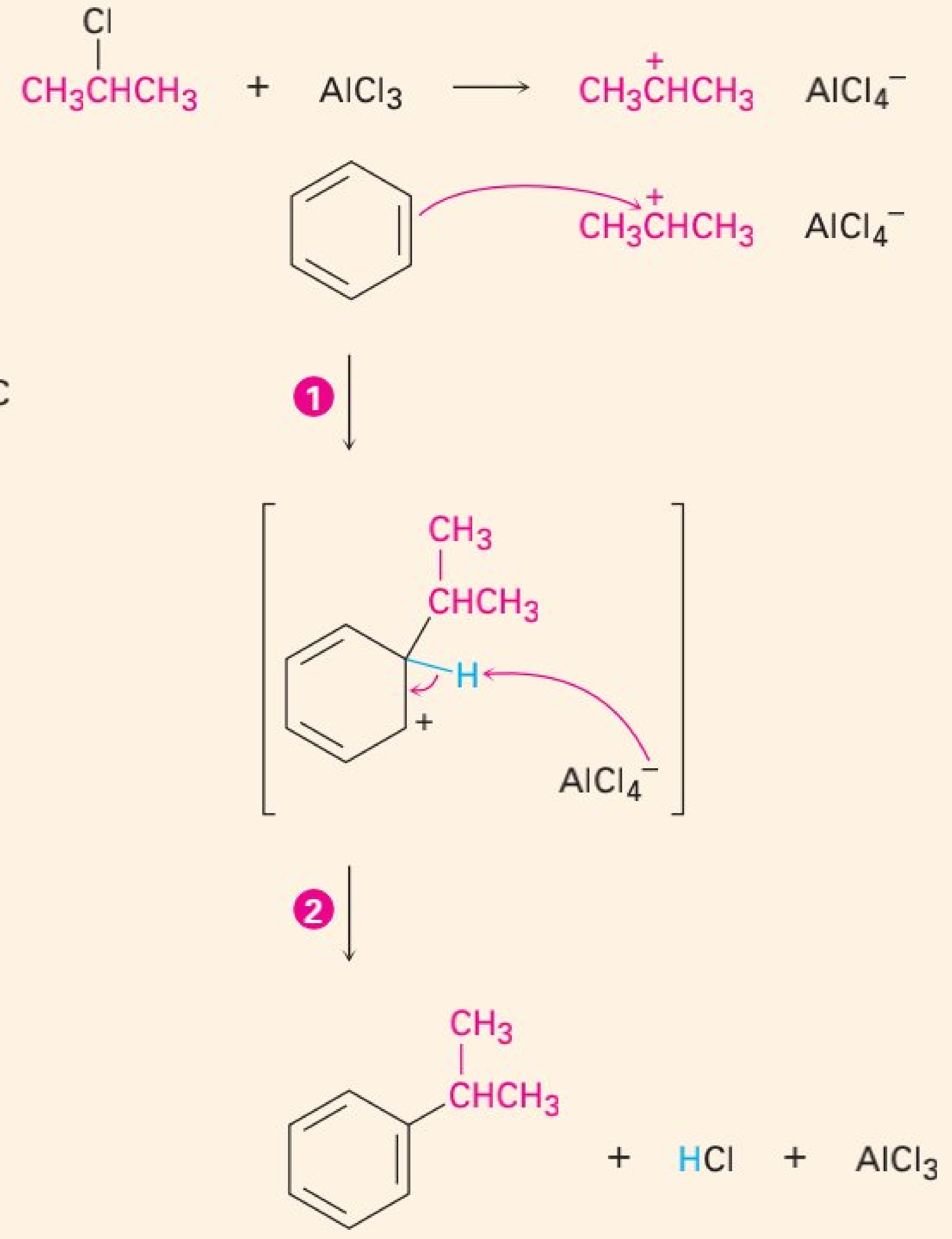
## 5.5 The Friedel–Crafts Alkylation and Acylation Reactions

One of the most useful electrophilic aromatic substitution reactions is *alkylation*—the introduction of an alkyl group onto the benzene ring. Called the **Friedel–Crafts alkylation reaction** after its discoverers, the reaction is carried out by treating the aromatic compound with an alkyl chloride, RCl, in the presence of $AlCl_3$ to generate a carbocation electrophile, $R^+$. Aluminum chloride catalyzes the reaction by helping the alkyl halide to dissociate in much the same way that $FeBr_3$ catalyzes aromatic brominations by helping $Br_2$ dissociate (Section 5.3). Loss of $H^+$ then completes the reaction (Figure 5.5).

**MECHANISM**

**Figure 5.5** **Mechanism of the Friedel–Crafts alkylation reaction. The electrophile is a carbocation, generated by $AlCl_3$-assisted ionization of an alkyl chloride.**



① An electron pair from the aromatic ring attacks the carbocation, forming a C–C bond and yielding a new carbocation intermediate.

② Loss of a proton then gives the neutral alkylated substitution product.

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Despite its utility, the Friedel–Crafts alkylation reaction has several limitations. For one, only *alkyl* halides can be used. Aromatic (aryl) halides such as chlorobenzene don't react. In addition, Friedel–Crafts reactions don't succeed on aromatic rings that are already substituted by the groups $-NO_2$, $-C{\equiv}N$, $-SO_3H$, or $-COR$. Such aromatic rings are much less reactive than benzene for reasons we'll discuss in the next two sections.

Closely related to the Friedel–Crafts alkylation reaction is the **Friedel–Crafts acylation reaction**. When an aromatic compound is treated with a carboxylic acid chloride (RCOCl) in the presence of $AlCl_3$, an **acyl** (**a**-sil) **group** (R—C=O) is introduced onto the ring. For example, reaction of benzene with acetyl chloride yields the ketone acetophenone.

**Benzene** **Acetyl chloride** **Acetophenone (95%)**

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**Problem 5.9** What products would you expect to obtain from the reaction of the following compounds with chloroethane and $AlCl_3$?

**(a)** Benzene **(b)** *p*-Xylene

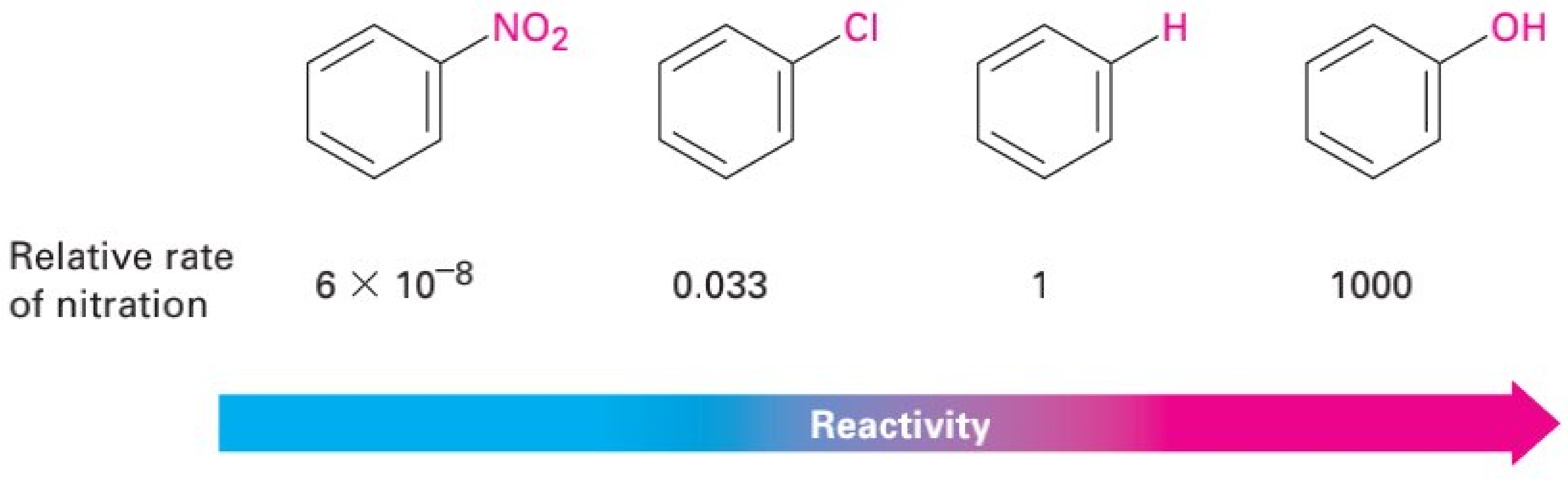
**Problem 5.10** What products would you expect to obtain from the reaction of benzene with the following reagents?

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

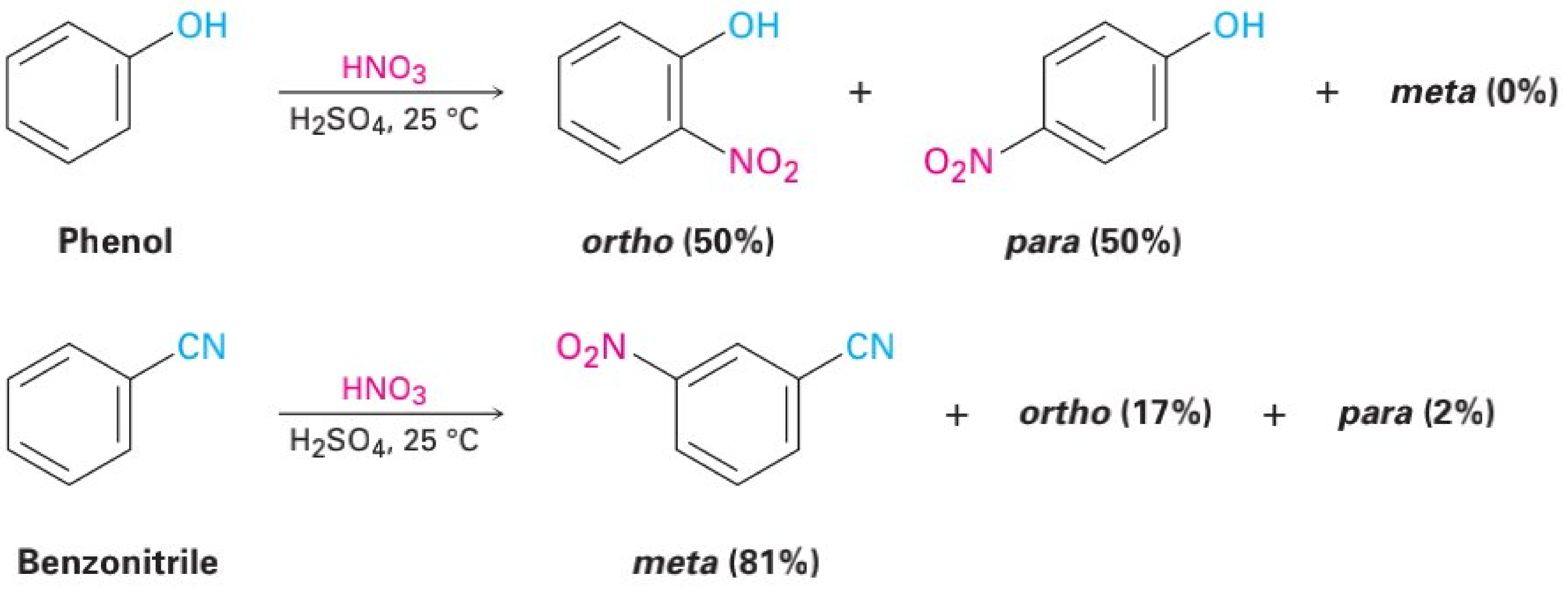
## 5.6 Substituent Effects in Electrophilic Aromatic Substitution

Only one product can form when an electrophilic substitution occurs on benzene, but what would happen if we were to carry out an electrophilic substitution on a ring that already has a substituent? A substituent already present on the ring has two effects:

- **Substituents affect the *reactivity* of an aromatic ring**. Some substituents activate a ring, making it more reactive than benzene, and some deactivate a ring, making it less reactive than benzene. In aromatic nitration, for instance, the presence of an –OH substituent makes the ring 1000 times more reactive than benzene, while an $-NO_2$ substituent makes the ring more than 10 million times less reactive.



- **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.



Substituents can be classified into three groups, as shown in Figure 5.6: *meta-directing deactivators, ortho- and para-directing deactivators,* and *ortho- and para-directing activators.* There are no meta-directing activators. Note how the directing effect of a group correlates with its reactivity. All meta-directing groups are deactivating, and all ortho- and para-directing groups other than halogen are activating. The halogens are unique in being ortho- and para-directing but deactivating.

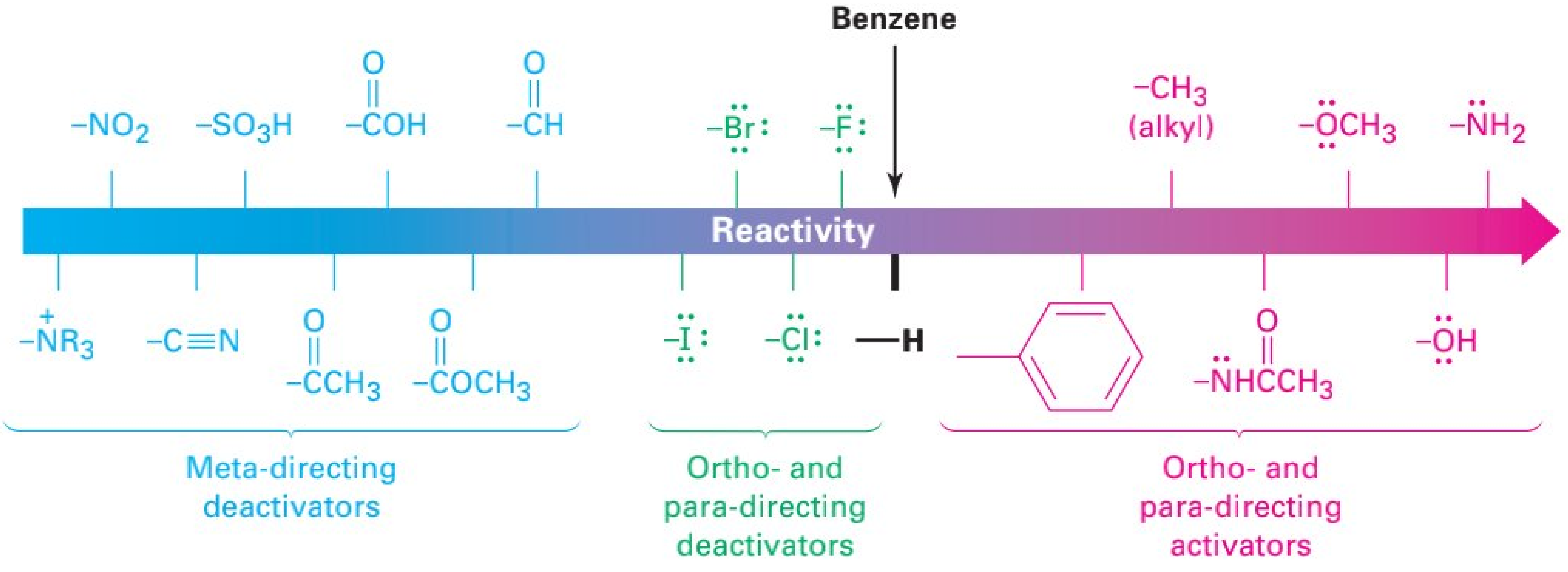


**Figure 5.6** Substituent effects in electrophilic aromatic substitutions. All activating groups are ortho- and para-directing, and all deactivating groups other than halogen are meta-directing. The halogens are unique in being deactivating but ortho- and para-directing.

## 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.

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**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)