

Worked Example 5.4

Predicting the Product of an Electrophilic Aromatic Substitution Reaction

What product(s) would you expect from bromination of aniline, $C_6H_5NH_2$?

Strategy

Look at Figure 5.6 to see whether the $-NH_2$ substituent is ortho- and para-directing or meta-directing. Because an amino group has a lone pair of electrons on the nitrogen atom, it is ortho- and para-directing and we expect to obtain a mixture of *o*-bromoaniline and *p*-bromoaniline.

Solution



Problem 5.13

What product(s) would you expect from sulfonation of the following compounds?

- (a) Nitrobenzene (b) Bromobenzene (c) Toluene
 (d) Benzoic acid (e) Benzonitrile

Problem 5.14

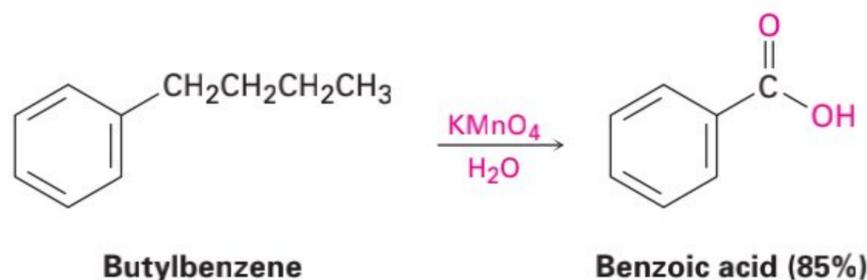
Draw resonance structures of the three possible carbocation intermediates to show how a methoxyl group ($-OCH_3$) directs bromination toward ortho and para positions.

Problem 5.15

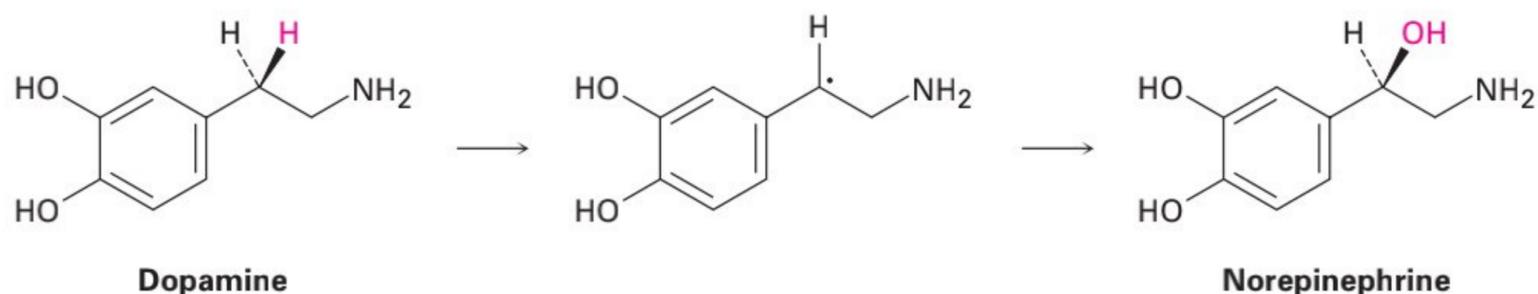
Draw resonance structures of the three possible carbocation intermediates to show how an acetyl group, $CH_3C=O$, directs bromination toward the meta position.

5.8 Oxidation and Reduction of Aromatic Compounds

Despite its unsaturation, a benzene ring does not usually react with strong oxidizing agents such as $KMnO_4$. (Recall from Section 4.6 that $KMnO_4$ cleaves alkene $C=C$ bonds.) Alkyl groups attached to the aromatic ring are readily attacked by oxidizing agents, however, and are converted into carboxyl groups ($-CO_2H$). For example, butylbenzene is oxidized by $KMnO_4$ to give benzoic acid. The mechanism of this reaction is complex and involves attack on the side-chain $C-H$ bonds at the position next to the aromatic ring (the **benzylic position**) to give radical intermediates.



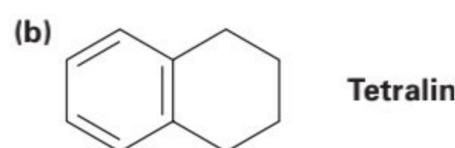
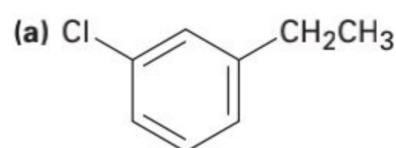
Analogous oxidations occur in various biological pathways. The neurotransmitter norepinephrine, for instance, is biosynthesized from dopamine by a benzylic hydroxylation reaction. The process is catalyzed by the copper-containing enzyme dopamine β -monooxygenase and occurs by a radical mechanism.



Just as aromatic rings are usually inert to oxidation, they are also inert to reduction under typical alkene hydrogenation conditions. Only if high temperatures and pressures are used does reduction of an aromatic ring occur. For example, *o*-dimethylbenzene (*o*-xylene) gives *cis*-1,2-dimethylcyclohexane if reduced at high pressure.

**Problem 5.16**

What aromatic products would you expect to obtain from oxidation of the following substances with KMnO_4 ?

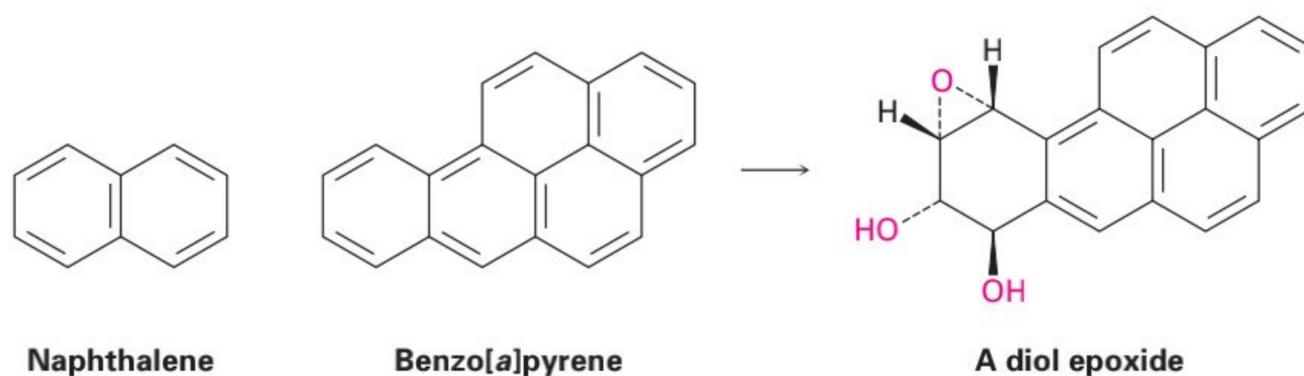


5.9 Other Aromatic Compounds

The concept of aromaticity—the unusual chemical stability present in cyclic conjugated molecules like benzene—can be extended beyond simple monocyclic hydrocarbons. Naphthalene, for instance, a substance familiar for its use in mothballs, has two benzene-like rings fused together and is thus a **polycyclic aromatic compound**.

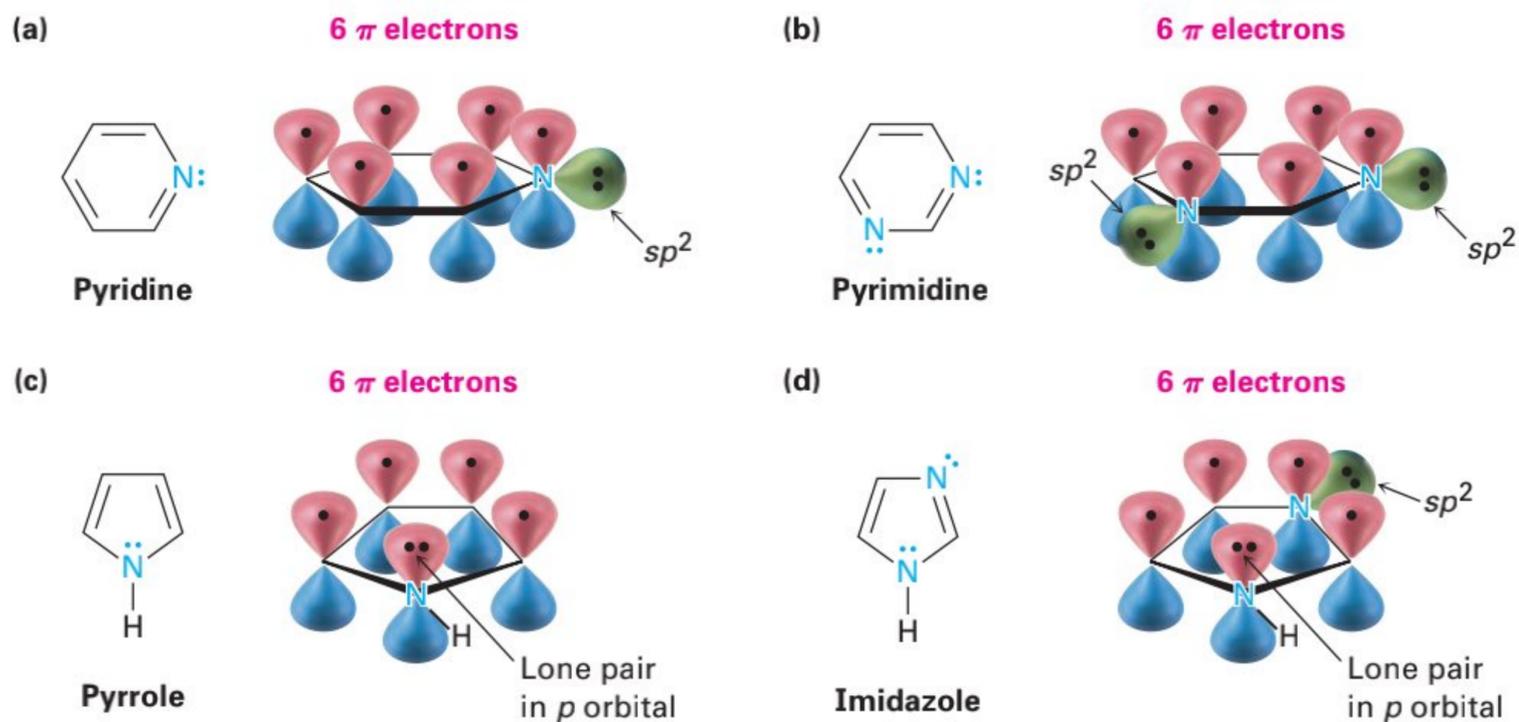
Perhaps the most notorious polycyclic aromatic hydrocarbon is benzo[*a*]pyrene, which has five benzene-like rings and is a major carcinogenic (cancer-causing) substance found in chimney soot, cigarette smoke, and well-done barbecued meat. Once in the body, benzo[*a*]pyrene is

metabolically converted into a diol epoxide that binds to DNA, where it induces mutations.



In addition to monocyclic and polycyclic aromatic hydrocarbons, some aromatic compounds are **heterocycles**—cyclic compounds that contain atoms of two or more elements in their rings. Nitrogen, sulfur, and oxygen atoms are all found along with carbon in various aromatic compounds. We'll see in Chapter 12, for instance, that the nitrogen-containing heterocycles pyridine, pyrimidine, pyrrole, and imidazole are aromatic, even though they aren't hydrocarbons and even though two of them have five-membered rather than six-membered rings (Figure 5.9). They are aromatic because they all, like benzene, contain a cyclic conjugated array of six π electrons. Pyridine and pyrimidine have one π electron on each of their six ring atoms. Pyrrole and imidazole have one π electron on each of four ring atoms and an additional two π electrons (the lone pair) on their N–H nitrogen.

Figure 5.9 Orbital views of the nitrogen-containing compounds (a) pyridine, (b) pyrimidine, (c) pyrrole, and (d) imidazole. All are aromatic because, like benzene, they contain a cyclic conjugated system of six π electrons. Pyridine and pyrimidine have one π electron on each of their six ring atoms. Pyrrole and imidazole have one π electron on each of four ring atoms and an additional two π electrons (the lone pair) on their N–H nitrogen.



Problem 5.17

There are three resonance structures of naphthalene, of which only one is shown. Draw the other two.

