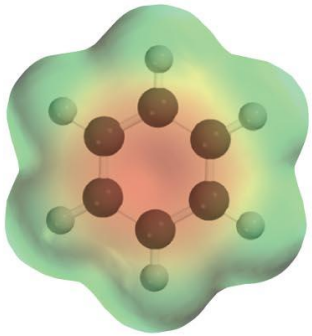
Organic Chemistry
2th Edition
Paula Yurkanis Bruice

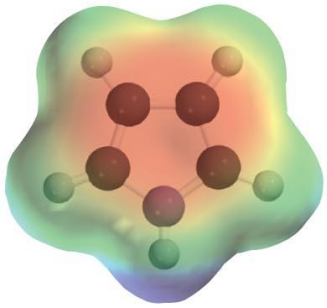
Chapter 8

Aromaticity • Reactions of Benzene

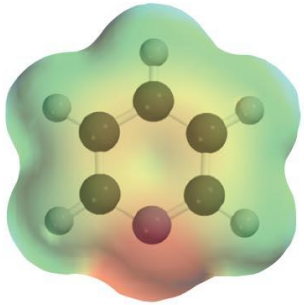
7.1-3



Benzene



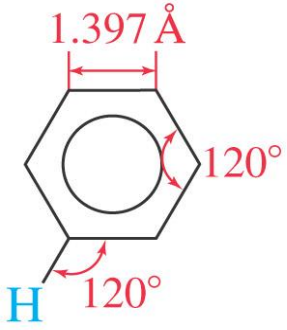
Pyrrole

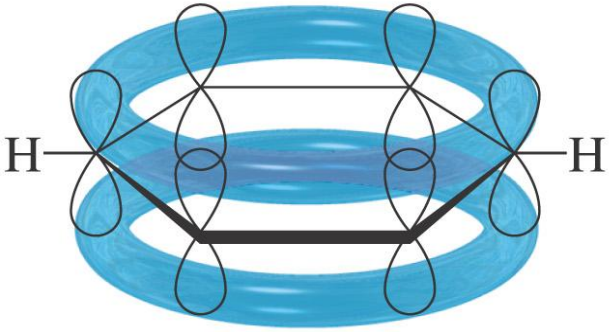


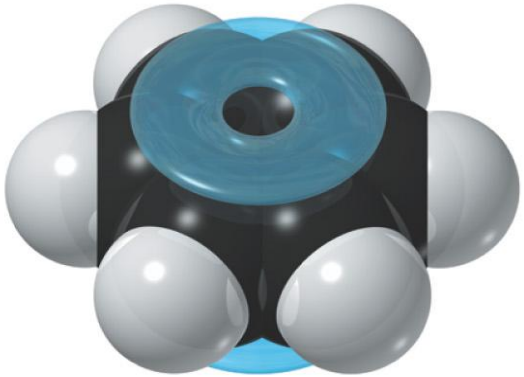
Pyridine

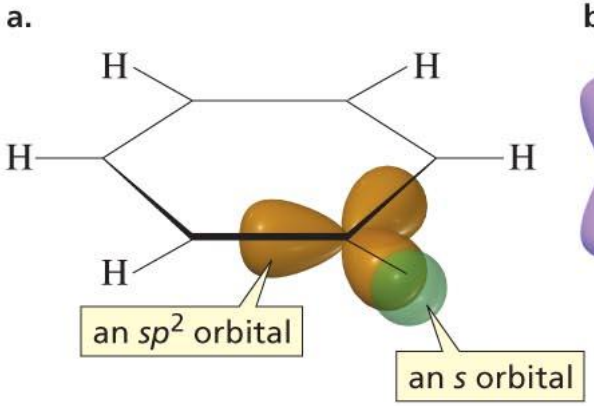
Benzene Has Delocalized Electrons

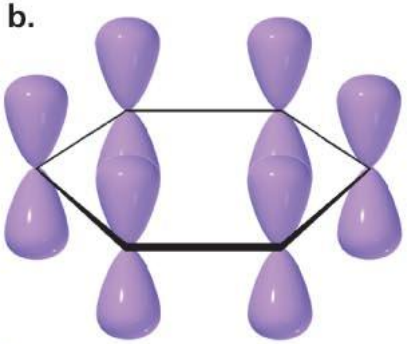
- A planar molecule
- Has six identical carbon–carbon bonds
- Each p electron is shared by all six carbons
- The p electrons are delocalized

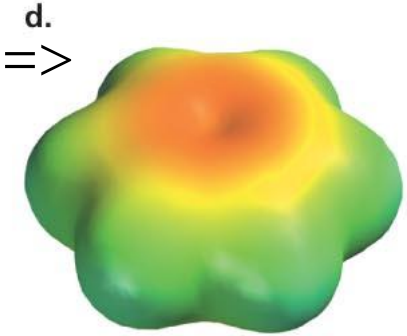




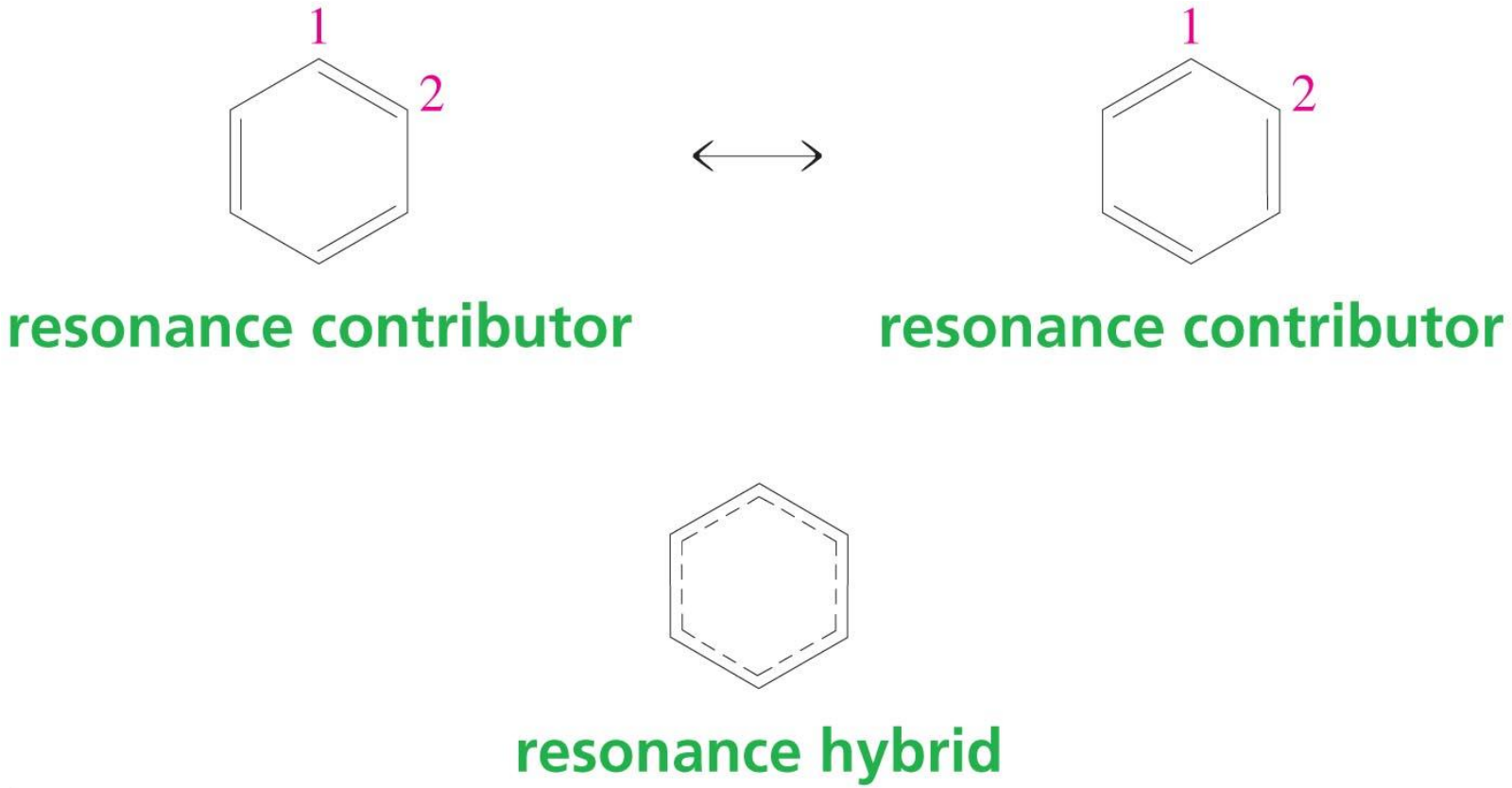








Resonance Contributors and the Resonance Hybrid

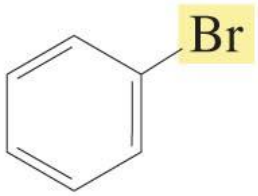


Resonance contributors do not depict any real electron distribution

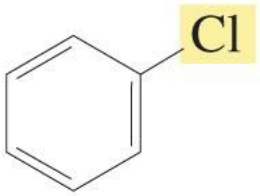
8.4

Nomenclature of Monosubstituted Benzenes

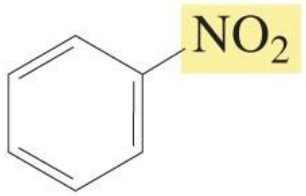
Some are named by attaching “benzene” after the name of the substituent:



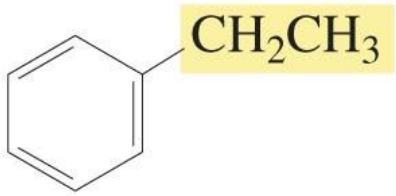
bromobenzene



chlorobenzene

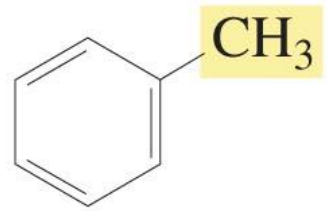


nitrobenzene
used as a solvent
in shoe polish

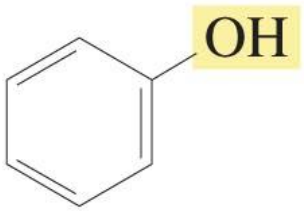


ethylbenzene

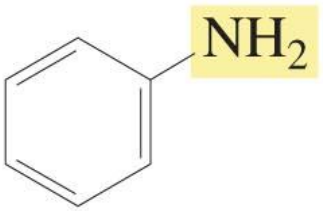
Some have to be memorized:



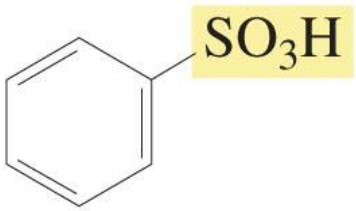
toluene



phenol



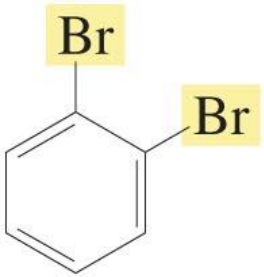
aniline



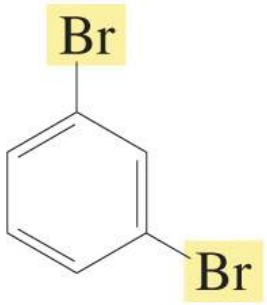
benzenesulfonic acid

Nomenclature of Substituted Benzenes

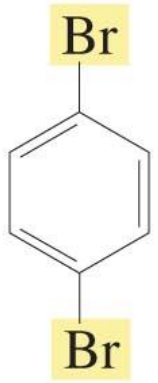
In disubstituted benzenes, the relative positions of the two substituents are indicated by numbers or by prefixes:



1,2-dibromobenzene
***ortho*-dibromobenzene**
***o*-dibromobenzene**

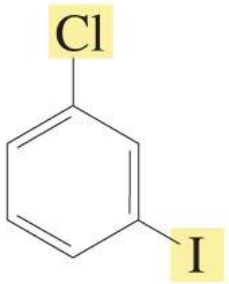


1,3-dibromobenzene
***meta*-dibromobenzene**
***m*-dibromobenzene**

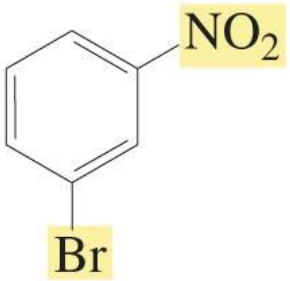


1,4-dibromobenzene
***para*-dibromobenzene**
***p*-dibromobenzene**

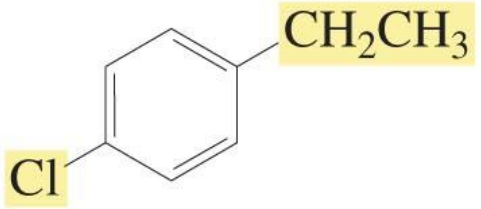
The two substituents are listed in alphabetical order:



1-chloro-3-iodobenzene
***meta*-chloroiodobenzene**
not
1-iodo-3-chlorobenzene or
***meta*-iodochlorobenzene**

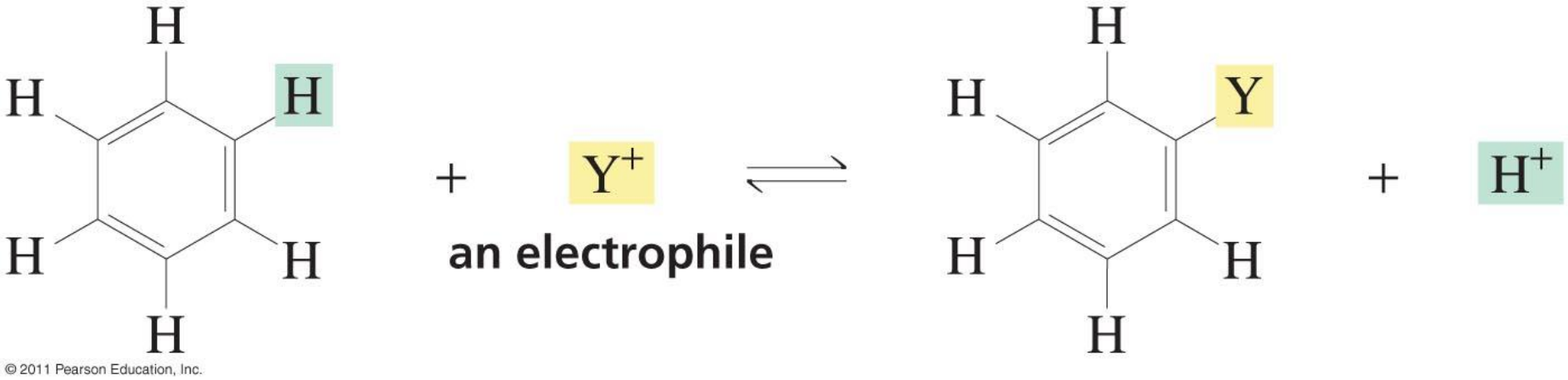


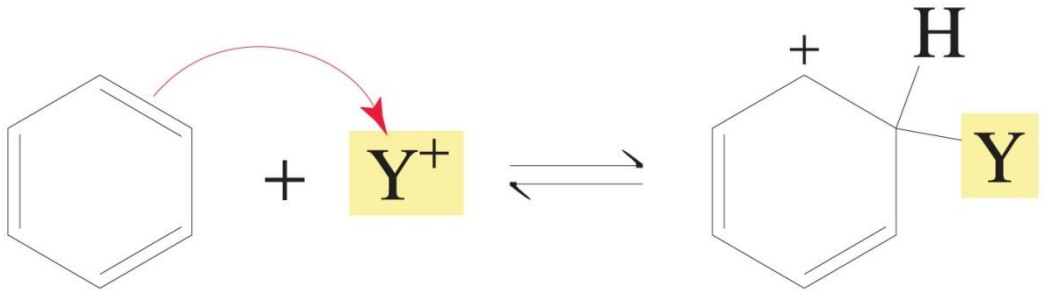
1-bromo-3-nitrobenzene
***meta*-bromonitrobenzene**



1-chloro-4-ethylbenzene
***para*-chloroethylbenzene**

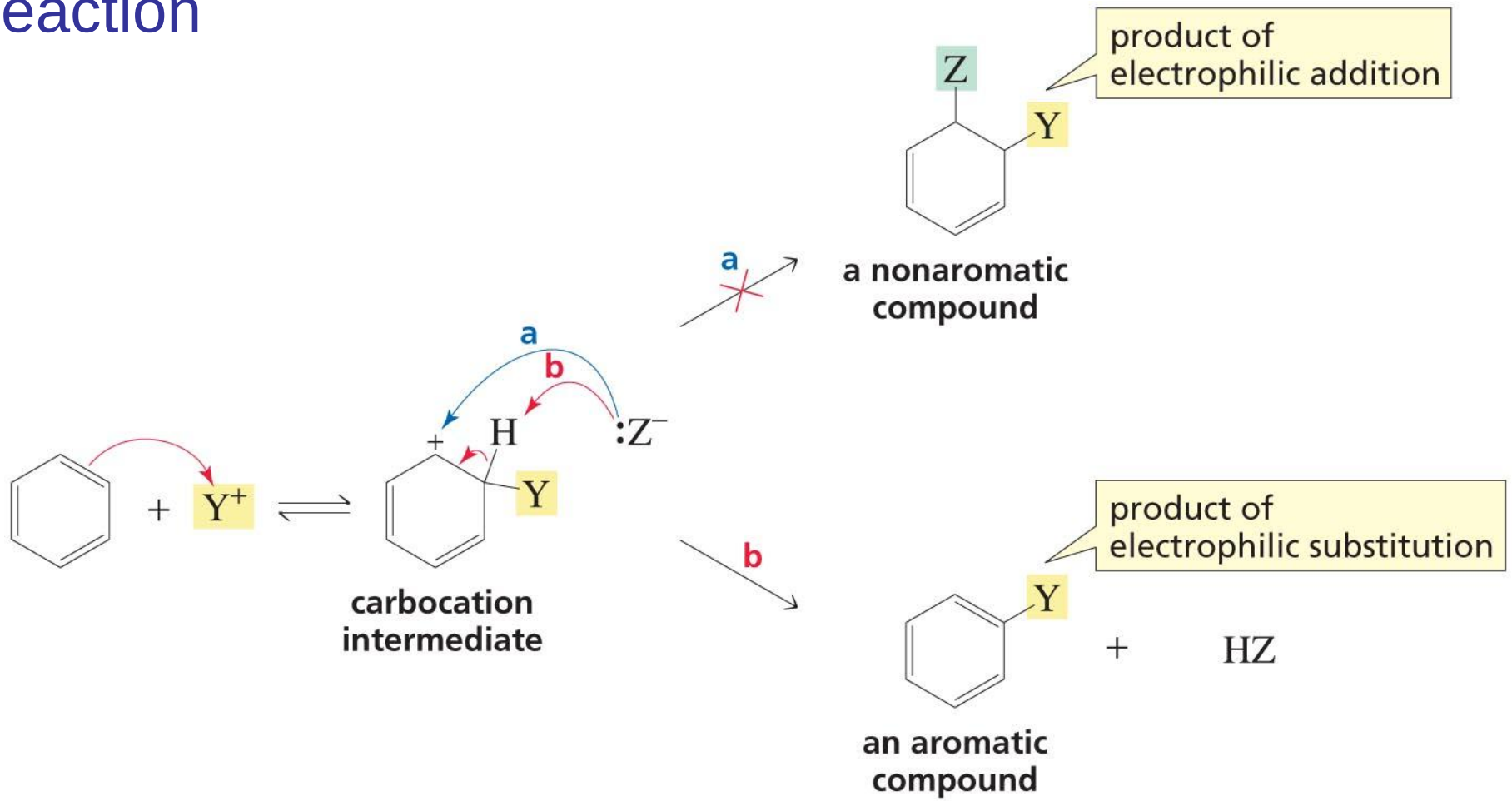
Aromatic compounds such as benzene undergo electrophilic aromatic substitution reactions:



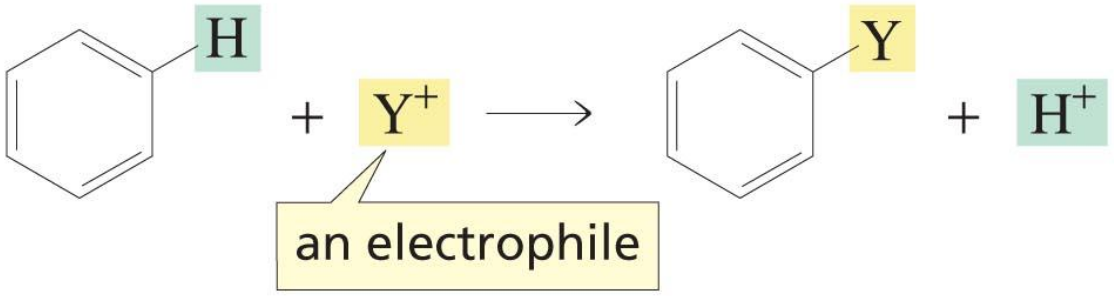


Benzene is a nucleophile that reacts with an electrophile

An electrophilic substitution yields an aromatic product, which is significantly more stable than the addition reaction

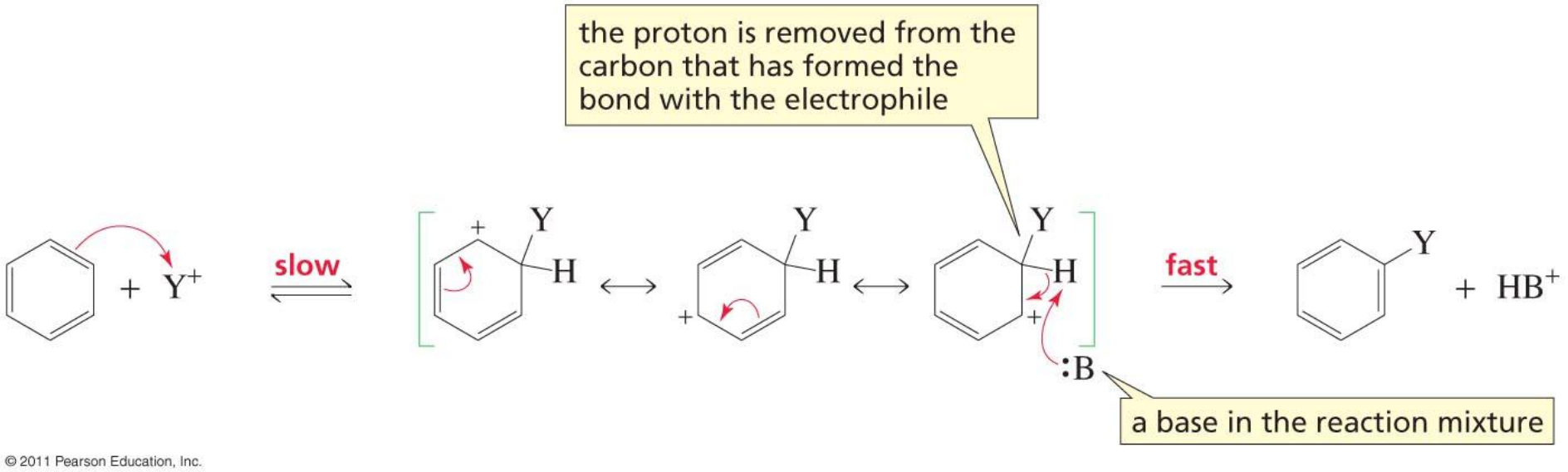


There are five common electrophilic aromatic substitution reactions:



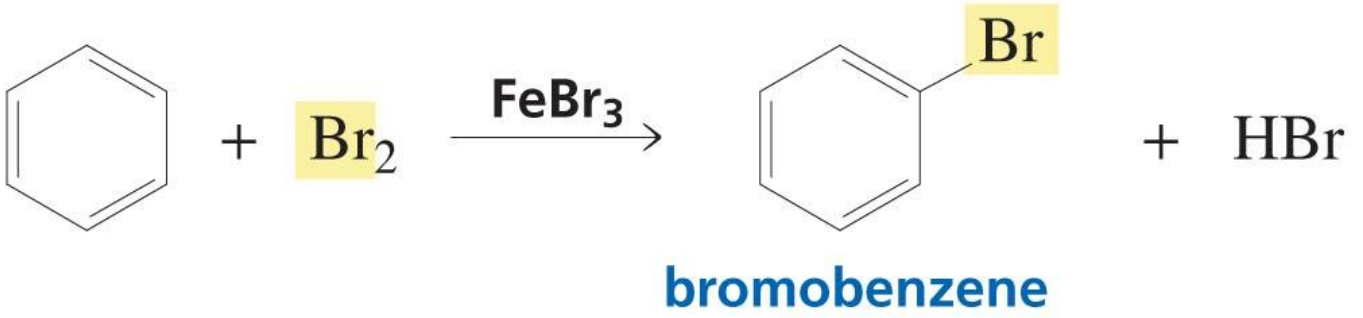
1. Halogenation
2. Nitration
3. Sulfonation
4. Friedel–Crafts acylation
5. Friedel–Crafts alkylation

General Mechanism for Electrophilic Aromatic Substitution of Benzene

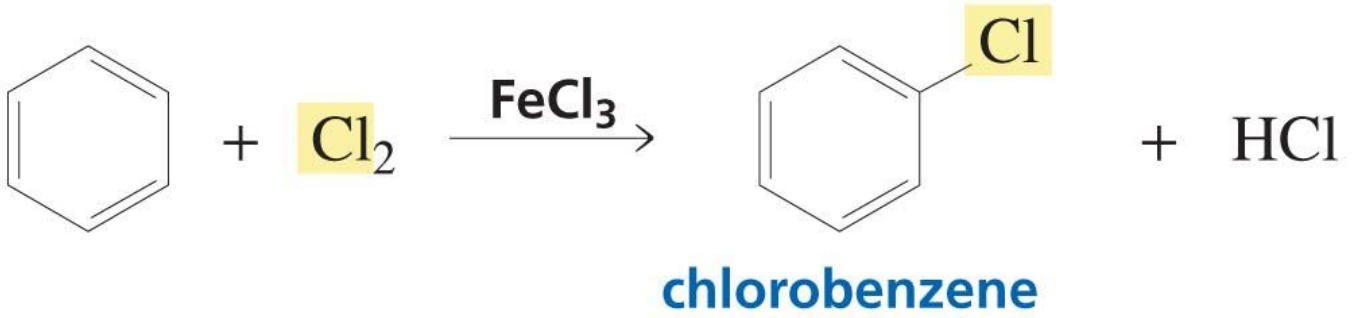


Halogenation of Benzene

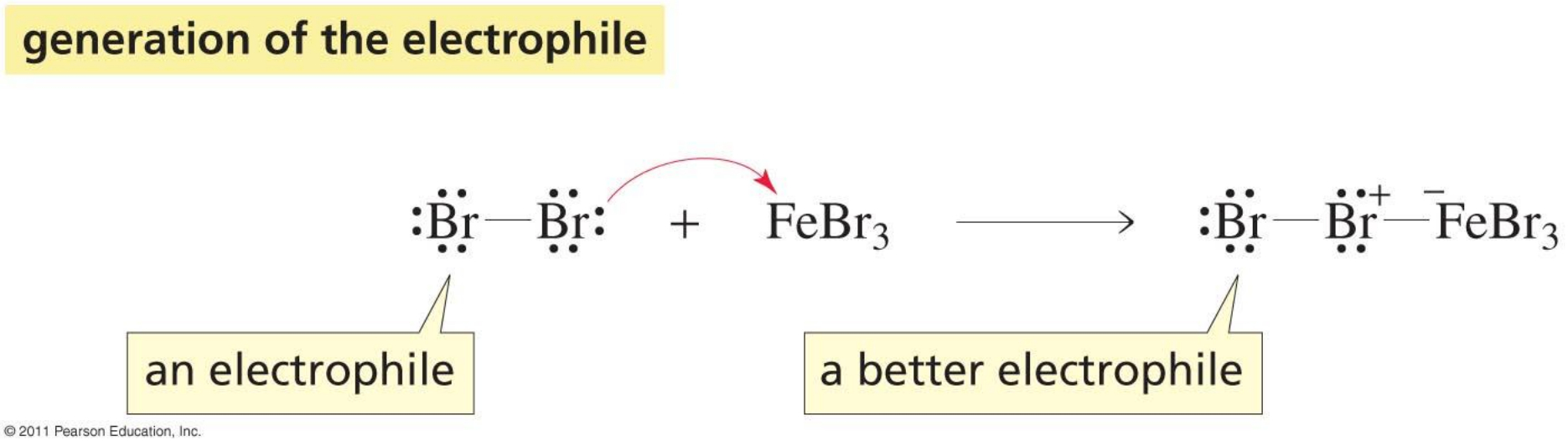
bromination



chlorination

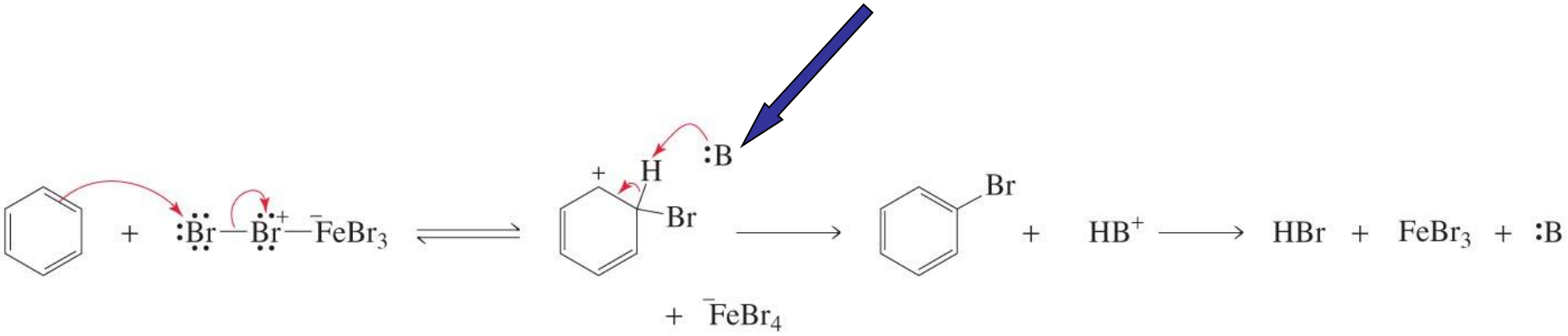


Lewis acid weakens the Br–Br (or Cl–Cl) bond, which makes the halogen a better electrophile:



Mechanism for bromination:

B: Bromide or Benzene

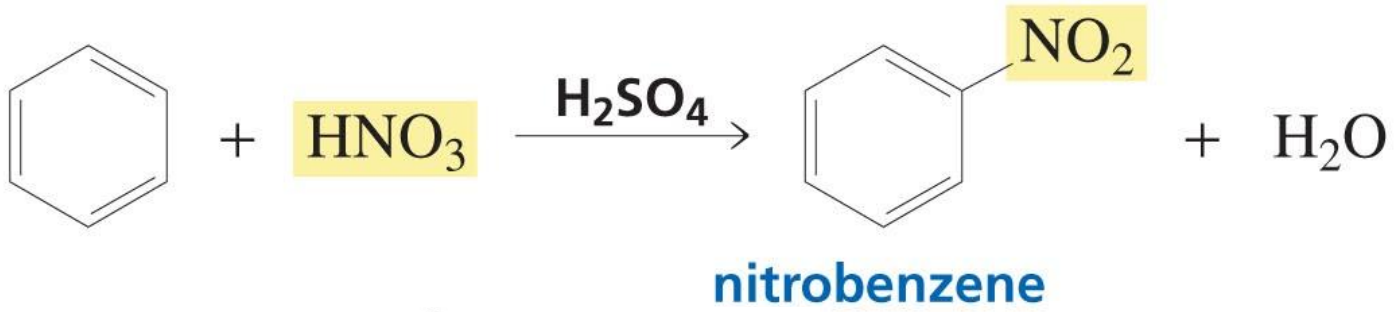


The catalyst is regenerated:

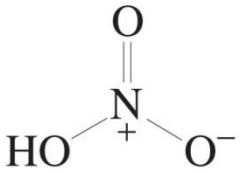
$$\bar{F}eBr_4 + HB^+ \longrightarrow HBr + FeBr_3 + :B$$

Nitration of Benzene

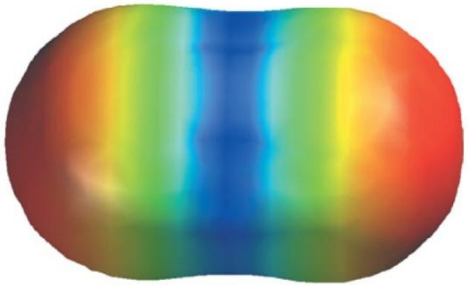
nitration



nitrobenzene



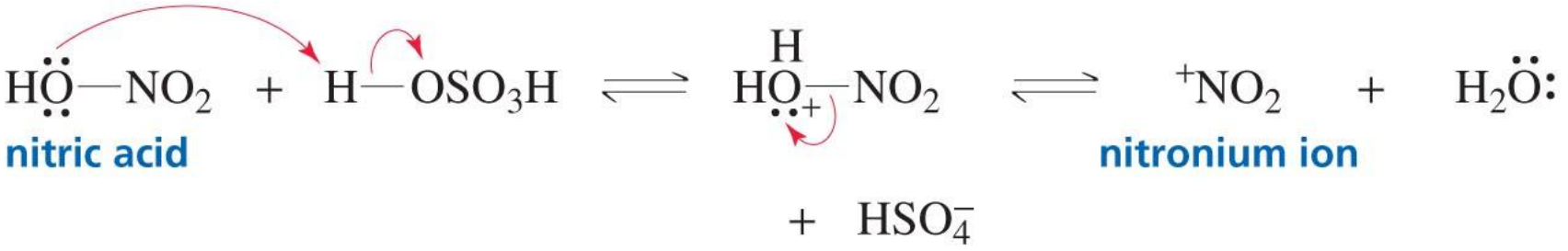
nitric acid



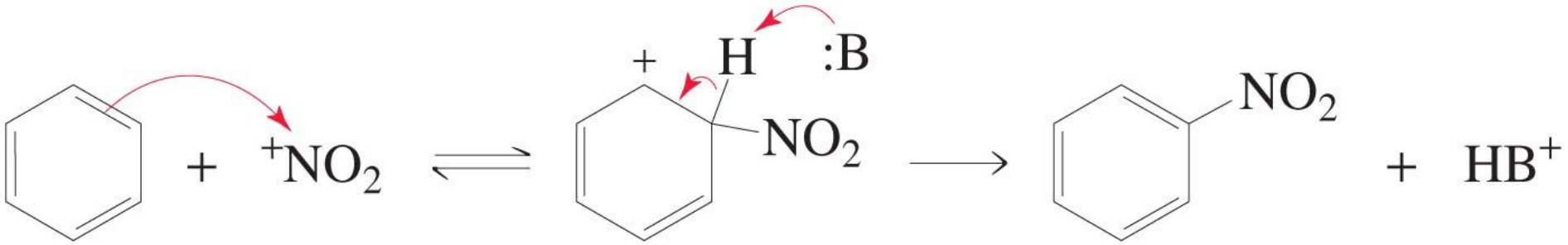
nitronium ion

Nitronium ion formation:

generation of the electrophile

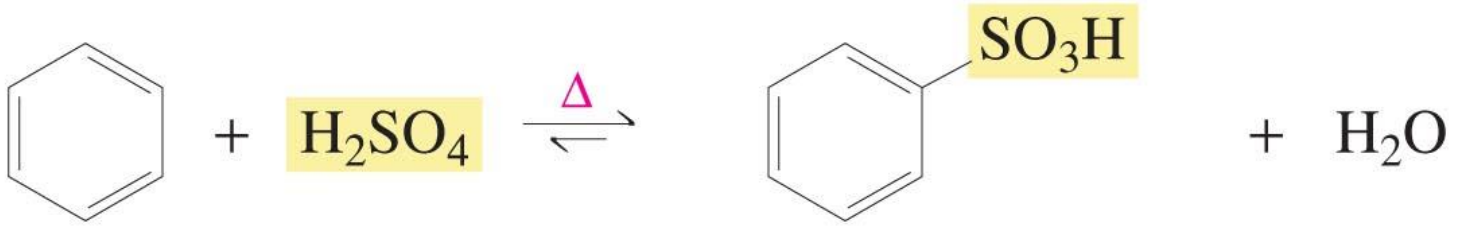


Electrophilic aromatic substitution:



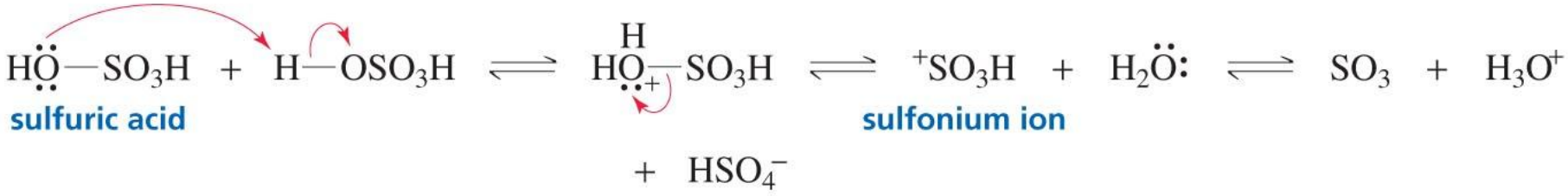
Sulfonation of Benzene

sulfonation

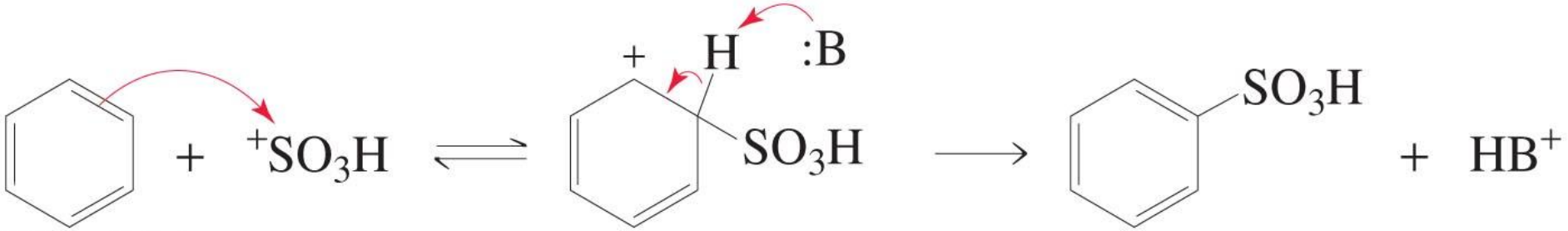


benzenesulfonic acid

generation of the electrophile

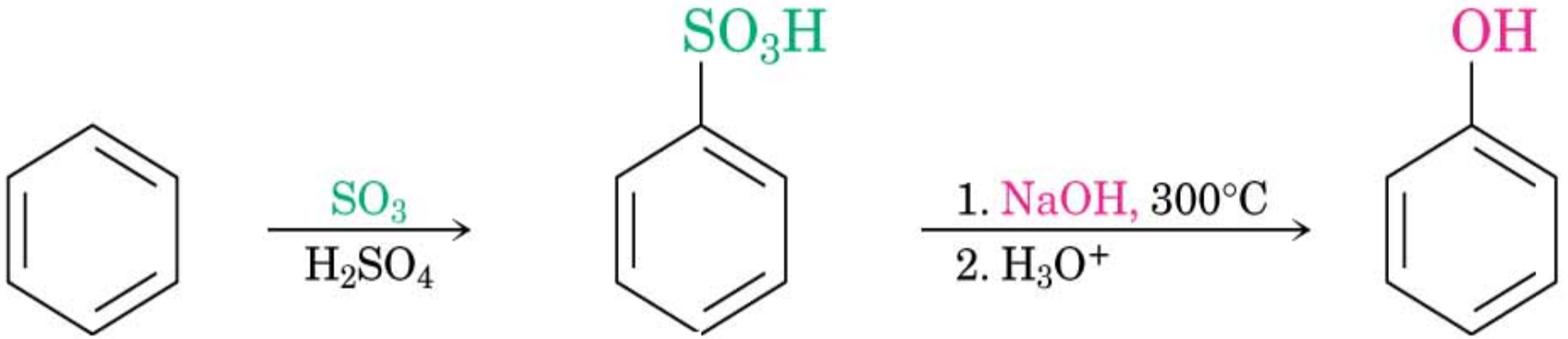


sulfuric acid **sulfonium ion**

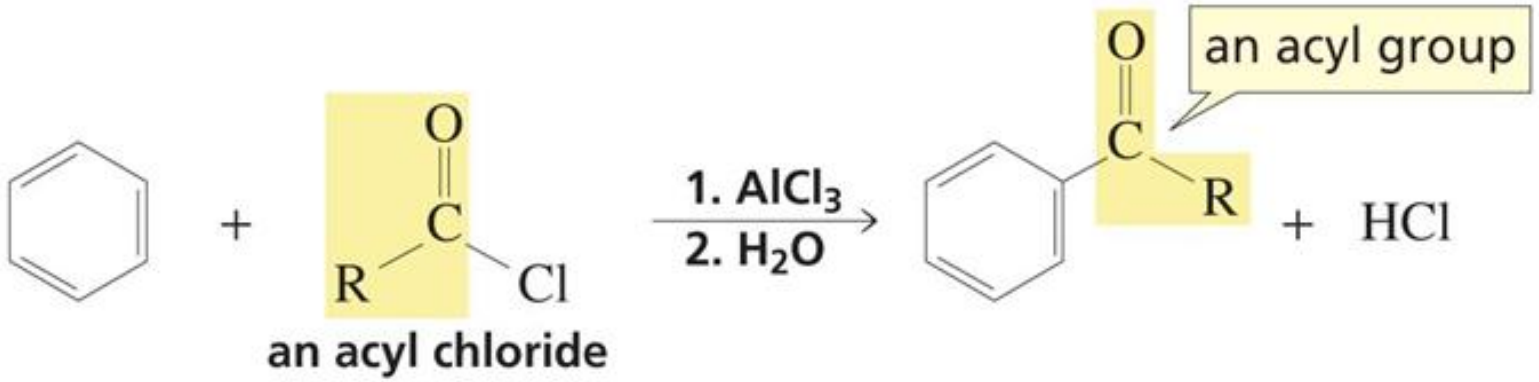


Preparation of Phenols

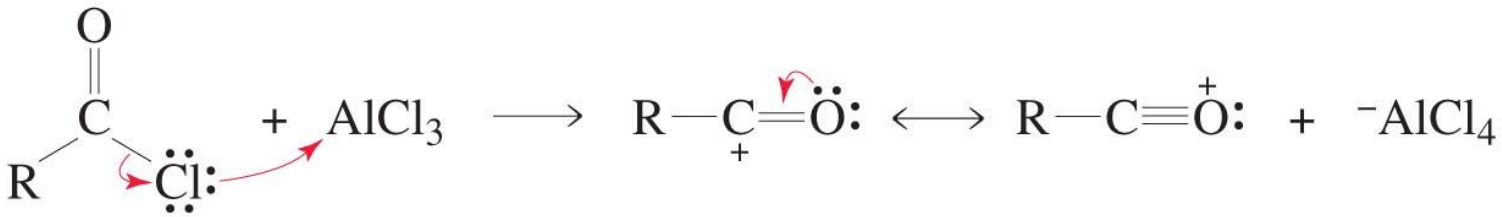
- From aromatic sulfonic acids with NaOH at high temperature

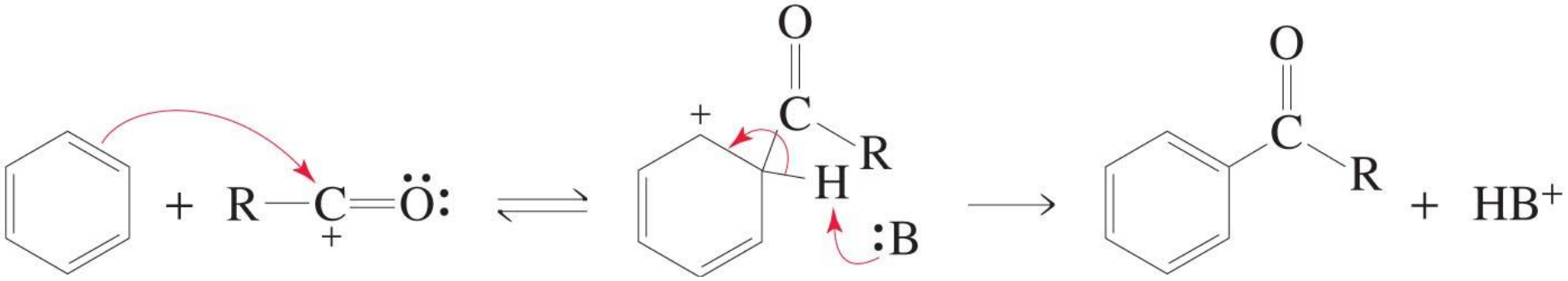


Friedel–Crafts Acylation Reactions



generation of the electrophile





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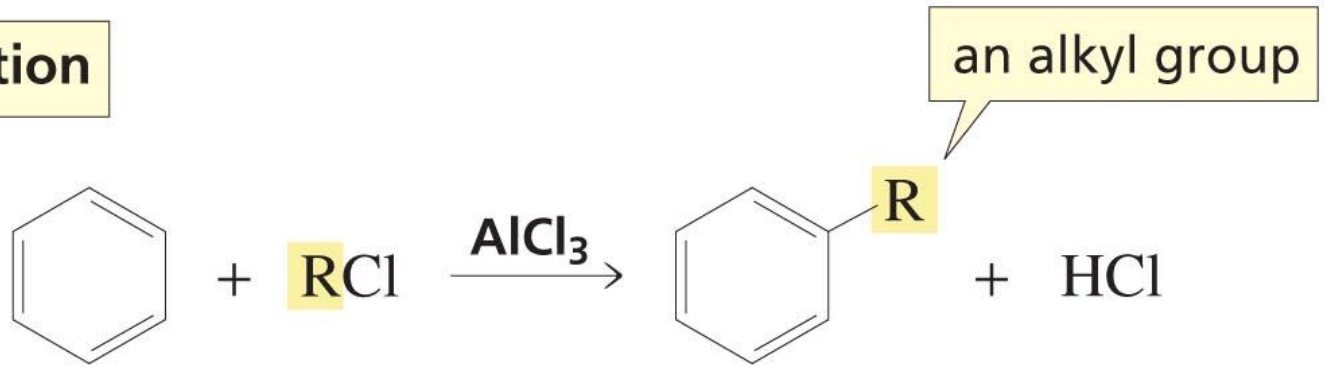
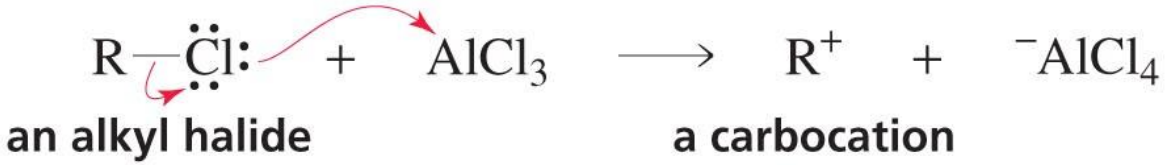
Friedel–Crafts Alkylation of Benzene

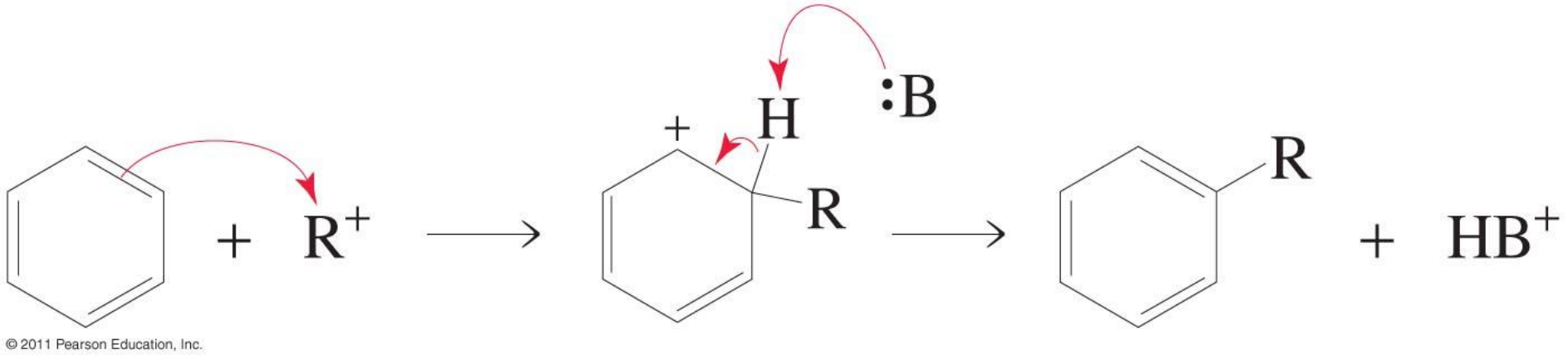
Friedel–Crafts alkylation



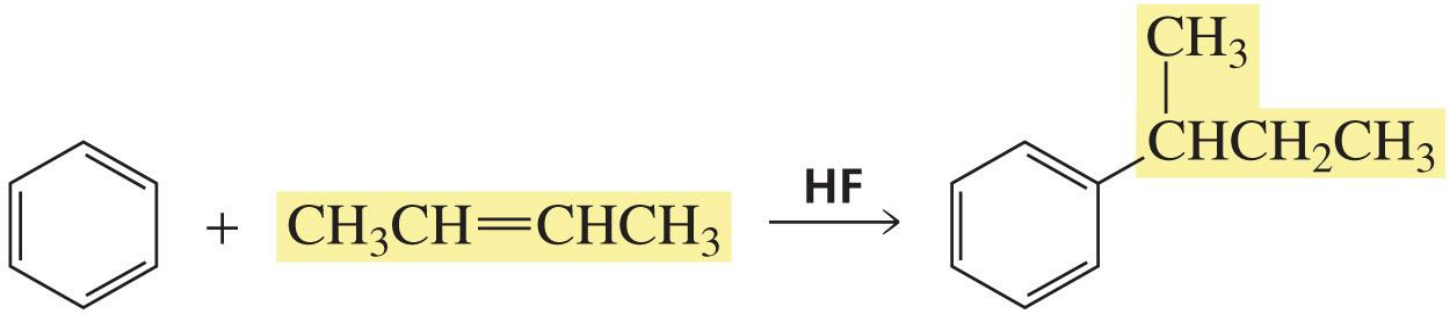
generation of the electrophile



Mechanism for Friedel–Crafts alkylation:



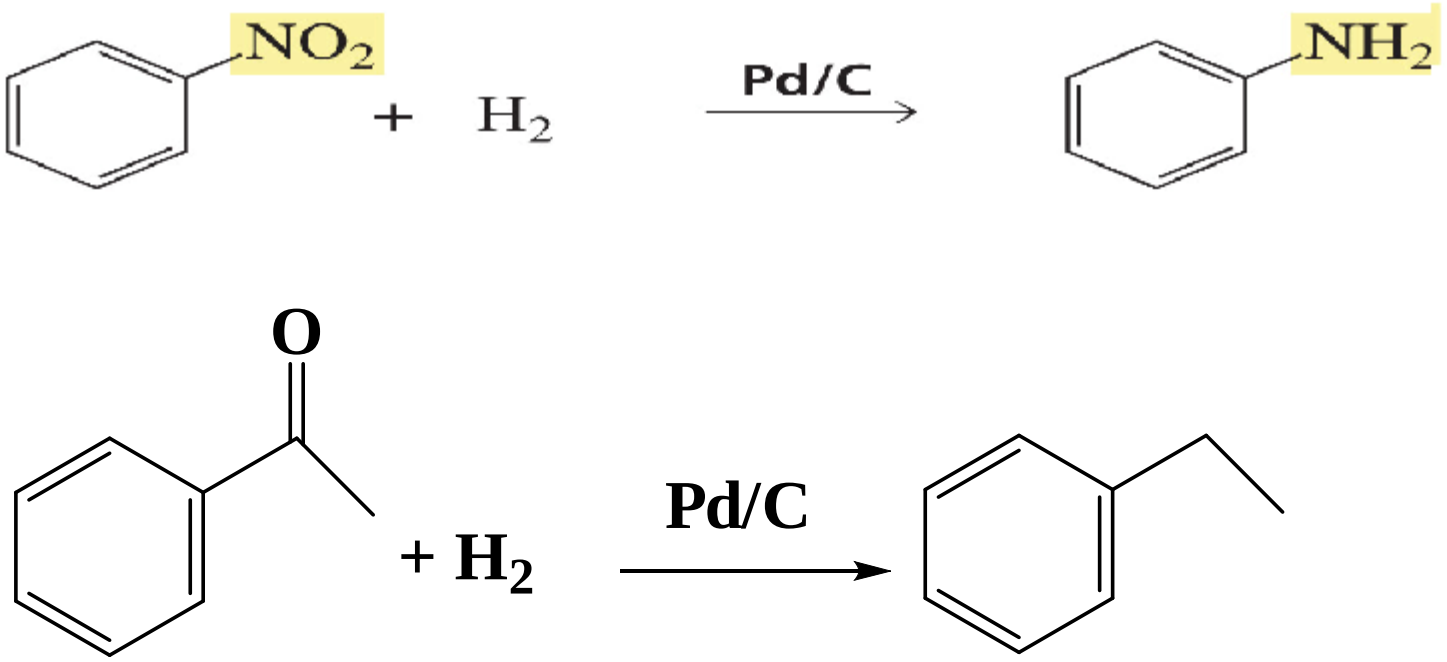
alkylation of benzene by an alkene



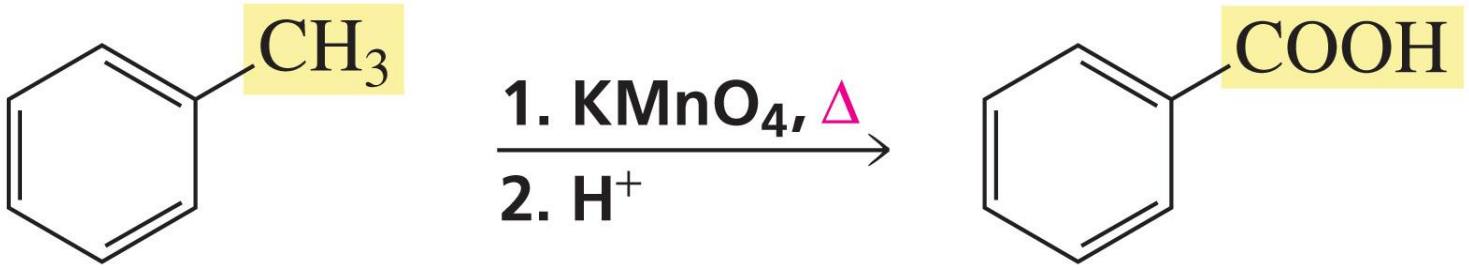
***sec*-butylbenzene**

Chemical Modification of Substituents of Benzene

Reactions of alkyl substituents:



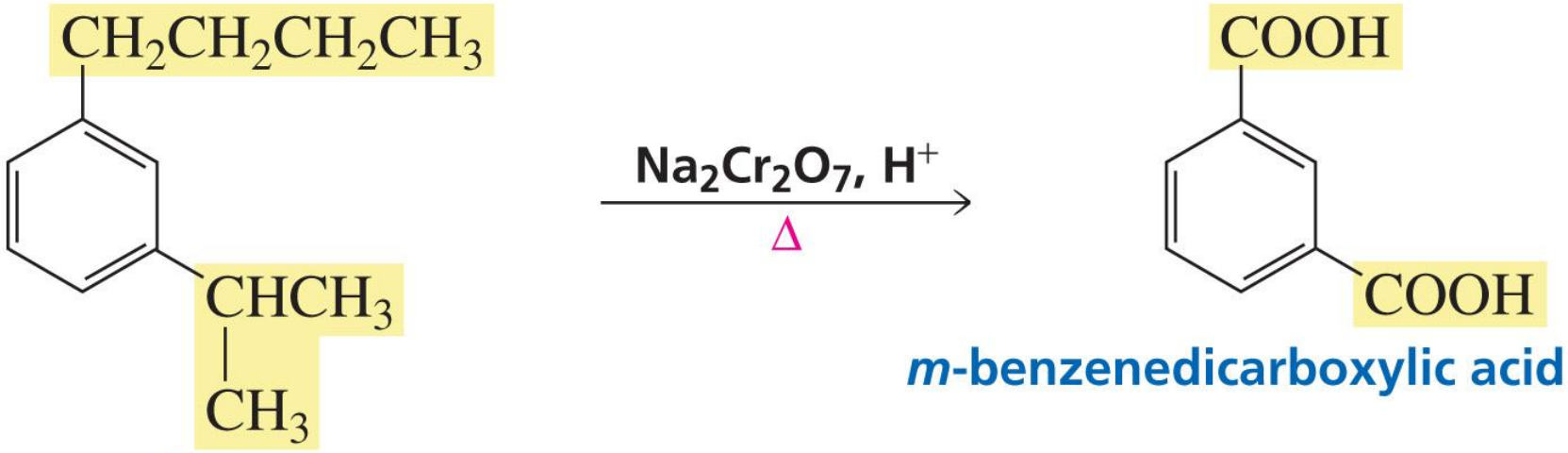
Oxidation of an alkyl group bonded to a benzene ring…



toluene

benzoic acid

Provided that a hydrogen is bonded to the benzylic carbon,



m-butylisopropylbenzene

m-benzenedicarboxylic acid