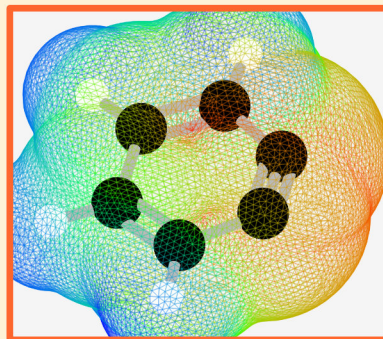


HIGHLIGHTS

- Nucleophilic aromatic substitution by elimination-addition.
- Mechanism of aryne formation and substitution reactions.
- Simple model of the structure of benzyne (or arynes).
- Influence of substituents on addition to the aryne intermediate.



The benzyne/aryne mechanism is the third version of nucleophilic aromatic substitution. If the nucleophile is a strong base, it can deprotonate the hydrogen adjacent to the leaving group. This is followed by elimination to give a triple bond on the outside of the aromatic ring, such species are called *arynes* or *benzyne*. The triple bond is formed from the poor overlap of the two sp^2 hybridized orbitals instead of the normal 2p orbitals. It is very weak and highly reactive. The triple bond is electrophilic, and the nucleophile can add to give a product that looks like substitution has occurred. In reality, the reaction was elimination and then addition. The nucleophile can add to either end of the triple bond and this can lead to regioisomers. Any substituent on the aryne can influence the regiochemistry. Simplistically, this is achieved by a combination of inductive and/or steric effects.

CHEMISTRY CLASSICS

NUCLEOPHILIC AROMATIC SUBSTITUTION

ELIMINATION- ADDITION & ARYNES

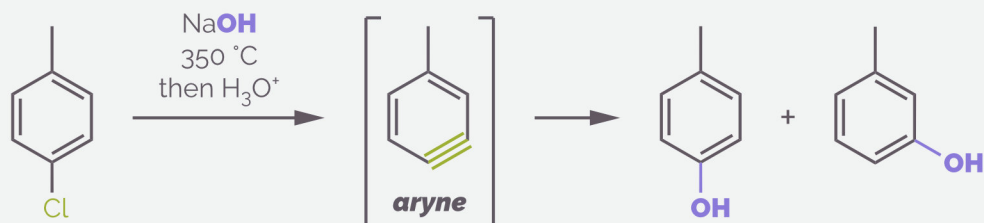


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Nucleophilic Aromatic Substitution 3

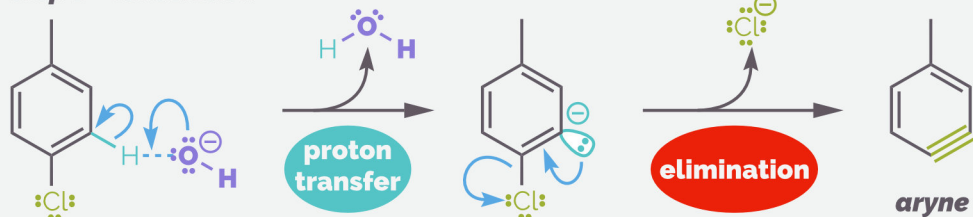
1. Nucleophilic aromatic substitution: Arynes



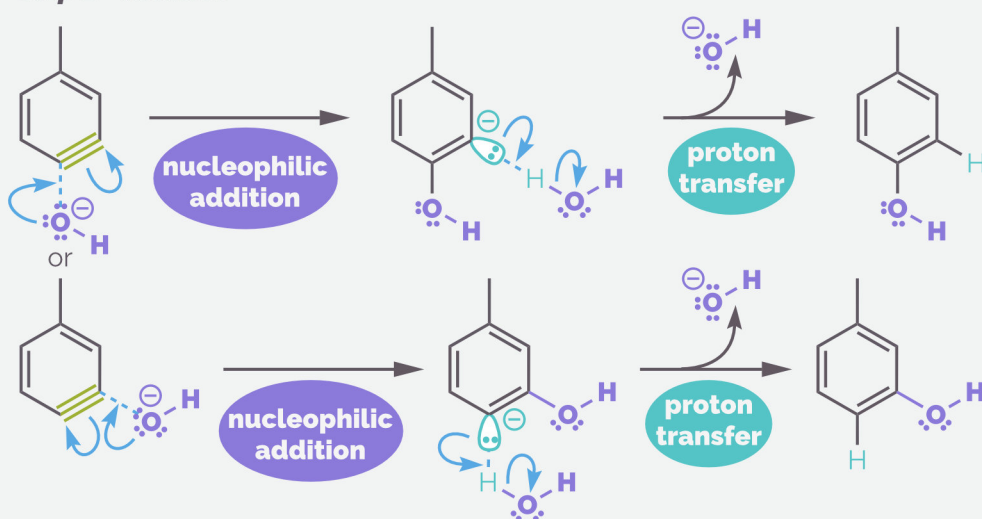
- Arynes are named after an **arene** ring containing an alky**ne**
- Requires a strong base to form - normally HO^- , RO^- or NH_2^-

2. Mechanism

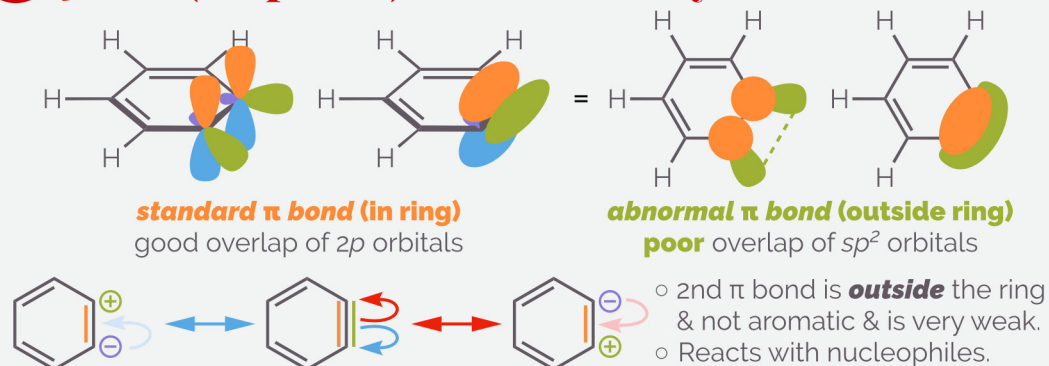
step 1 - elimination



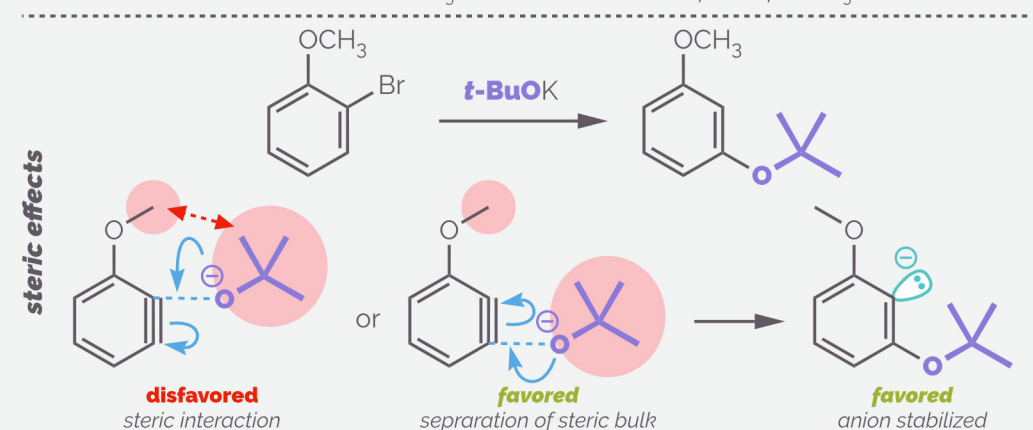
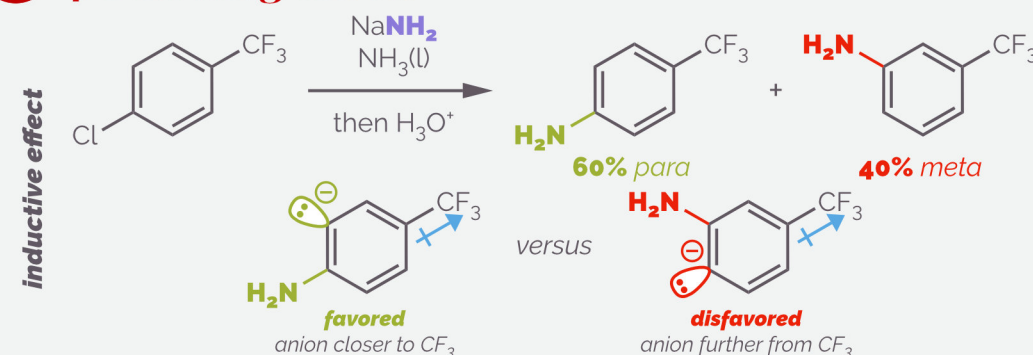
step 2 - addition



3. The (simplified) structure of arynes



4. Directing effects



Aryne distortion model now favored - <https://pubs.acs.org/doi/10.1021/ja5099935>