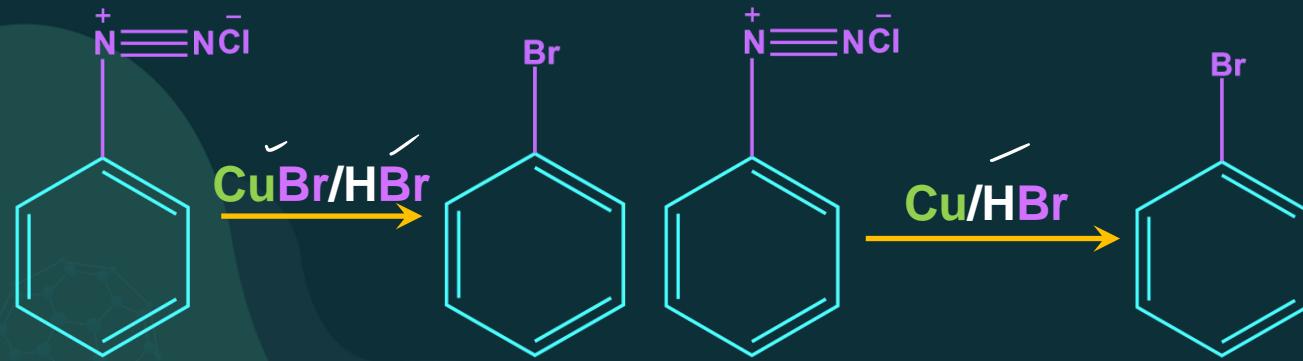
Sandmeyer reaction

Higher yield



Gattermann
reaction

Replacement by $-Br$



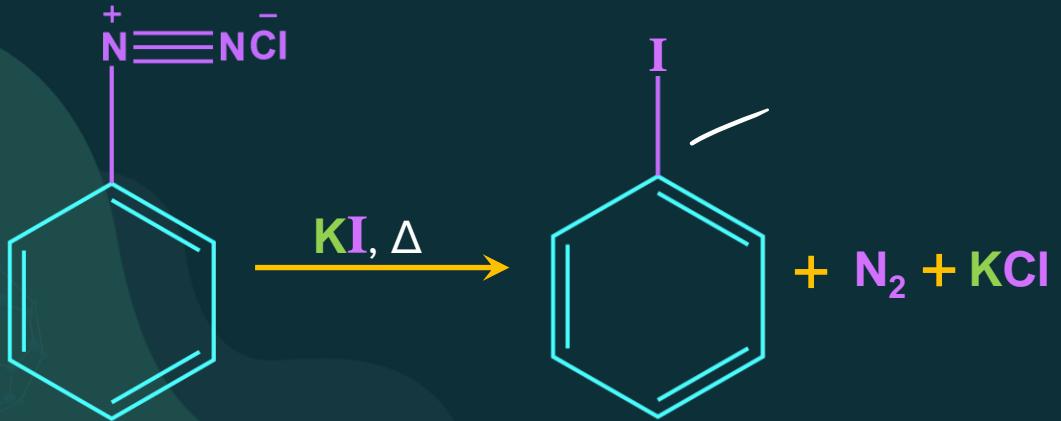
Sandmeyer reaction

Gattermann reaction



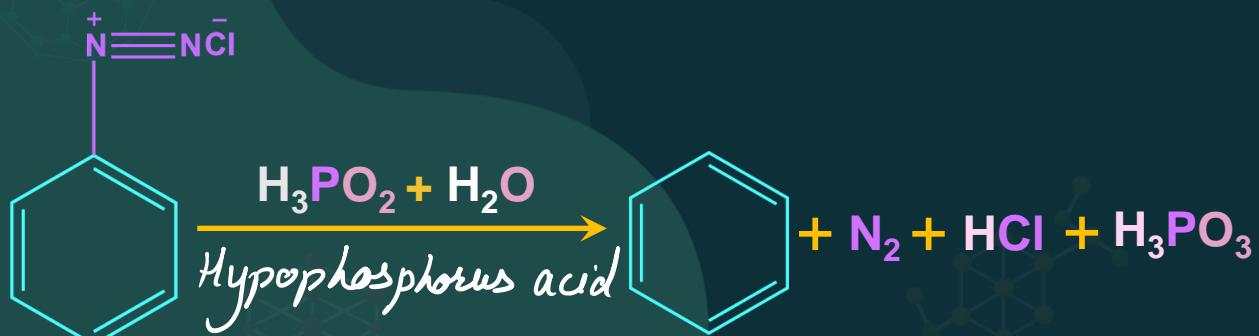
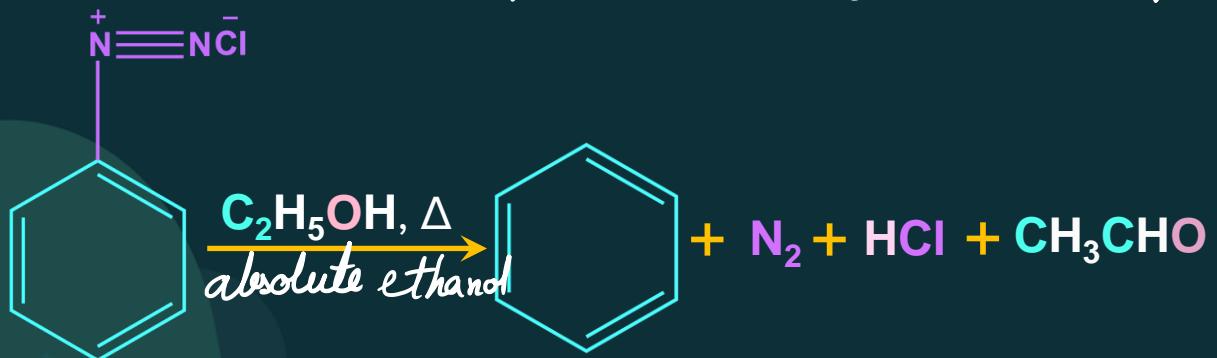
The **yield** in **Sandmeyer** reaction is found to be **better** than **Gattermann** reaction.

Replacement by $-I$

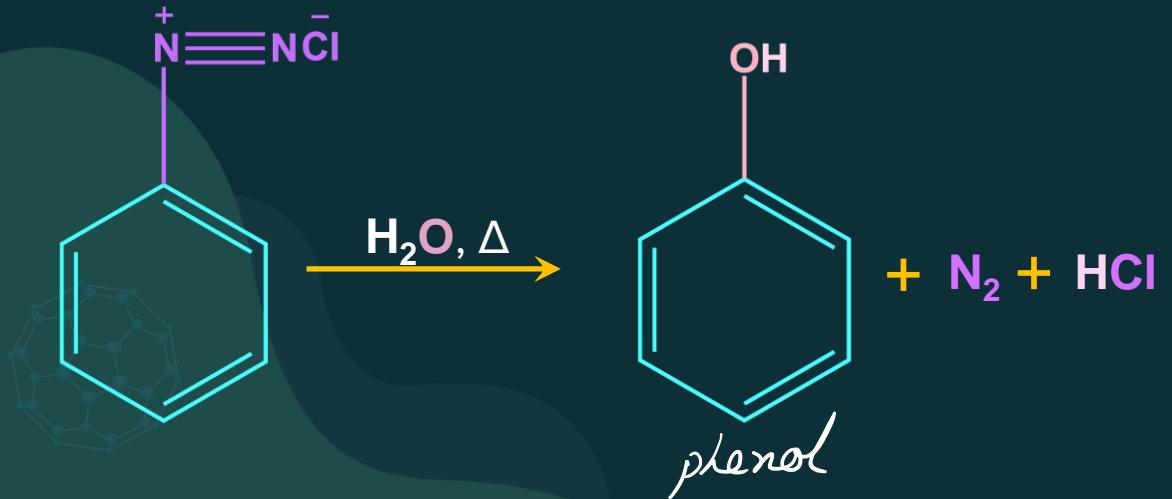


Replacement by $-H$

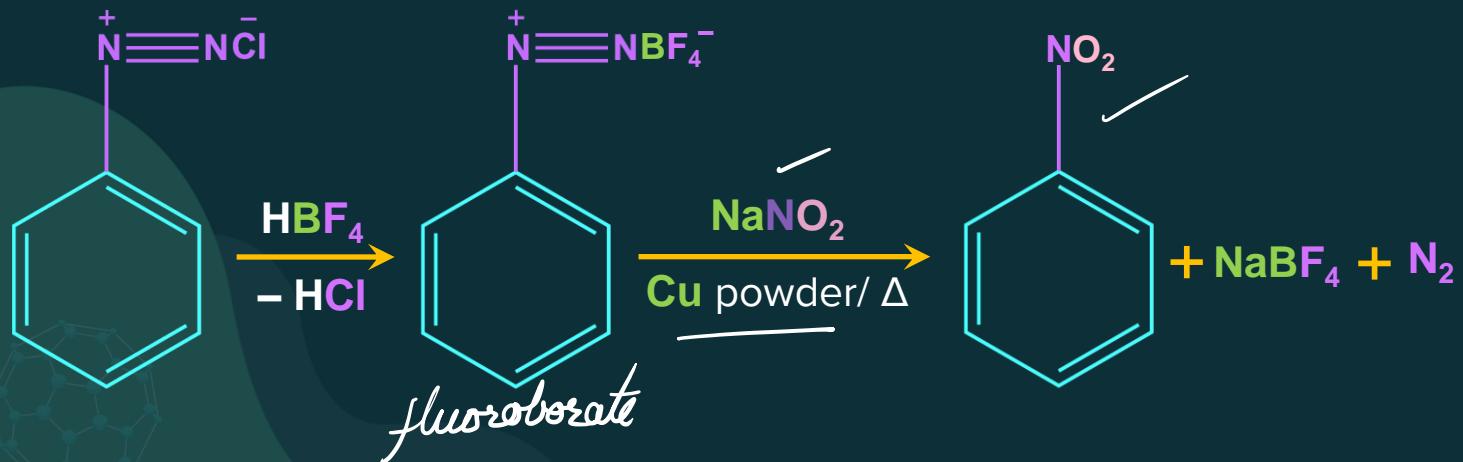
Used for removal of Nb group from benzene.



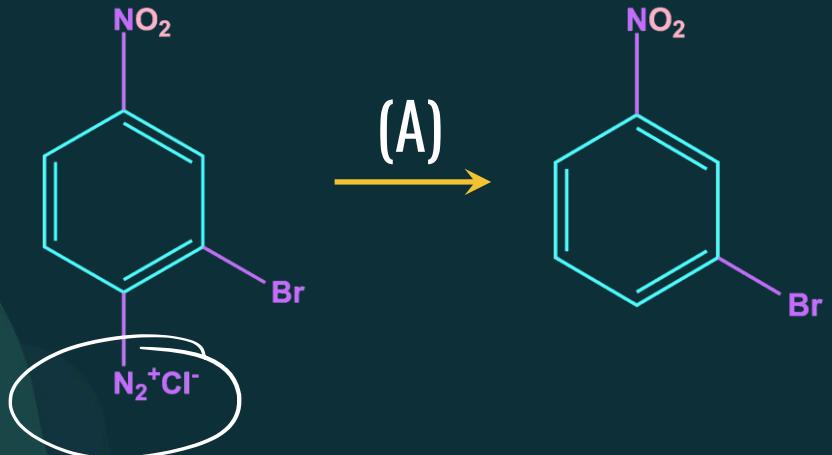
Replacement by $-OH$



Replacement by $-\text{NO}_2$



In the reaction, (A) is:



a) H_3PO_2 and H_2O

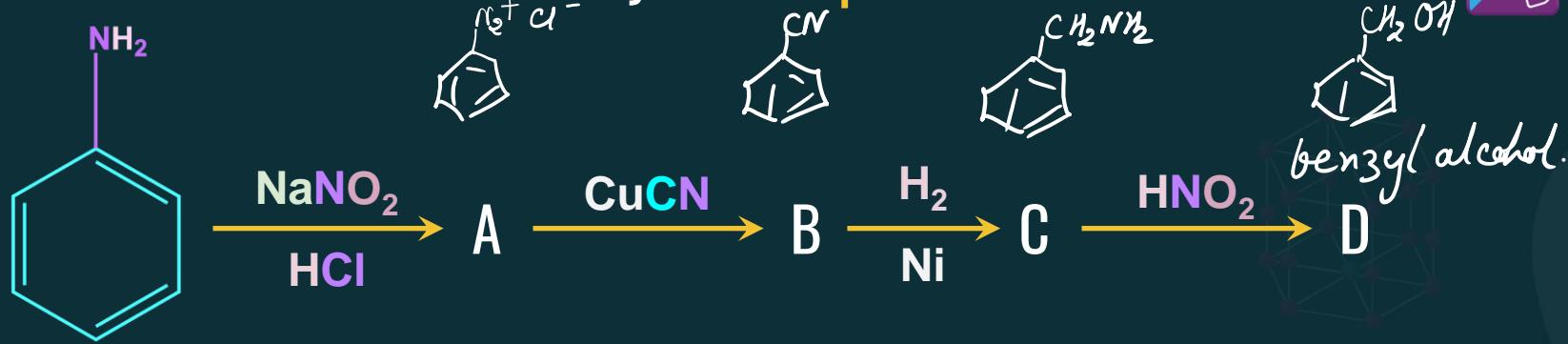
b) $\text{H}^+/\text{H}_2\text{O}$

c) $\text{HgSO}_4/\text{H}_2\text{SO}_4$

d) Cu_2Cl_2

NEET 2013

Aniline in a set of reactions yielded a product D.

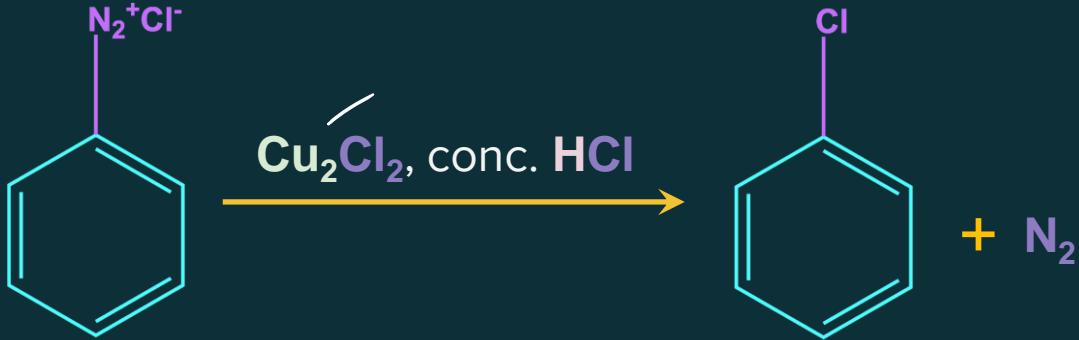


The structure of product D would be:

AIPMT 2005

- a) C6H5NHOH
- b) C6H5NHCH2CH3
- c) C6H5CH2NH2
- d) C6H5CH2OH

The following reaction is known as



AIIMS 2000

- a) Strecker's reaction
- ~~b) Sandmeyer's reaction~~
- c) Wohl-Ziegler reaction
- d) Stephen's reaction

Diagonium ion reacts as ~~electrophile~~

Coupling Reactions

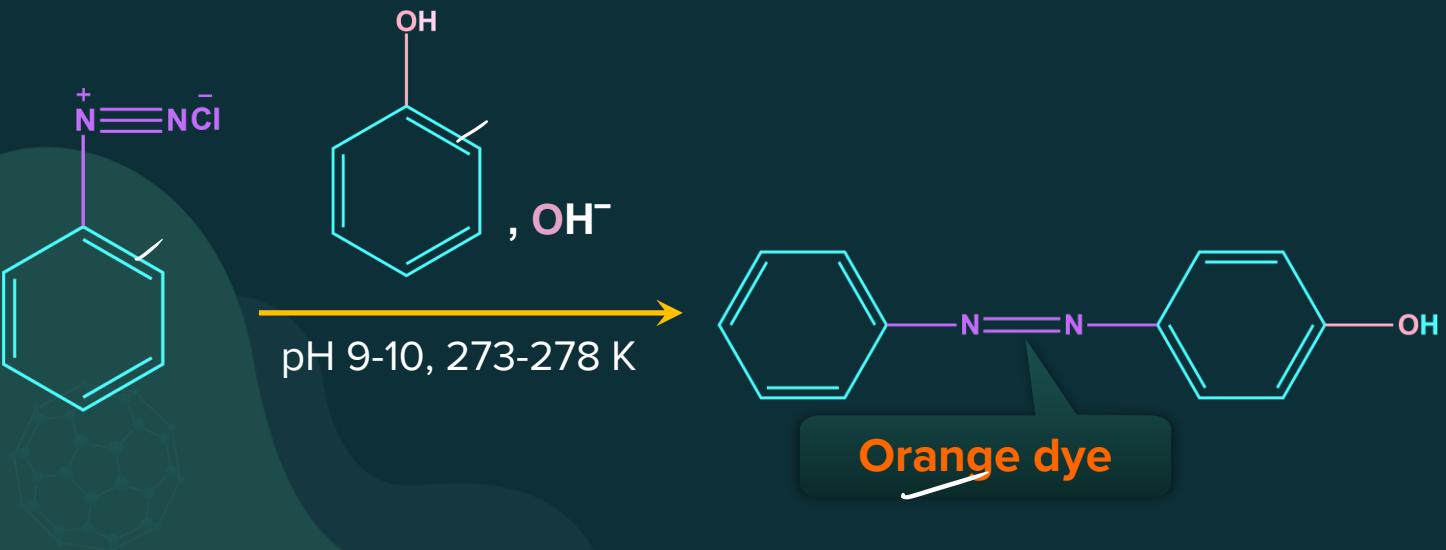
Coupling Reactions



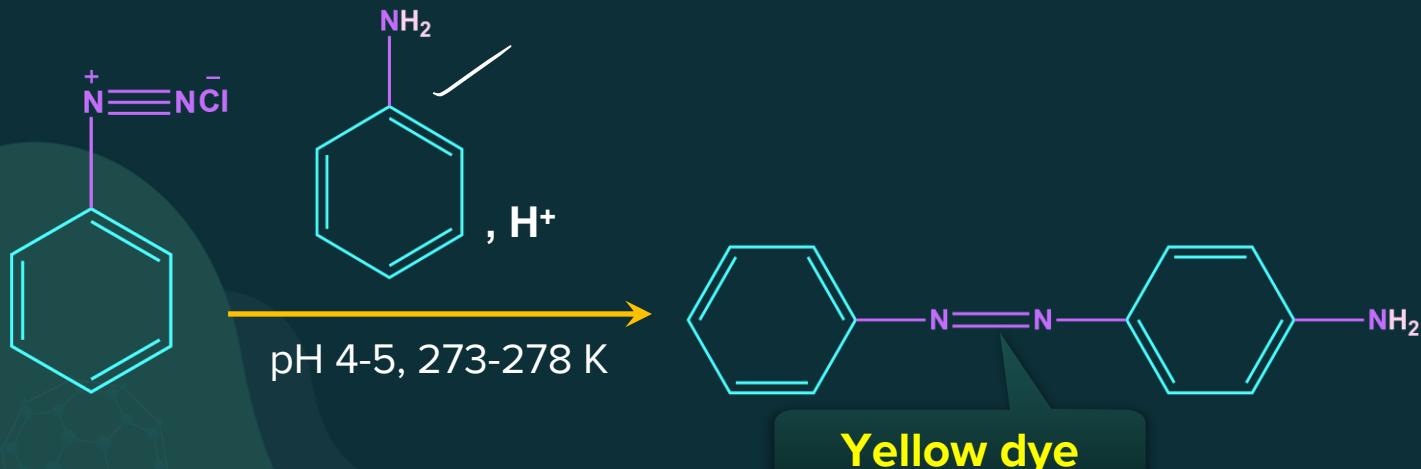
✓ Arene diazonium ions are **weak electrophiles** and they react with **highly reactive** aromatic compounds like phenols and arylamines to yield **azo compounds**.

This electrophilic aromatic substitution is often called a **diazo coupling reaction**.

Coupling Reactions



Coupling Reactions



Coupling Reactions



Azo compounds are usually intensely coloured because of the azo linkage (-N=N-).

chromophore

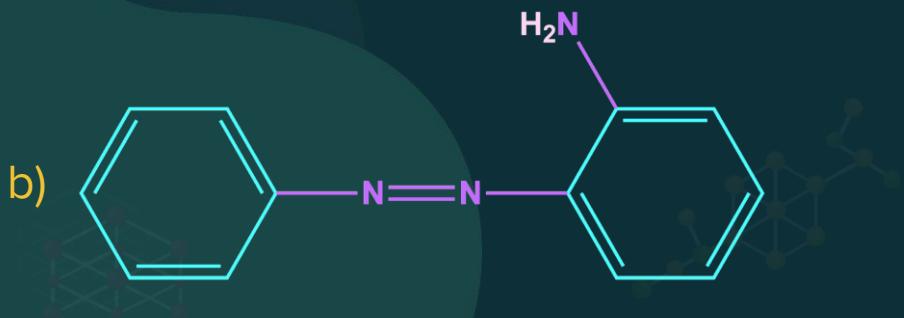
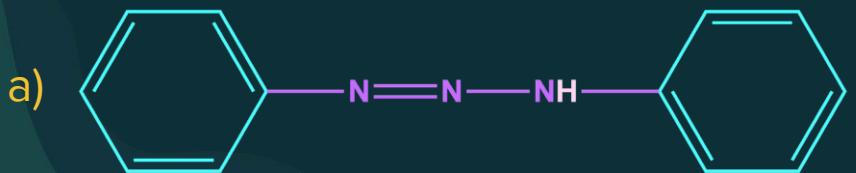
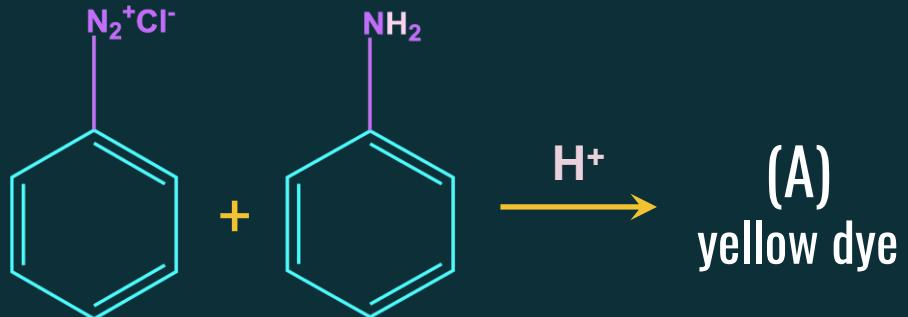
Azo linkage brings the two aromatic rings into **conjugation** and gives an extended system of delocalized π electrons and allows **absorption** of light in the **visible region**.

Coupling Reactions



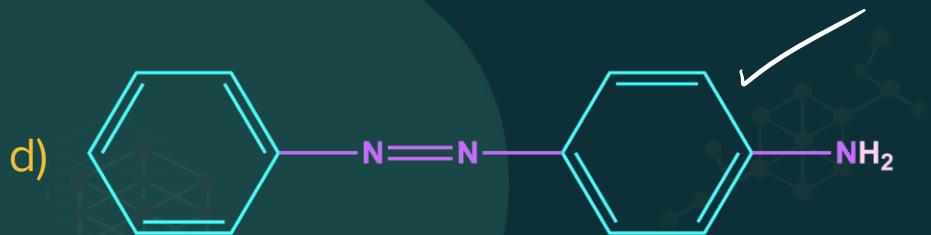
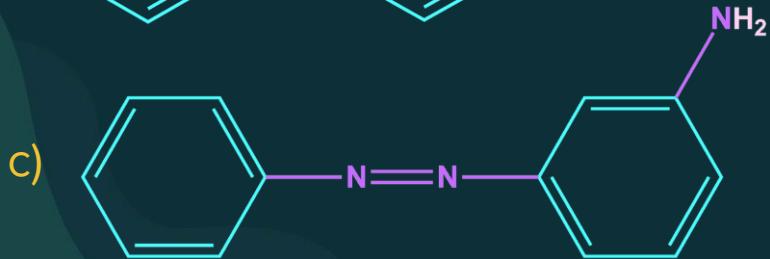
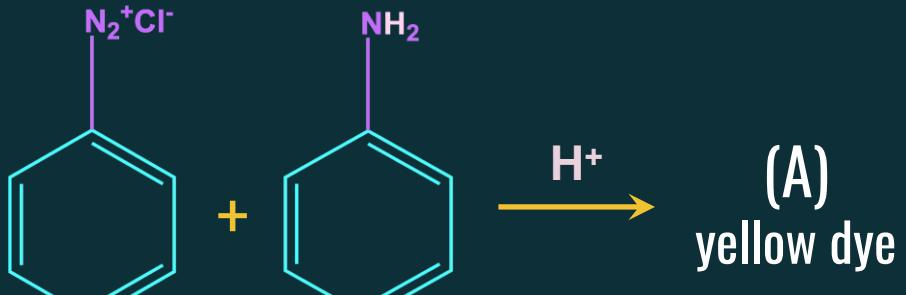
Azo compounds because of their **intense colors** and because they can be synthesized from relatively **inexpensive compounds**, are used extensively as **dyes**. → *azo dyes*

In the following reaction, the product (A) is:



NEET 2014

In the following reaction, the product (A) is:



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Importance of Diazonium Salts

Importance of Diazonium Salt



1

Diazonium salts are good intermediates for the introduction of **$-F$** , **$-Cl$** , **$-Br$** , **$-I$** , **$-CN$** , **$-OH$** , **$-NO_2$** groups into the aromatic ring.

Importance of Diazonium Salt



2

Aryl fluorides and **iodides** cannot be prepared by direct halogenation but they can be obtained from **diazonium salt**.

3

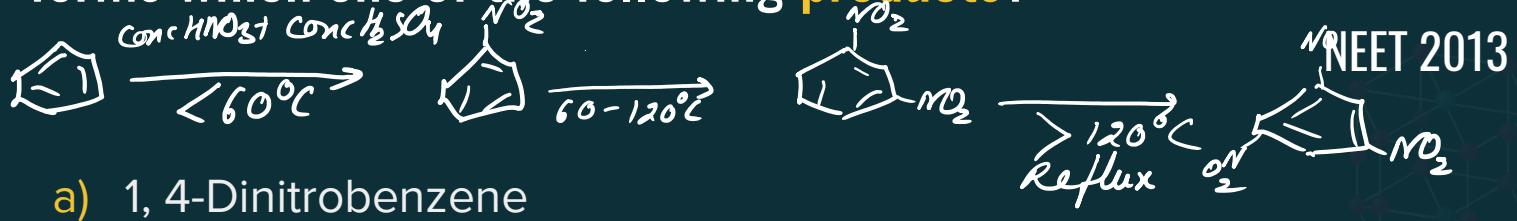
Cyano group can't be introduced by nucleophilic substitution of -Cl in **chlorobenzene** but cyanobenzene can be obtained from **diazonium salt**.

Which of the following compound will **not** undergo azo coupling reaction with benzene diazonium chloride?

AIIMS 2016

- a) Aniline
- b) Phenol
- c) Anisole
- d) Nitrobenzene
T deactivating group

Nitrobenzene on reaction with conc. $\text{HNO}_3/\text{H}_2\text{SO}_4$ at $80-100^\circ\text{C}$ forms which one of the following **products**?



- a) 1, 4-Dinitrobenzene
- b) 1, 2, 4-Trinitrobenzene
- c) 1, 2-Dinitrobenzene
- ~~d) 1, 3-Dinitrobenzene~~

Which of the following is involved in Sandmeyer's reaction?

AIIMS 2002

- a) Ferrous salt
- ~~b) Diazonium salt~~
- c) Ammonium salt
- d) Cuprammonium salt

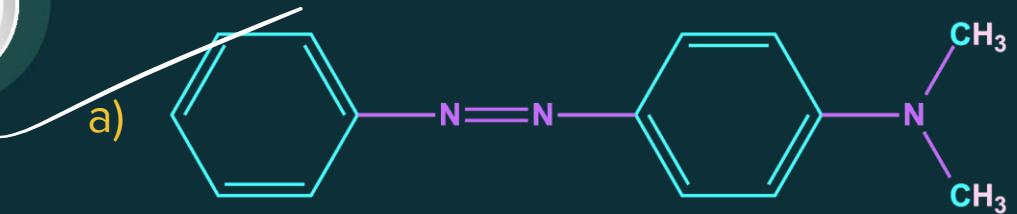
Aniline in a set of following reactions yielded a product Y.



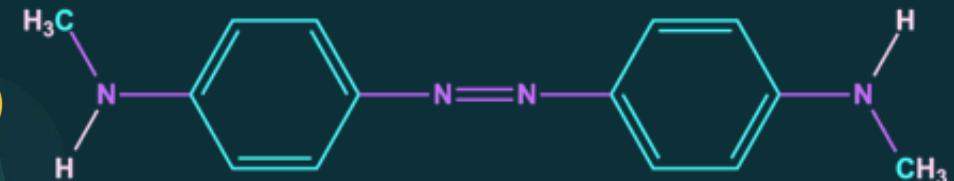
The structure of product Y would be:

AIPMT 2010

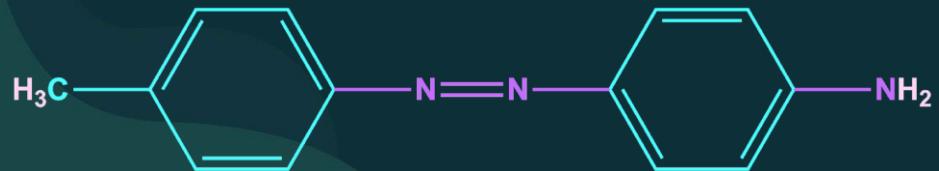
a)



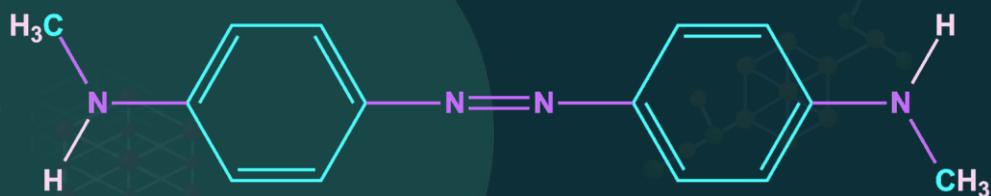
b)



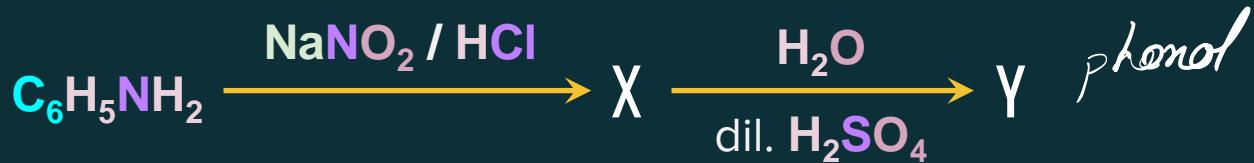
c)



d)



Identify Y in the reaction:



AIIMS 1998



Aromatic nitriles (ArCN) are not prepared by reaction:

- a) $\text{ArX} + \text{KCN}$
- b) $\text{ArN}_2^+ \text{Cl}^- + \text{CuCN}$
- c) $\text{ArCONH}_2 + \text{P}_2\text{O}_5$
- d) None of these

Assertion: Benzene diazonium chloride does not give test for nitrogen. *in Lassaigne method*

Reason: Loss of N_2 gas takes place during heating.

AIIMS 1999

- a)** If both assertion and reason are correct and the reason is a correct explanation of the assertion
- b)** If both assertion and reason are correct but reason is not a correct explanation of the assertion.

Assertion: Benzene diazonium chloride does not give test for nitrogen.

Reason: Loss of N_2 gas takes place during heating.

AIIMS 1999

- c) If the assertion is correct but reason is incorrect.

- d) If both the assertion and reason are incorrect.

Assertion: Benzene diazonium salt on boiling with water forms phenol.

Reason: C—N bond is polar.

AIIMS 2007

a) If both assertion and reason are correct and the reason is a correct explanation of the assertion

b) If both assertion and reason are correct but reason is not a correct explanation of the assertion.

Assertion: Benzene diazonium salt on boiling with water forms phenol.

Reason: C—N bond is polar.

AIIMS 2007

- c) If the assertion is correct but reason is incorrect.

- d) If both the assertion and reason are incorrect.



“Stay Positive, Work Hard. Make It Happen!”

THANK YOU