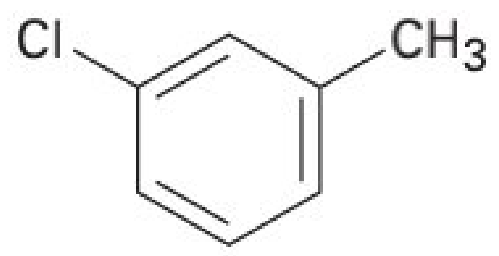
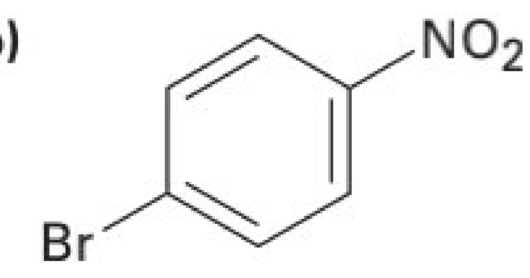
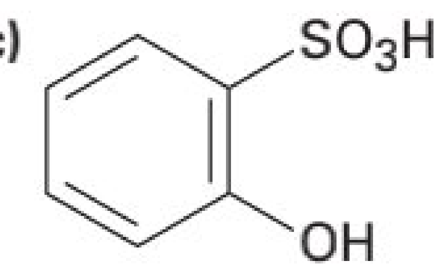
Solution Because the nitro group ($-NO_2$) and chloro group are on carbons 1 and 3, they have a meta relationship. Citing the two substituents in alphabetical order gives the IUPAC name *m*-chloronitrobenzene.

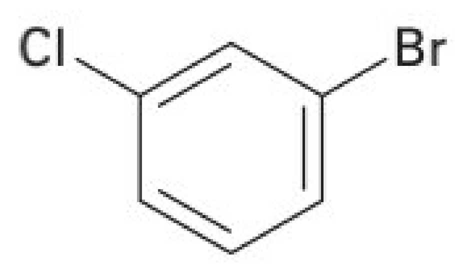
Problem 5.2 Tell whether the following compounds are ortho, meta, or para disubstituted:

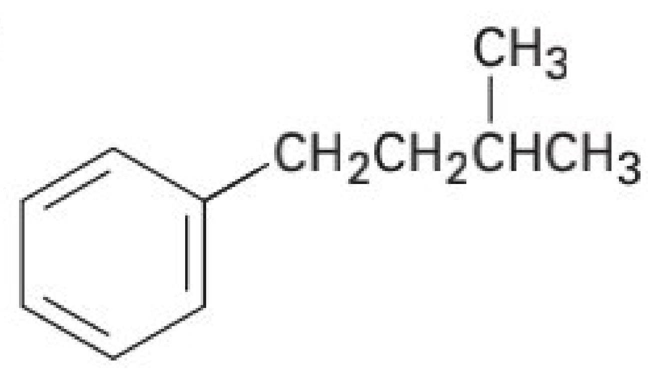
(a) 

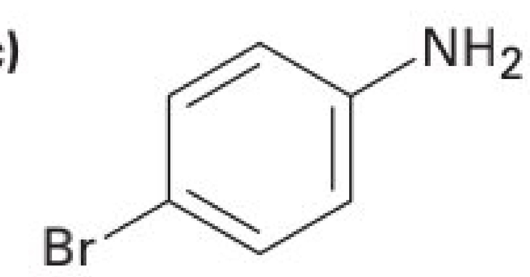
(b) 

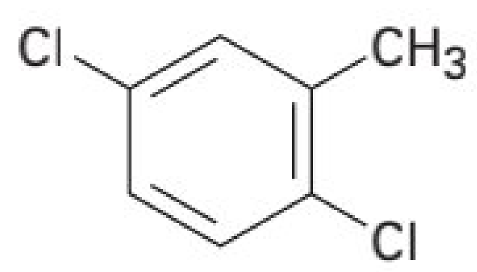
(c) 

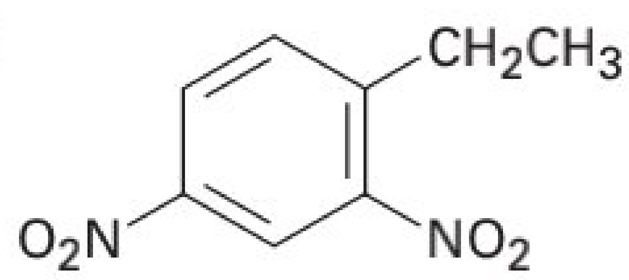
Problem 5.3 Give IUPAC names for the following compounds:

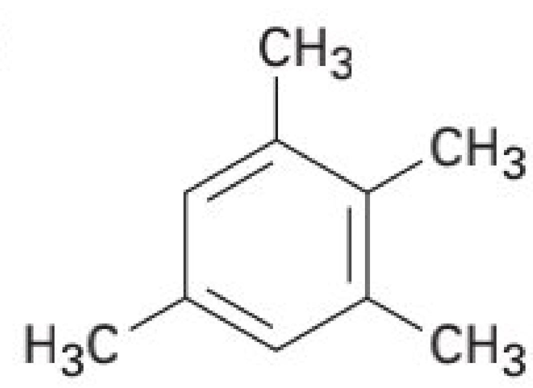
(a) 

(b) 

(c) 

(d) 

(e) 

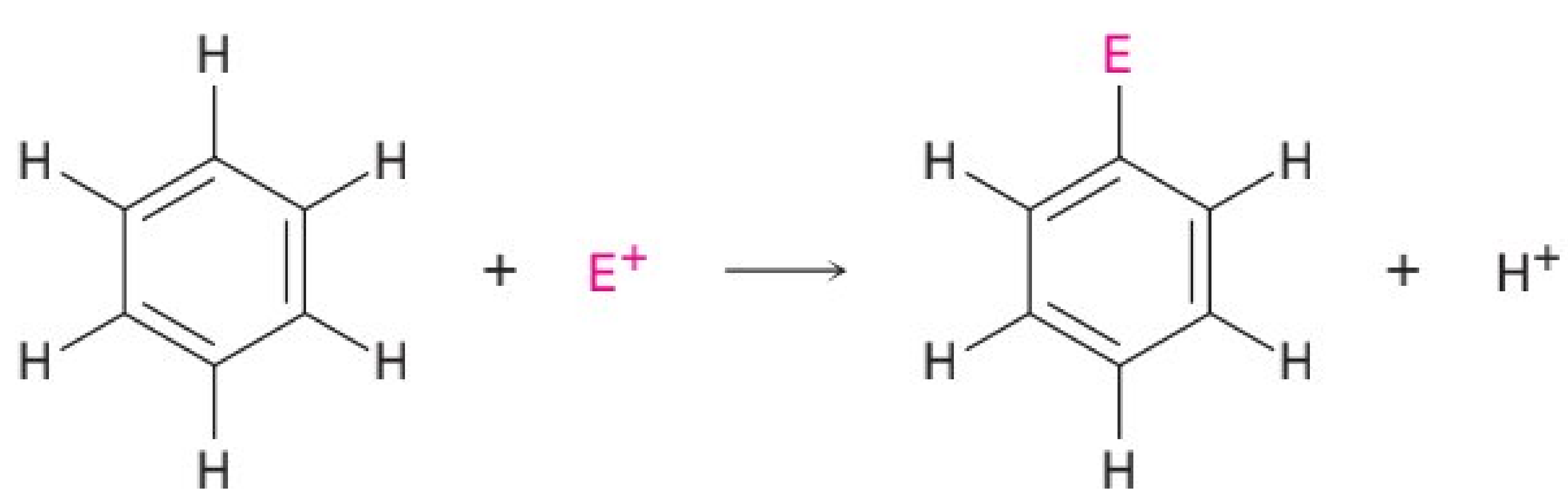
(f) 

Problem 5.4 Draw structures corresponding to the following IUPAC names:

(a) *p*-Bromochlorobenzene **(b)** *p*-Bromotoluene
(c) *m*-Chloroaniline **(d)** 1-Chloro-3,5-dimethylbenzene

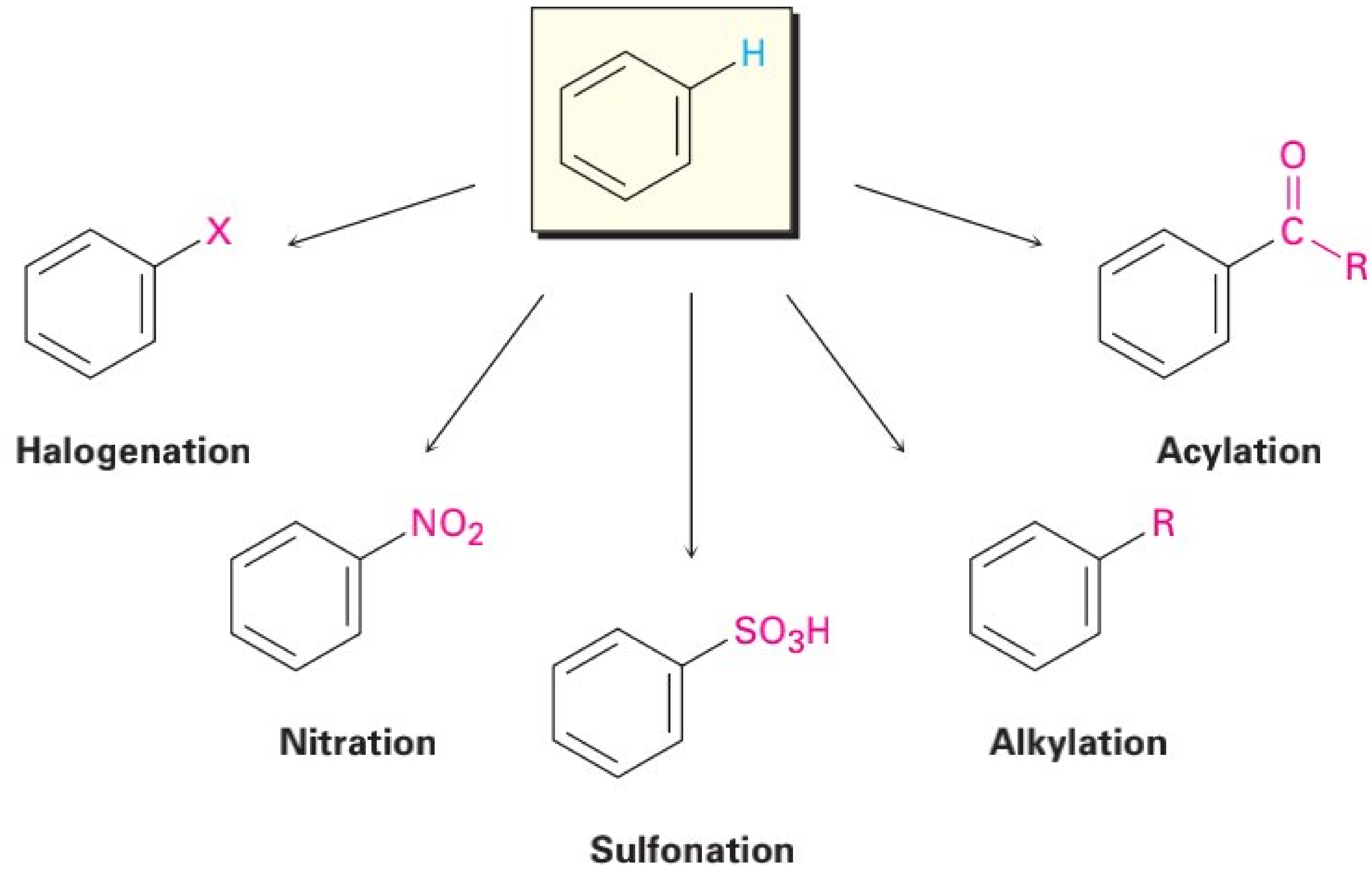
5.3 Electrophilic Aromatic Substitution Reactions: Bromination

The most common reaction of aromatic compounds is **electrophilic aromatic substitution**, a process in which an electrophile (E^+) reacts with an aromatic ring and substitutes for one of the hydrogens.

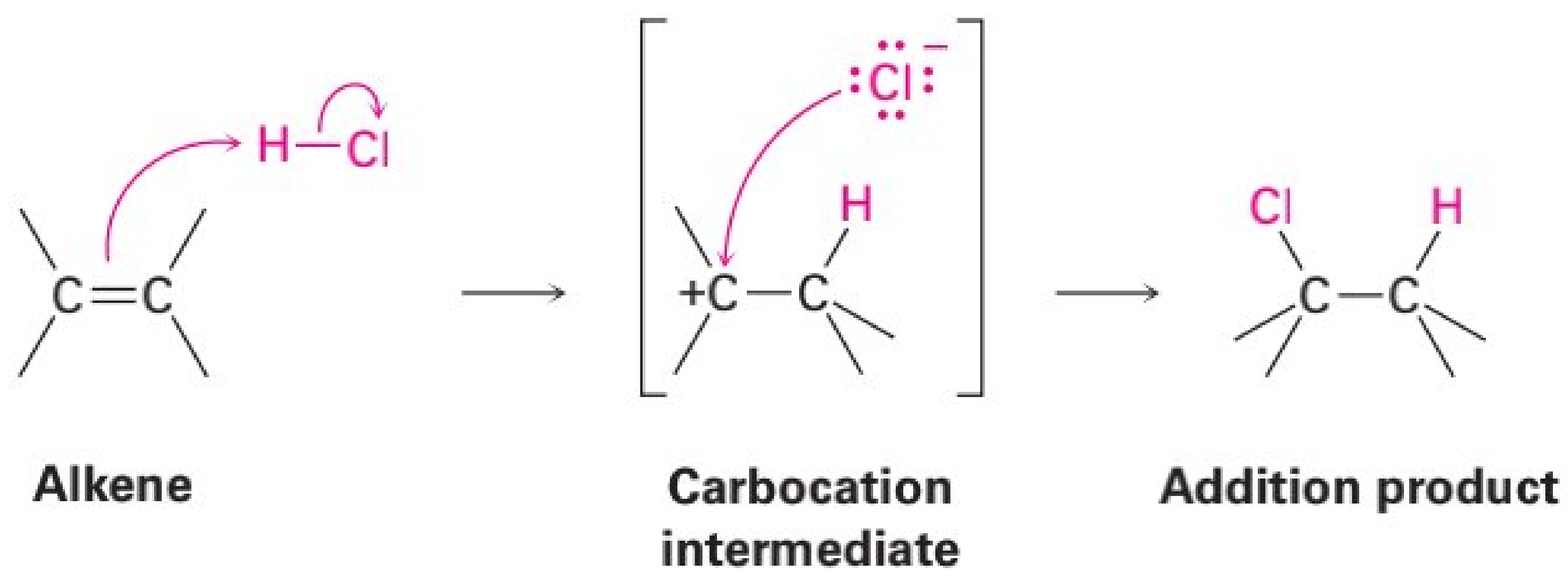


Many different substituents can be introduced onto the aromatic ring by electrophilic substitution. To list some possibilities, an aromatic ring can be substituted by a halogen (−Cl, −Br, −I), a nitro group ($-NO_2$), a sulfonic acid group ($-SO_3H$), an alkyl group (−R), or an acyl group (−COR). Starting from only a few simple materials, it's possible to prepare many thousands of substituted aromatic compounds (Figure 5.2).

Figure 5.2 Some electrophilic aromatic substitution reactions.

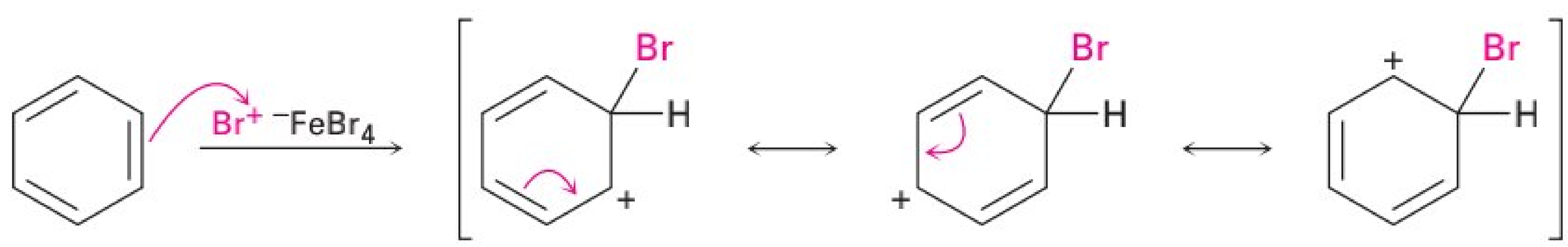


Before seeing how these electrophilic substitution reactions occur, let's briefly recall what was said in Sections 3.7 and 3.8 about electrophilic addition reactions of alkenes. When a reagent such as HCl adds to an alkene, the electrophilic H^+ approaches the π electrons of the double bond and forms a bond to one carbon, leaving a positive charge at the other carbon. This carbocation intermediate then reacts with the nucleophilic Cl^- ion to yield the addition product.



An electrophilic aromatic substitution reaction begins in a similar way, but there are a number of differences. One difference is that aromatic rings are less reactive toward electrophiles than alkenes are. For example, Br_2 in CH_2Cl_2 solution reacts instantly with most alkenes but does not react with benzene at room temperature. For bromination of benzene to take place, a catalyst such as $FeBr_3$ is needed. The catalyst makes the Br_2 molecule more electrophilic by reacting with it to give $FeBr_4^-$ and Br^+. The electrophilic Br^+ then reacts with the electron-rich (nucleophilic) benzene ring to yield a nonaromatic carbocation intermediate. This carbocation is doubly allylic (Section 4.9) and is a hybrid of three resonance forms.

$$Br{-}Br \; + \; FeBr_3 \longrightarrow Br^+ \; ^-FeBr_4$$

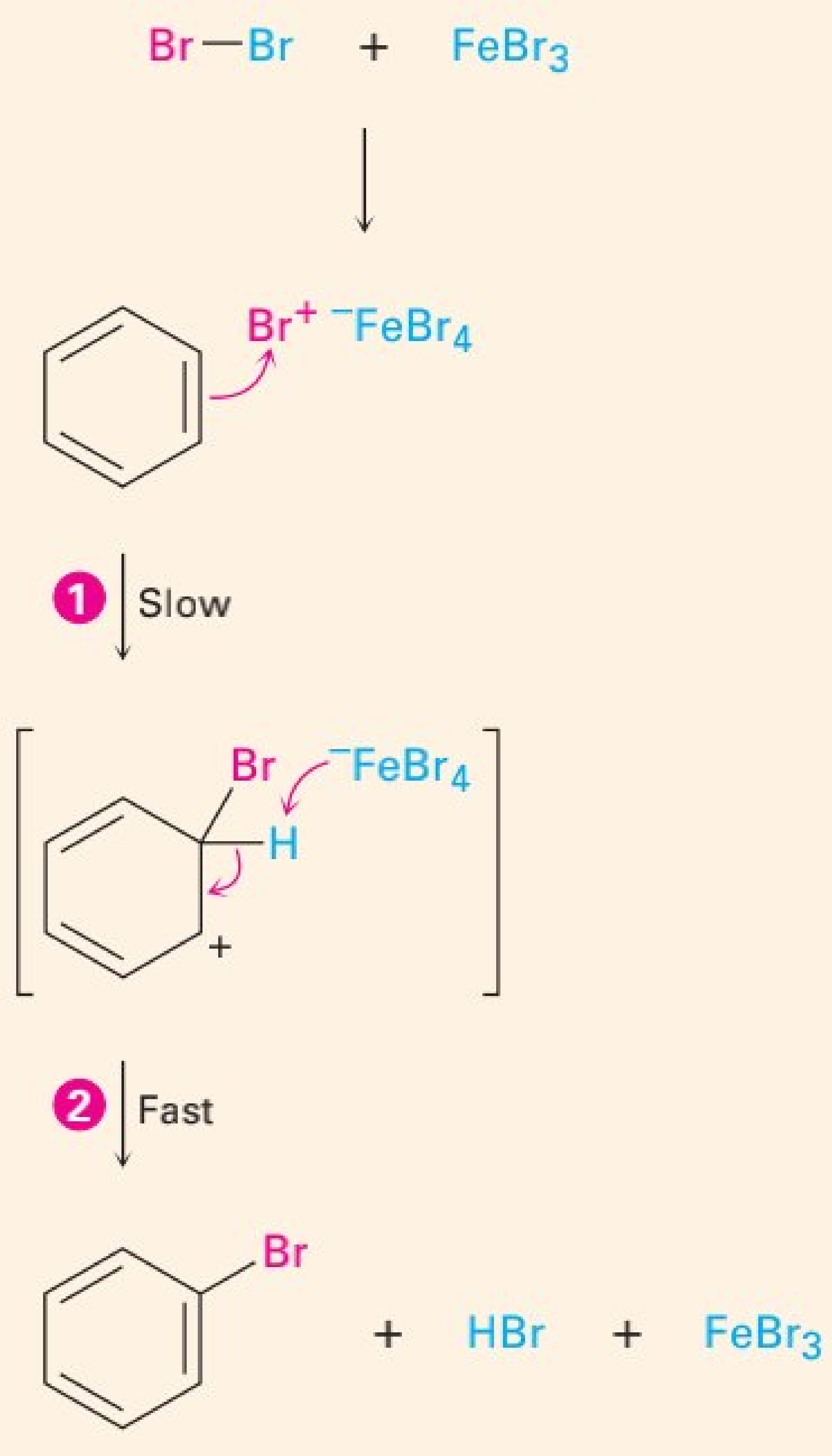


Although more stable than a typical nonallylic carbocation because of resonance, the intermediate in electrophilic aromatic substitution is much less stable than the starting benzene ring itself. Thus, reaction of an electrophile with a benzene ring has a relatively high activation energy and is rather slow.

Another difference between alkene addition reactions and aromatic substitution reactions occurs after the electrophile has added to the benzene ring and the carbocation intermediate has formed. Instead of adding Br^- to give an addition product, the carbocation intermediate loses H^+ from the bromine-bearing carbon to give a substitution product. The net effect is the substitution of H^+ by Br^+ by the overall mechanism shown in Figure 5.3.

MECHANISM

Figure 5.3 **The mechanism of the electrophilic bromination of benzene. The reaction occurs in two steps and involves a resonance-stabilized carbocation intermediate.**



1 An electron pair from the benzene ring attacks the positively polarized bromine, forming a new C–Br bond and leaving a nonaromatic carbocation intermediate.

2 A base removes H^+ from the carbocation intermediate, and the neutral substitution product forms as two electrons from the C–H bond move to re-form the aromatic ring.

Why does the reaction of Br_2 with benzene take a different course than its reaction with an alkene? The answer is straightforward: if *addition* occurred, the resonance stabilization of the aromatic ring would be lost and the overall reaction would be energetically unfavorable. When *substitution* occurs, though, the resonance stability of the aromatic ring is retained and