



# Chapter 5. Aromatic Compounds

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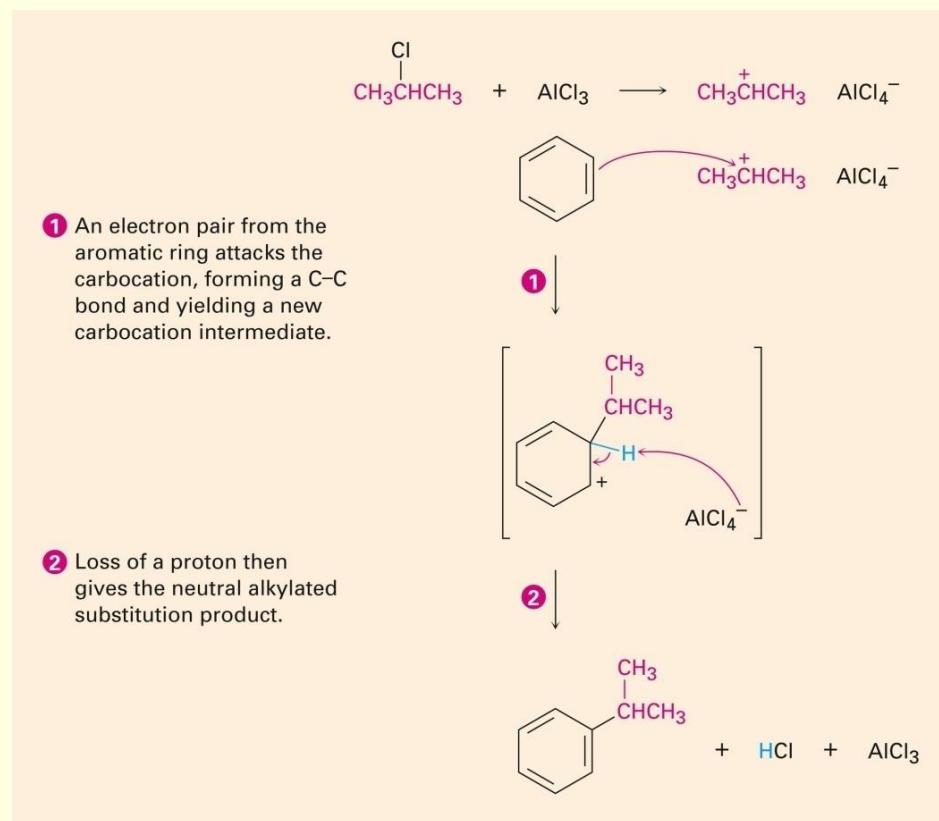
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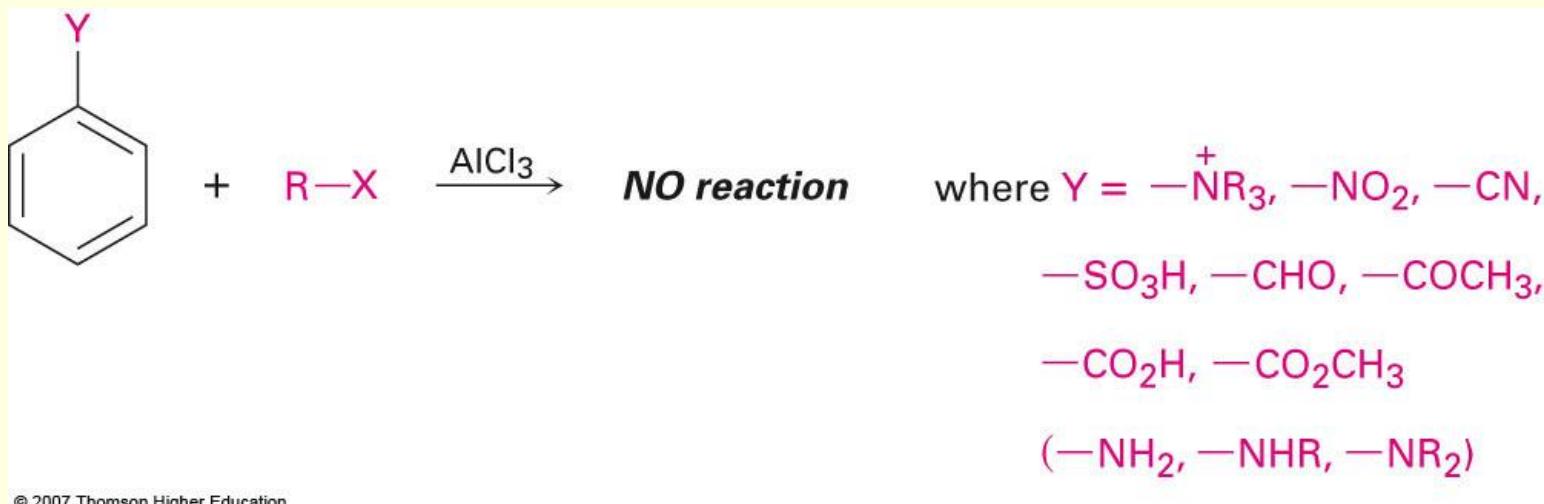
# 5.5 Friedel-Crafts Alkylation and Acylation Reactions

- Alkylation among most useful electrophilic aromatic substitution reactions
- Aromatic substitution of  $R^+$  for  $H^+$
- Aluminum chloride promotes the formation of the carbocation



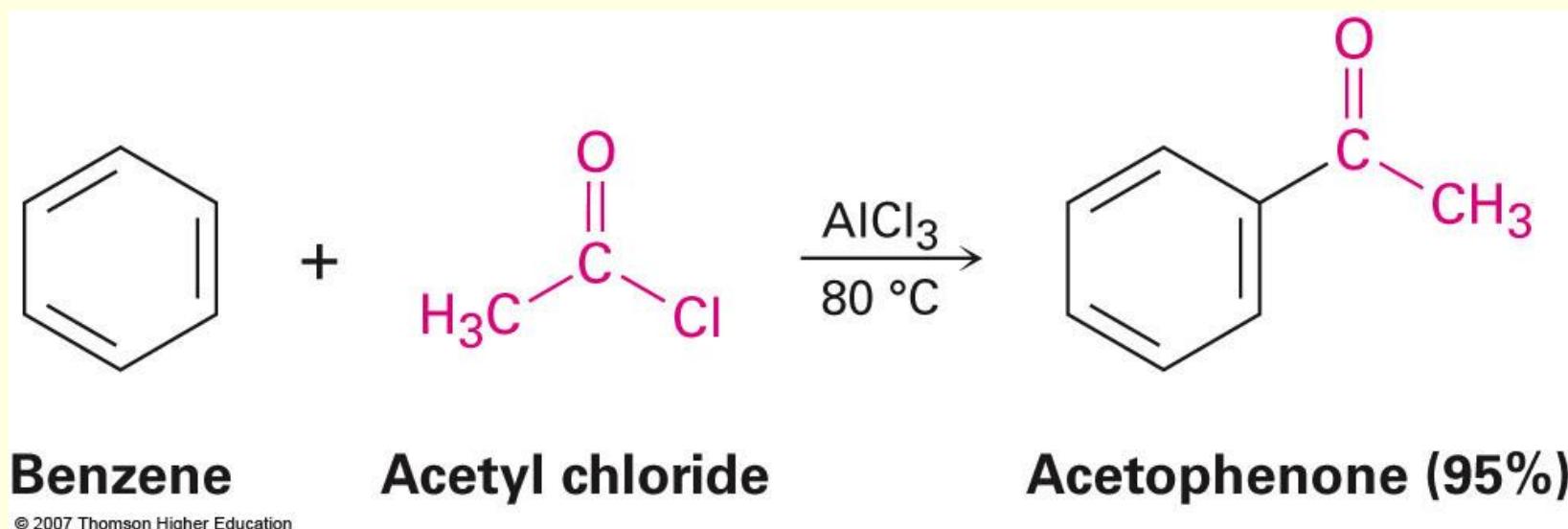
# Limitations of the Friedel-Crafts Alkylation

- Only *alkyl* halides can be used (F, Cl, I, Br)
- *Aryl* halides and *vinylic* halides do not react (their carbocations are too hard to form)
- Will not work with rings containing an amino group substituent or a strongly electron-withdrawing group



# Friedel-Crafts Acylation Reaction

- Reaction of an acid chloride ( $\text{RCOCl}$ ) and an aromatic ring in the presence of  $\text{AlCl}_3$  introduces **acyl group**,  $-\text{COR}$ 
  - Benzene with acetyl chloride yields acetophenone



**Problem 5.9**

What products would you expect to obtain from the reaction of the following compounds with chloroethane and AlCl<sub>3</sub>?

- (a) Benzene      (b) *p*-Xylene

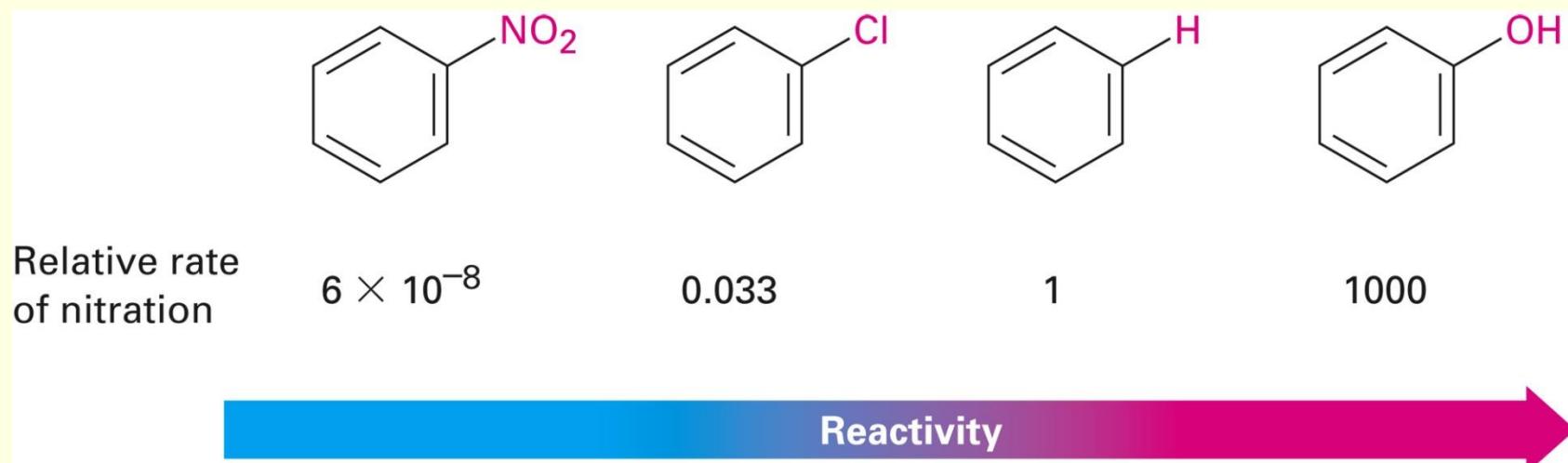
**Problem 5.10**

What products would you expect to obtain from the reaction of benzene with the following reagents?

- (a)  $(CH_3)_3CCl$ ,  $AlCl_3$       (b)  $CH_3CH_2COCl$ ,  $AlCl_3$

# 5.6 Substituent Effects in Electrophilic Aromatic Substitution

- Substituents can cause a compound to be (much) more or (much) less reactive than benzene

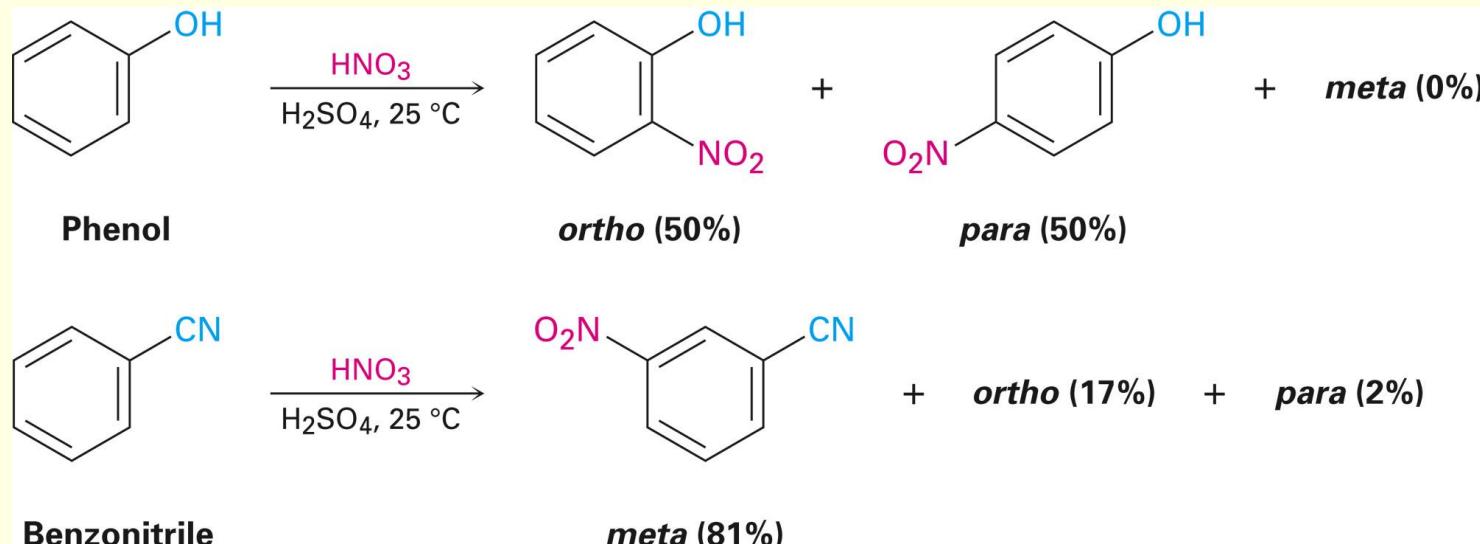


## Substituents affect the *orientation* of a reaction.

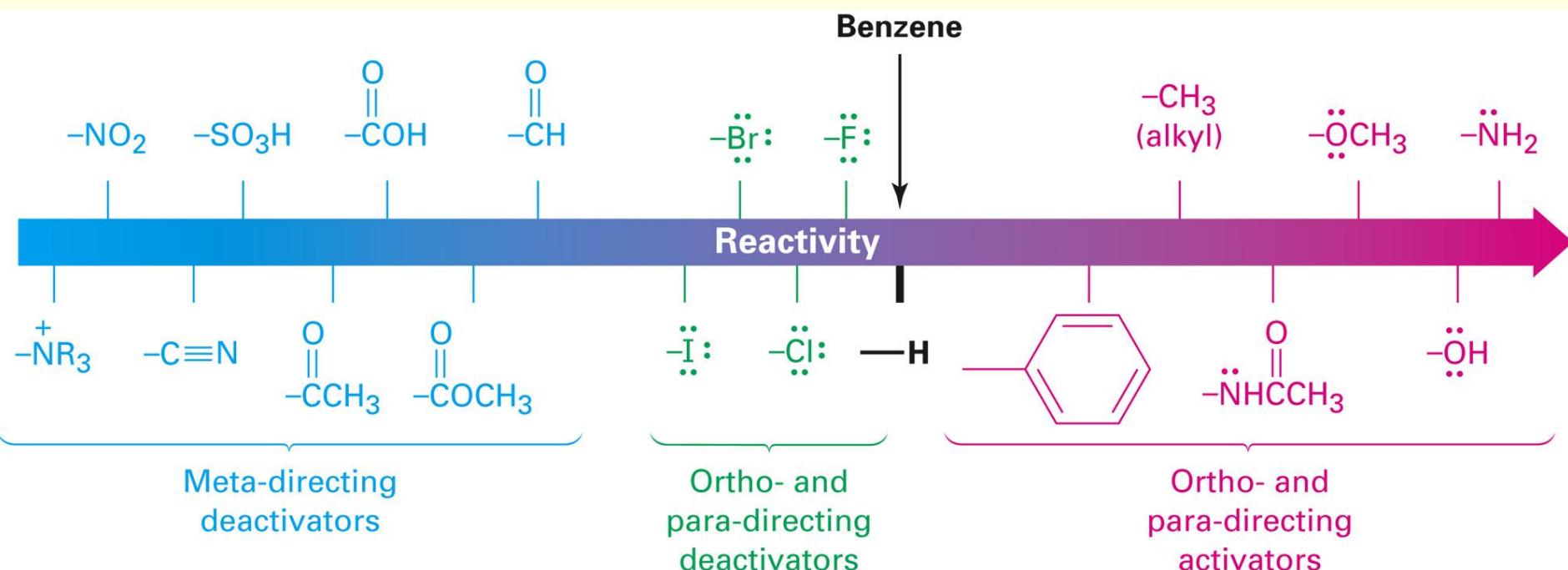
The three possible disubstituted products—ortho, meta, and para—are usually not formed in equal amounts.

Instead, the nature of the substituent already present on the ring determines the position of the second substitution.

An OH group directs further substitution toward the ortho and para positions, for instance, while a CN directs further substitution primarily toward the meta position.



# Summary: Effect of Substituents in Aromatic Substitution



**Figure 5.6** Substituent effects in electrophilic aromatic substitutions.

All activating groups are ortho- and para-directing, and all deactivating groups other than halogen are meta-directing.

The halogens are unique in being deactivating but ortho- and para-directing.

## Worked Example 5.3

### Predicting Relative Reactivity in Electrophilic Aromatic Substitution Reactions

Which would you expect to react faster in an electrophilic aromatic substitution reaction, chlorobenzene or ethylbenzene? Explain.

#### Strategy

Look at Figure 5.6, and compare the relative reactivities of chloro and alkyl groups.

#### Solution

A chloro substituent is deactivating, whereas an alkyl group is activating. Thus, ethylbenzene is more reactive than chlorobenzene.

**Problem 5.11**

Use Figure 5.6 to rank the compounds in each of the following groups in order of their reactivity toward electrophilic aromatic substitution:

- (a) Nitrobenzene, phenol (hydroxybenzene), toluene
- (b) Phenol, benzene, chlorobenzene, benzoic acid
- (c) Benzene, bromobenzene, benzaldehyde, aniline (aminobenzene)

