

UNIT 9 • AMINES

JEE WEIGHTAGE: HIGH

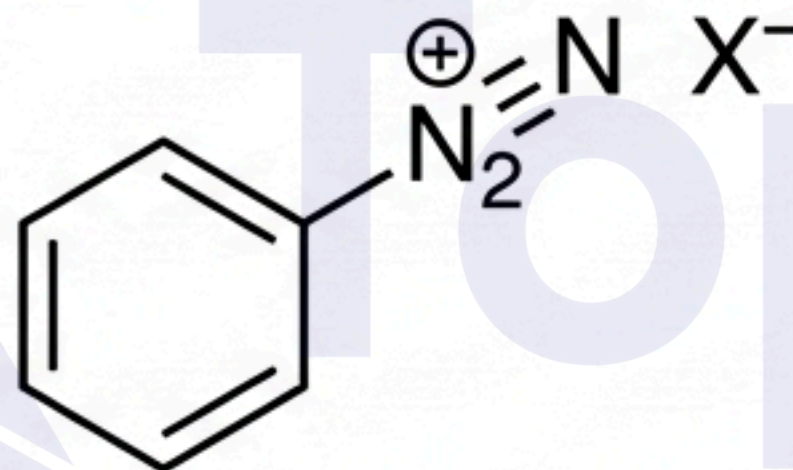
9.9 Chemical Reactions of Diazonium Salts

From one central intermediate to a universe of aromatic compounds.

The Diazonium Synthetic Hub

Family 1: Displacement of Nitrogen (N₂ escapes)

Family 2:
Retention of Diazo
Group (N₂ retained)



The Ultimate Intermediate

Sandmeyer

Gattermann

Iodide (I)

Fluoride (F)

Hydrogen (H)

Hydroxyl (OH)

Nitro (NO₂)

Coupling (Azo)

Family 1: Displacement

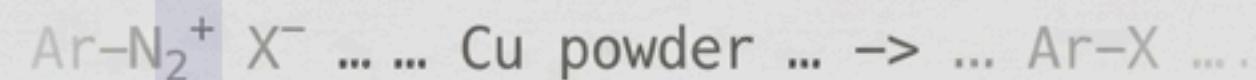
Replacement by Halide/Cyanide

Sandmeyer Reaction (Cu(I) catalyzed)



Note: Sandmeyer yield is better.

Gattermann Reaction (Cu powder)



Note: Sandmeyer yield is better.



Sandmeyer

Gattermann

Iodide (I)

Fluoride (F)

Hydrogen (H)

Hydroxyl (OH)

Nitro (NO₂)

Coupling (Azo)

Family 1: Displacement

Replacement by Halide (Alternative)

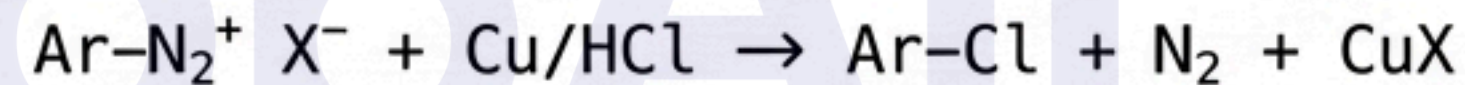
Sandmeyer Reaction
(Cu(I) catalyzed)



Note: Sandmeyer yield is better.

Gattermann Reaction

(Cu powder + HX)



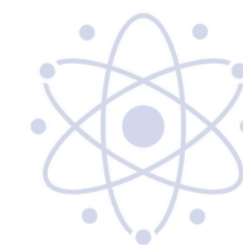
Uses **Copper powder** instead of Cu(I) ion.
Introduced by Gattermann for Cl and Br.

Note: Sandmeyer yield is better.



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$$E=mc^2$$



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Sandmeyer

Gattermann

Iodide (I)

Fluoride (F)

Hydrogen (H)

Hydroxyl (OH)

Nitro (NO₂)

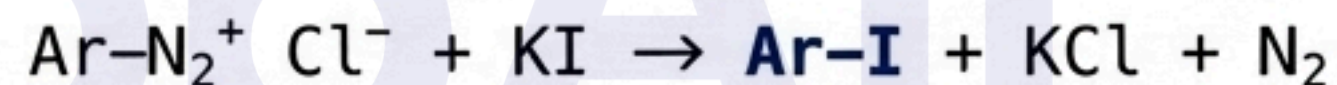
Coupling (Azo)

Family 1: Displacement

Direct Iodination

Iodine cannot easily be introduced into the benzene ring directly.

However, treating the diazonium salt solution directly with Potassium Iodide (KI) **easily** forms Iodobenzene.



No Copper Catalyst Required!

Sandmeyer

Gattermann

Iodide (I)

Fluoride (F)

Hydrogen (H)

Hydroxyl (OH)

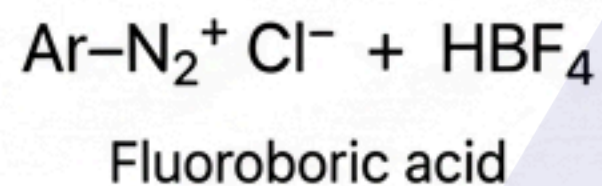
Nitro (NO₂)

Coupling (Azo)

Family 1: Displacement

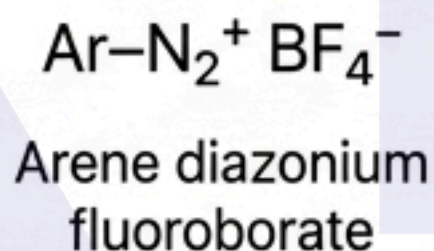
Fluorination via Fluoroborate

Step 1



Precipitation

Step 2



Water insoluble,
stable at room temp

Heat (Δ)

Step 3

**Aryl Fluoride**

Aryl fluorides cannot be prepared by direct halogenation. This 2-step thermal decomposition is the primary synthetic route.

Family 1: Displacement

Reduction to Arenes (Deamination)

Hypophosphorous Acid (Phosphinic Acid)



Note: H₃PO₂ oxidizes to Phosphorous acid (H₃PO₃).

Ethanol Reduction



Note: Ethanol oxidizes to Ethanal (CH₃CHO).

Sandmeyer

Gattermann

Iodide (I)

Fluoride (F)

[Hydrogen (H)]

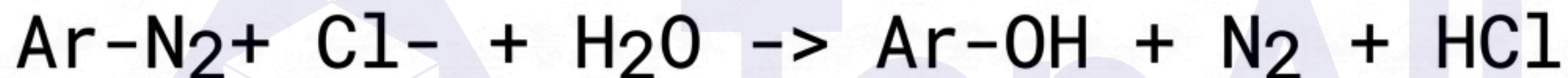
[Hydroxyl (OH)]

Nitro (NO₂)

Coupling (Azo)

Family 1: Displacement

Hydrolysis to Phenol

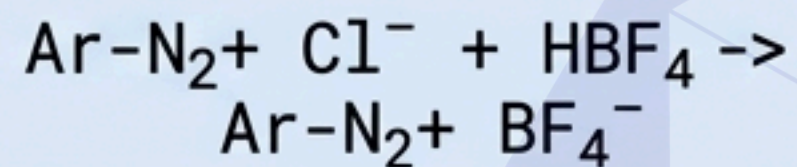


Temperature is Key (283 K)

Diazonium salts are stable in cold aqueous solutions (273–278 K). Allowing the temperature to gently rise up to **283 K** forces hydrolysis, replacing the diazonium group with a hydroxyl group to form Phenol.

Family 1: Displacement

Nitration via Fluoroborate



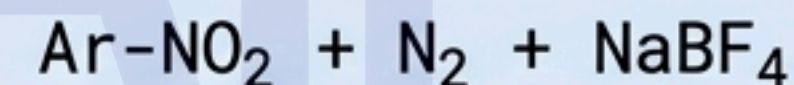
(Diazonium fluoroborate)



Aqueous NaNO₂
Copper (Cu) catalyst
Heat (Δ)



Nitrobenzene



Requires the stable fluoroborate intermediate rather than directly heating the chloride salt.

Sandmeyer

Gattermann

Iodide (I)

Fluoride (F)

[Hydrogen (H)]

Hydroxyl (OH)

Nitro (NO₂)

Coupling (Azo)

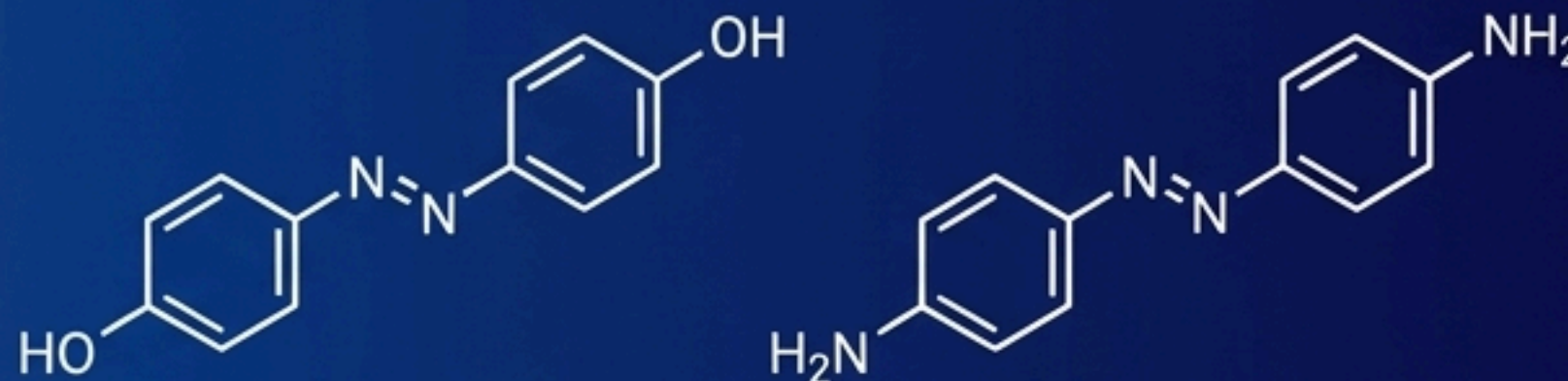
Family 2: Retention

Retention: Azo Dye Formation

The azo products possess an **extended conjugate system** where both aromatic rings are joined through the -N=N- bond. This extended conjugation makes them highly colored.

Reaction 1:

$\text{Ar-N}_2^+ + \text{Phenol} \rightarrow p\text{-Hydroxyazobenzene}$
(Electrophilic substitution at para position)



Key Takeaways: Diazonium Reactions

- **Versatility:** Diazonium salts act as critical intermediates to synthesize compounds otherwise impossible to make directly (e.g., Aryl fluorides, cyanides, iodides).
- **Displacement vs. Retention:** Reactions fall into two main categories based on whether Nitrogen gas (N_2) escapes or the $-N=N-$ bond is retained.
- **Catalysts Matter:** Sandmeyer uses $Cu(I)$ for better yields; Gattermann uses Cu powder.
- **Coupling:** Electrophilic substitution at the *para* position of phenol or aniline yields brightly colored Azo dyes.

Try 9.10 Importance of Diazonium Salts next →



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