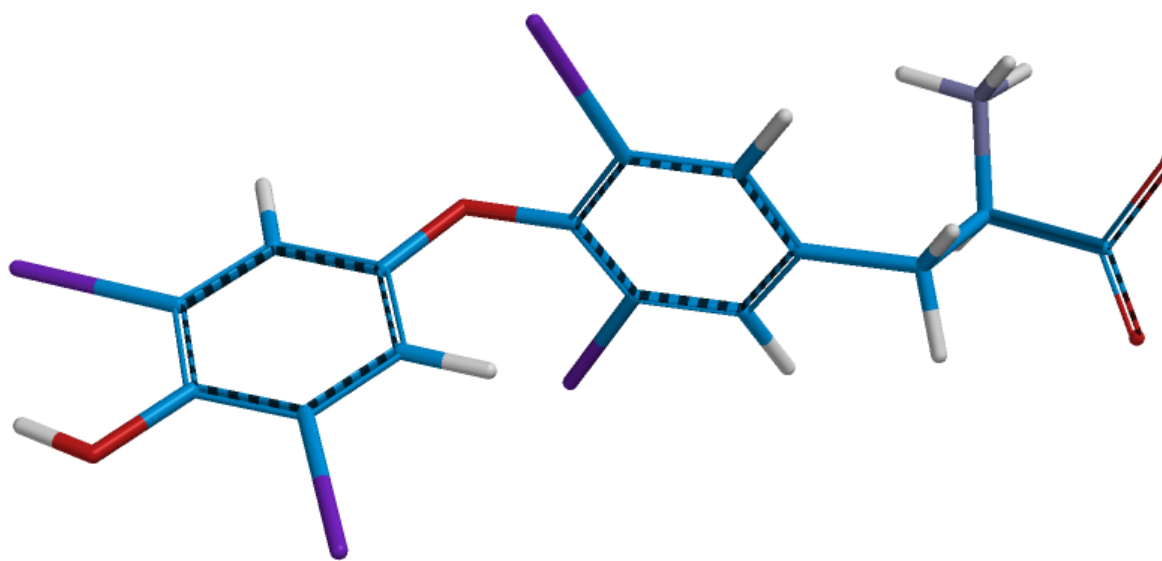


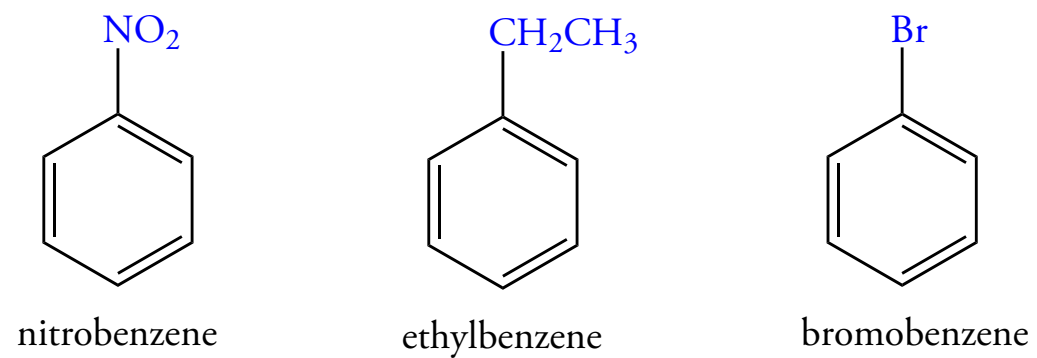
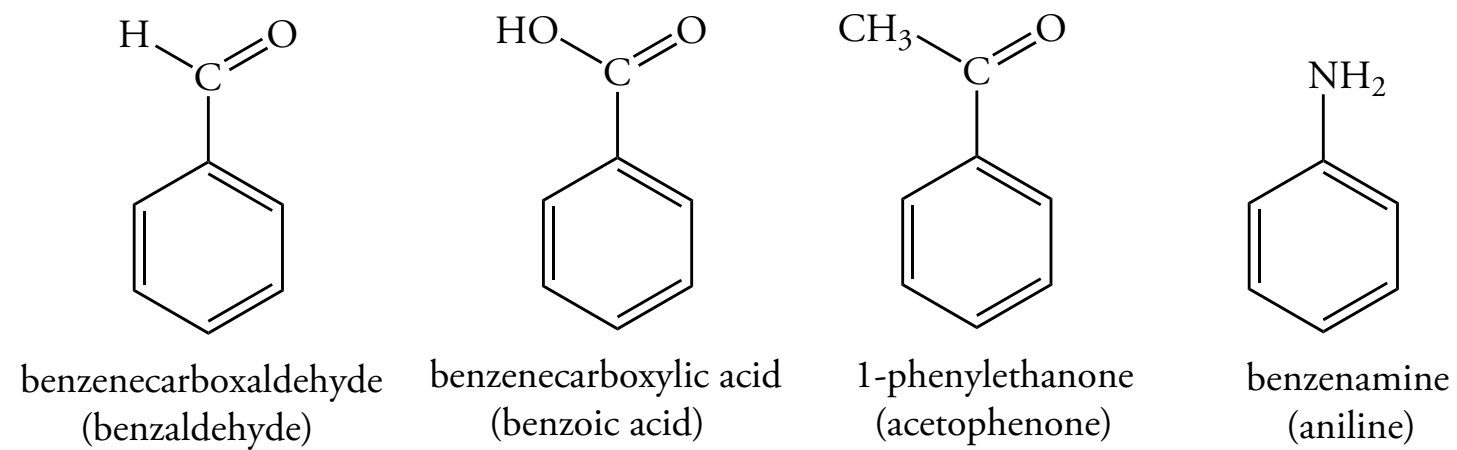
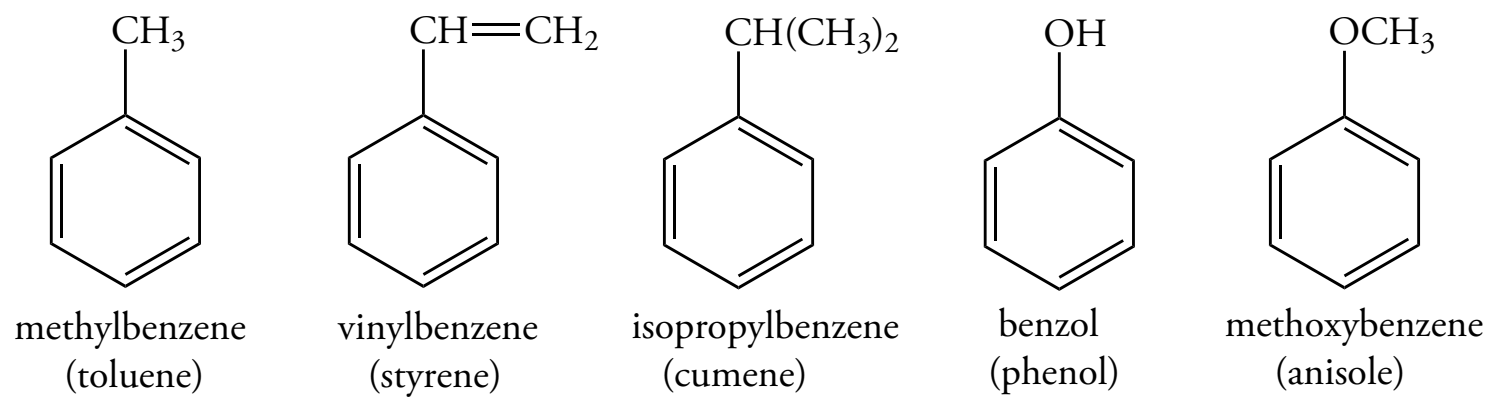
13

ELECTROPHILIC AROMATIC SUBSTITUTION

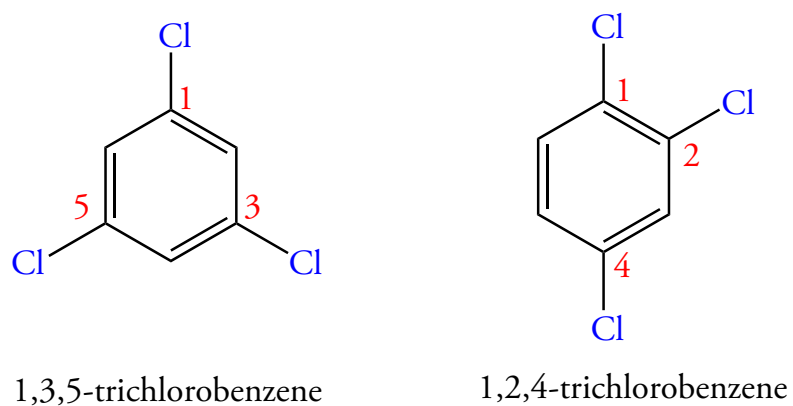
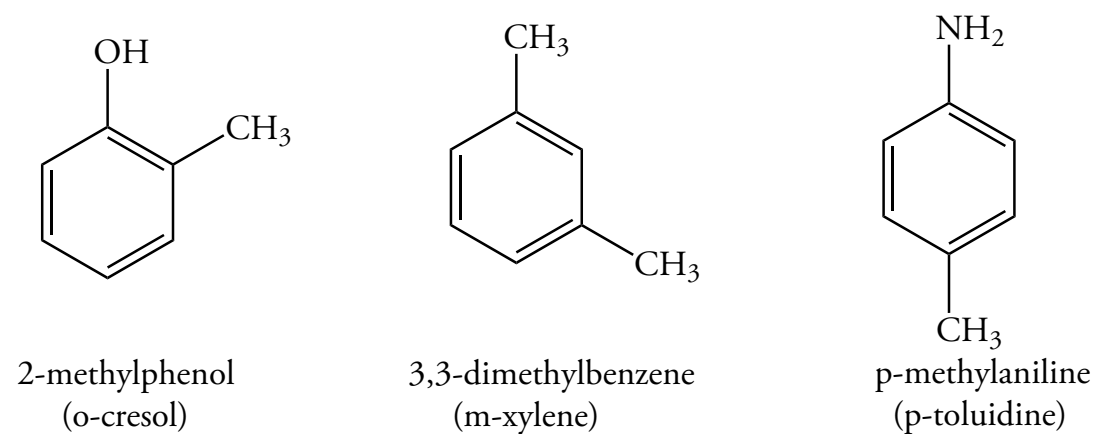
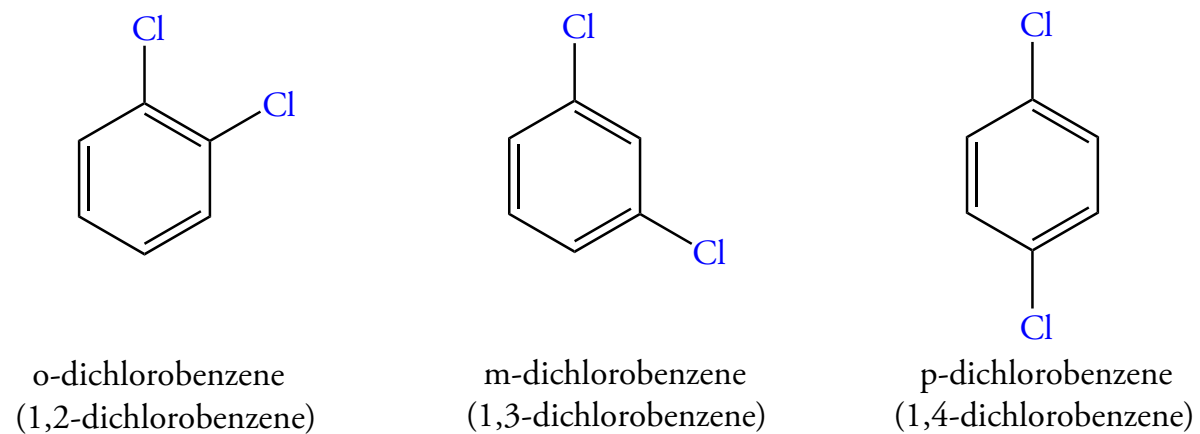
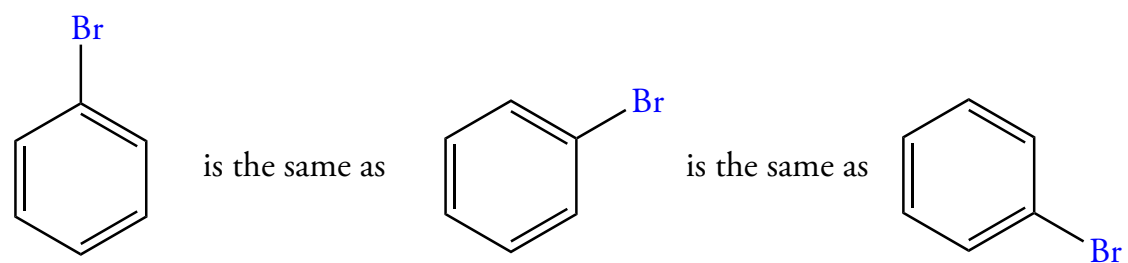


thyroxine

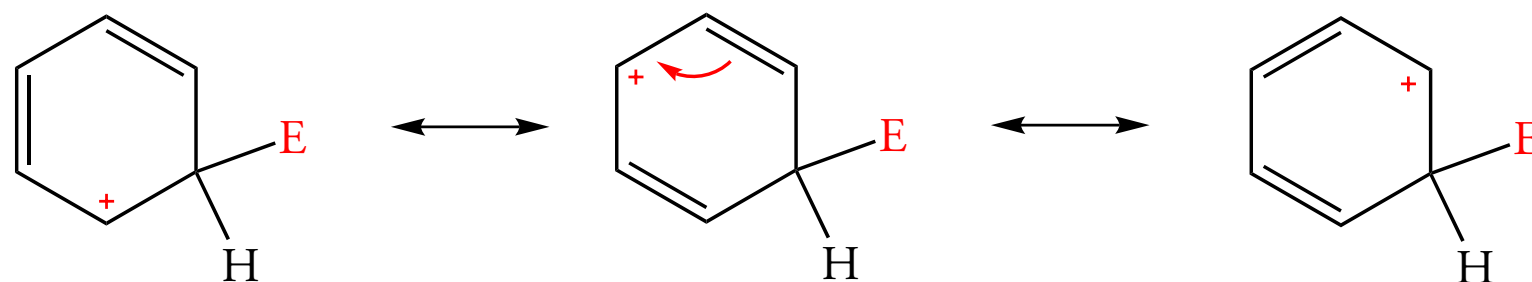
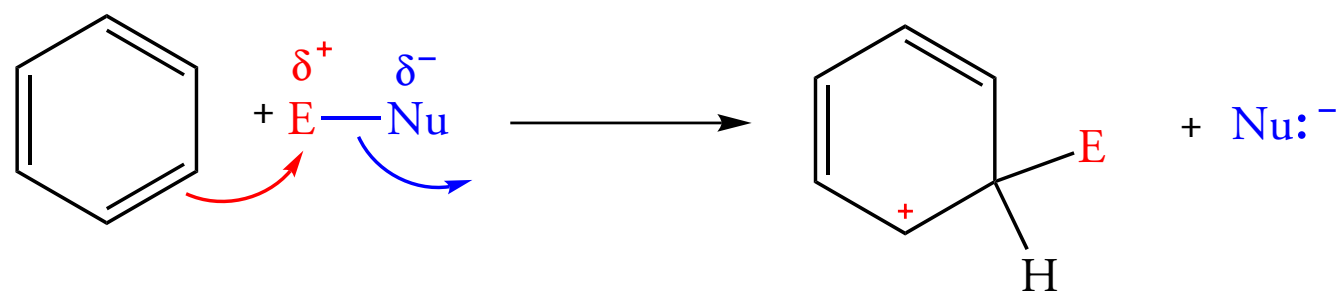
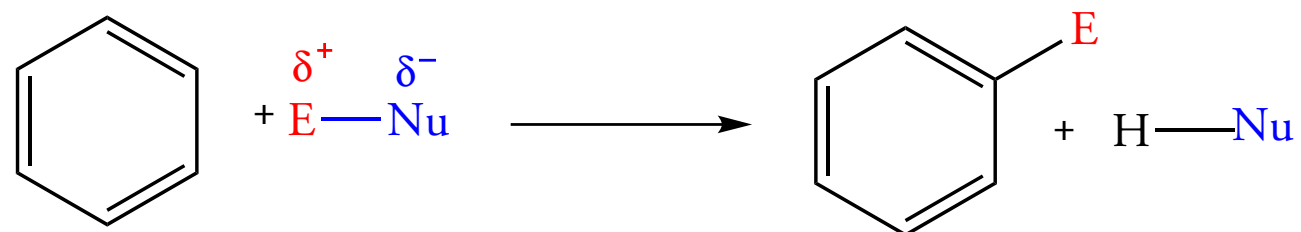
13.1 NOMENCLATURE OF BENZENE DERIVATIVES, I



13.1 NOMENCLATURE OF BENZENE DERIVATIVES, II



13.2 MECHANISM OF ELECTROPHILIC AROMATIC SUBSTITUTION



resonance forms of a cyclohexadienyl carbocation

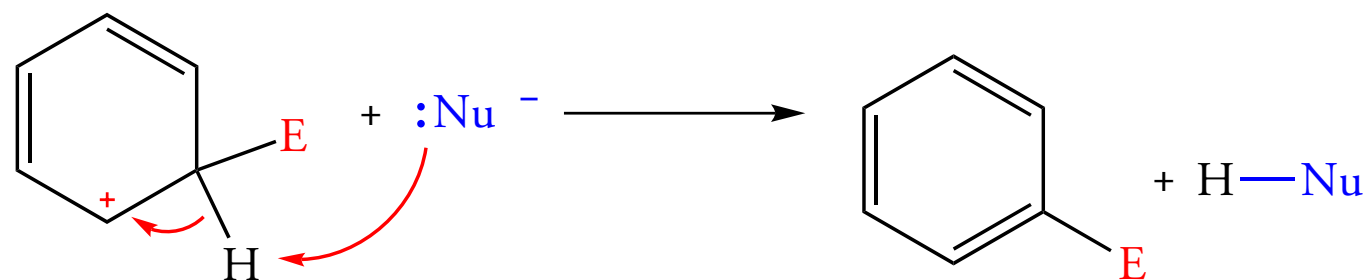
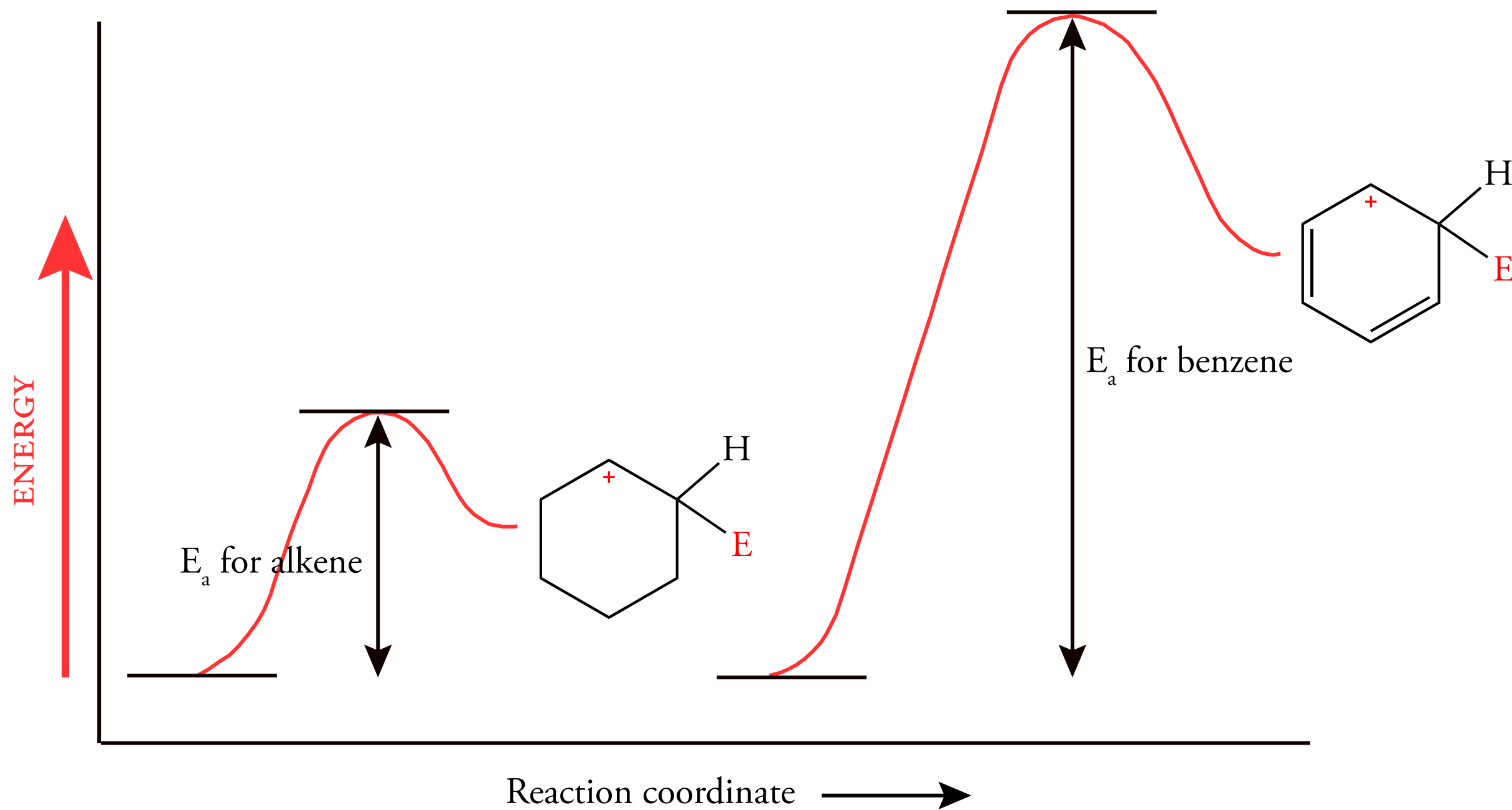
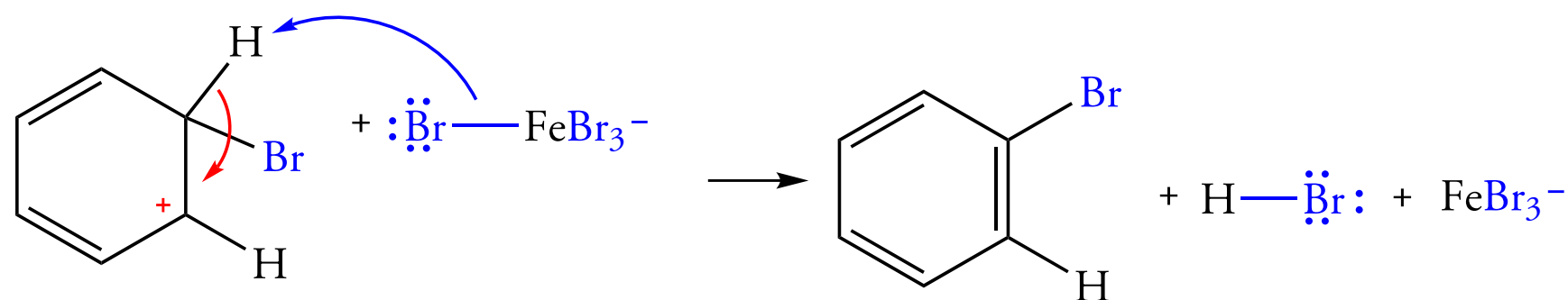
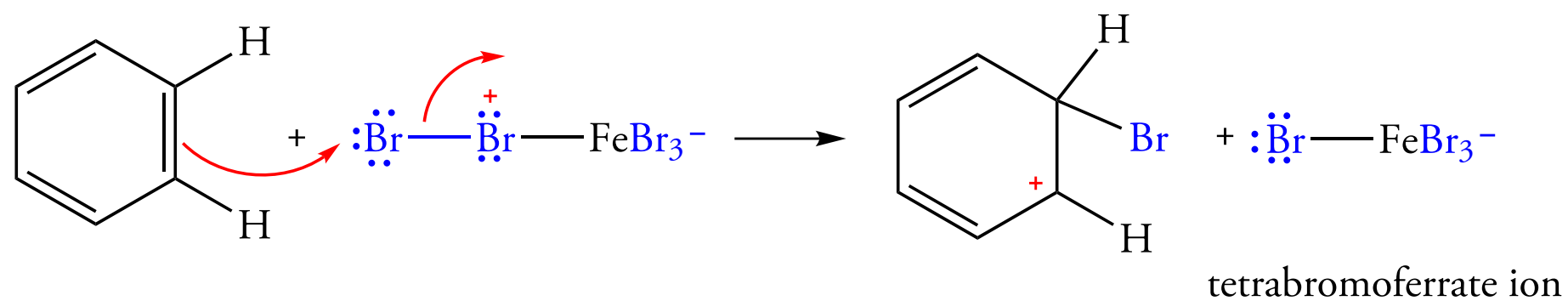
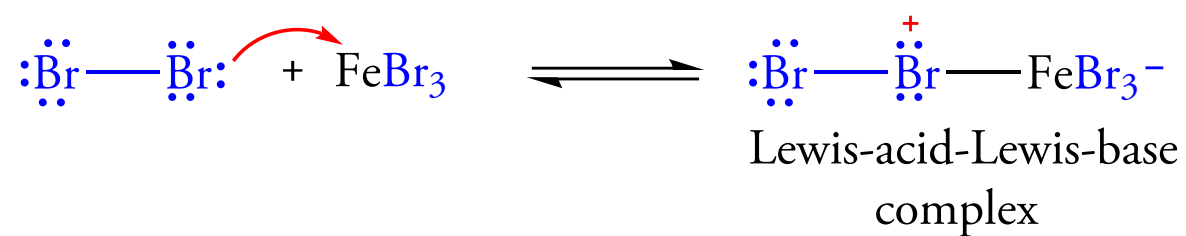
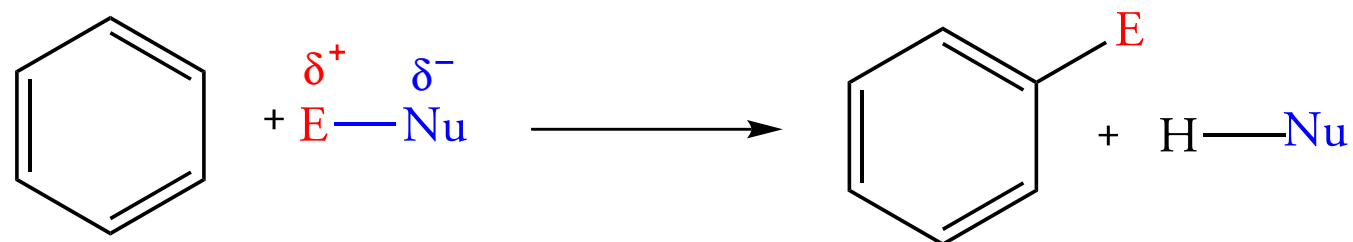


Figure 13.1 Electrophilic Addition to Cyclohexene Compared to Benzene

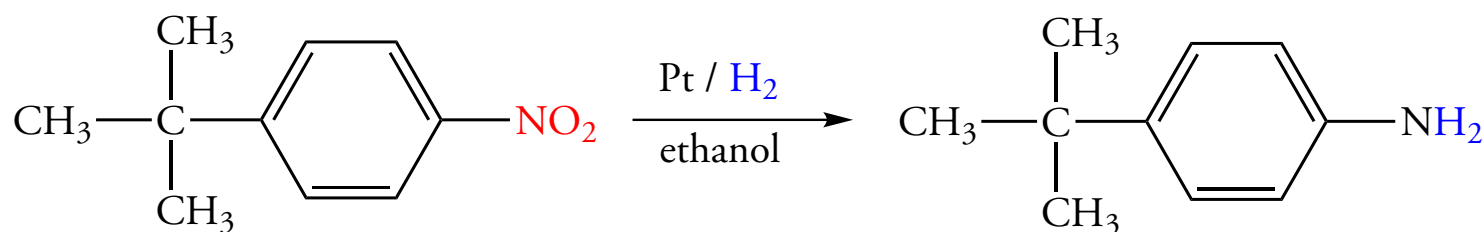
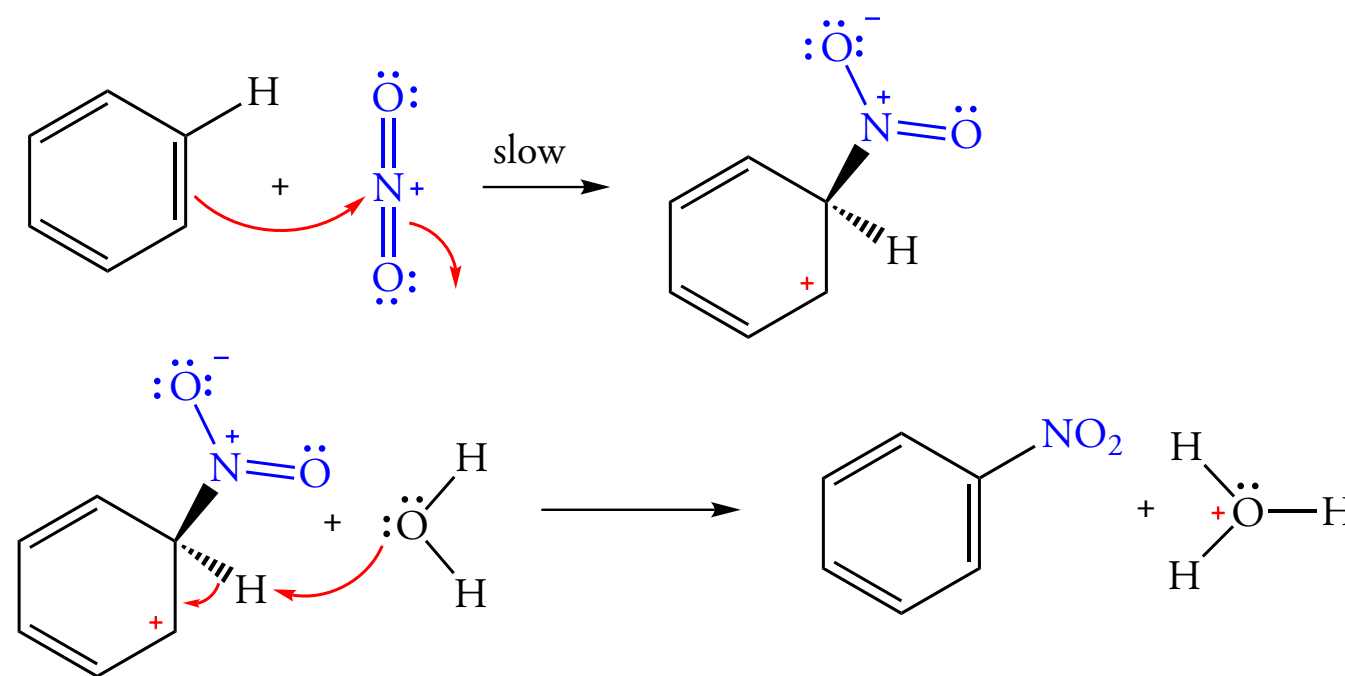
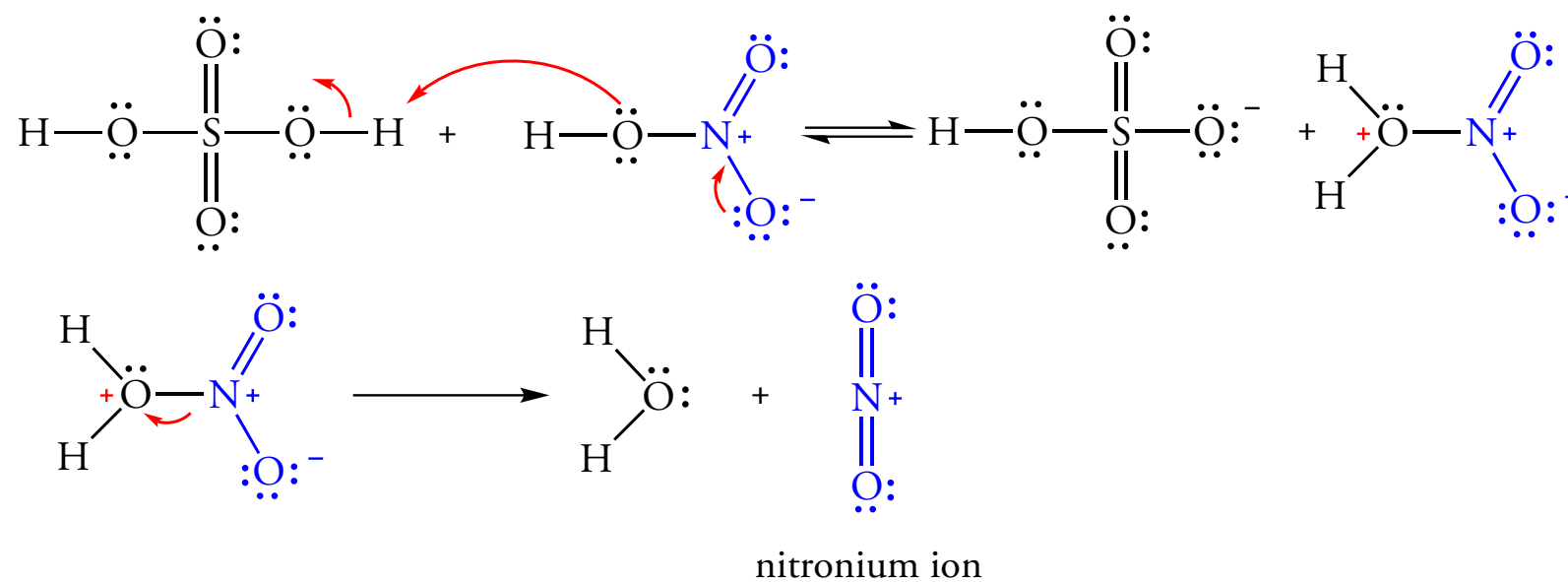
The activation energy for adding an electrophile to benzene is higher than for the activation energy for adding an electrophile to an alkene because some of the resonance energy of benzene is lost in the transition state.



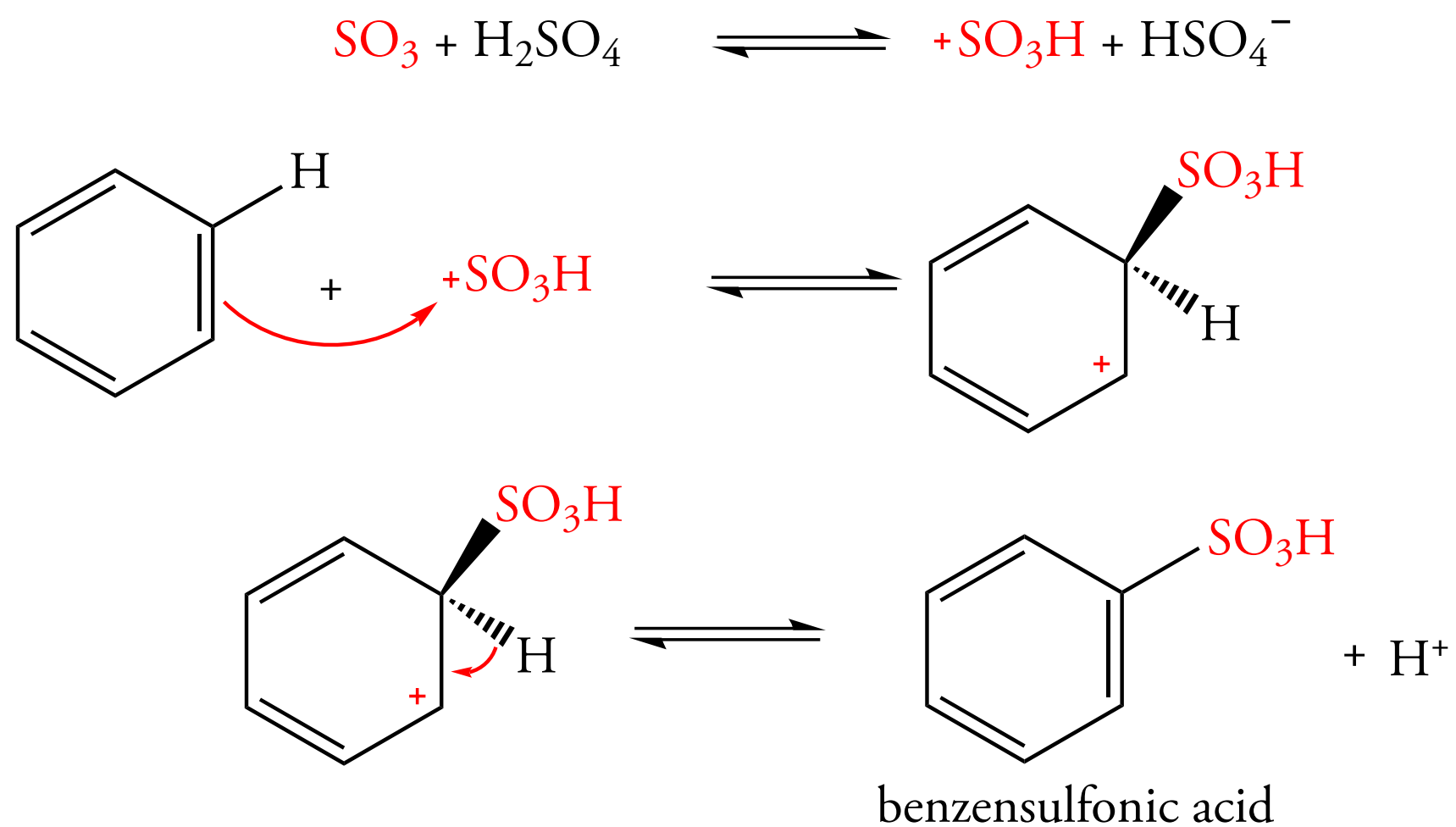
13.3 COMMON ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS: HALOGENATION



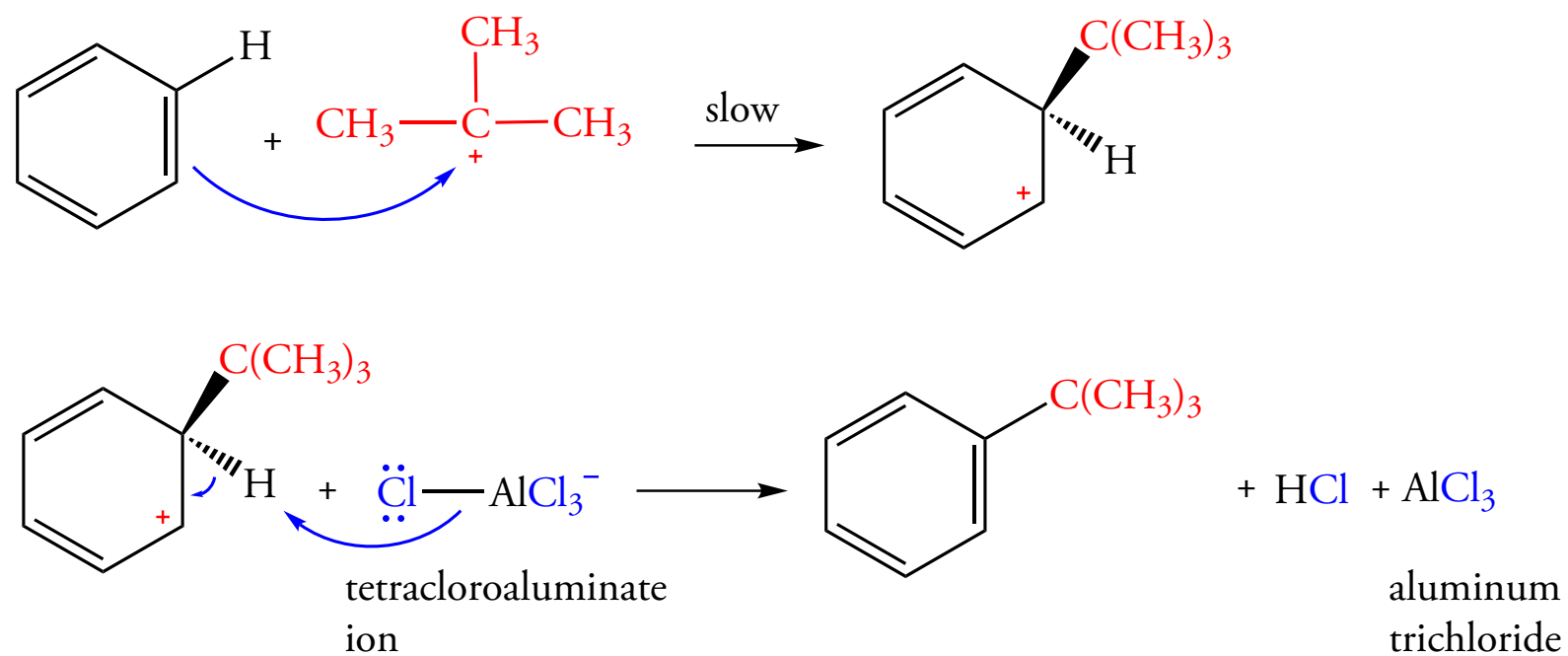
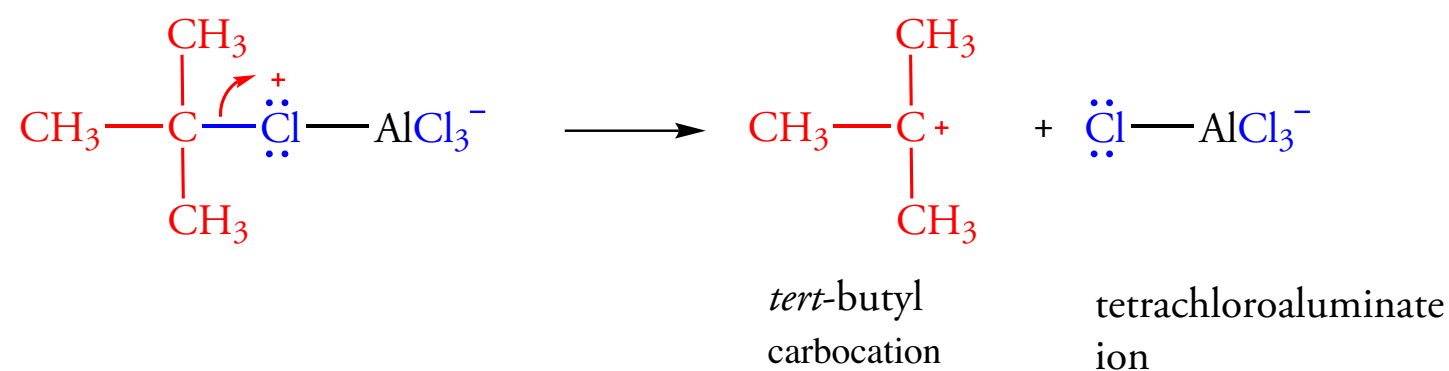
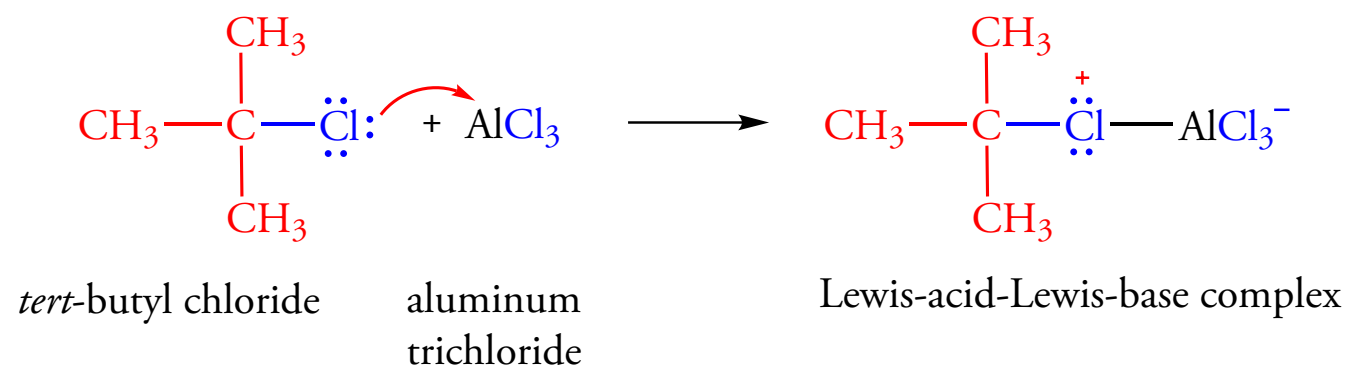
13.3 COMMON ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS: NITRATION



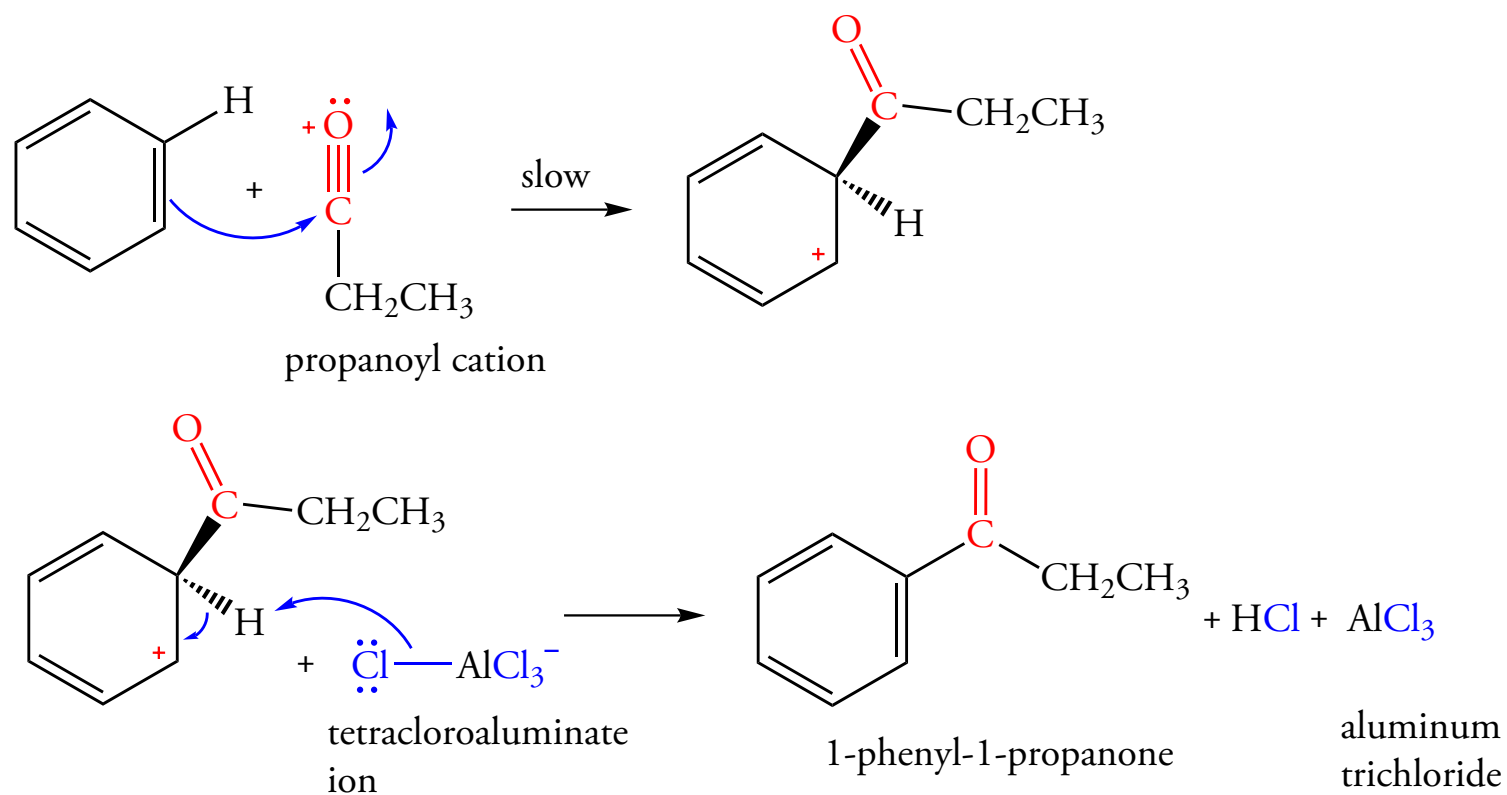
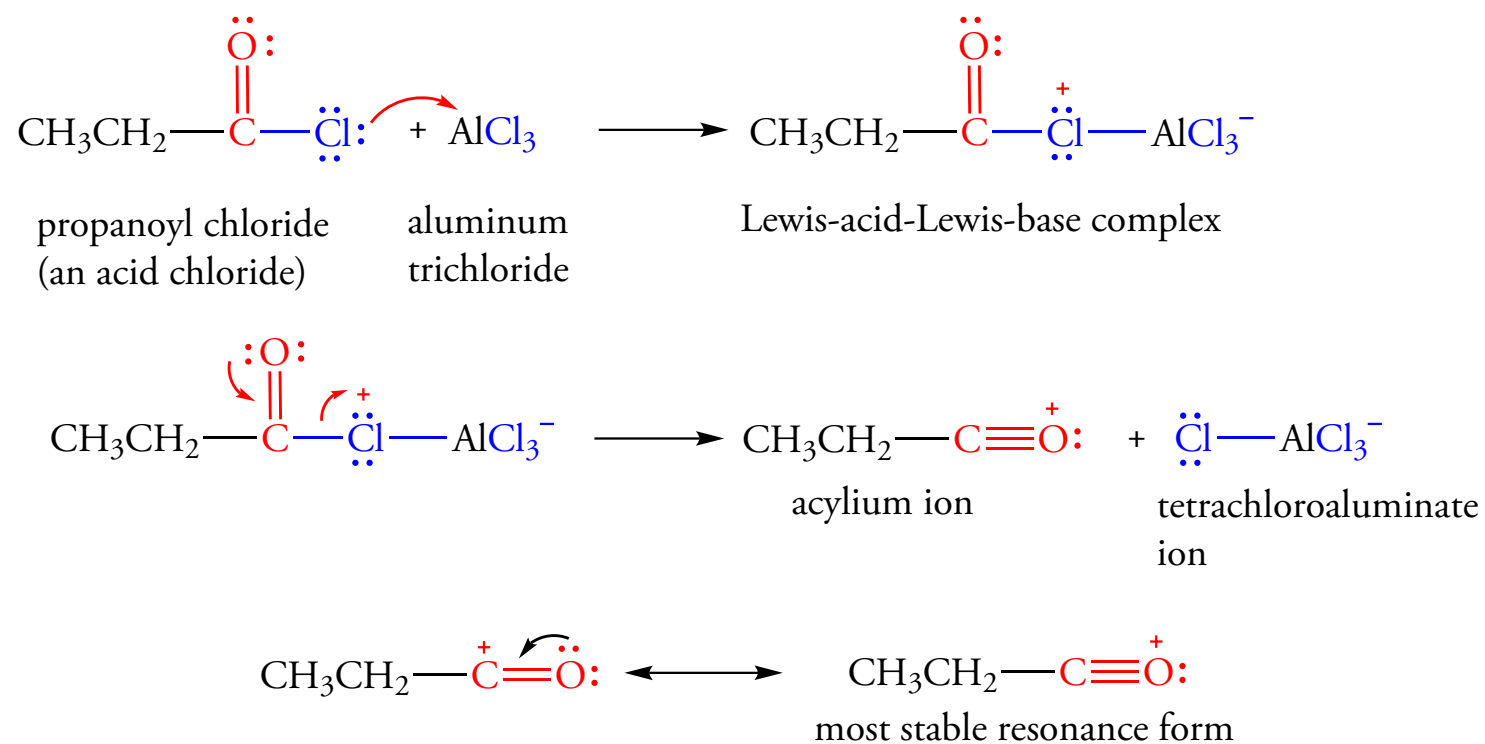
13.3 COMMON ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS: SULFONATION



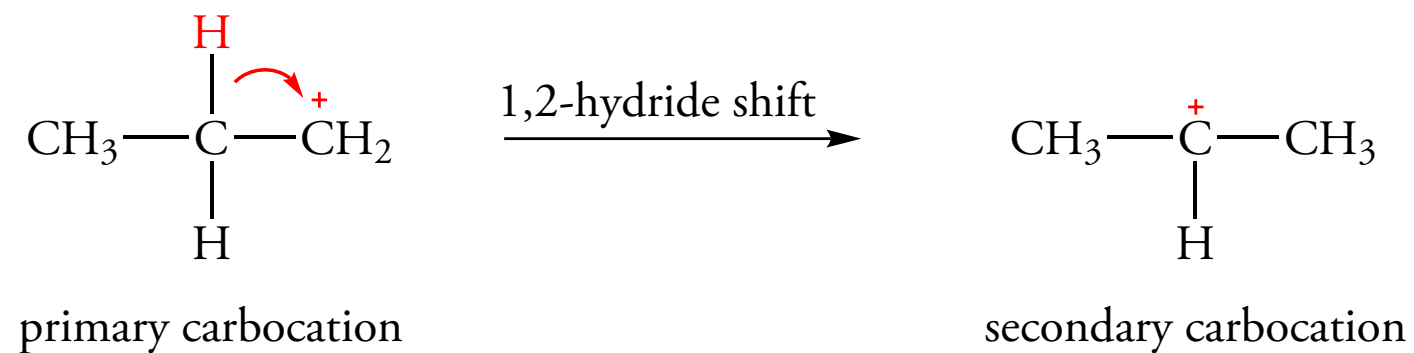
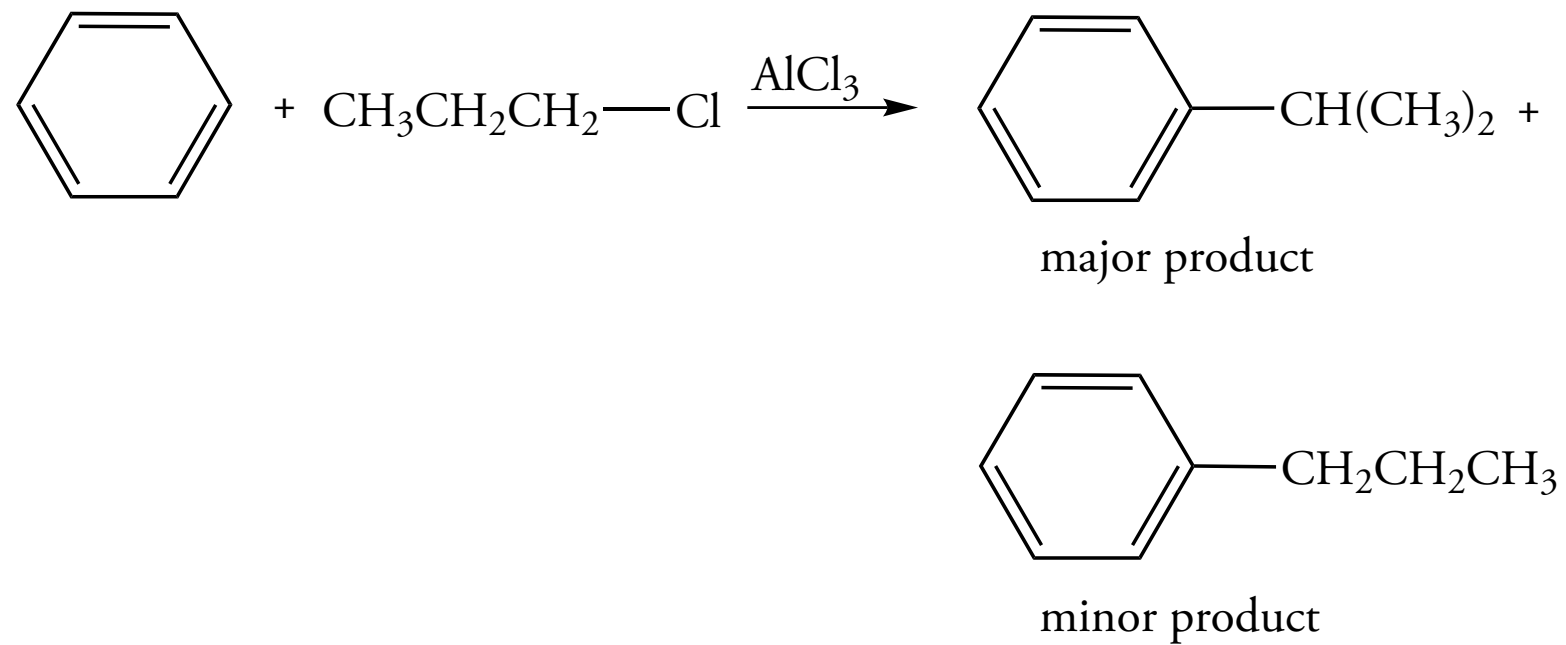
13.3 COMMON ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS: FRIEDEL-CRAFTS ALKYLATION



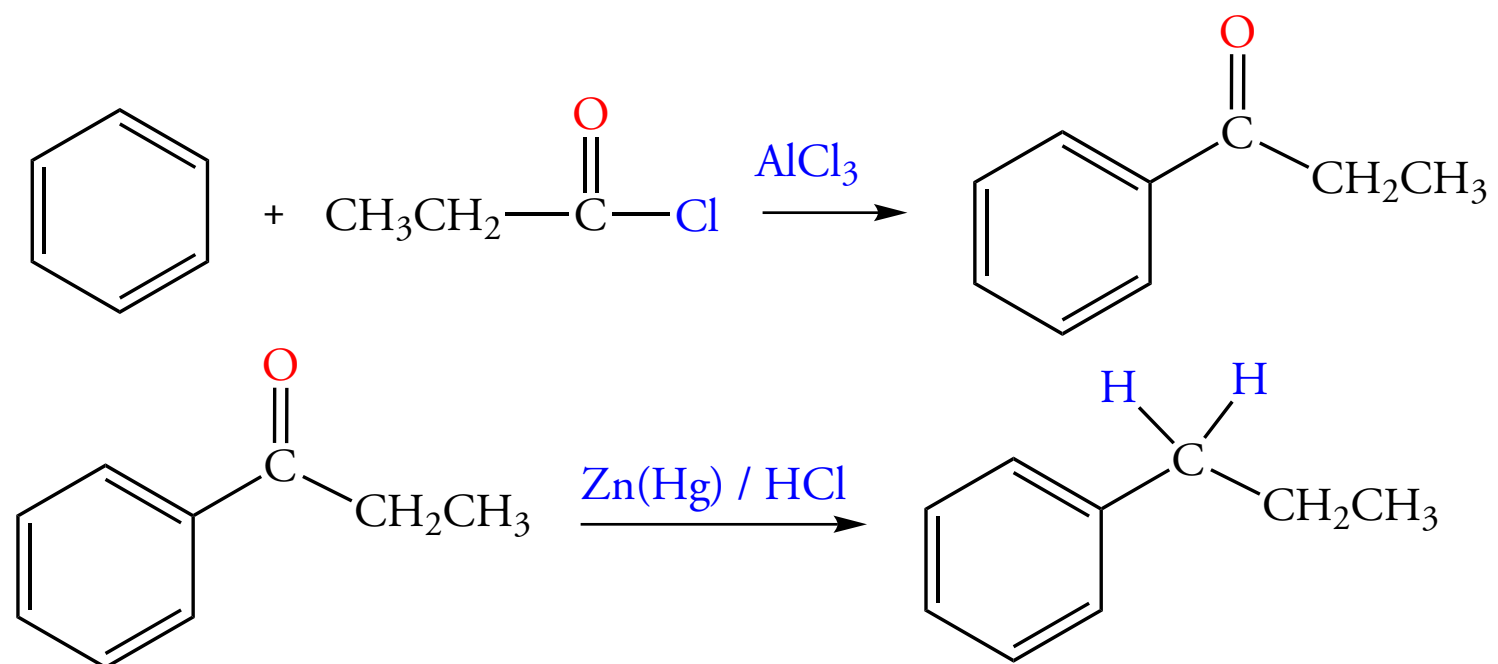
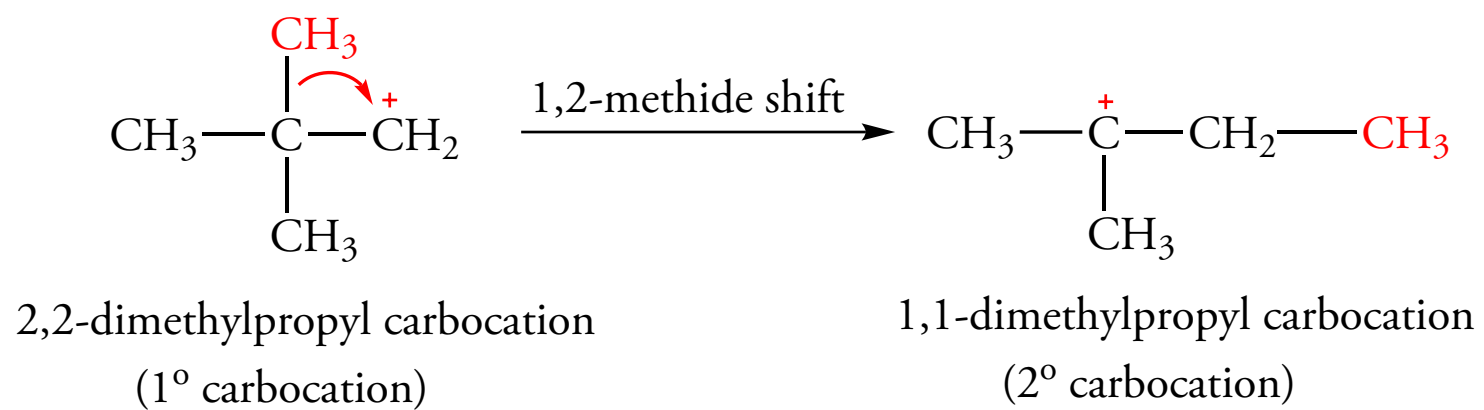
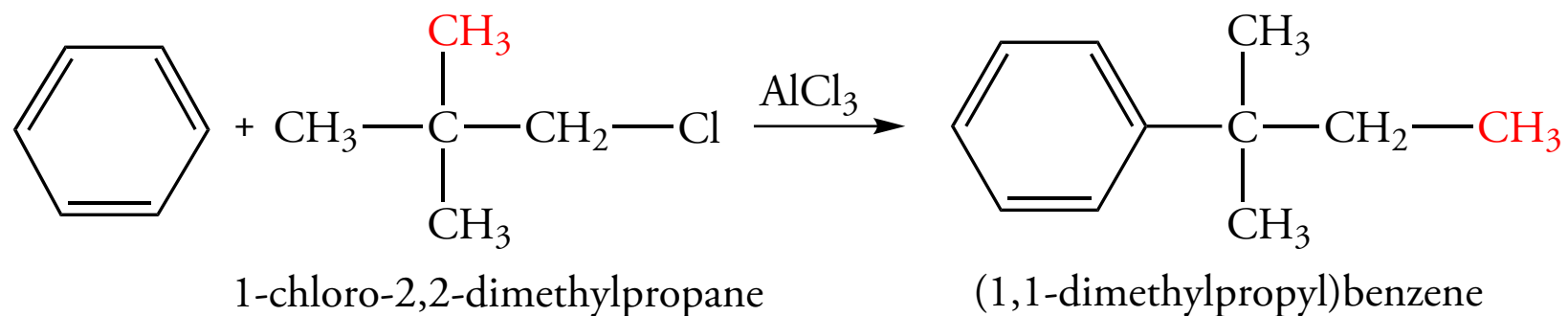
13.3 COMMON ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS: FRIEDEL-CRAFTS ACYLATION



13.3 LIMITATIONS OF THE FRIEDEL-CRAFTS REACTION, I



13.3 LIMITATIONS OF THE FRIEDEL-CRAFTS REACTION, II

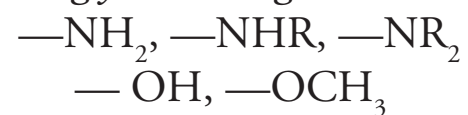


13.4 SUBSTITUENT EFFECTS ON THE REACTIVITY OF BENZENE RINGS

Effects of Ring Substituents on Reaction Rate

Table 13.1
Effect of Substituents on
Aromatic Substitution

Strongly activating



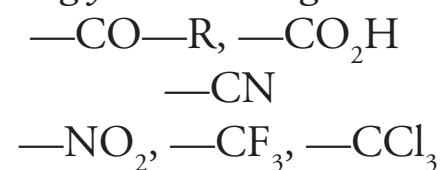
Weakly activating



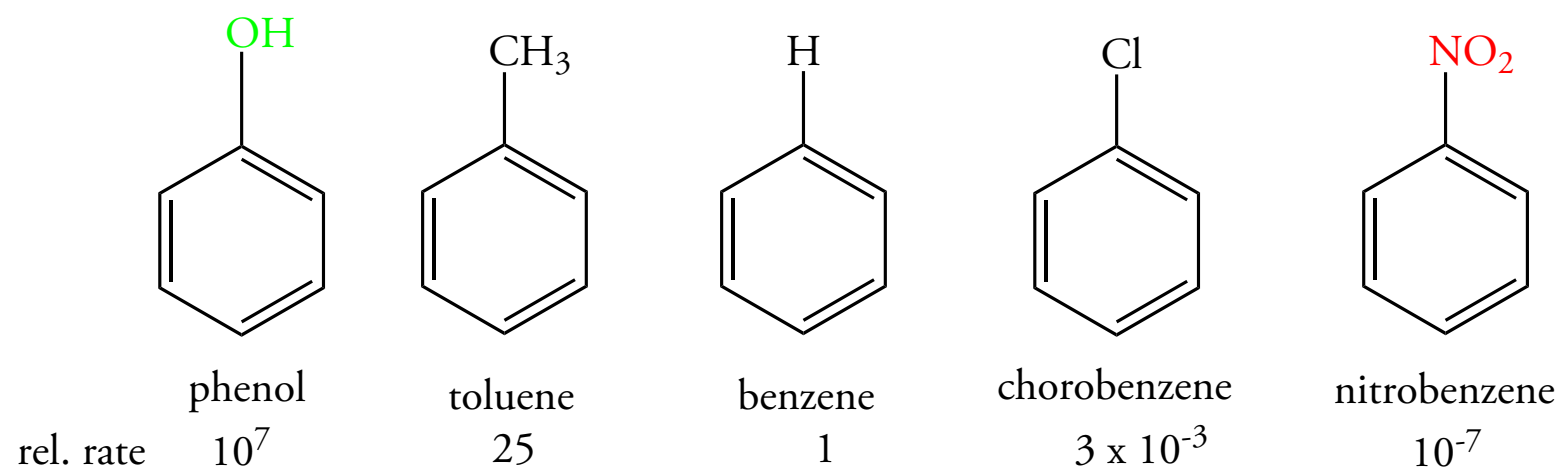
Weakly deactivating



Strongly deactivating

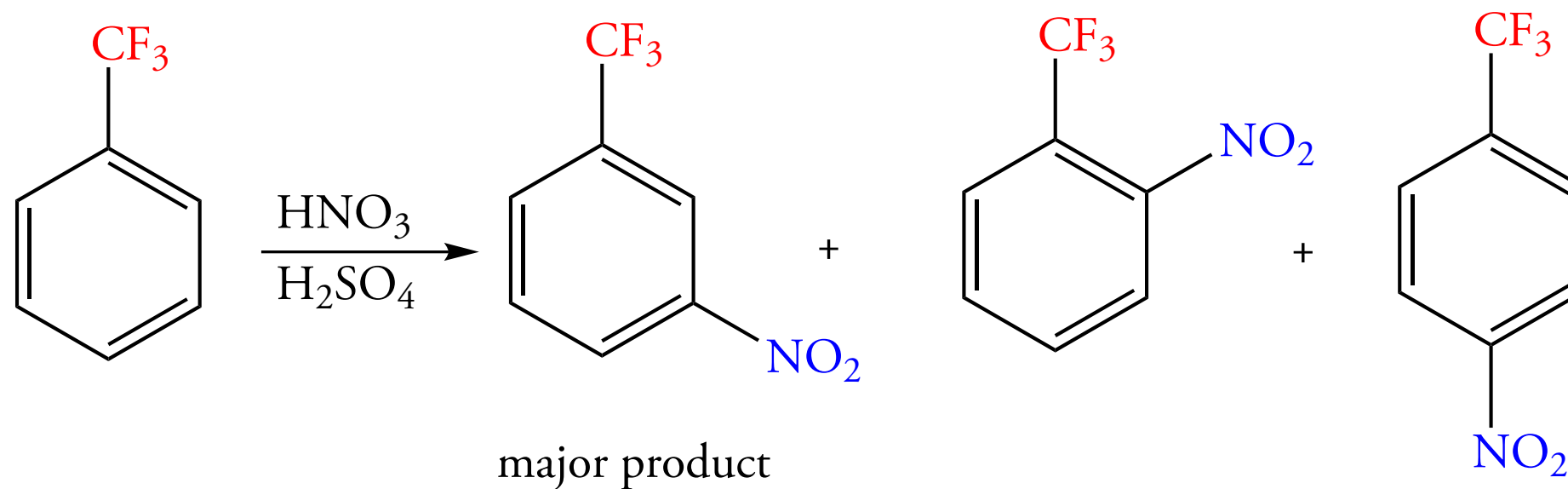
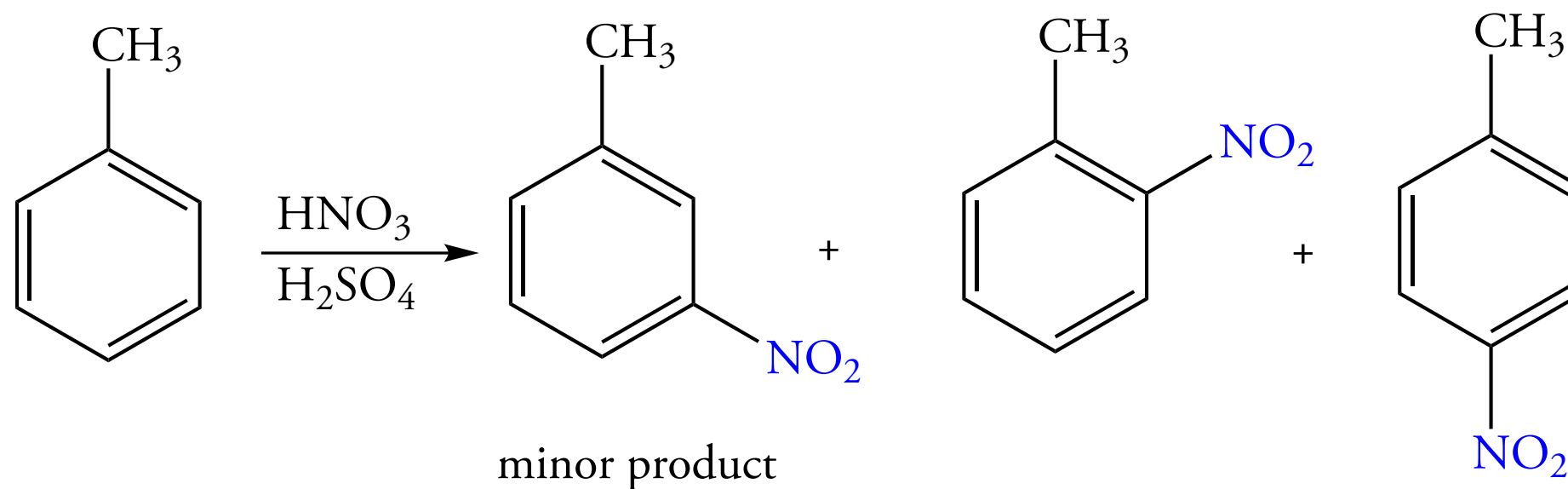


Relative rates of nitration of benzene and its derivatives

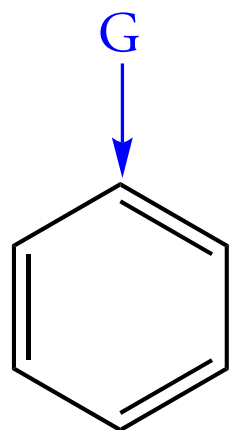


13.4 SUBSTITUENT EFFECTS ON THE REACTIVITY OF BENZENE RINGS

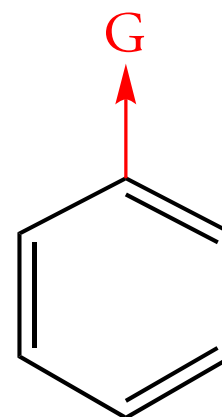
Orientation Effects of Ring Substituents



13.5 INTERPRETATION OF THE EFFECT OF SUBSTITUENTS ON REACTION RATES



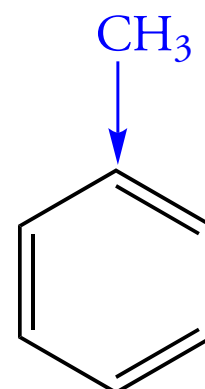
If G is an electron donating group, the ring gains electron density.



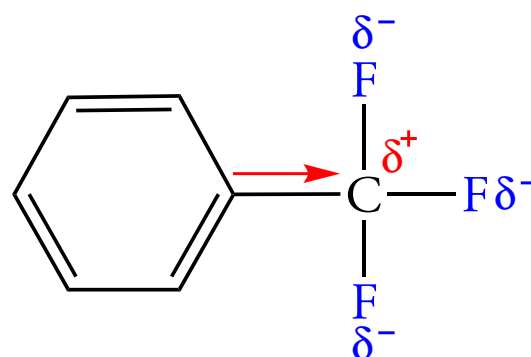
If G is an withdrawing group, the ring loses electron density.

13.5 INTERPRETATION OF THE EFFECT OF SUBSTITUENTS ON REACTION RATES

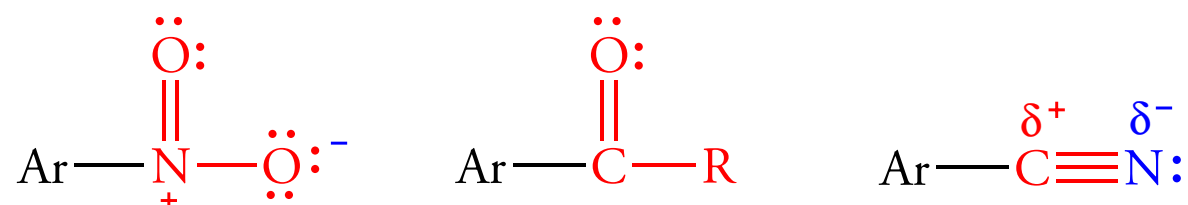
Inductive Effects of Substituents



An alkyl group donates electron density to the ring by an inductive effect.

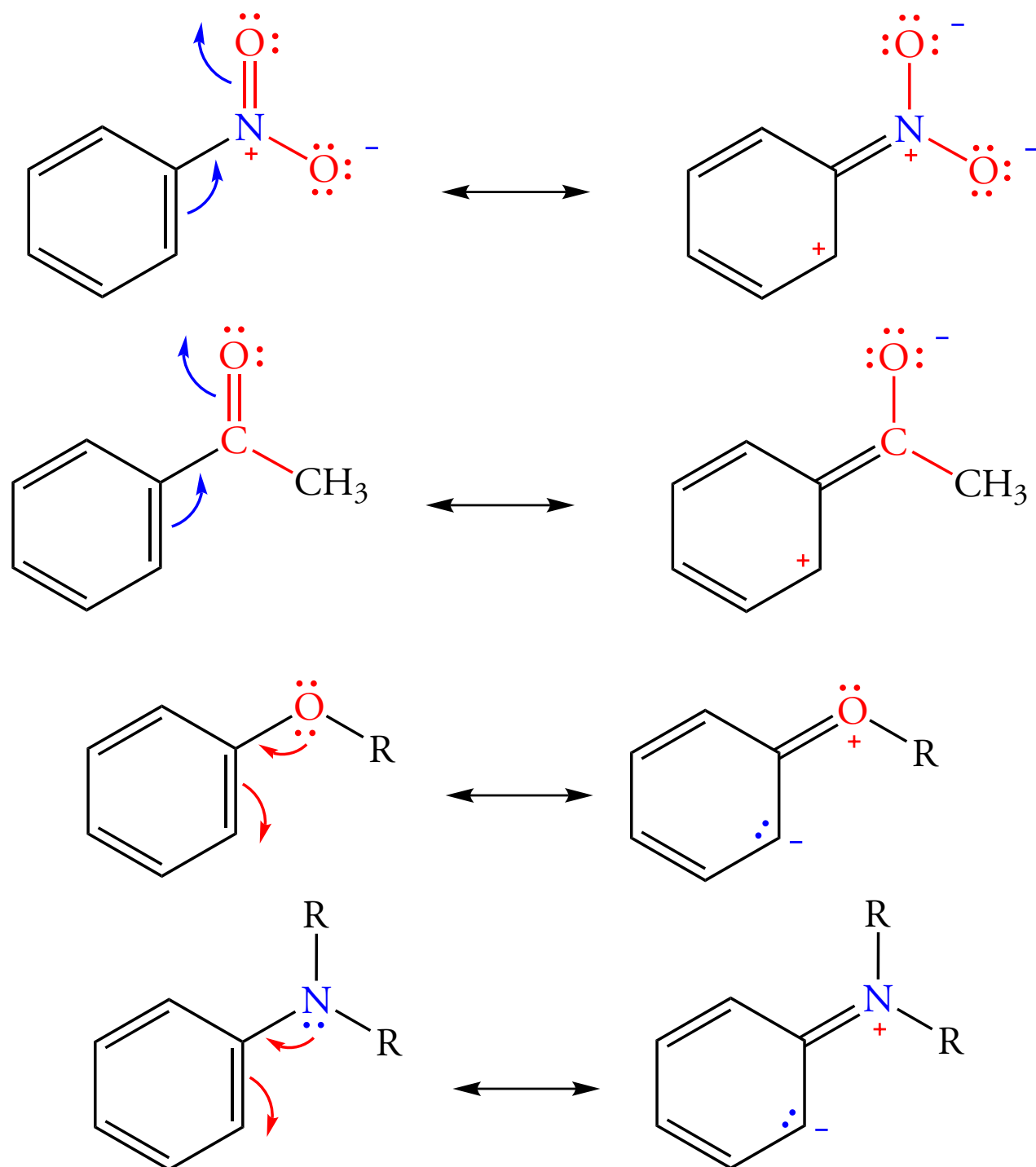


the trifluoromethyl group withdraws electron density from the benzene ring by an inductive effect.



13.5 INTERPRETATION OF THE EFFECT OF SUBSTITUENTS ON REACTION RATES

Resonance Effects of Substituents



13.6 INTERPRETATION OF DIRECTING EFFECTS, I

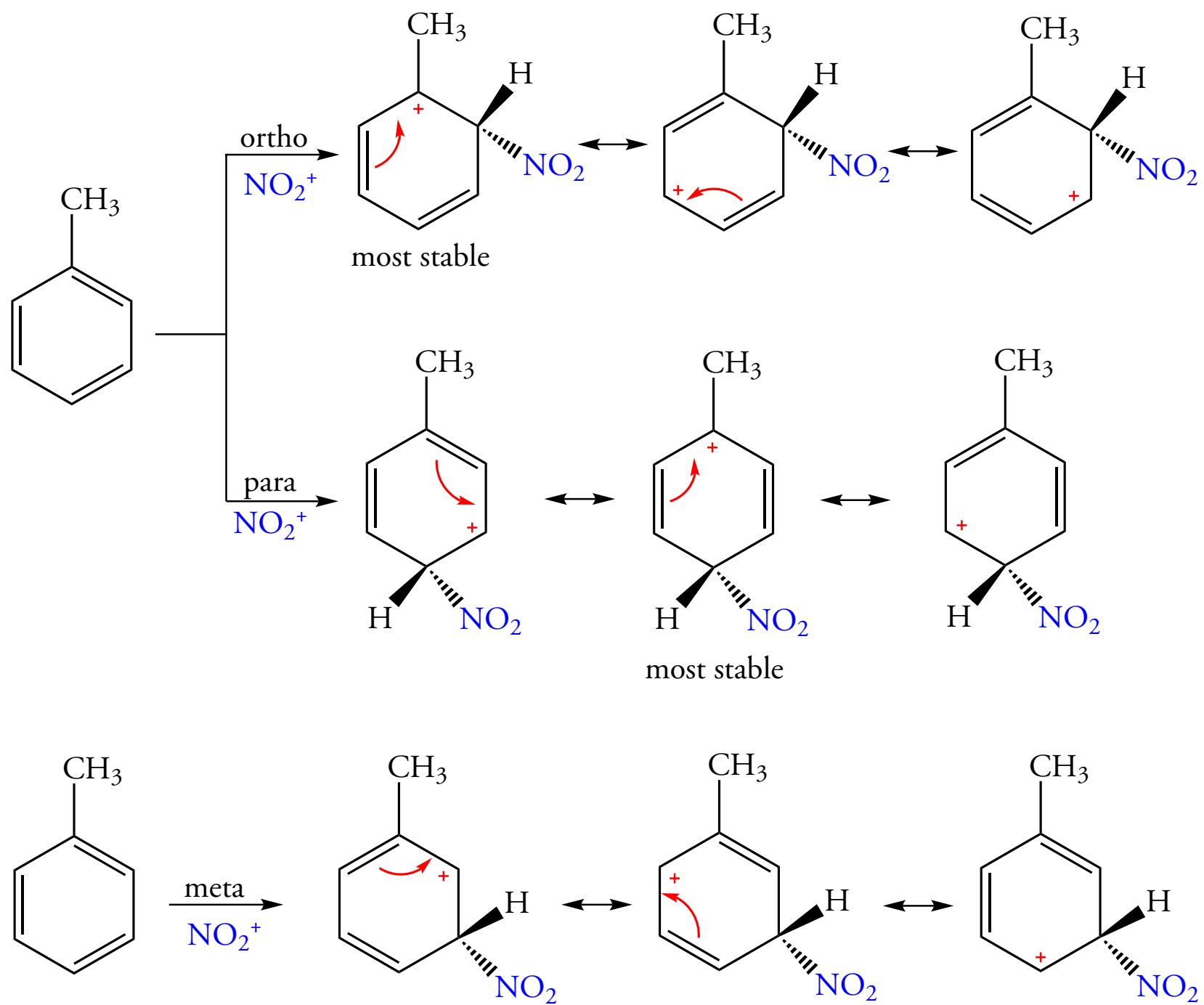
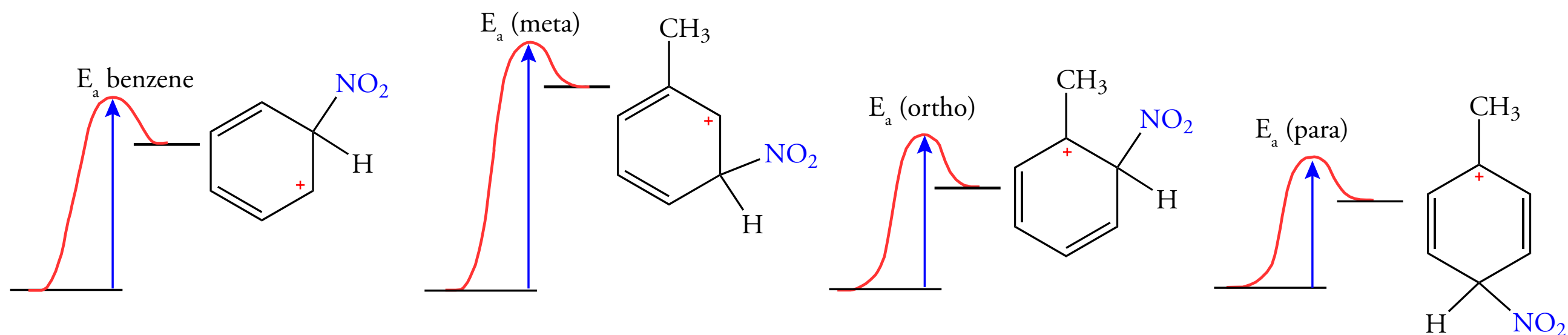
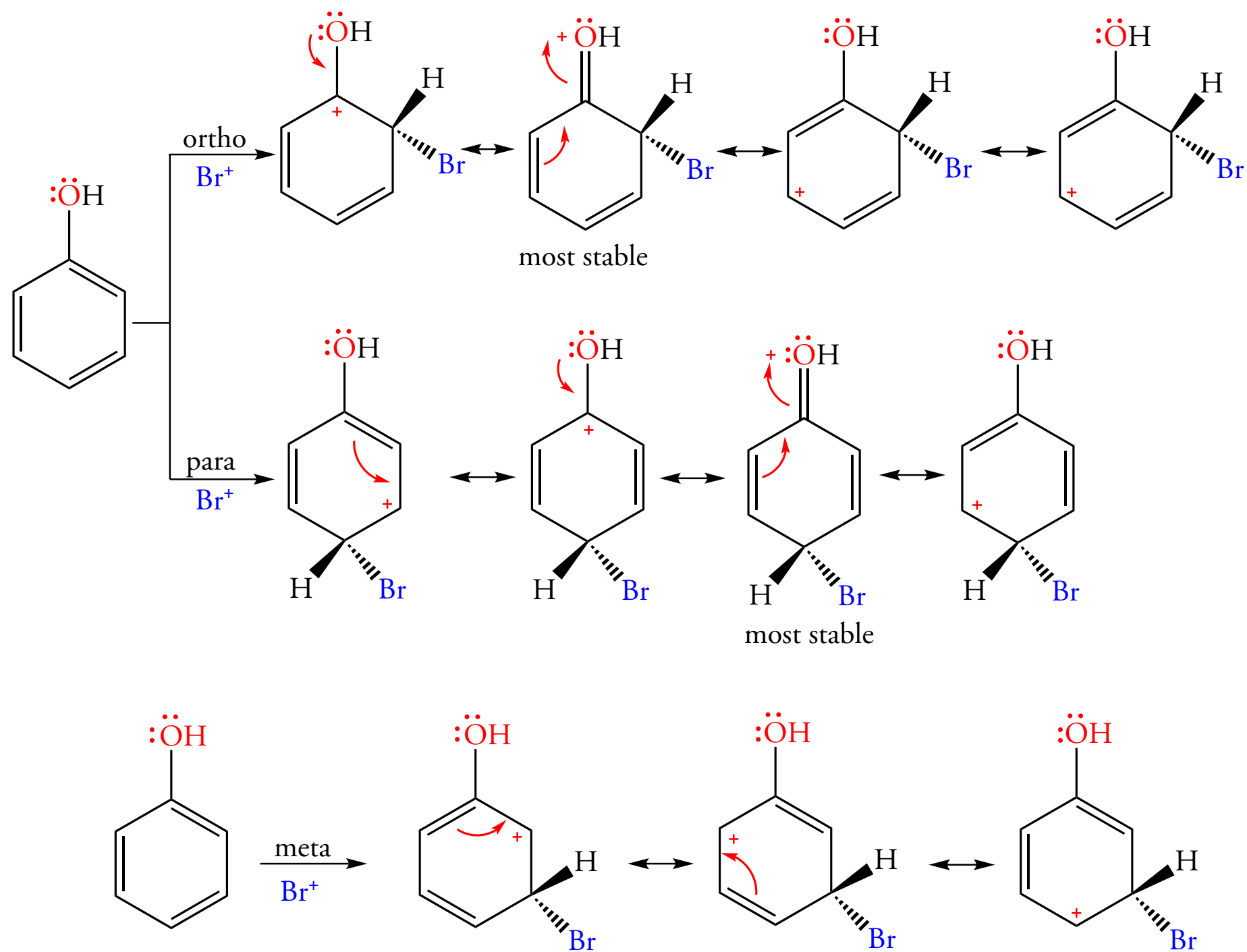


Figure 13.3 Transition State Energies for the Nitration of Toluene

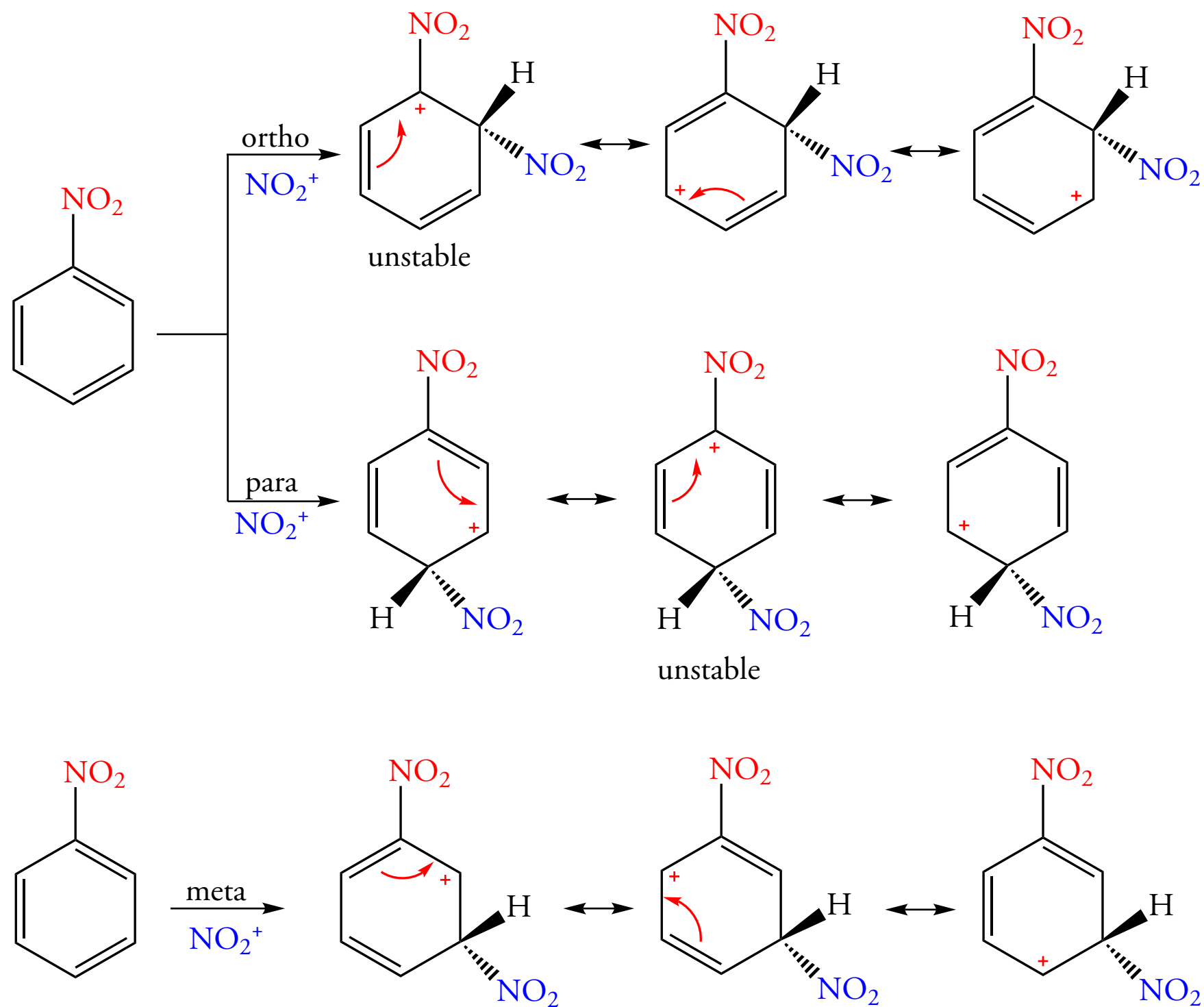
Substitution at any position of toluene occurs at a faster rate than substitution of benzene. However, substitution occurs faster at the ortho and para positions than at the meta position.



13.6 INTERPRETATION OF DIRECTING EFFECTS, II

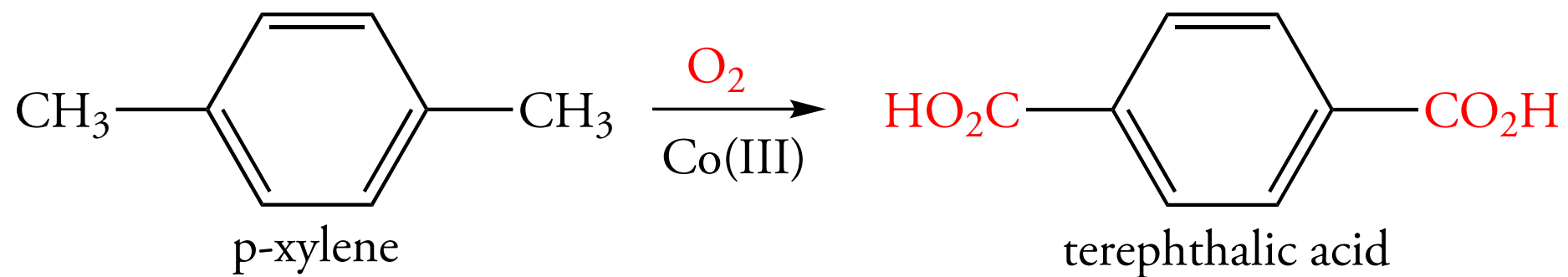
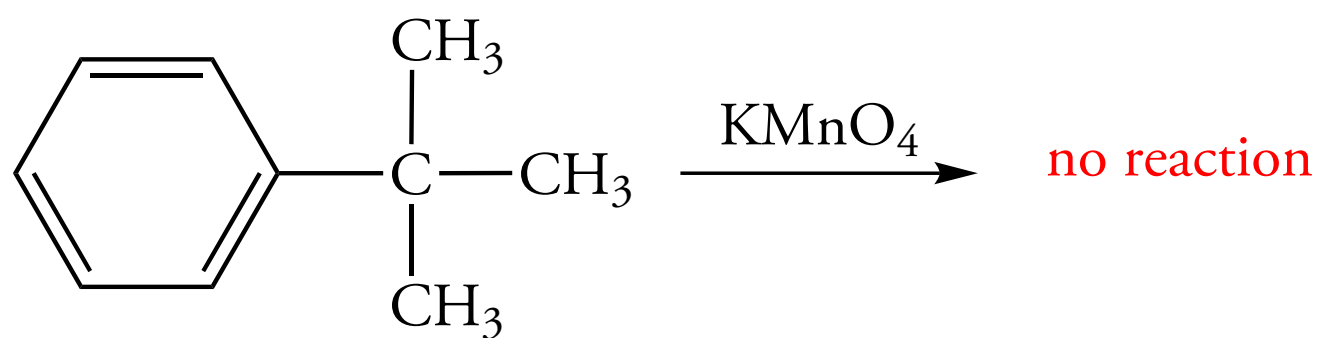
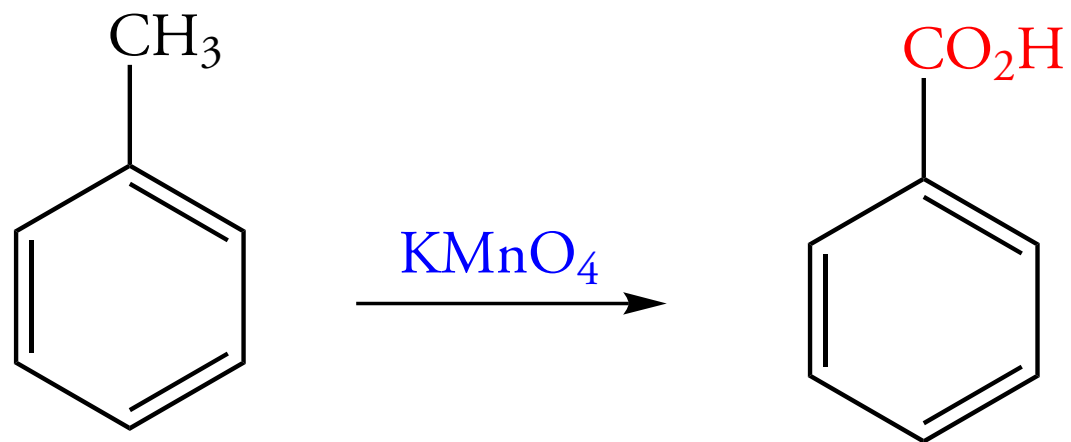


13.6 INTERPRETATION OF DIRECTING EFFECTS, III



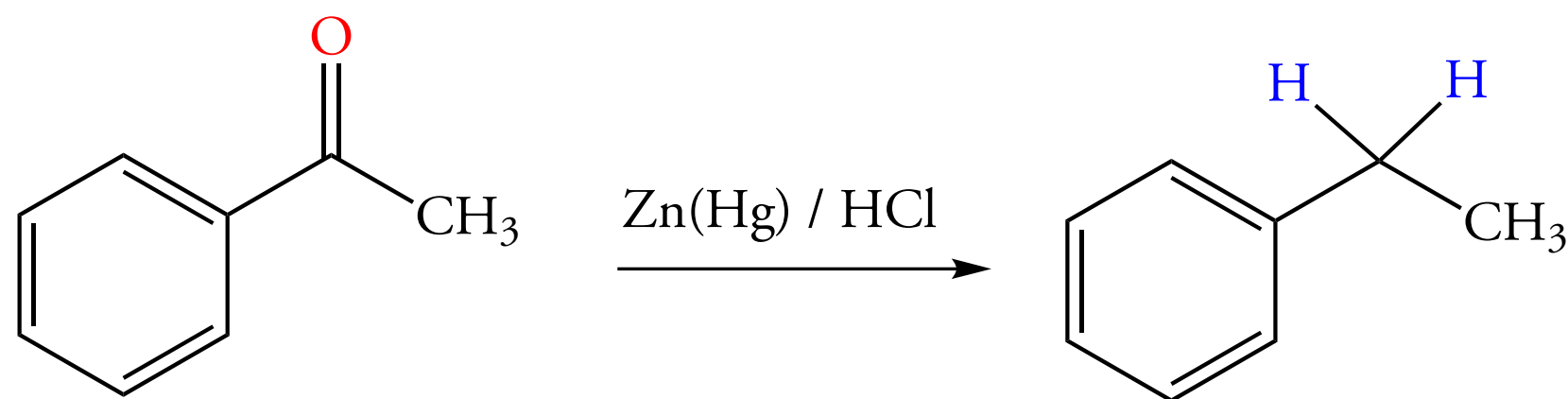
13.7 FUNCTIONAL GROUP MODIFICATION

Alkyl Side Chain Oxidation



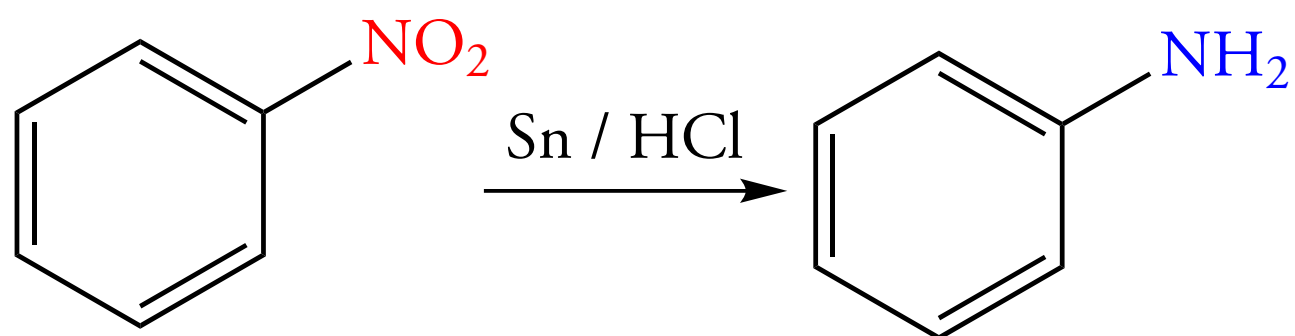
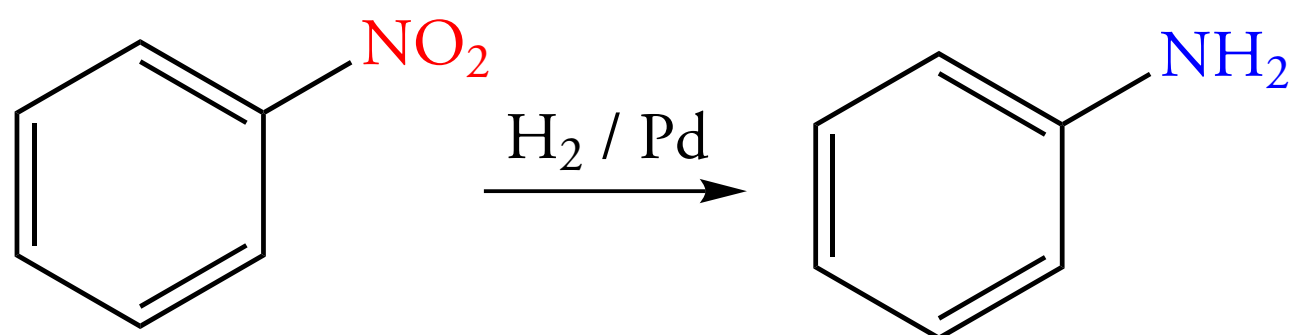
13.7 FUNCTIONAL GROUP MODIFICATION

Conversion of an Acyl Group to an Alkyl Group



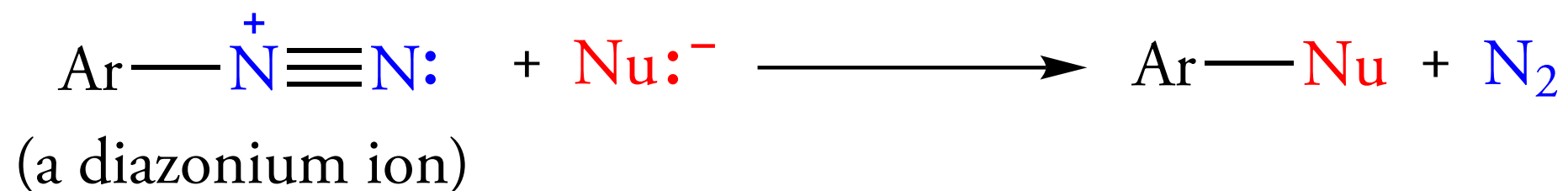
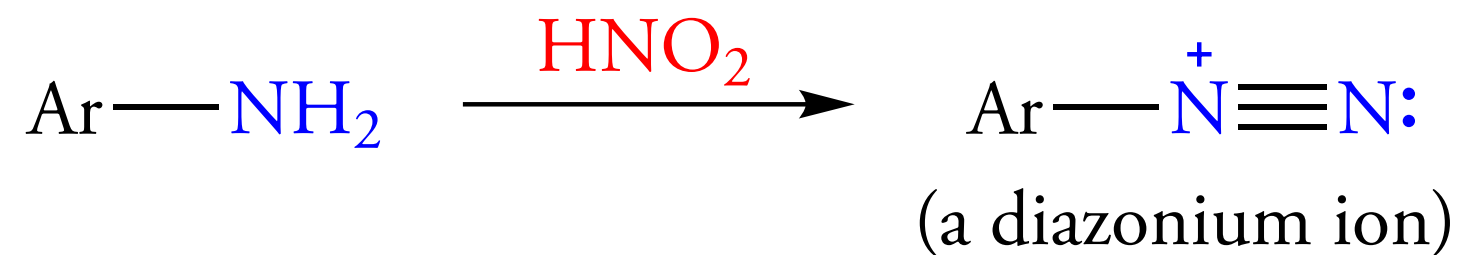
13.7 FUNCTIONAL GROUP MODIFICATION

Reduction of a Nitro Group to an Amino Group



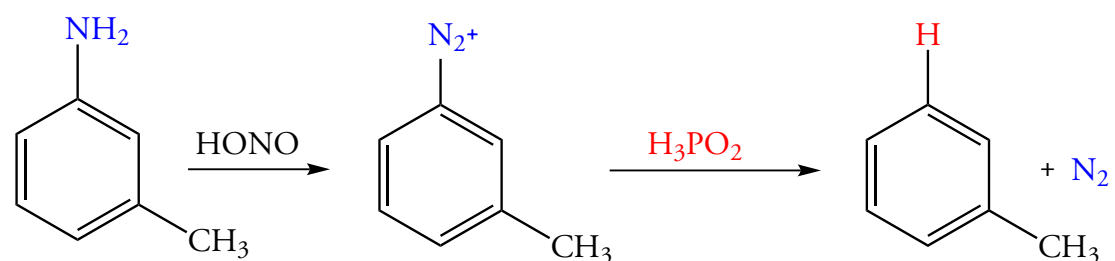
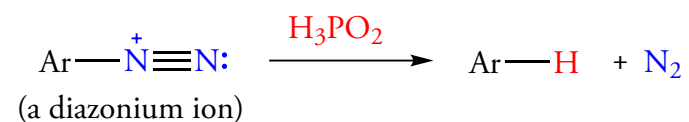
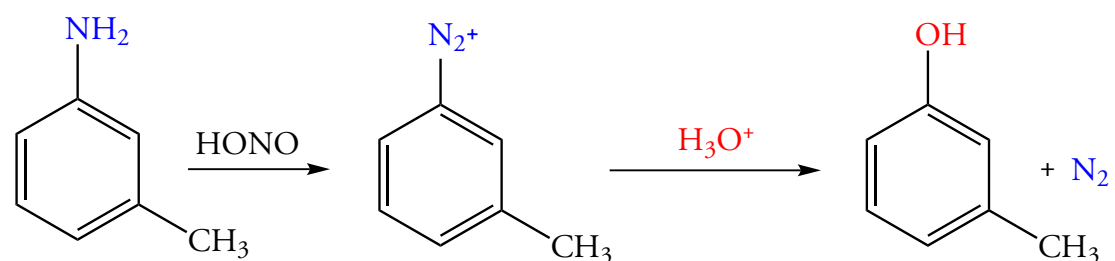
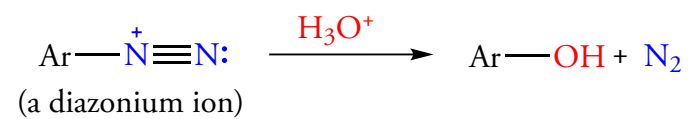
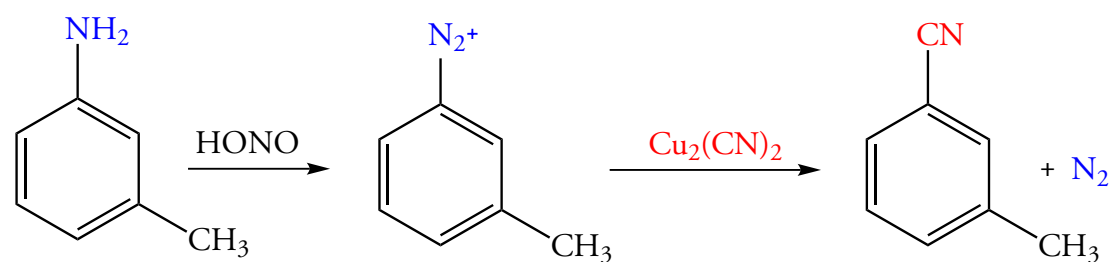
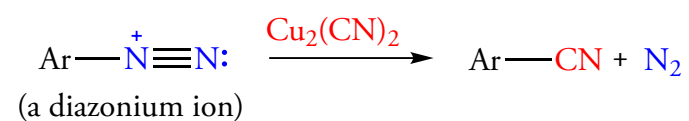
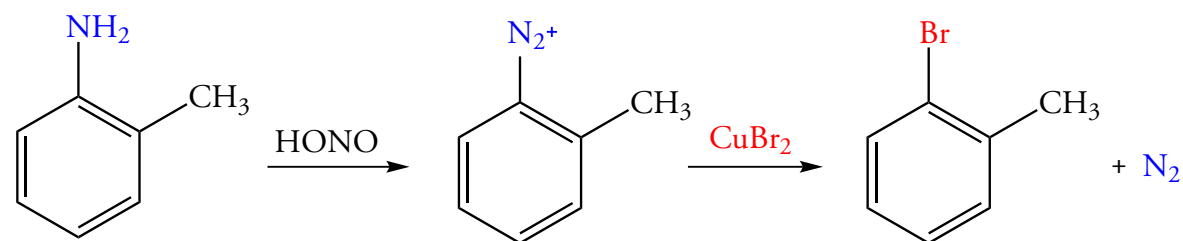
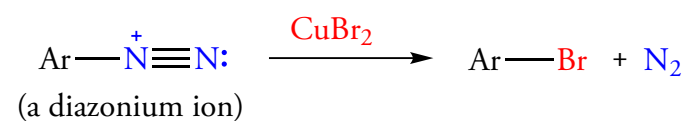
13.7 FUNCTIONAL GROUP MODIFICATION

Converting an Amino Group to a Diazonium Ion: The Sandmeyer Reaction

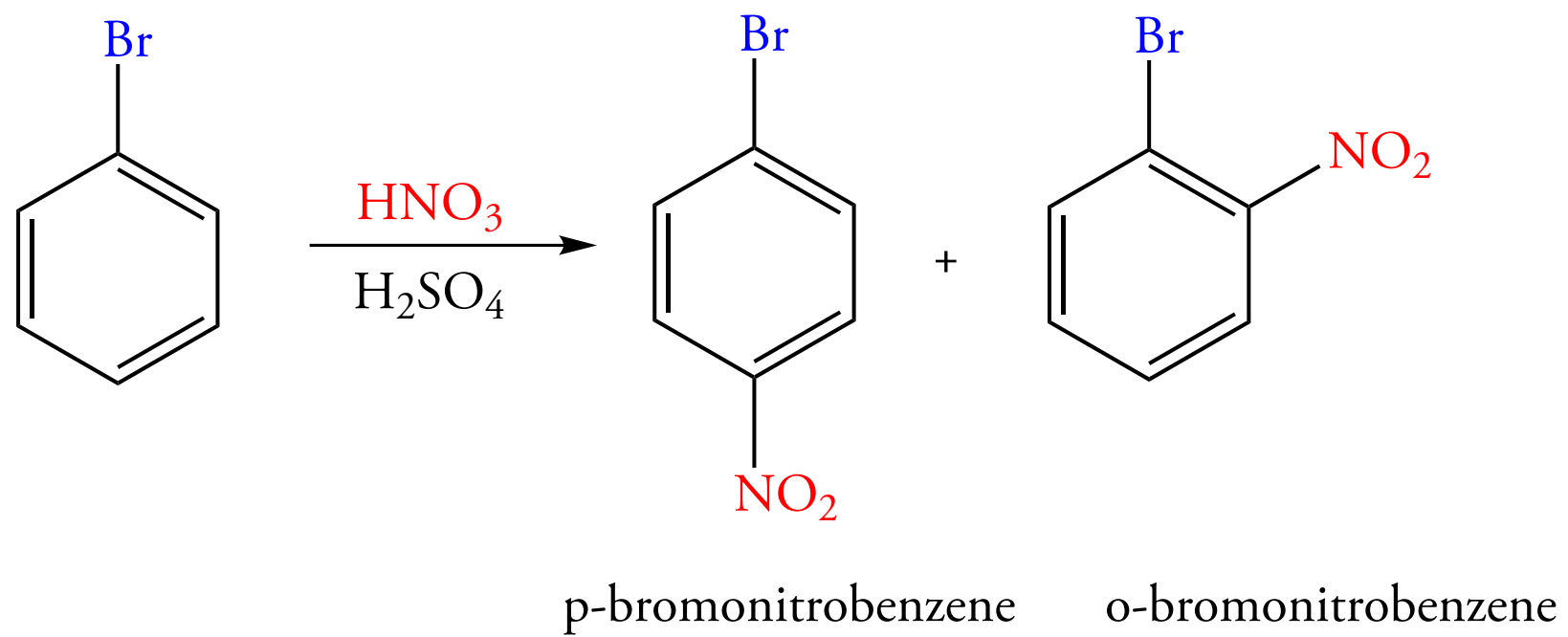
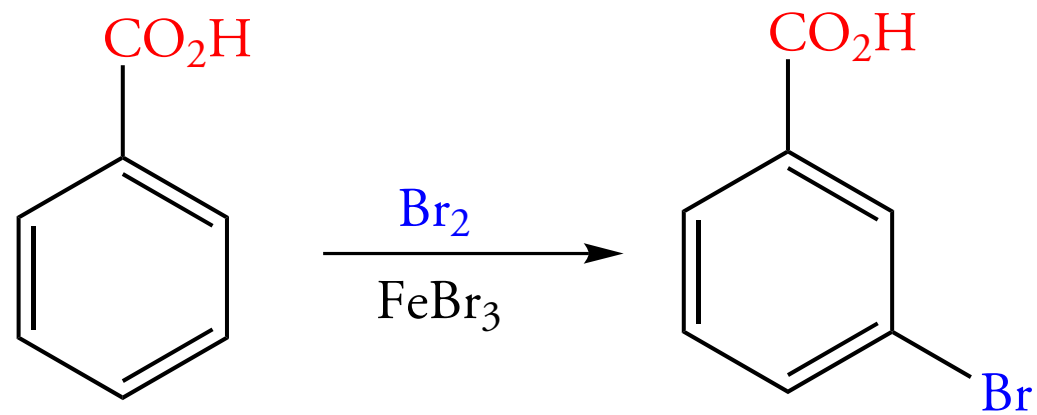


13.7 FUNCTIONAL GROUP MODIFICATION

Reactions of Diazonium Ions

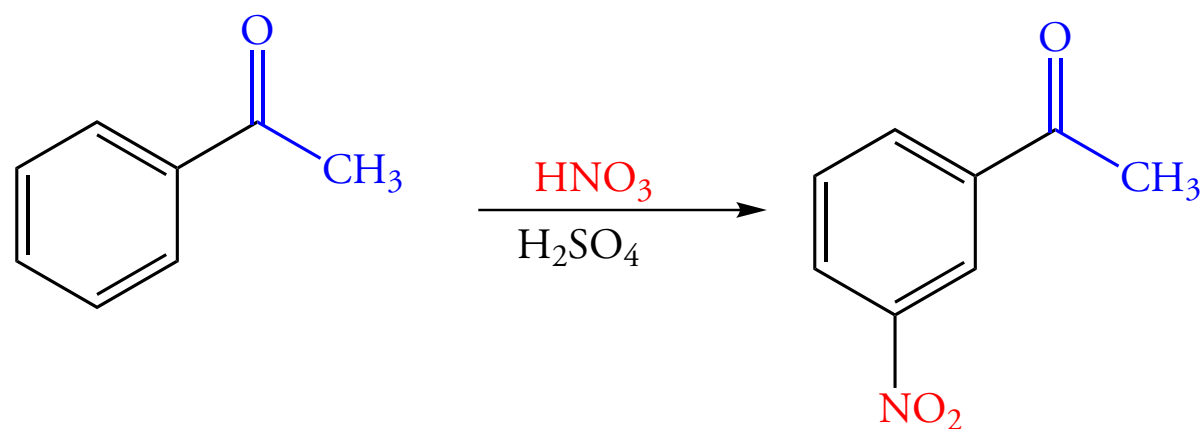
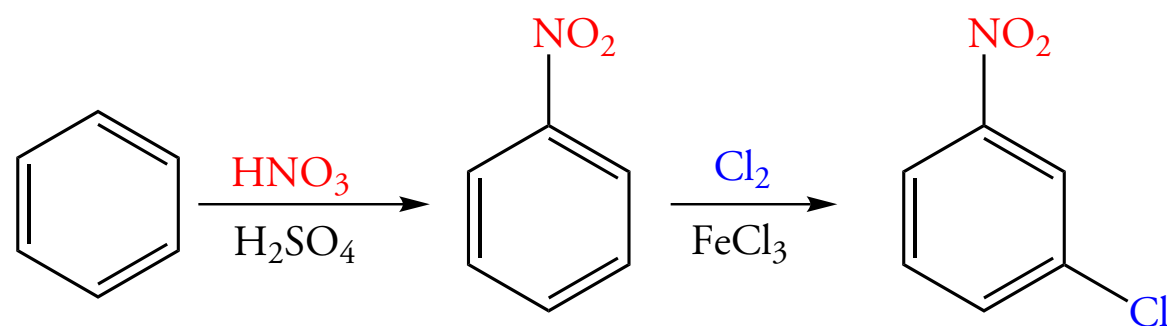
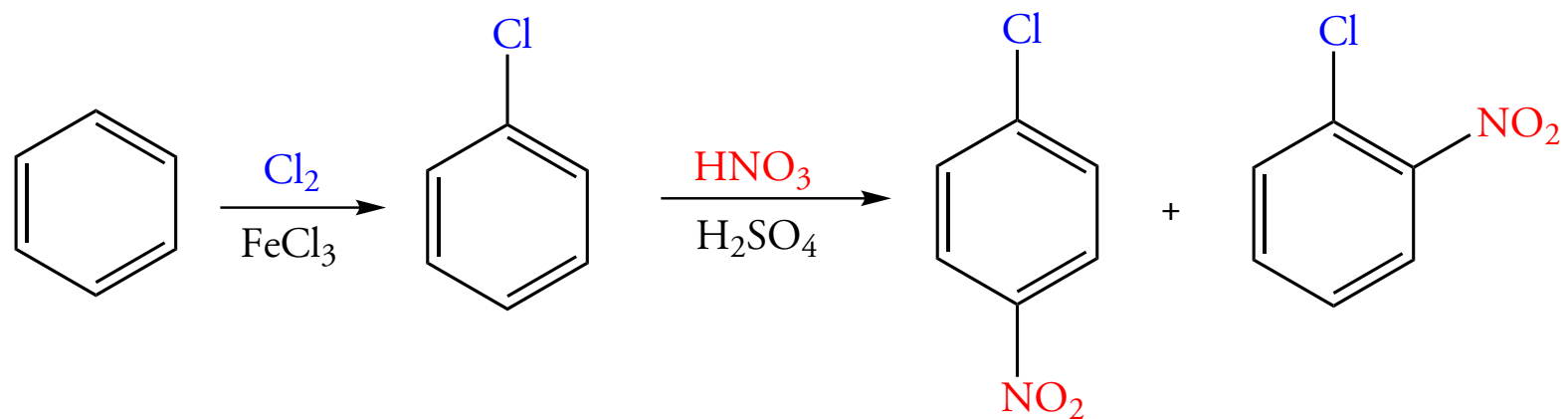


13.8 SYNTHESIS OF SUBSTITUTED AROMATIC COMPOUNDS



13.8 SYNTHESIS OF SUBSTITUTED AROMATIC COMPOUNDS

Strategies for Aromatic Synthesis: Order of Group Substitution



13.8 SYNTHESIS OF SUBSTITUTED AROMATIC COMPOUNDS

Modifying Ring Substituents

