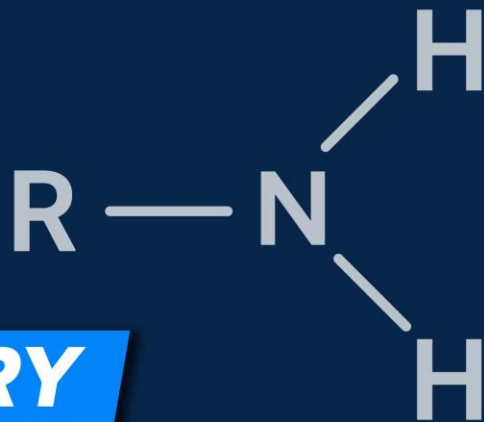




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<https://t.me/neetaakashdigital>



Diazonium Salts

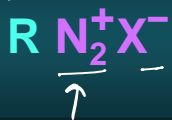
2 N cation

Diazonium Salts



alkyl diazonium salts can not be isolated

General formula



R stands for an **aryl** group
X⁻ ion may be **Cl⁻**, **Br⁻**, **BF₄⁻** etc.

Example

$\text{C}_6\text{H}_5 \text{N}_2^+ \text{Cl}^-$
Benzenediazonium
chloride

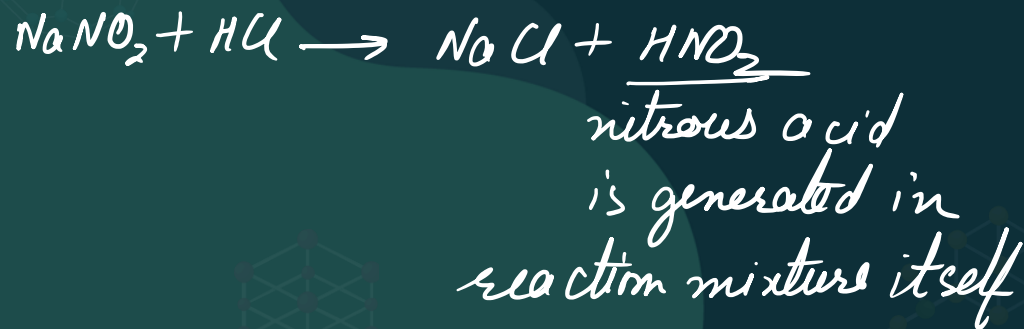
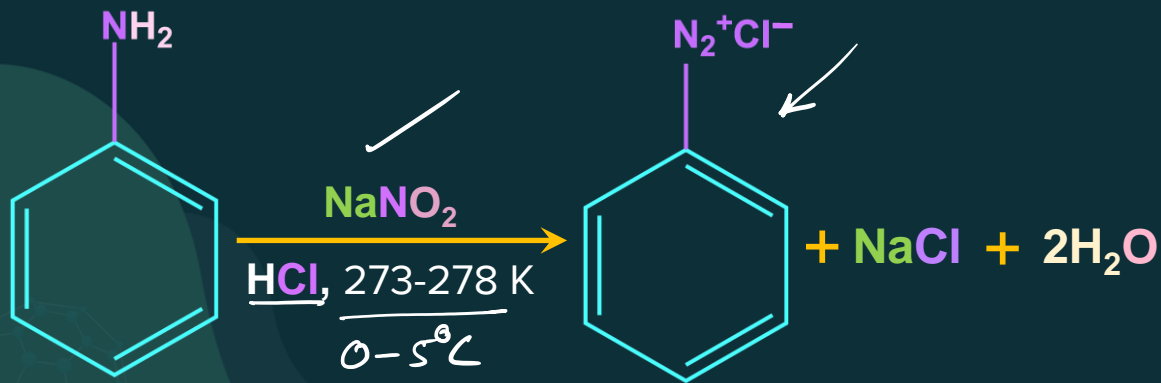
Diazonium Salts



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 **arene diazonium salts**.

Preparation of Diazonium Salts

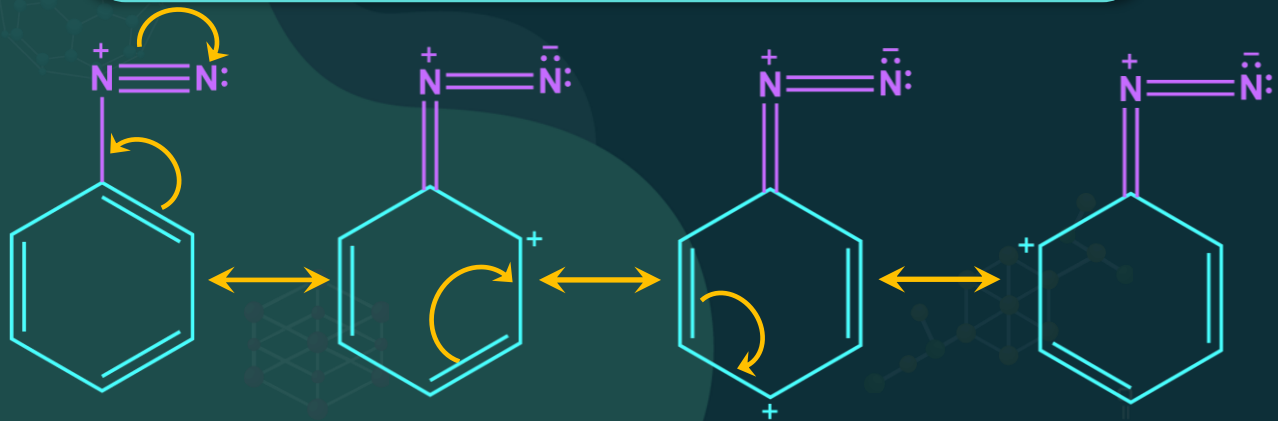


Diazonium Salts

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**. ✓



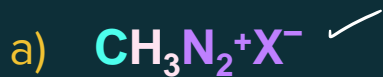


Which of the following will be **most stable** diazonium salt $RN_2^+X^-$?



NEET 2014

*a, c, d → alkyl diazonium salts.
so are highly unstable.*





Physical Properties

Benzenediazonium Chloride

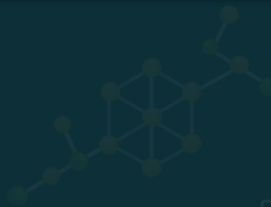


It is a **colorless crystalline solid**. ✓

It is **readily soluble in water**.

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

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

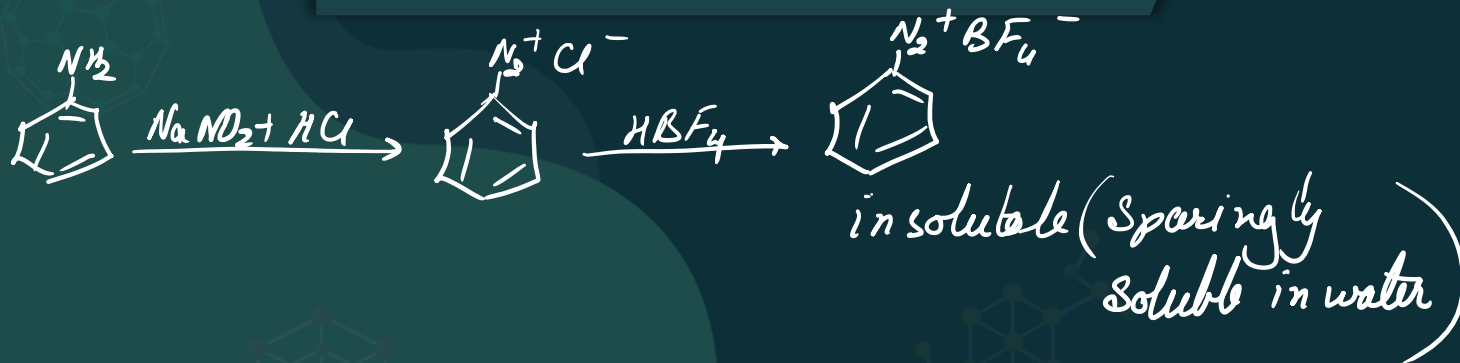


Benzenediazonium Fluoroborate



It is **water insoluble**.

It is **stable at room temperature**.





Chemical Reactions of Benzene Diazonium Chloride



$\eta = 0$

Chemical Reactions

Reactions
involving
displacement
of nitrogen

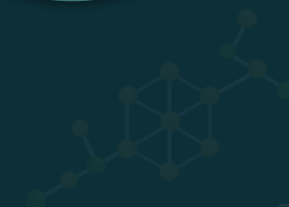
electrophile



nucleophile



Reactions
involving
retention of
diazio group



Reactions Involving Displacement of Nitrogen

Replacement by $-\text{CN}$ ✓

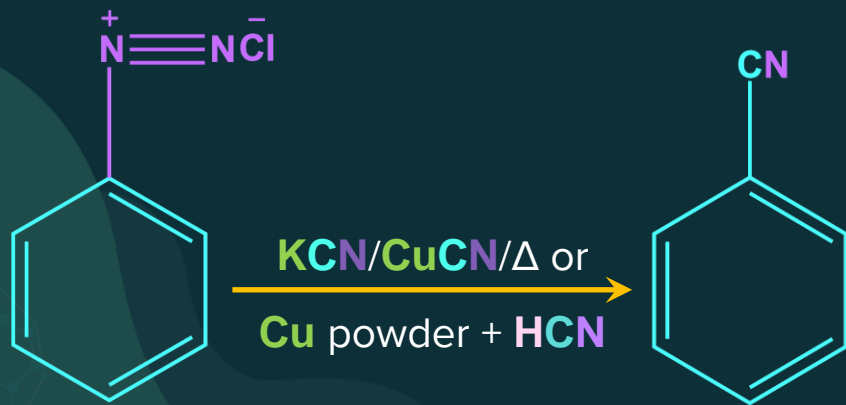
Replacement by $-\text{X}$ ✓

Replacement by $-\text{H}$ ✓

Replacement by $-\text{OH}$ ✓

Replacement by $-\text{NO}_2$ ✓

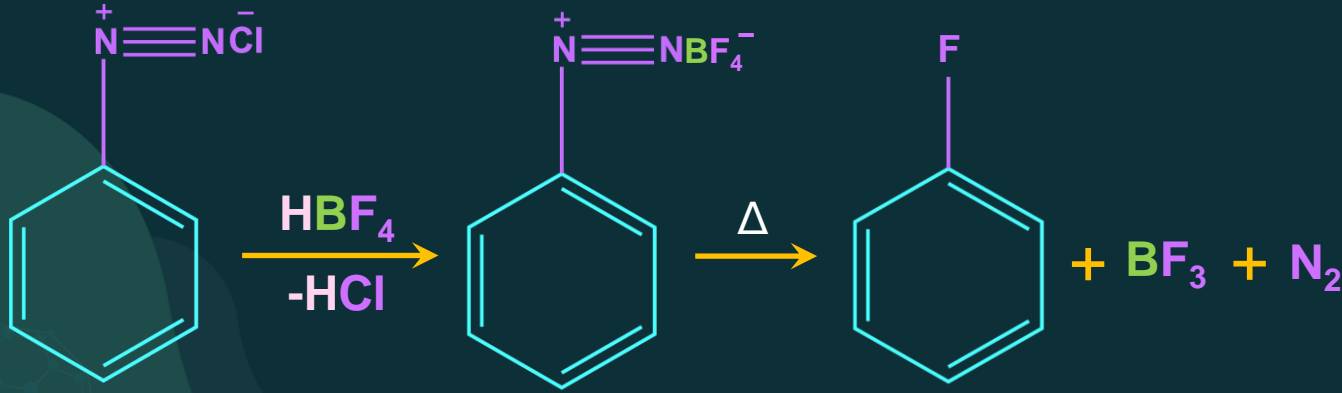
Replacement by -CN





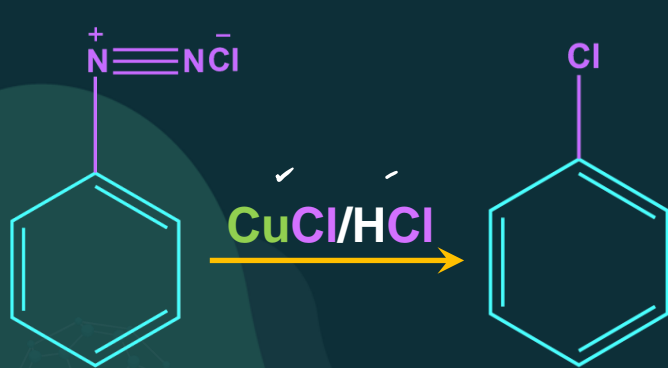
Replacement by -F

Only practical method of preparation of fluorobenzene.



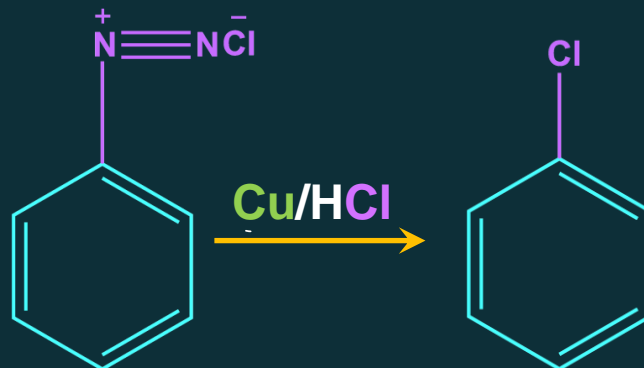
✓
Balz-Schiemann reaction

Replacement by -Cl



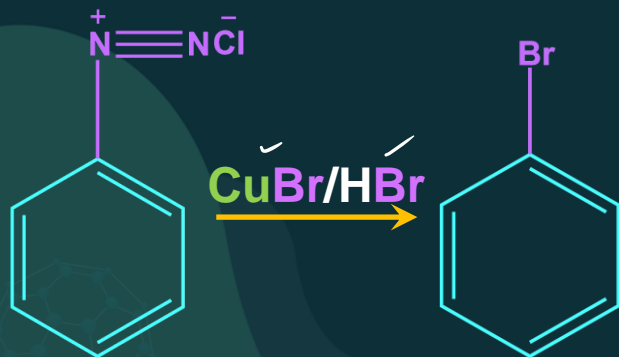
Sandmeyer reaction

Higher yield

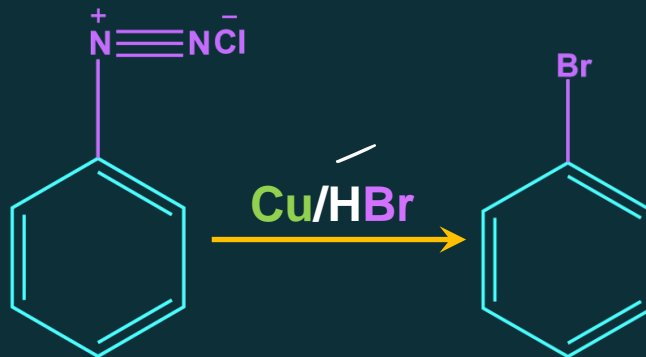


**Gattermann
reaction**

Replacement by -Br



Sandmeyer reaction



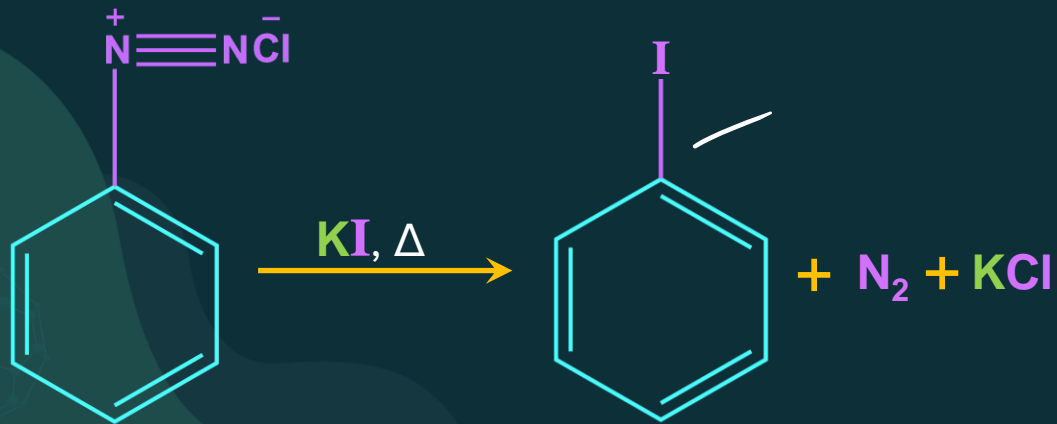
Gattermann reaction

Note



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

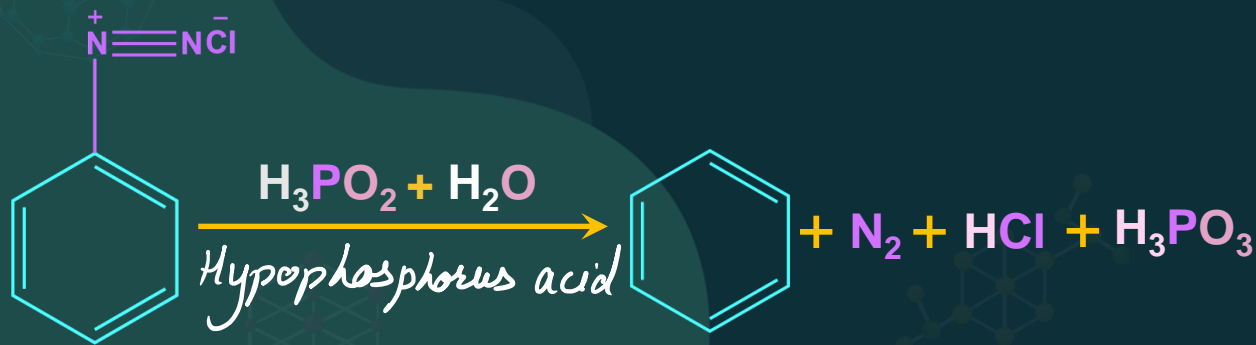
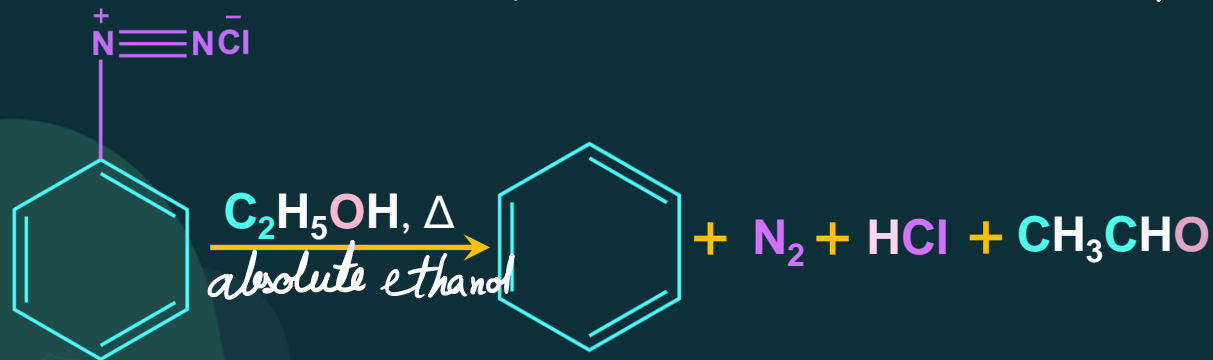
Replacement by –I



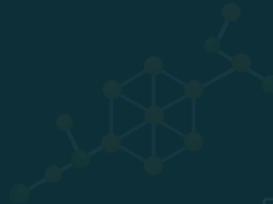
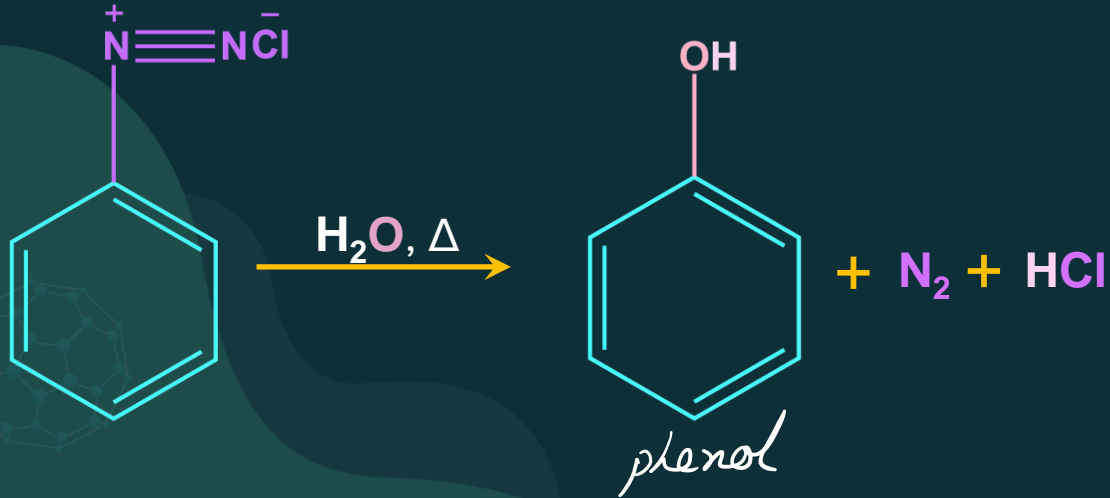


Replacement by -H

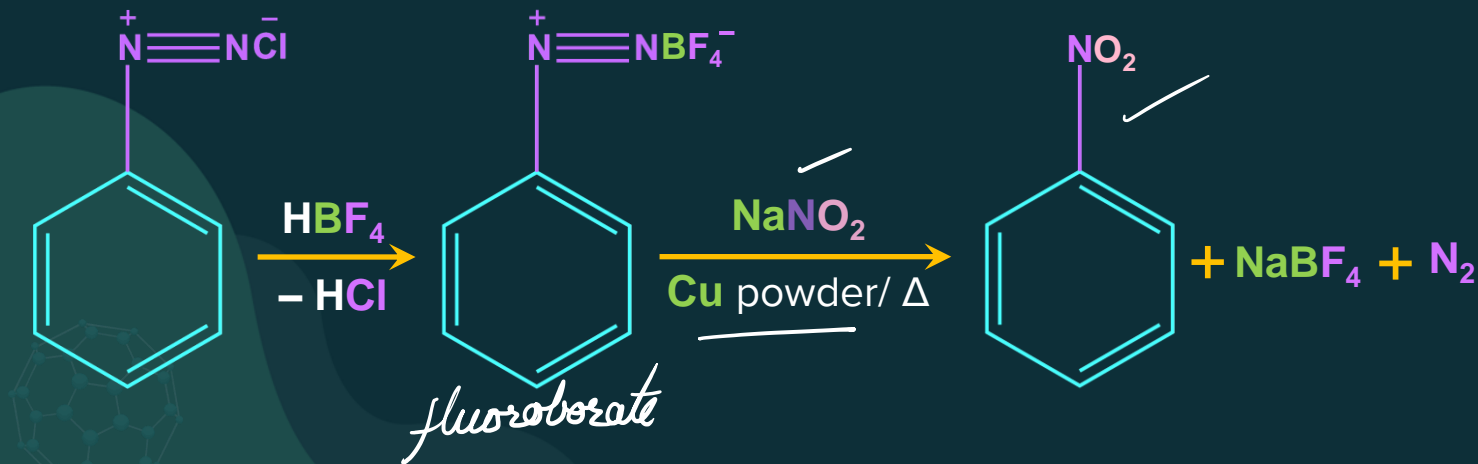
Used for removal of NH_2 group from benzene.



Replacement by -OH

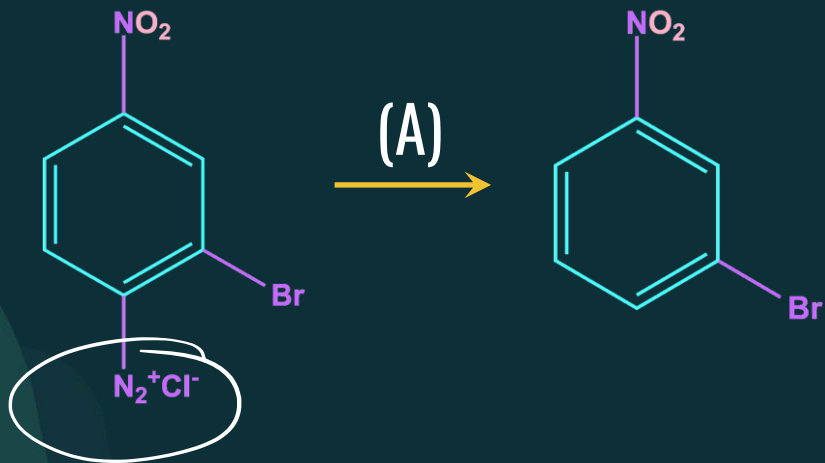


Replacement by $-\text{NO}_2$





In the reaction, (A) is:



a) H_3PO_2 and H_2O

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

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

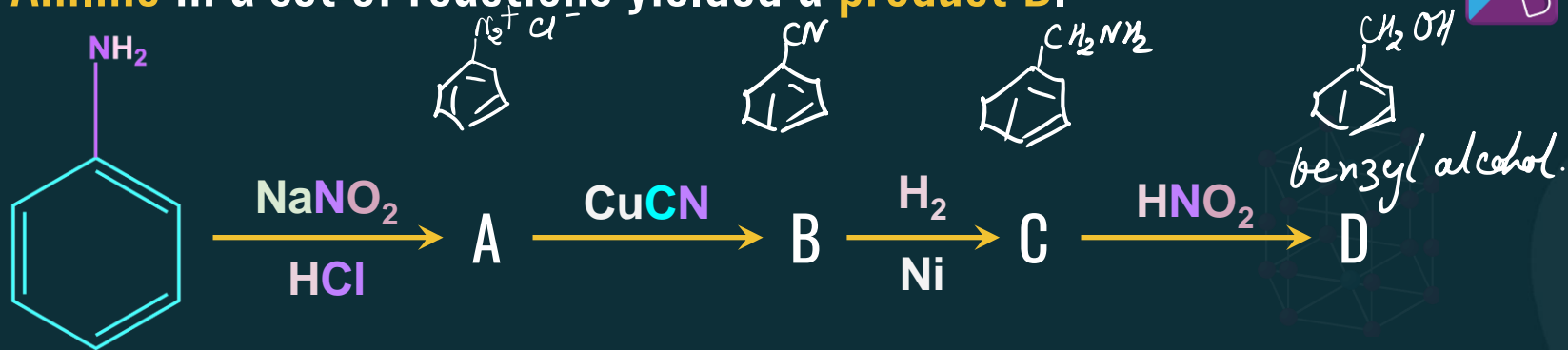
d) Cu_2Cl_2



NEET 2013

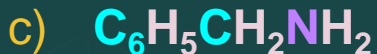
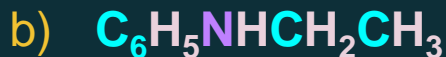


Aniline in a set of reactions yielded a product D.



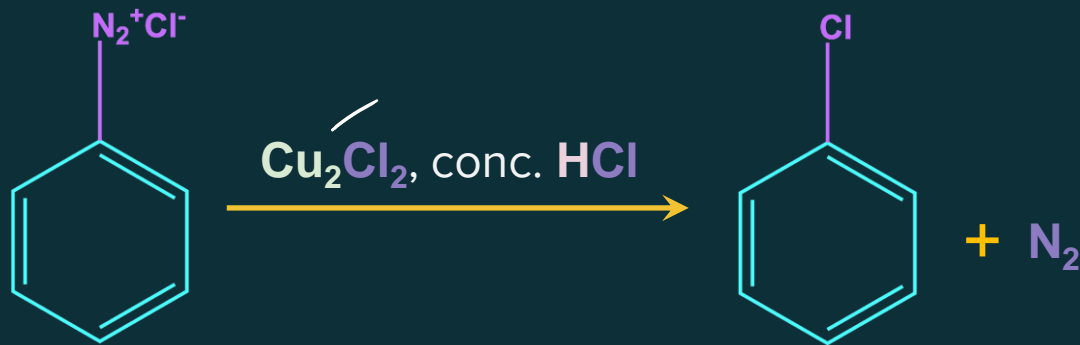
The structure of product D would be:

AIPMT 2005





The following reaction is known as



AIIMS 2000

a) Strecker's reaction

~~b) Sandmeyer's reaction~~

c) Wohl-Ziegler reaction

d) Stephen's reaction



Diazonium ion reacts as electrophile

Coupling Reactions

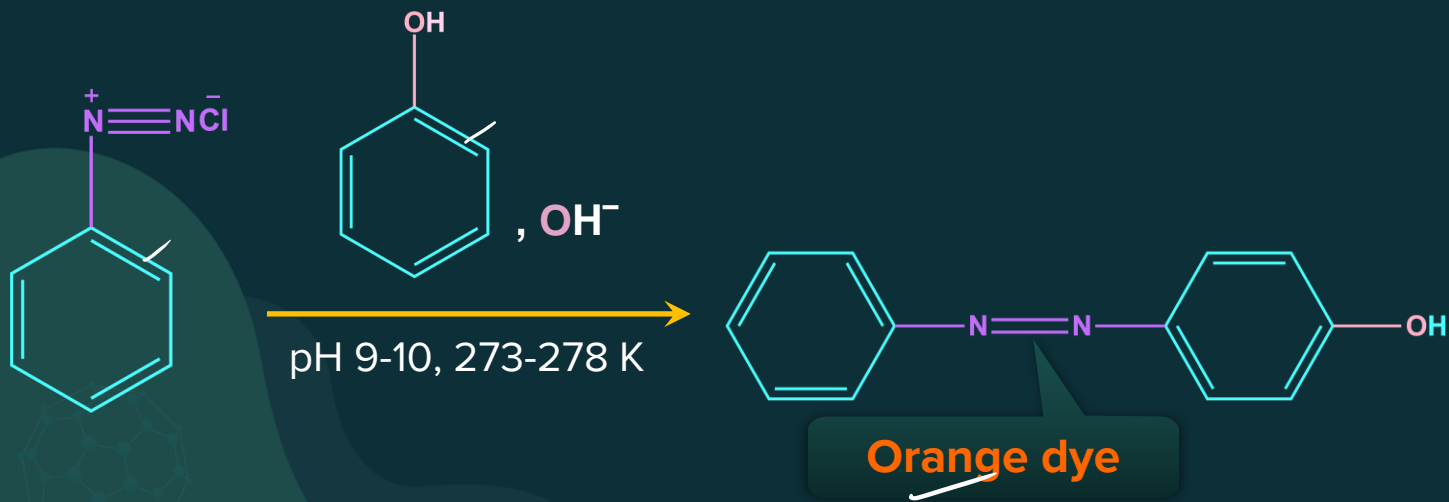
Coupling Reactions



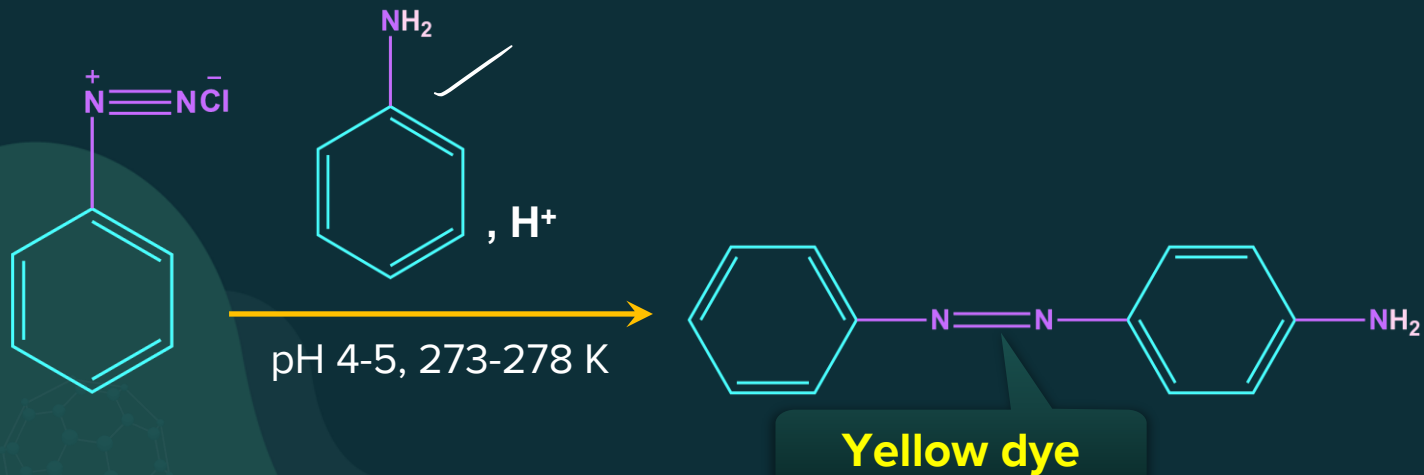
Arene diazonium ions are **weak electrophiles** and they react with **highly reactive** aromatic compounds like phenols and arylamines to yield **azo compounds**.

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

Coupling Reactions



Coupling Reactions



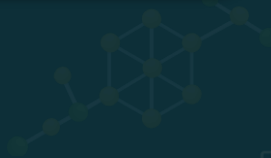
Coupling Reactions



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

chromophore

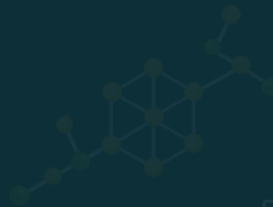
Azo linkage brings the two aromatic rings into **conjugation** and gives an extended system of delocalized π electrons and allows **absorption** of light in the **visible region**.



Coupling Reactions

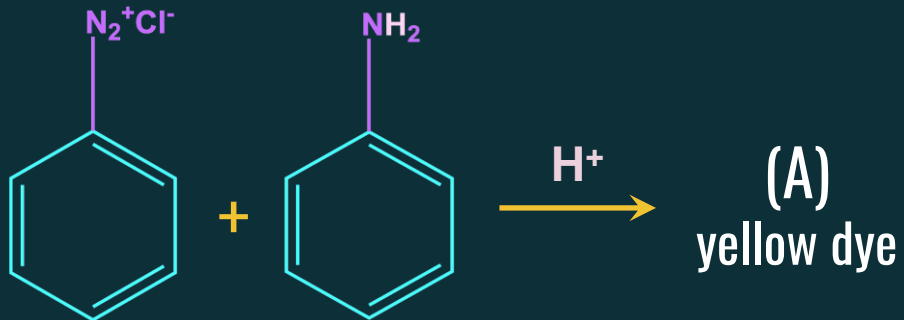


Azo compounds because of their **intense colors** and because they can be synthesized from relatively **inexpensive compounds**, are used extensively as **dyes**. *→ azo dyes*

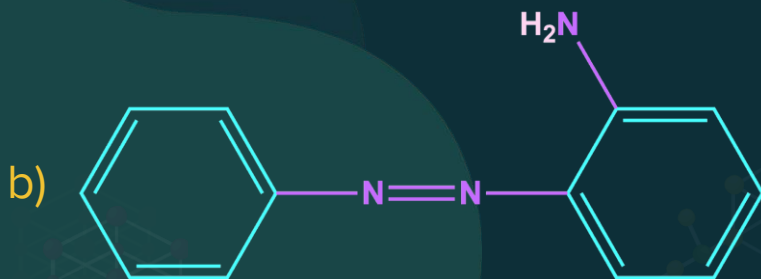
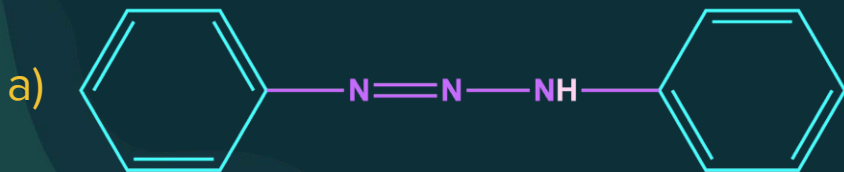




In the following reaction, the **product (A)** is:

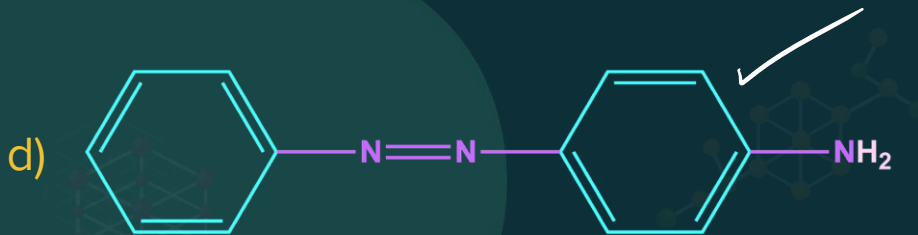
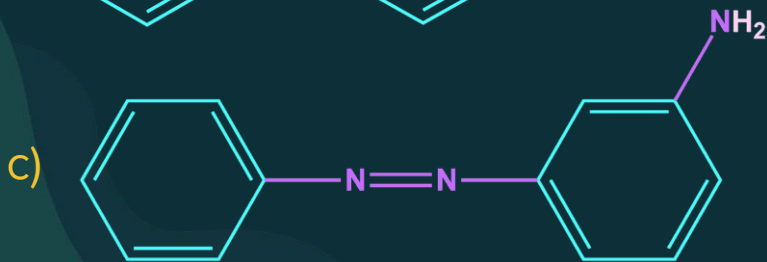
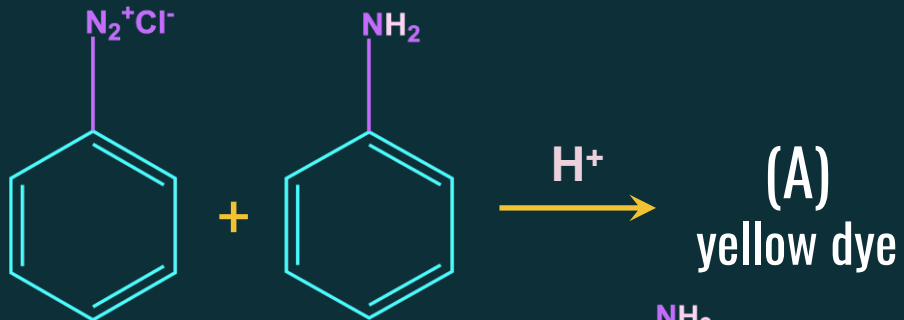


NEET 2014





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



NEET 2014



Importance of Diazonium Salts

Importance of Diazonium Salt



1

Diazonium salts are good intermediates for the introduction of $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{CN}$, $-\text{OH}$, $-\text{NO}_2$ 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

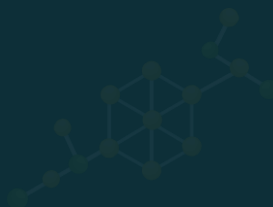
a) Aniline

b) Phenol

c) Anisole

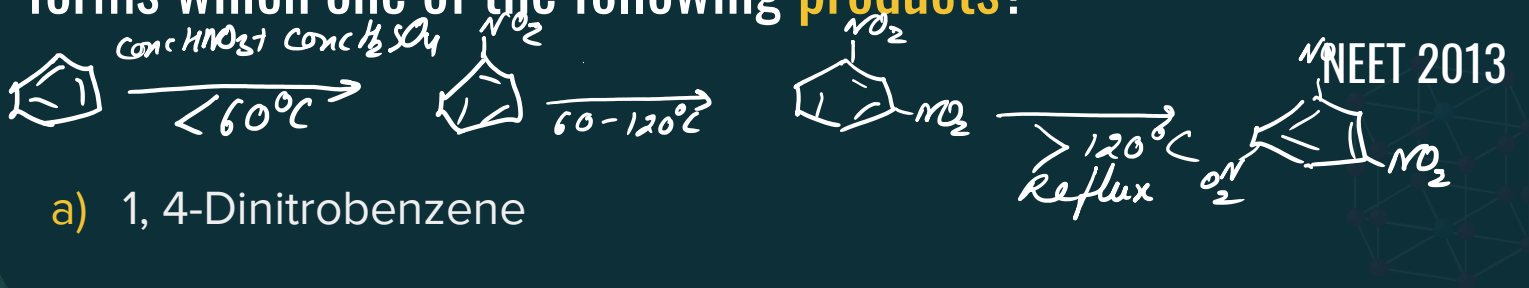
~~d) Nitrobenzene~~

*↑
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

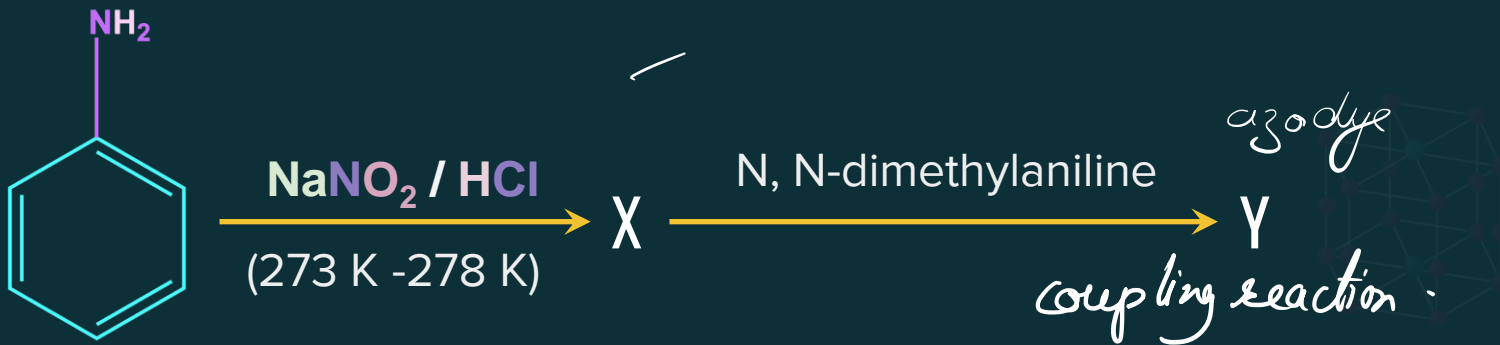
☒ b) Diazonium salt

c) Ammonium salt

d) Cuprammonium salt



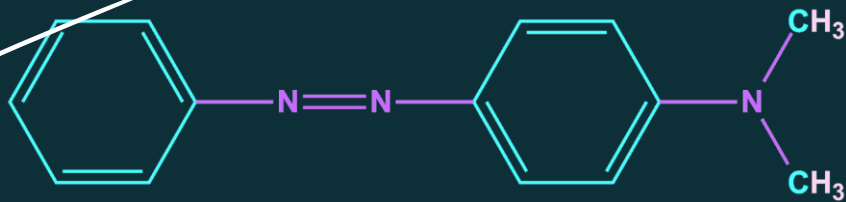
Aniline in a set of following reactions yielded a **product Y**.



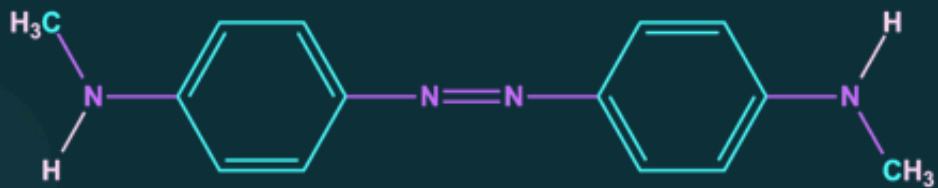
The **structure** of product Y would be:

AIPMT 2010

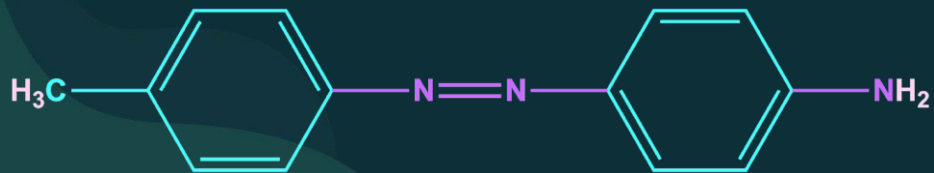
a)



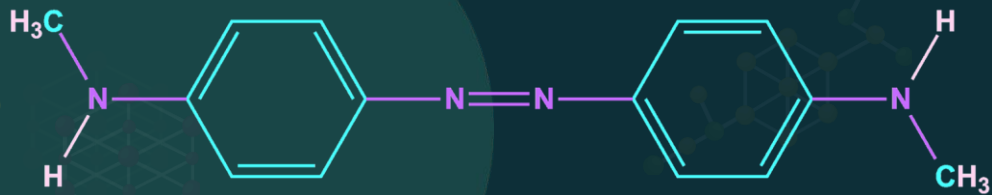
b)



c)

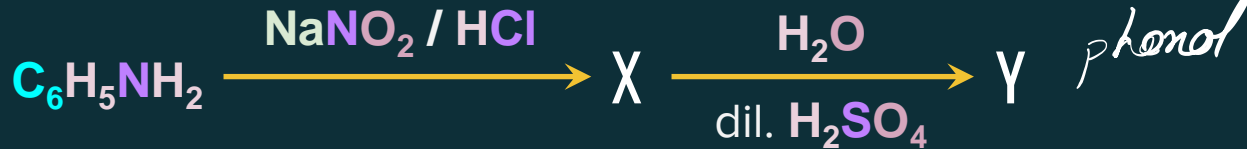


d)

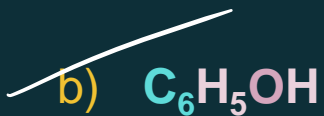
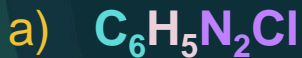




Identify **Y** in the reaction:

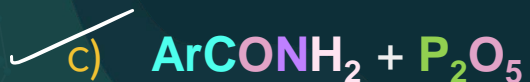
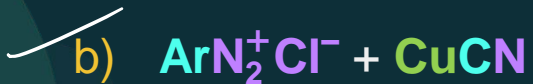


AIIMS 1998





Aromatic nitriles (**ArCN**) are **not prepared** by reaction:



d) None of these



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