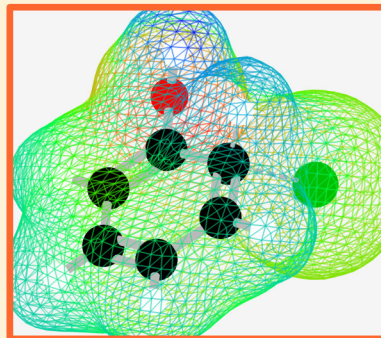


HIGHLIGHTS

- Naming the positions of the ring.
- Strongly activating groups are *ortho,para*-directing and involve the conjugation of a lone pair of electrons.
- Weakly activating groups are *ortho,para*-directing but tend to be less selective. They involve the inductive effect.
- Strongly deactivating groups are conjugated with the ring but remove electron density. They are *meta*-directing.
- Weakly deactivating groups are inductively electron withdrawing. They are *meta*-directing but with less selectivity.
- Halides are deactivating but *ortho,para*-directing.



The addition of a substituent onto a benzene ring has two effects on electrophilic aromatic substitution. It alters the reactivity, either **activating** the ring, making reactions faster and more easy, or **deactivating the ring**. The substituent also controls the position of the reaction (it controls the **regioselectivity**).

Electron donating groups activate the ring either by delocalization of a conjugated lone pair, or through σ conjugation. They are ***ortho,para***-directing.

Electron withdrawing groups behave in the opposite manner. They deactivate the ring and direct to the ***meta*** position. Again, either delocalization or the inductive effect drag electrons from the ring.

Halides are a pain. They are deactivating but ***ortho,para***-directing.

CHEMISTRY CLASSICS

π NUCLEOPHILES PART 5

ACTIVATION AND DIRECTING EFFECTS IN S_EAr

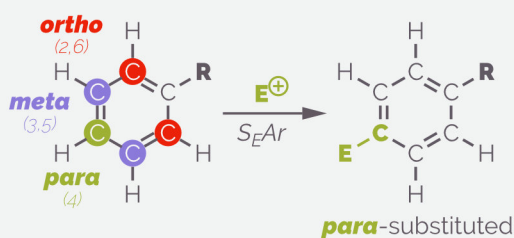


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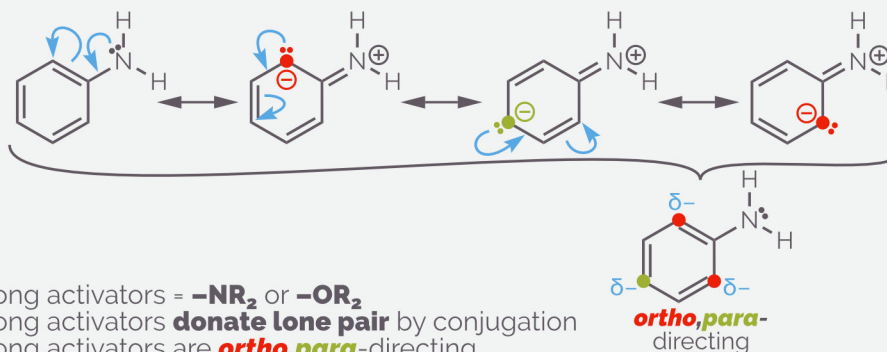
S_EAr - Activation & directing

1. Introduction

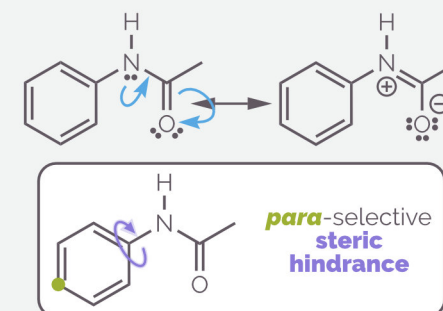


- Reaction can occur at 3 positions
- Named relative to original substituent

2. Strong activating groups

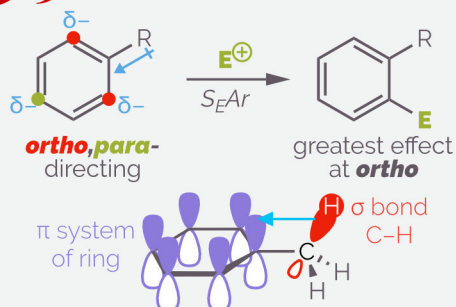


- Strong activators = $-NR_2$ or $-OR_2$
- Strong activators **donate lone pair** by conjugation
- Strong activators are **ortho,para**-directing

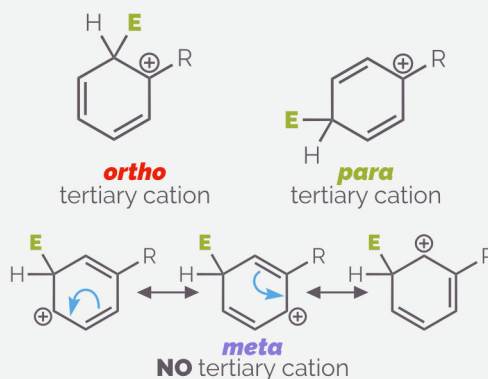


- Control reactivity by forming amides/esters - steric hindrance favors **para**

3. Weak activators

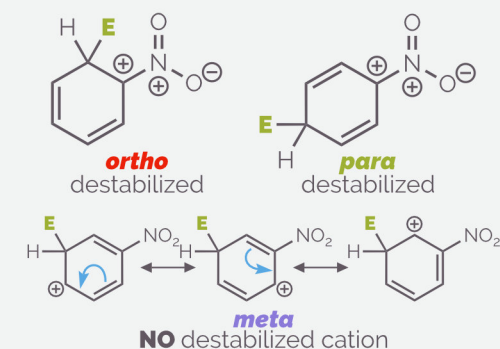
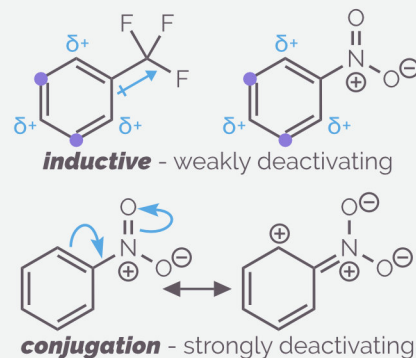


- Weak activators - alkyl groups
- Inductive effect or σ conjugation



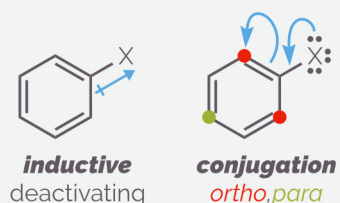
- Stability of carbocation intermediate

4. Deactivating groups



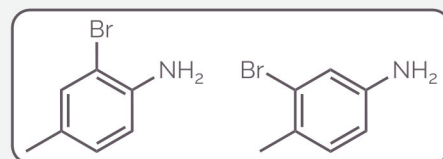
- **Meta**-directing as least deactivated C
- **Meta**-directing as no destabilized cation

5. Halides



- Weakly deactivating
- **Ortho,para**-directing

6. Example



- How can each regioisomer be selectively formed?
- Use directing group effects and functional group interconversion

