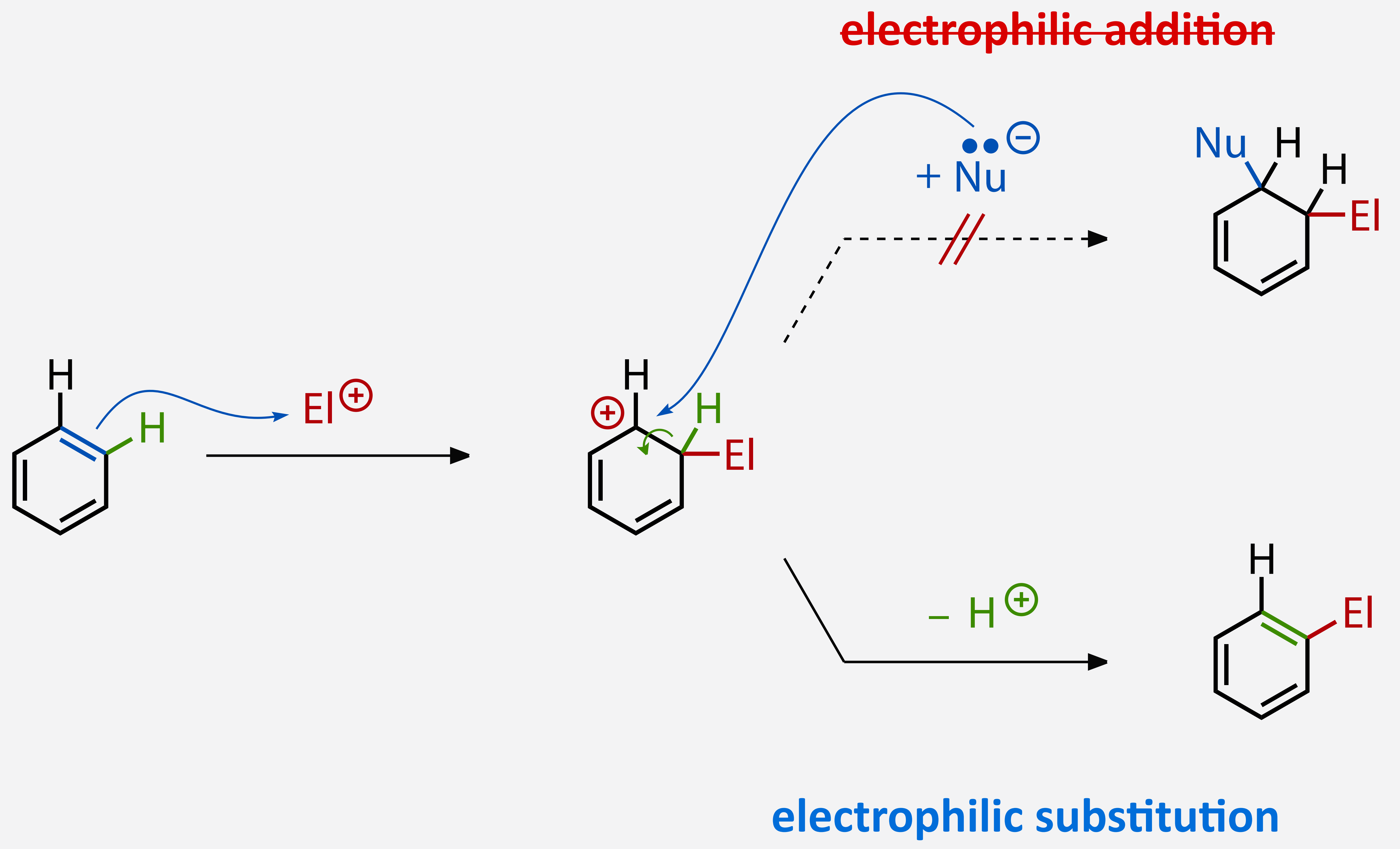
# 4.7 Electrophilic Substitutions on Aromatic Systems ($S_E$)

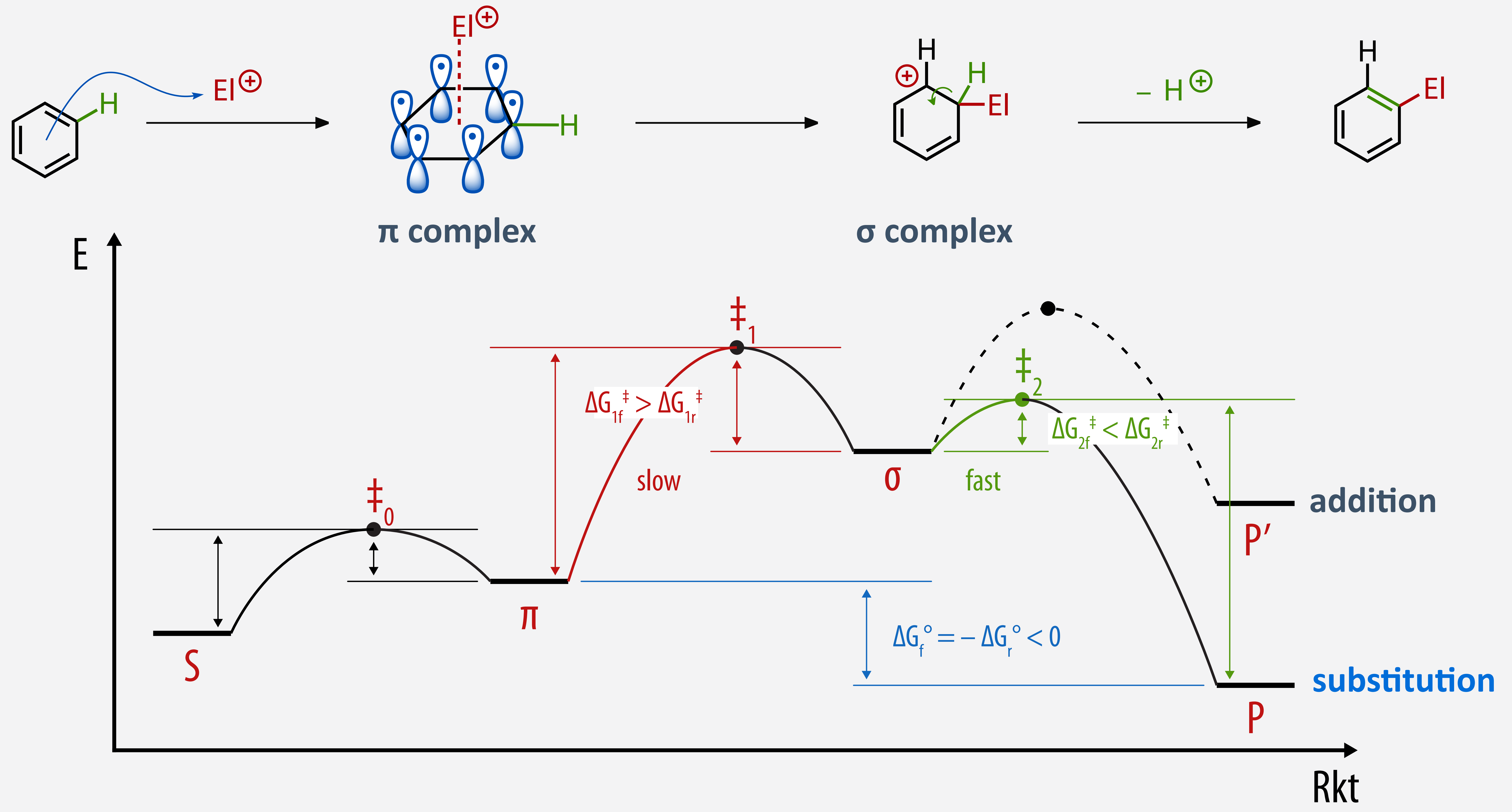
# Multiple Bonds in Aromatic Compounds Do Not React Like Olefins

- aromatic π systems are also weak nucleophiles; electrophiles add to one of the double bonds




- **addition of the nucleophile to complete electrophilic addition results in loss of aromaticity**
- **instead, proton elimination results in substitution and re-establishes aromatic π system!**

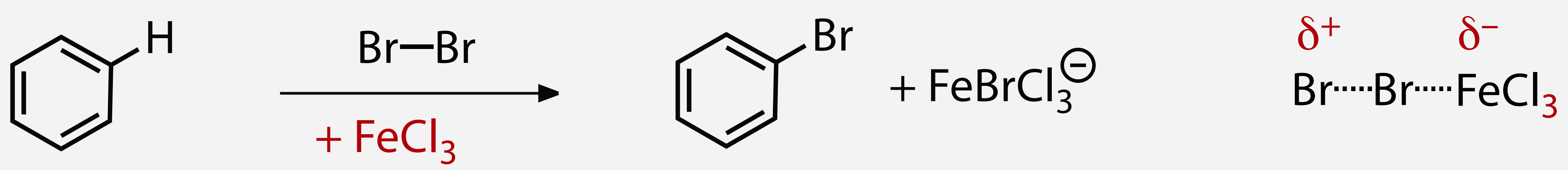
# Mechanism of Electrophilic Aromatic Substitutions ($S_EAR$)



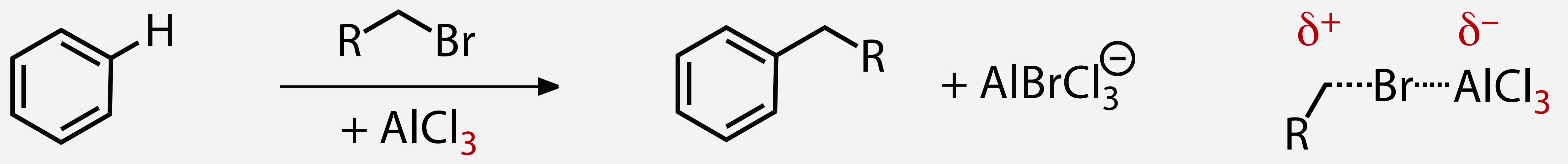

- π complex allows electrophile to find most favorable reaction path towards σ complex
- electrophilic substitution is **regioselective**: "most acidic" proton is replaced

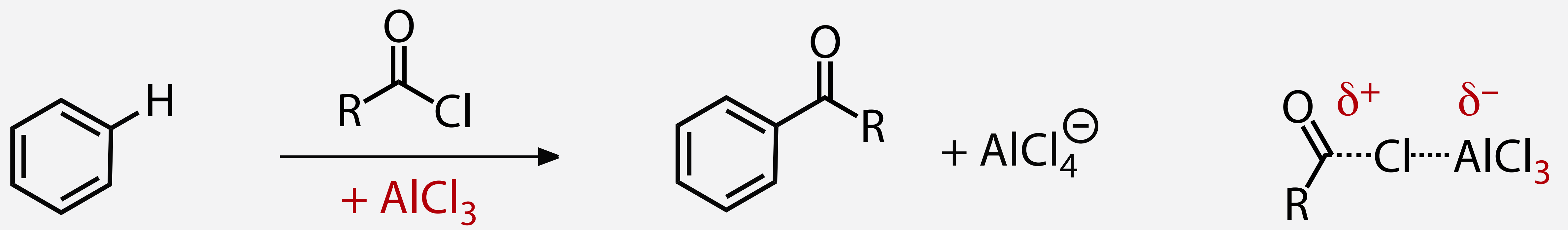
# Simple Examples

- **bromination**

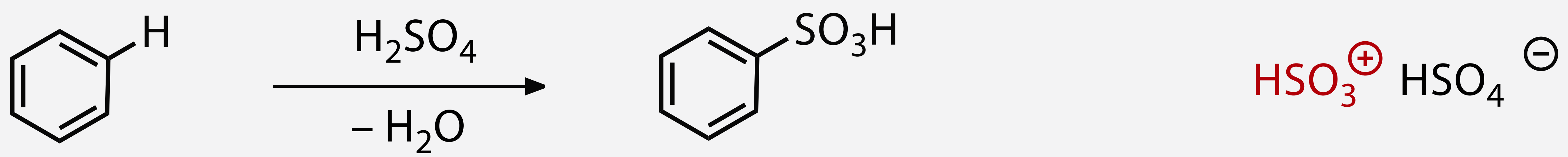


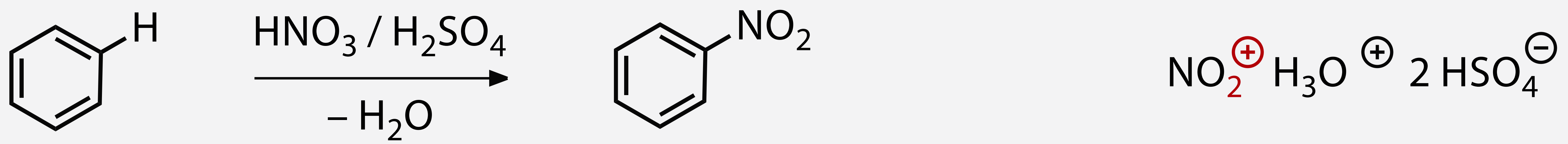

- **Friedl-Crafts alkylation and acylation**



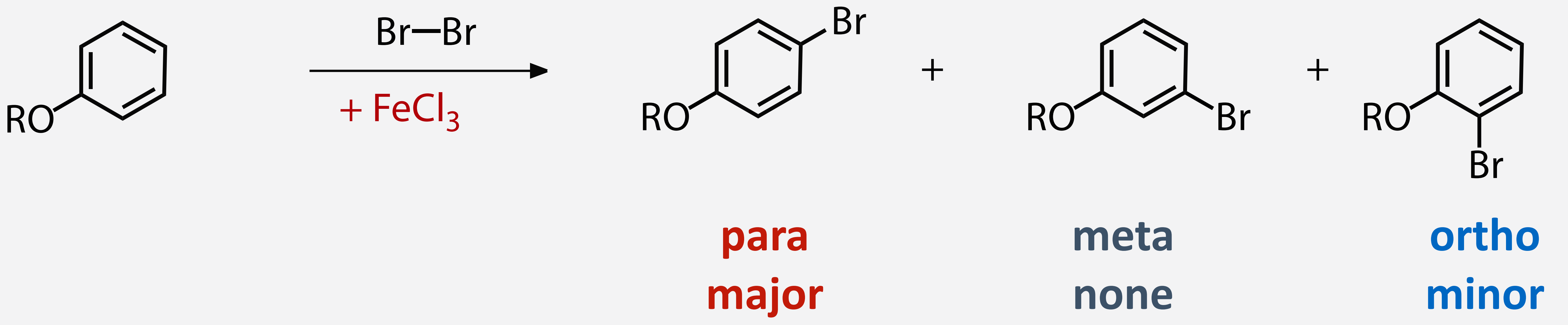

- **sulfonation and nitration**

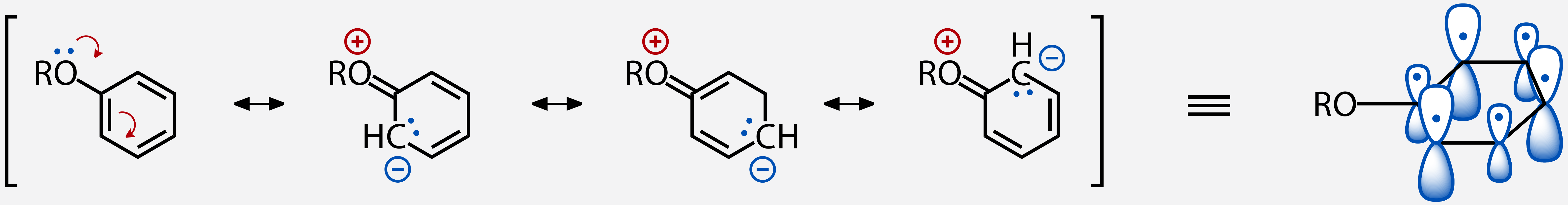


# Regioselectivity in Electrophilic Aromatic Substitutions

- regioselectivity in electrophilic substitutions is directed by previous substituents



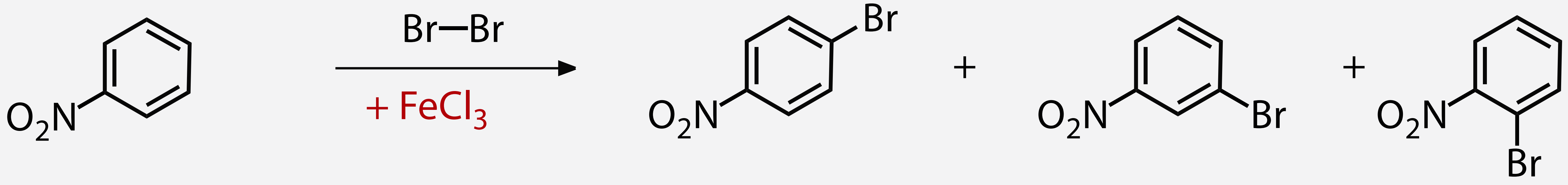





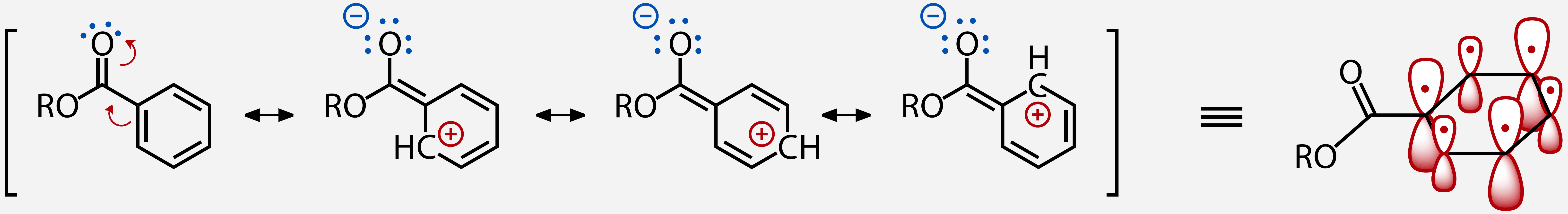
- **substituents with +M effect direct the electrophile into *para* (and *ortho*) positions**
- **substituents with +M effect increase electron density and reactivity towards electrophile**

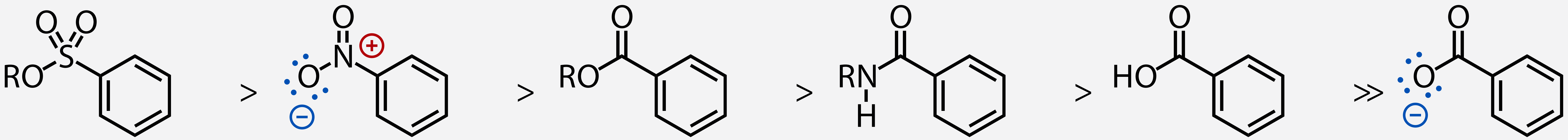
# Regioselectivity in Electrophilic Aromatic Substitutions

- regioselectivity in electrophilic substitutions is directed by previous substituents




para traces | **meta major** | ortho traces




sulfonate | nitro | carboxylic esters | carboxylic amides | carboxylic acids | carboxylates

- **substituents with –M effect direct the electrophile into *meta* positions**
- **substituents with –M effect decrease electron density and reactivity towards electrophile**

# Learning Outcomes

- aromatic π systems are weak nucleophiles
- electrophiles add to one of the double bonds
- but subsequent nucleophile addition would result in loss of aromaticity
- instead, loss of a proton results in substitution product
- reaction is regioselective, directed by other substituents