Amines

Part C

B. Pharm. Semester-1
Course Code: 0510210; Session: 2022-2023

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Learning Outcomes

At the end of this lesson, students will be able to describe

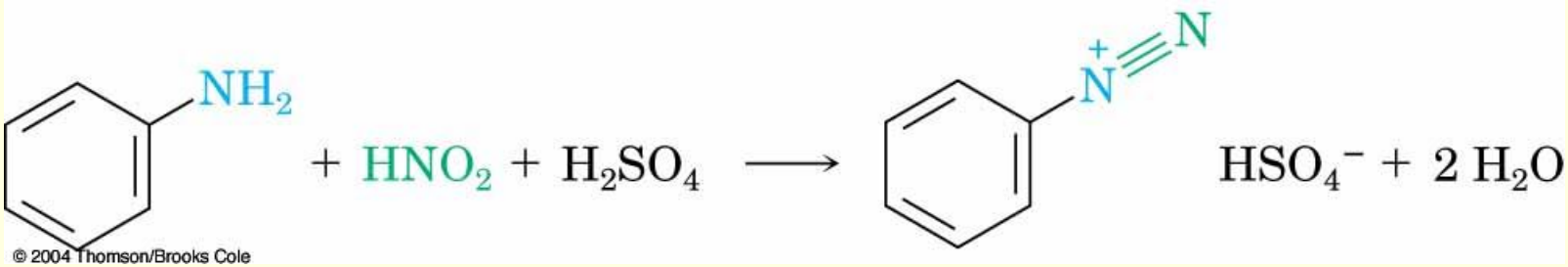
- **Aryldiazonium salts: Preparations and Reactions**

Objective

The objective of this course is to give to the students of pharmacy the basic knowledge about the organic chemistry.

Aryldiazonium Salts

- Primary arylamines react with nitrous acid, HNO_2, to yield stable arenediazonium salts, $Ar\text{-}N^+{\equiv}N\text{-}X^-$, a process called a diazotization reaction.
- Alkylamines also react with nitrous acid, but the corresponding alkanediazonium products.



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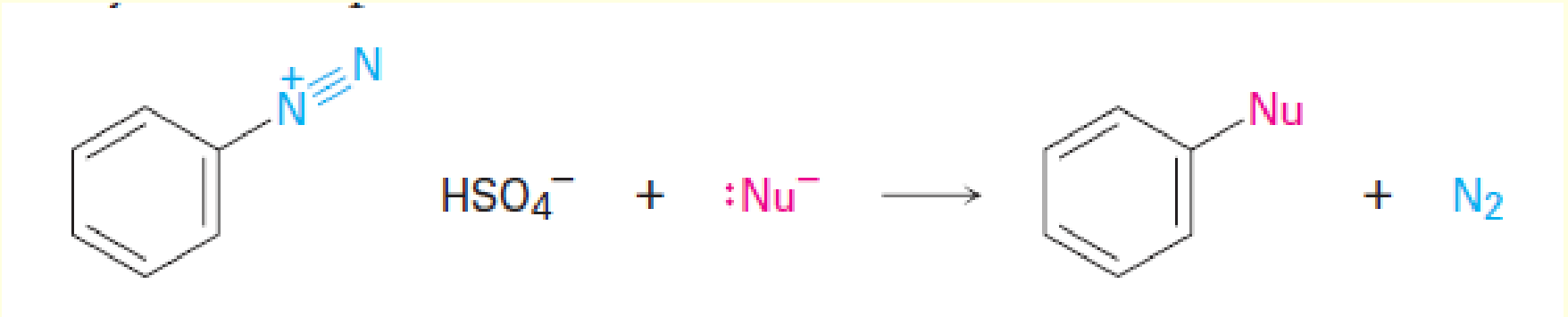


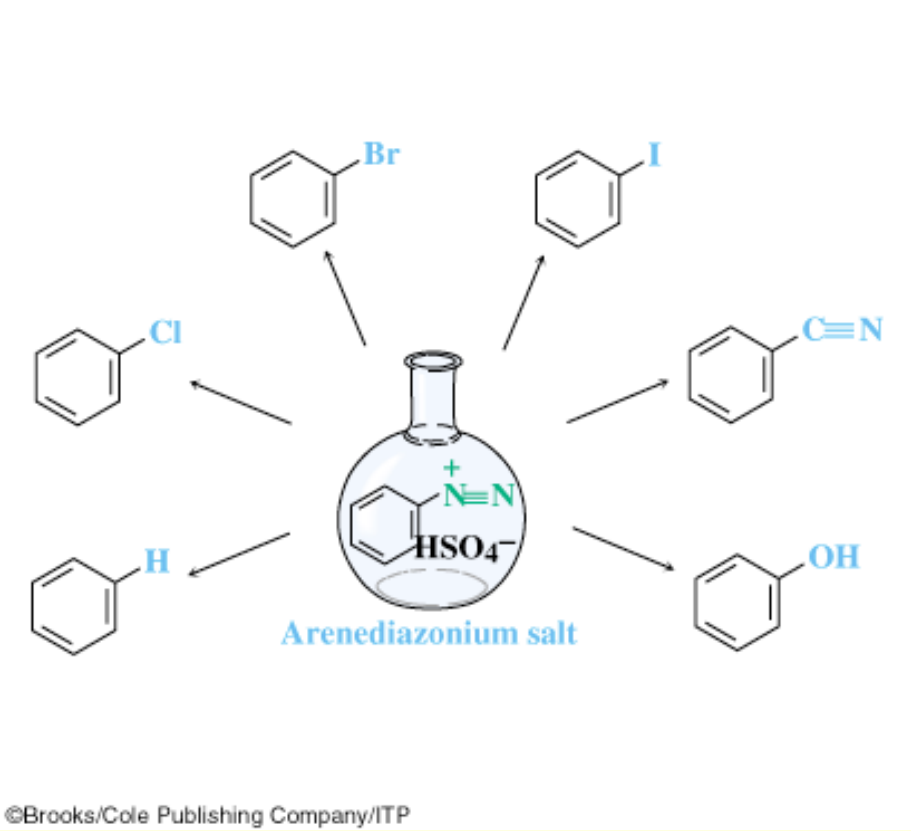
Aryldiazonium Salts

- Many different nucleophiles—halide, hydride, cyanide, and hydroxide among others—react with arene diazonium salts, yielding many different kinds of substituted benzenes.

- Like:-
  (1) nitration
  (2) reduction
  (3) diazotization
  (4) nucleophilic substitution

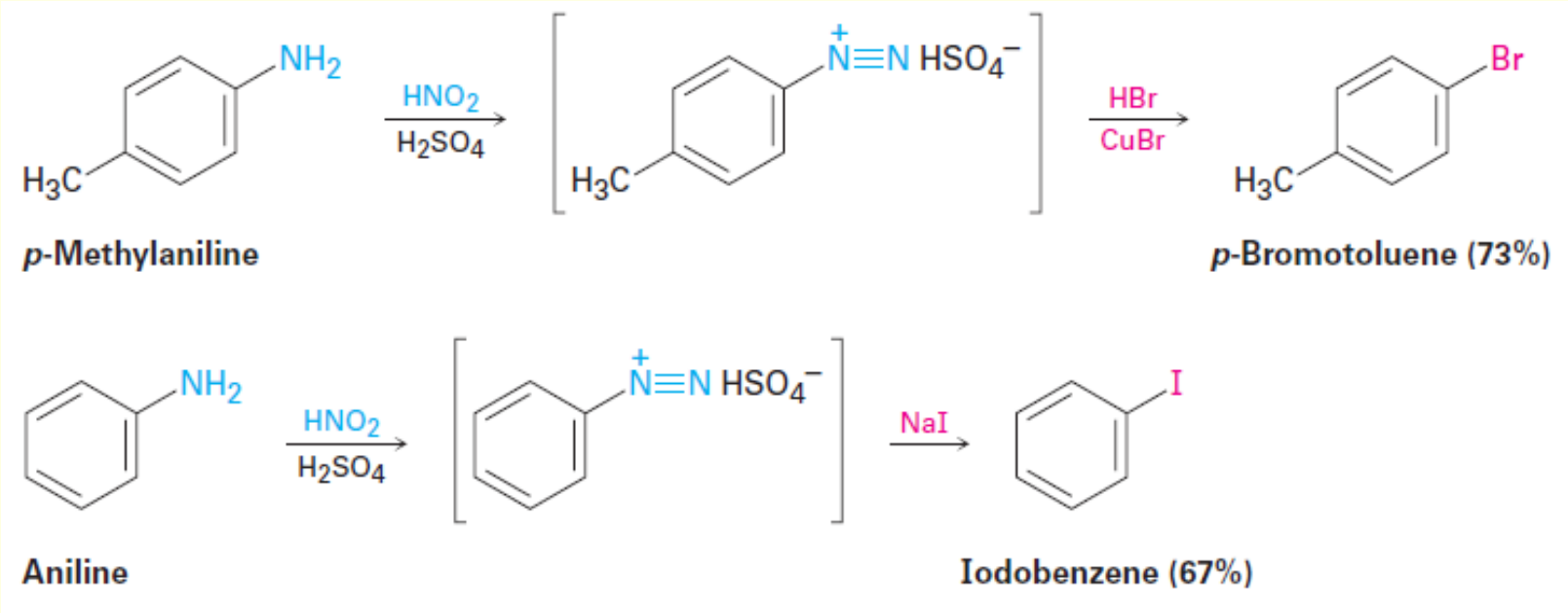
Aryldiazonium Salts: Reactions

Diazonium salts act as intermediate compounds for preparing different other compounds as mentioned below:-



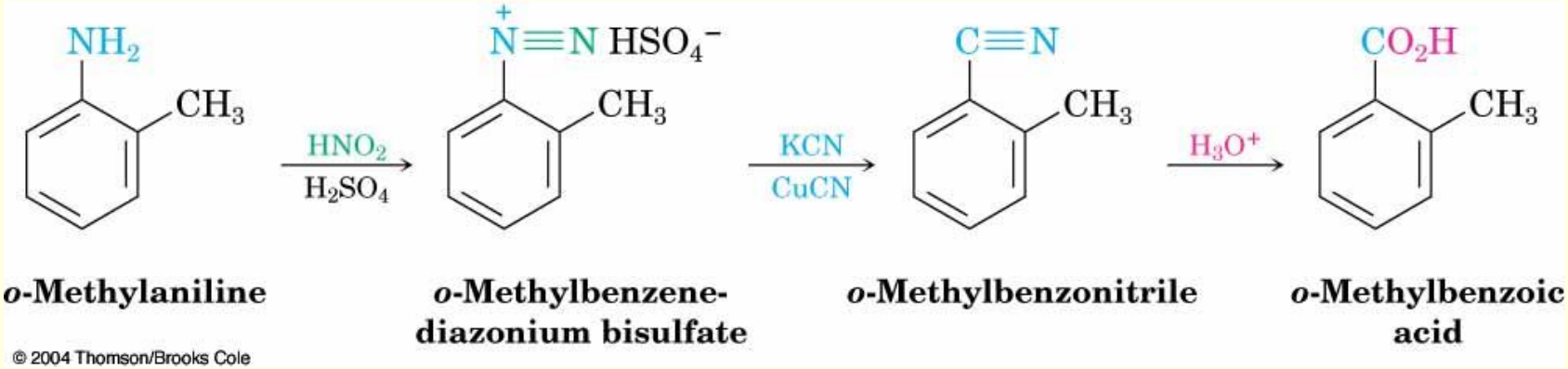
The Sandmeyer Reaction
(Preparation of Aryl Halides

- Aryl chlorides and bromides are prepared by reaction of an arenediazonium salt with the corresponding copper(I) halide, CuX, a process called the Sandmeyer reaction.
- Aryl iodides can be prepared by direct reaction with NaI without using a copper(I) salt.



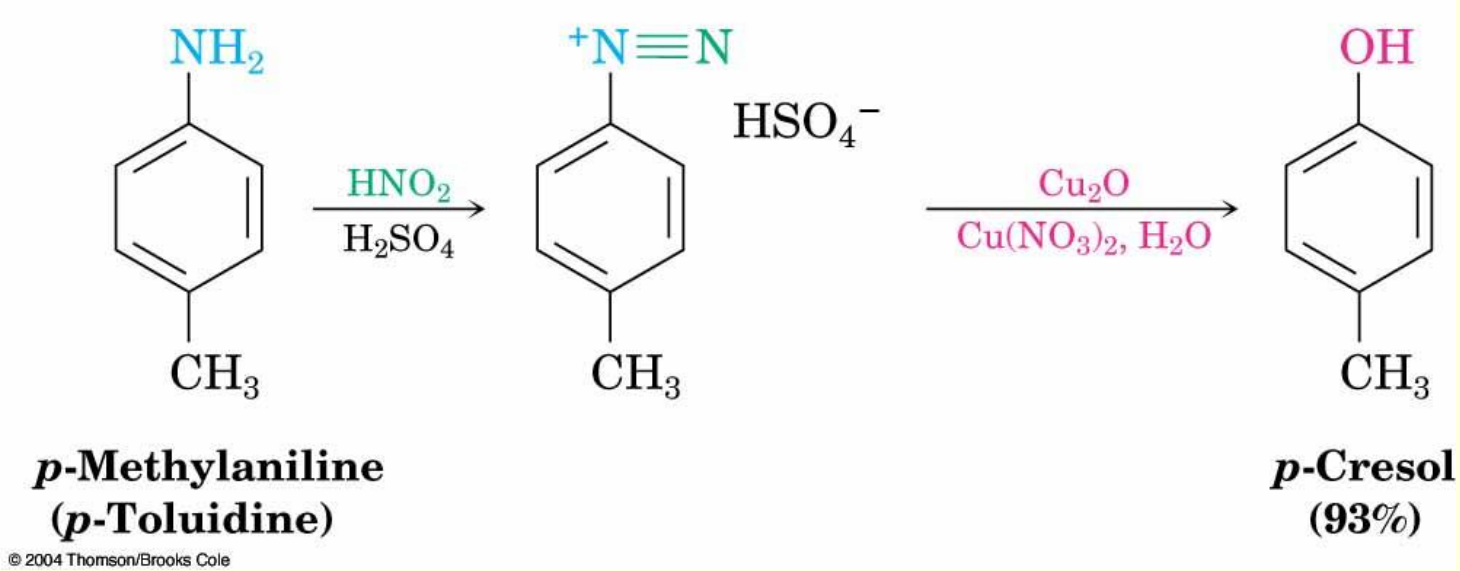
Preparation of Aryl Nitriles and Carboxylic Acids

Treatment of an arenediazonium salt with CuCN yields the nitrile, ArCN, which can then be further converted into other functional groups such as carboxyl group.



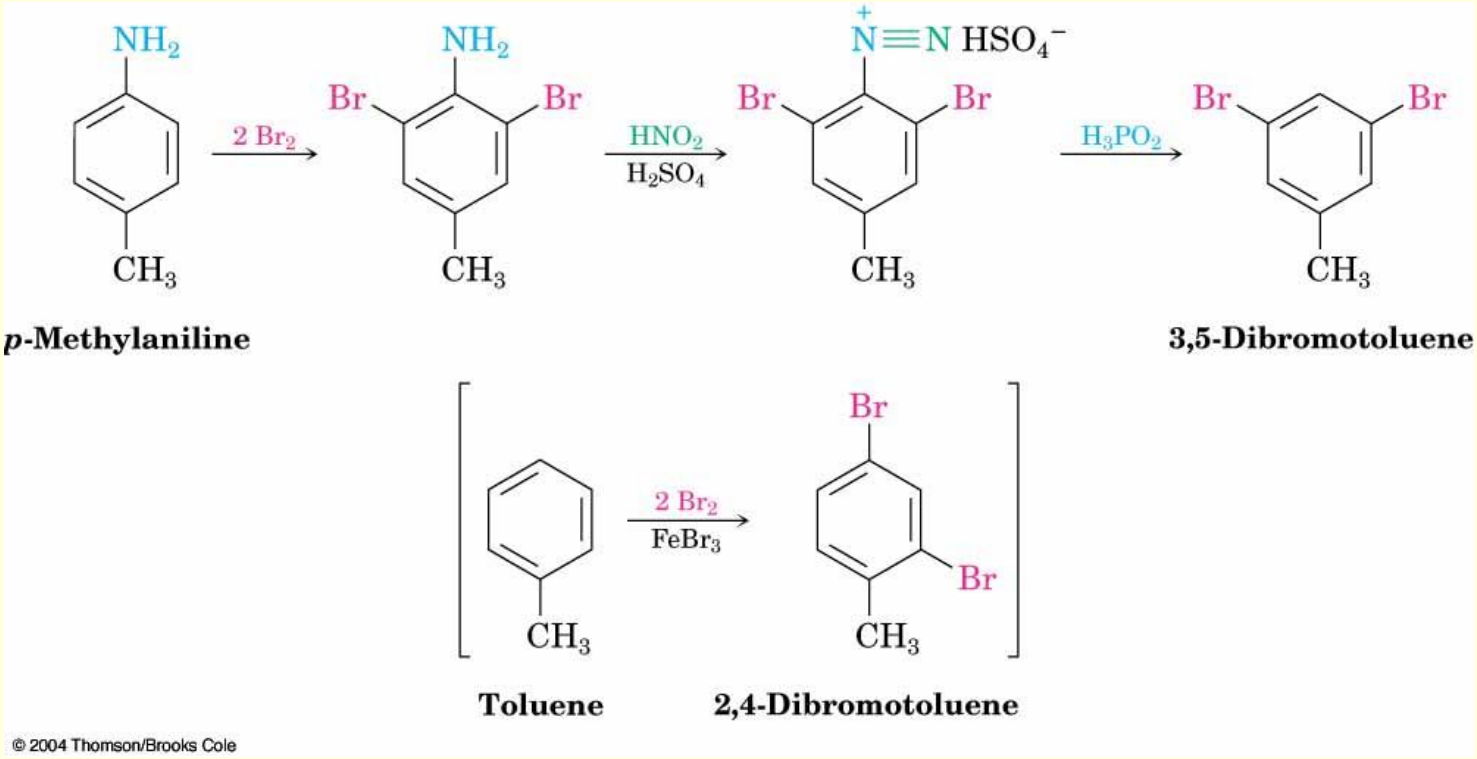
Preparation of Phenol

A phenol is prepared by reaction of the arenediazonium salt with copper(I) oxide in an aqueous solution of copper(II) nitrate, a reaction that is especially useful because few other general methods exist for introducing an -OH group onto an aromatic ring.



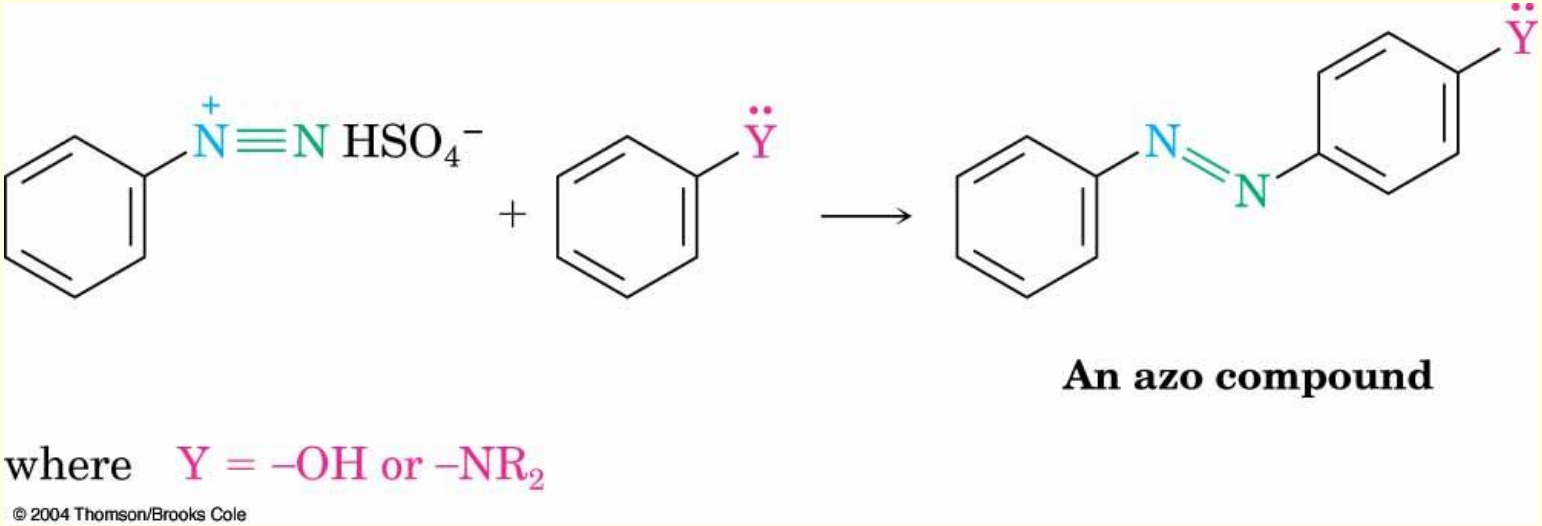
Reduction to a Hydrocarbon

Reduction of a diazonium salt to give an arene occurs on treatment with hypophosphorous acid, H_3PO_2



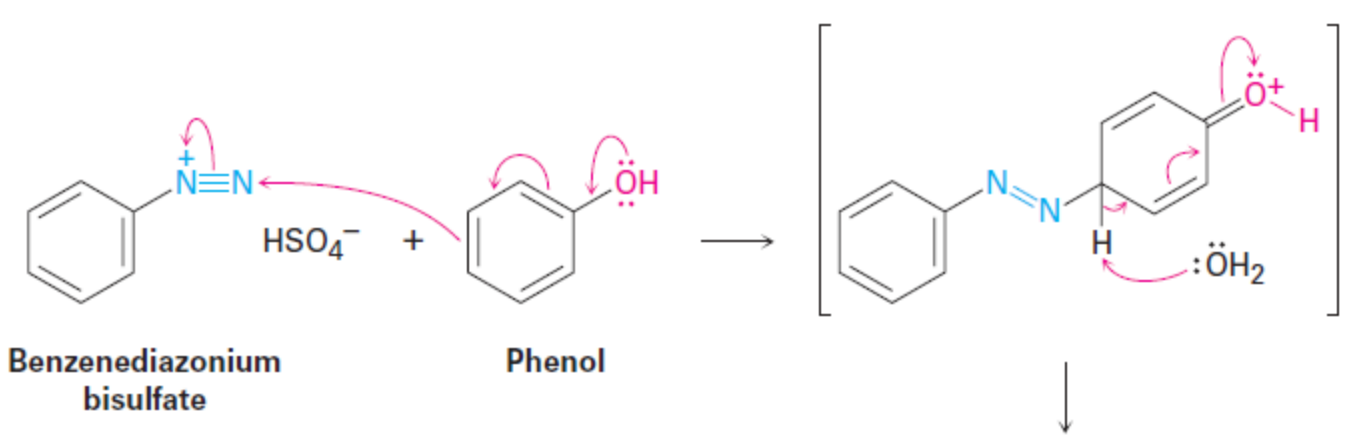
Diazonium Coupling Reactions

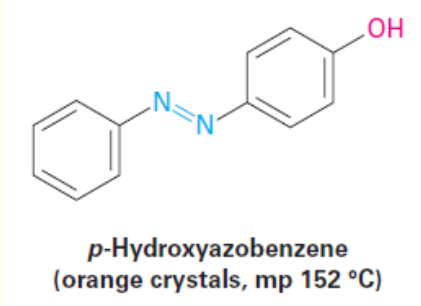
Arenediazonium salts undergo a coupling reaction with activated aromatic rings such as phenols and arylamines to yield brightly colored azo compounds, Ar-N=N-Ar'.



Diazonium Coupling Reactions

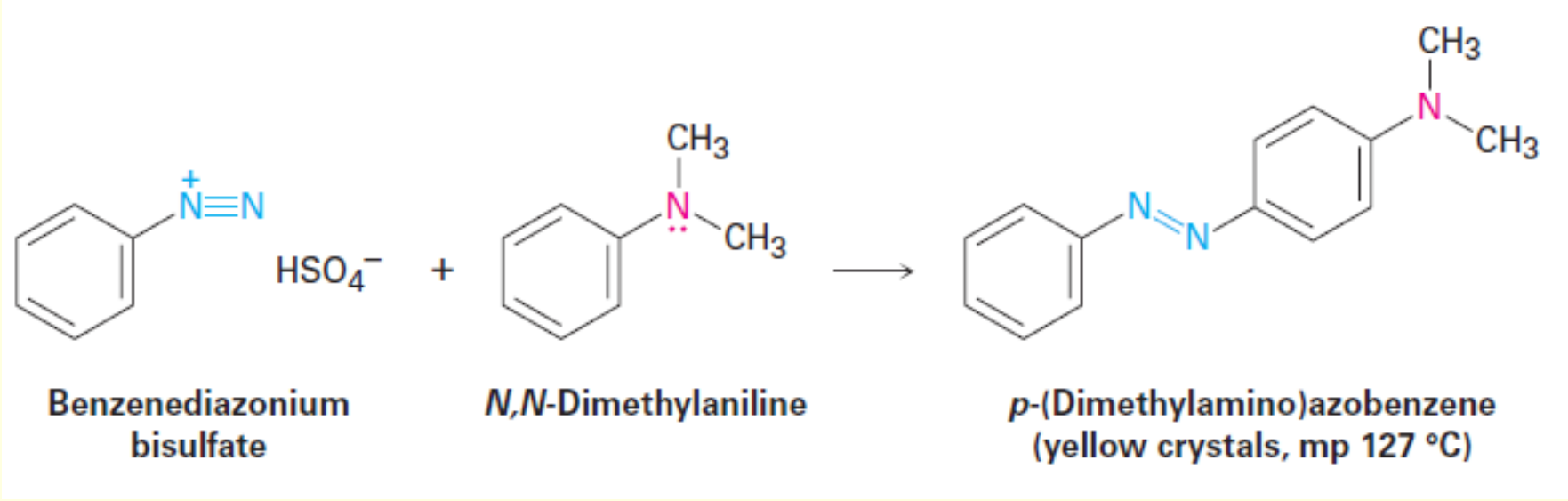
Diazonium coupling reactions are typical electrophilic aromatic substitutions in which the positively charged diazonium ion is the electrophile that reacts with the electron-rich ring of a phenol or arylamine. Reaction usually occurs at the **para position**.





Diazonium Coupling Reactions

Azo-coupled products are widely used as dyes for textiles because their extended conjugated π-electron system causes them to absorb in the visible region of the electromagnetic spectrum.



Benzenediazonium bisulfate + ***N,N*-Dimethylaniline** → ***p*-(Dimethylamino)azobenzene (yellow crystals, mp 127 °C)**

REFERENCES

Textbooks:

1. **Organic Chemistry, 9th Edition, 2015, Author: John E. McMurry, Publisher: Cengage Learning, ISBN: 978-1305080485.**
2. **Organic Chemistry, 7th Edition, 2010, Authors: Saibal Kanti Bhattacharjee, Robert Thornton Morrison, Robert Neilson Boyd, Publisher: Pearson India, ISBN: 978-0199270293.**
3. **Textbook of Organic Chemistry, 22nd Edition, 2022, Authors: Arun Bahl & B S Bahl, Publisher: S Chand, ISBN: 978-9352531967.**

Supplementary book:

Organic Chemistry, 11th Edition, 2015, Authors: Francis Carey Robert Giuliano Neil Allison Susan Bane, Publisher: McGraw Hill, ISBN: 978-1260148923.