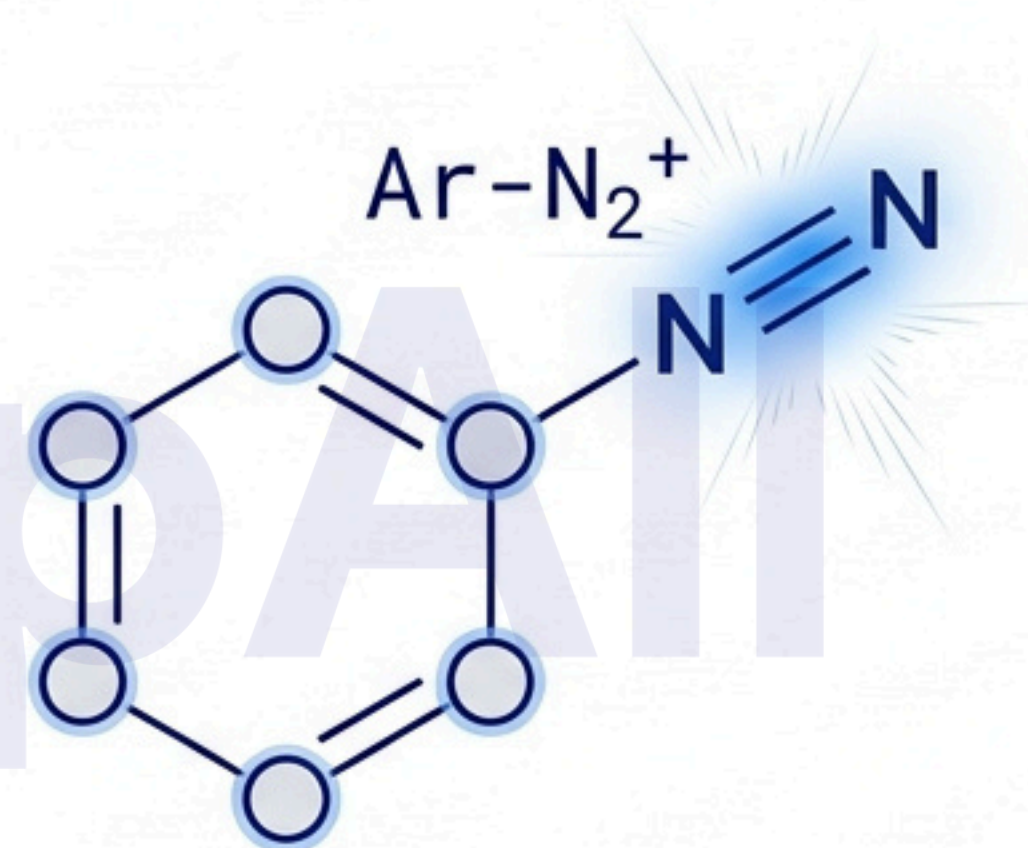


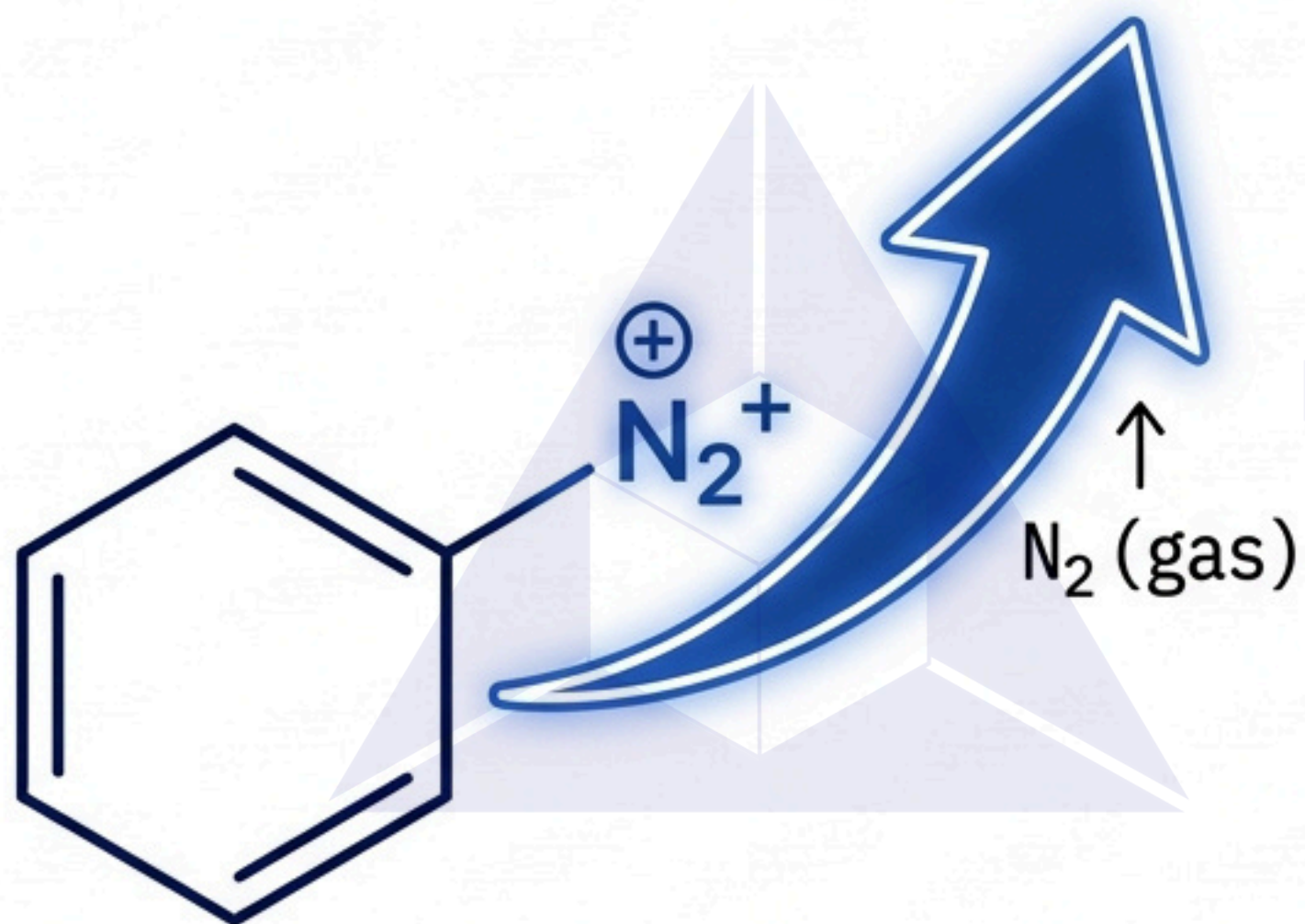
NEET REVISION • CHAPTER 9: AMINES

9.9.1 Displacement Reactions of Diazonium Salts

The ultimate master key intermediate
in aromatic synthesis.



Why the Diazonium Group is Highly Reactive



Excellent Leaving Group

The diazonium group is highly prone to substitution by nucleophiles (Cl^- , Br^- , I^- , CN^- , OH^-).

Thermodynamic Driving Force

Quantitative Evolution of N_2 gas

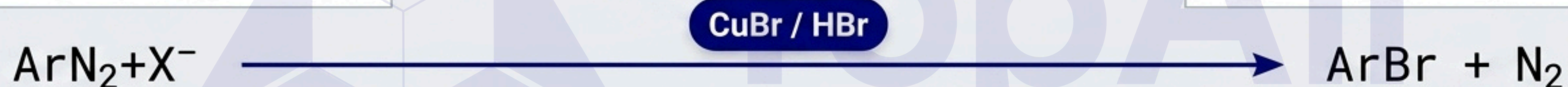
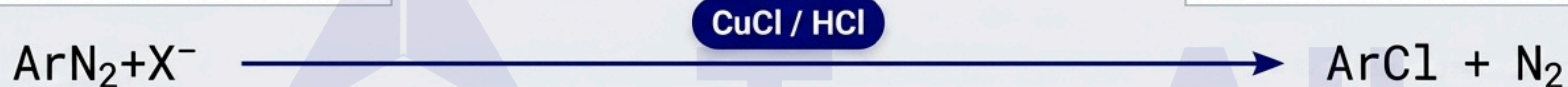
Because nitrogen gas is highly stable and escapes the reaction mixture, it heavily drives the equilibrium forward.

Displacement reactions substitute the nitrogen with a new functional group, fundamentally transforming the aromatic ring.

NAME REACTION

Sandmeyer Reaction

Introduction of Cl, Br, or CN nucleophiles using a Copper(I) ion catalyst.



Requires Cu(I) salts. Provides excellent yields for aromatic halides and cyanides.



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Gattermann Reaction

Alternative halogen introduction using copper powder instead of Copper(I) salts.



Sandmeyer vs. Gattermann

	Sandmeyer	Gattermann
Catalyst	Cu(I) salt (CuCl/CuBr)	Cu powder
Yield	Higher Yield	Lower Yield

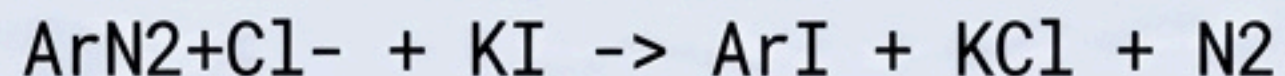
Both achieve the same aromatic substitution, but Sandmeyer is practically preferred due to better product yield.

Introduction of Iodide and Fluoride

No Cu required

Direct Potassium Iodide

Iodine is introduced without any copper catalyst. Simply treat the salt solution with KI.

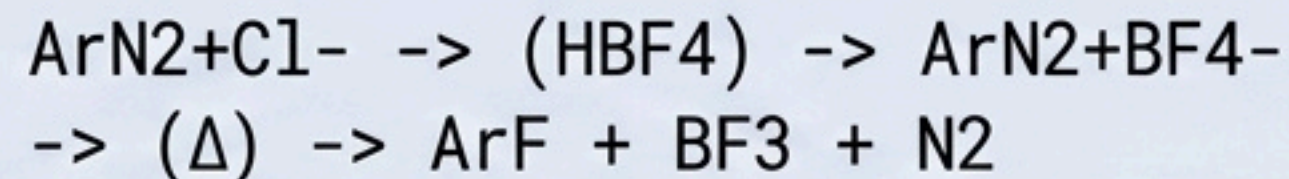


No Cu required

Fluoroborate Route

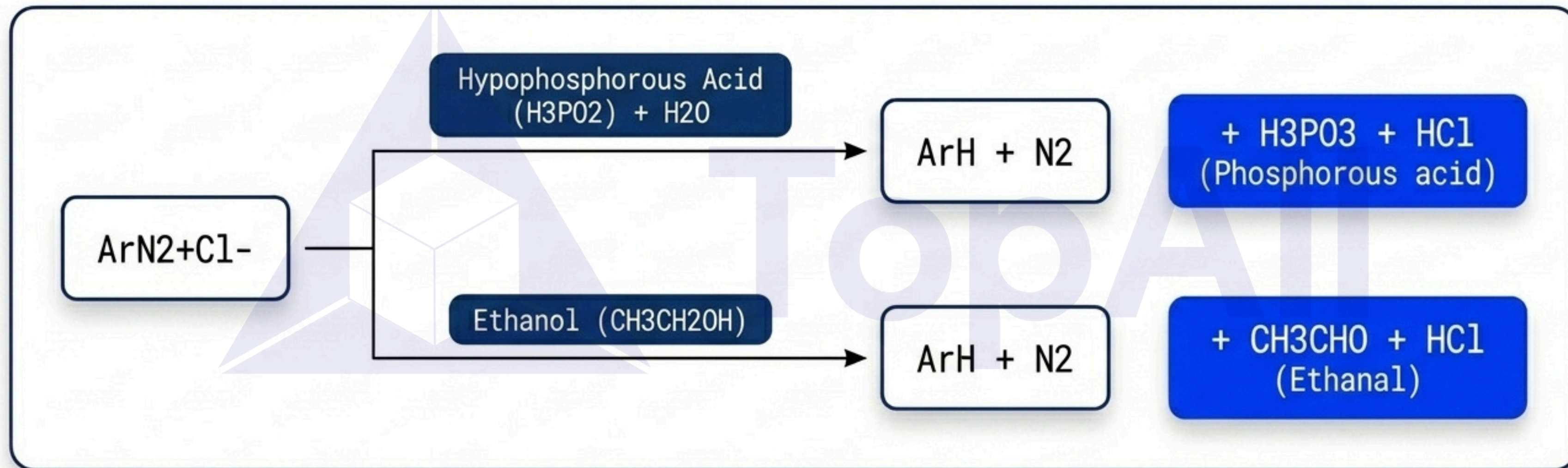
Fluorine requires a two-step precipitation and heating process.

1. Precipitate arene diazonium fluoroborate using fluoroboric acid (HBF_4).
2. Heat to decompose.



Replacement by Hydrogen (Mild Reduction)

Mild reducing agents convert diazonium salts back to the base arene (benzene).

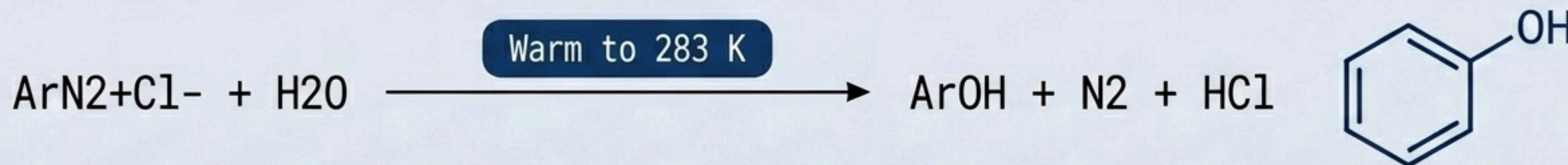


The reducing agents themselves get oxidized to phosphorous acid and ethanal, respectively.

Replacement by Hydroxyl Group (-OH)



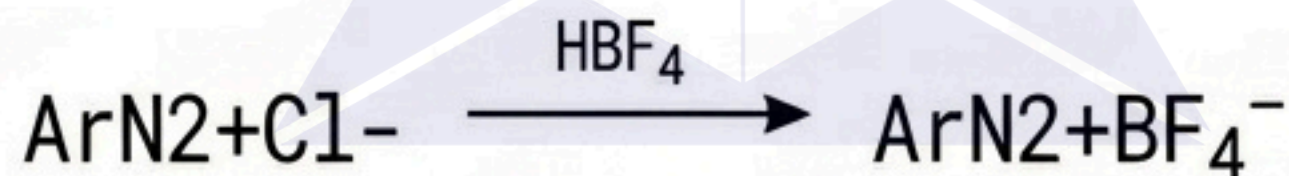
Simple hydrolysis to phenol occurs if the solution is allowed to warm up slightly.



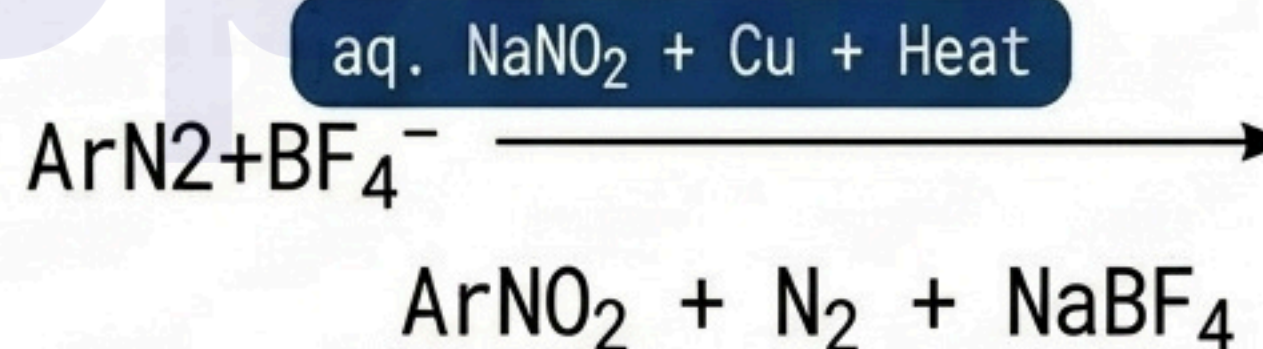
Replacement by Nitro Group (-NO₂)

Nitro introduction relies on the same stable fluoroborate intermediate used for fluorination, followed by displacement with aqueous nitrite.

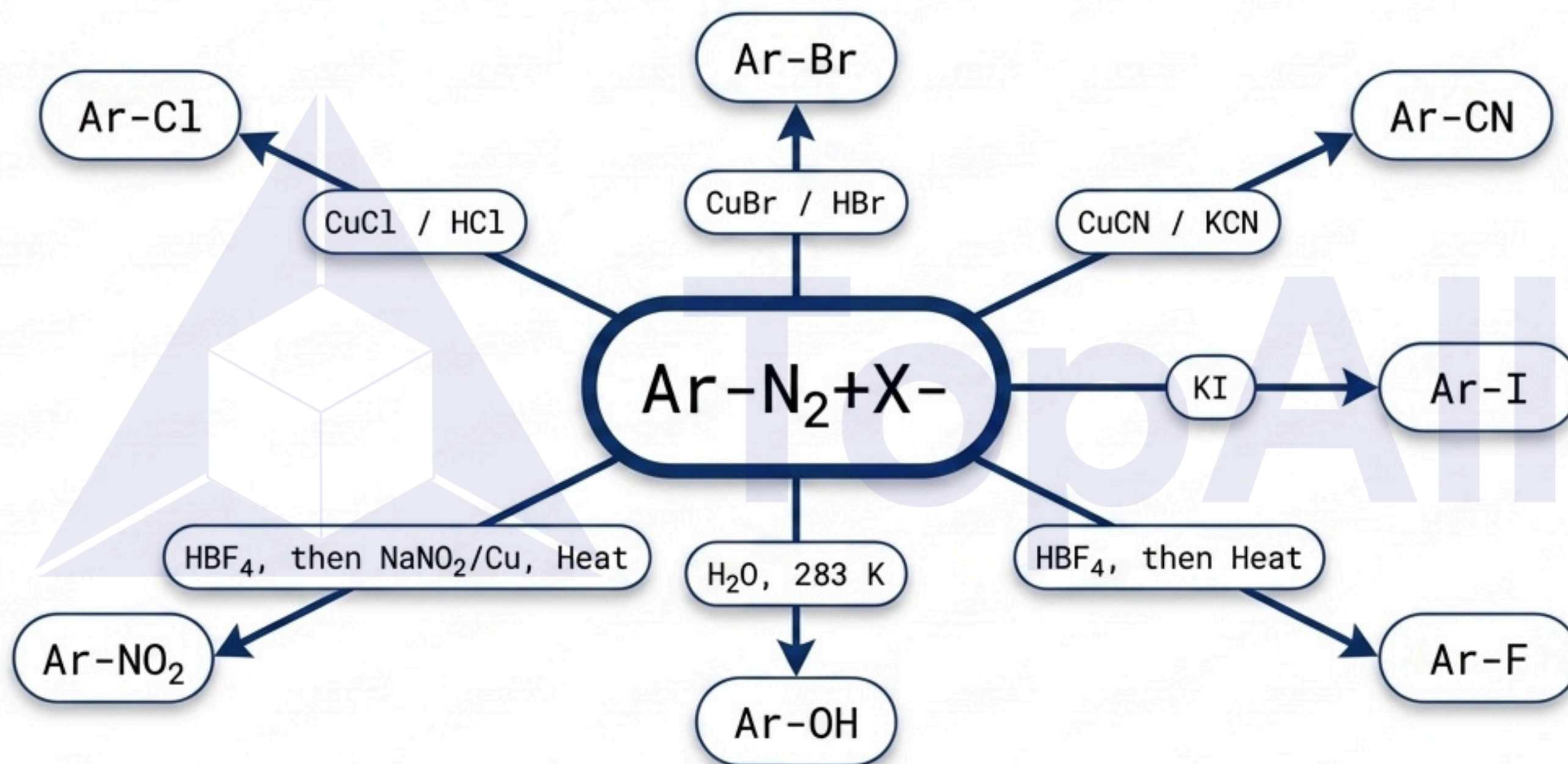
Step 1: Form Fluoroborate



Step 2: Heat with Nitrite & Copper



One Intermediate, Infinite Possibilities



Diazonium salts allow the introduction of substituents ($-\text{F}$, $-\text{I}$, $-\text{CN}$, $-\text{OH}$) that cannot be easily introduced via direct benzene substitution.



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