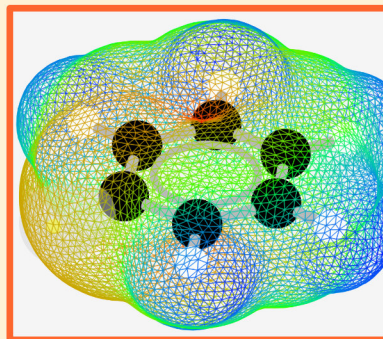


HIGHLIGHTS

- Synthesis of diazonium salts from anilines using acidic sodium nitrite to create a nitrosonium and then dehydration.
- Common substitutions of aryl diazonium salts to give halides, phenols and nitriles.
- The ionic mechanism for the reaction of nucleophiles with diazonium salts.
- The radical mechanism for the reaction of copper(I) salts with aryl diazonium species.



Classic S_NAr is restricted to activated benzene rings, those with powerful electron-withdrawing groups. An alternative is more general, all it requires is one very good leaving group. The **leaving group** is **nitrogen gas** and the substrate is a **diazonium salt**. Anilines are readily converted into diazonium salts, which on heating eliminate nitrogen to give an **aryl cation**. This is readily attacked by a number of heteroatom nucleophiles. When the substitution is performed in the presence of a copper(I) salt it is a radical reaction. The copper(I) reduces the diazonium salt to an **aryl radical** which then adds to a range of copper complexes. Such radical reactions are often called Sandmeyer reactions (although this strictly refers to the synthesis of halides).

The substitution of diazonium salts demonstrates the usefulness of nitrogen-containing functional groups in the synthesis of aromatic compounds.

CHEMISTRY CLASSICS

NUCLEOPHILIC AROMATIC SUBSTITUTION

CHEMISTRY OF ARYL DIAZONIUM SALTS



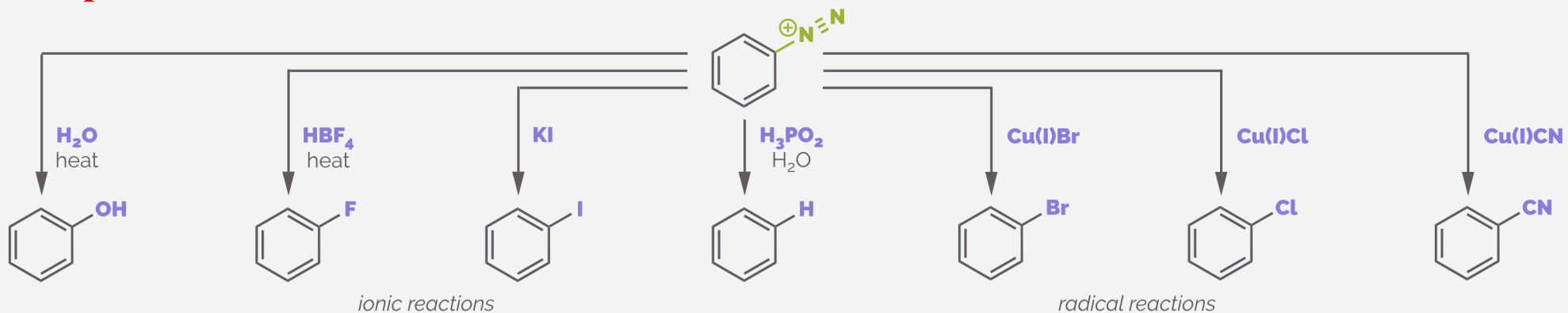
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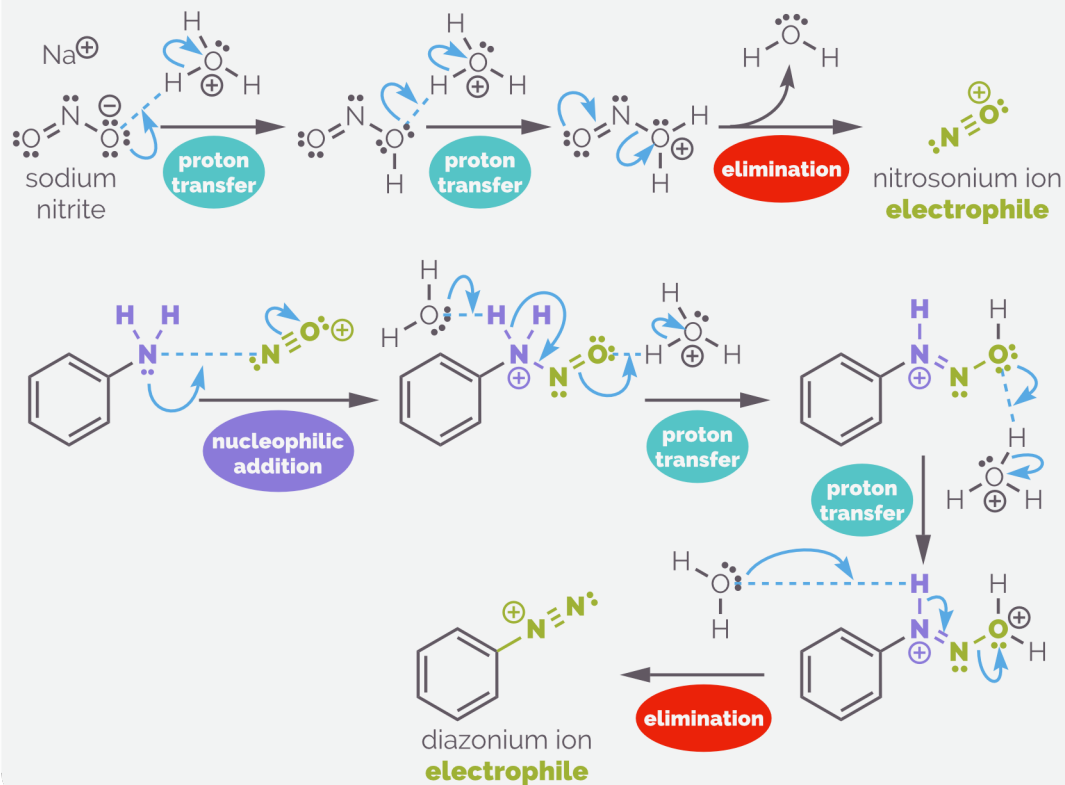
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Nucleophilic Aromatic Substitution 2

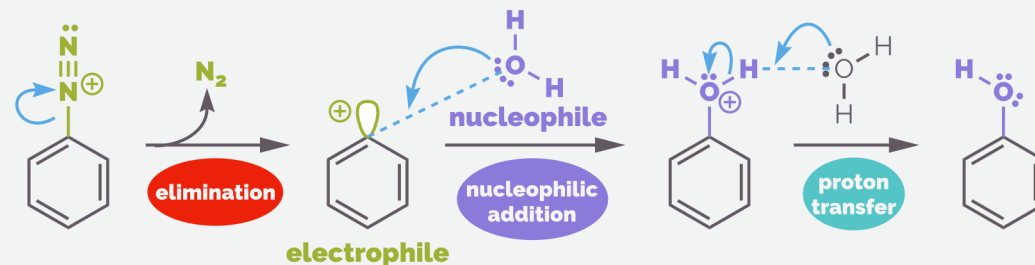
1. Nucleophilic substitution of diazonium salts



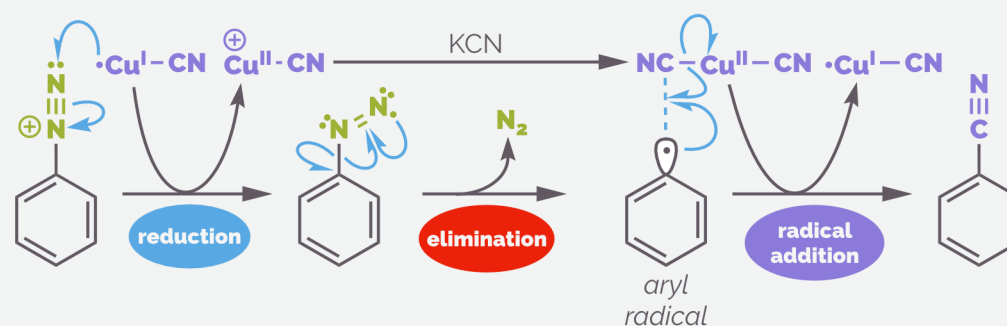
2. Synthesis of diazonium salts from anilines



3. Mechanism for ionic substitution



4. Mechanism of radical substitution



Two possible mechanisms for radical or **Sandmeyer-like** reactions. Both start with Cu(I) reducing diazonium salt to **aryl radical**. One involves direct radical addition of 'nucleophile' (shown). The other forms a Cu(III) species then reductive elimination.