30

BENZENE AND ITS DERIVATIVES

30.1 | The Structure of Benzene

The history of benzene and the discovery of its unusual structure is an interesting story. In 1825, Michael Faraday isolated a pure compound from the oily mixture that condensed from illuminating gas, the fuel burned in gaslights common at the time in England. The compound had a boiling point of 80 °C and a pungent odour. Elemental analysis of the compound showed it had a carbon-to-hydrogen ratio of 1:1, corresponding to an empirical formula of CH. About nine years later, German chemist Eilhard Mitscherlich (1794–1863) synthesized the same compound by heating benzoic acid in the presence of lime:

$$C_6H_5COOH \quad + \quad CaO \quad \xrightarrow{heat} \quad C_6H_6 \quad + \quad CaCO_3$$

| gum of benzoin (benzoic acid) | calcium oxide | | benzene | calcium carbonate |

He further used vapor-density measurements to determine the molecular weight of 78 u. He named the new compound *benzin*, after the gum benzoin from which he derived it. We now know this compound as benzene.

However, benzoic acid had been known for several hundred years before Mitscherlich's experiment. Benzoic acid is the white odourless compound isolated from benzoin resin, a substance extruded by several types of Southeast Asian trees of the genus *Styrax*. It is often used as a topical fungicide.

Although the experiments of Mitscherlich showed that benzene must have the formula C_6H_6, it was not clear what the structure of the molecule could be. Only after 1860, when the concept of unsaturation was introduced, did August Kekulé (1829–1896) propose a suitable model. Kekulé was instrumental in developing much of the structural theory of organic chemistry, but he is best known for his work on benzene (1865). How he came to propose the structure of benzene is the truly fascinating part of this story. Kekulé recalled falling asleep on a London bus, and while he was dozing, he conjured images of "dancing atoms" that connected into snakes. As the snakes twisted and turned, eventually one caught its own tail, giving the image leading to the now famous structure of alternating double and single bonds. In his theory, however, two interconvertible structures were possible. As we know now, the structure is subtly different, but considering the level of chemical knowledge at this point in time, and more importantly, on the chemistry of benzene, Kekulé's proposed structure was revolutionary.

By the end of this section, you should be able to:

• Understand the unusual structure that benzene possesses.

In Chapter 26, we discussed the structure of both alkenes and alkynes and described the carbon atoms that form the molecular skeleton as *unsaturated*. The trigonal-planar bonding geometry of an alkene carbon was rationalized based on the hybridization of one $2s$ and two $2p$ orbitals available to carbon. Recall that the overlap of unhybridized p orbitals forms a π-bond. One other class of hydrocarbon also takes advantage of π-bonding—the *aromatic hydrocarbons*.
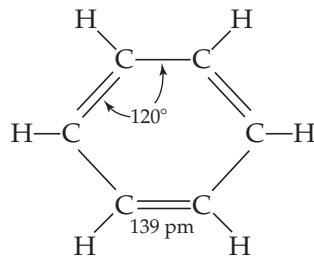
Benzene is the simplest example of an **aromatic hydrocarbon** (also called an **arene**). This class of hydrocarbon contains a planar ring structure, usually drawn with either a circle in the middle (for reasons we discuss shortly), or alternating single and double bonds (**Figure 30.1**). Although aromatic hydrocarbons involve sp^2-hybridized carbons, they are not alkenes, and undergo very different chemical reactions.

Bonding in Benzene

In many of the molecules we have discussed so far, the bonding electrons are *localized*. By this we mean that the σ- and π-electrons are associated totally with the two atoms that form the bond. In some molecules, however, we cannot adequately describe the bonding as being entirely localized. One molecule that cannot be described with localized π-bonds is benzene (C_6H_6).
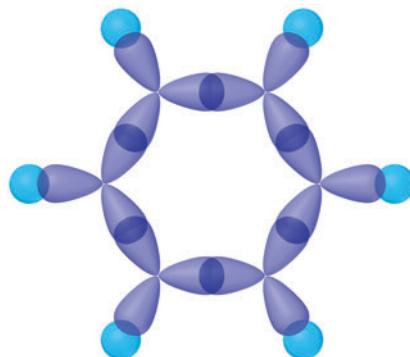
Go Figure   How does the structure of benzene relate to cyclohexane?

C_6H_6
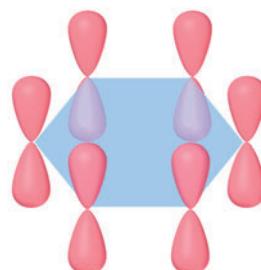
▲ Figure 30.1 **Benzene.** Molecular formulas and geometrical representations for benzene.

To describe the bonding in benzene, we first choose a hybridization scheme consistent with the geometry of the molecule (see Figure 30.1). As each carbon is surrounded by three atoms at 120° angles, the appropriate carbon hybrid orbital set is sp^2. Six localized C—C σ-bonds and six localized C—H σ-bonds are formed from the sp^2 hybrid orbitals, as shown in **Figure 30.2(a)**. This leaves a $2p$ orbital on each carbon atom that is oriented perpendicularly to the plane of the hydrocarbon ring. The situation is very much like that in ethene, except we now have six carbon $2p$ orbitals arranged in a ring (Figure 30.2(b)). Each of the unhybridized $2p$ orbitals is occupied by one electron, meaning a total of six electrons have to be accounted for by π-bonding.

We could imagine using the unhybridized $2p$ orbitals of benzene to form three *localized* π-bonds—that is, π-bonds defined formally between neighboring carbon atoms. As shown in **Figure 30.3(a) and (b)**, there are two equivalent ways to make these localized bonds and each diagram corresponds to one of the resonance structures of the molecule. A representation that reflects *both* resonance structures has the six π-electrons distributed among all six carbon atoms, as shown in Figure 30.3(c). Notice how this figure corresponds to the "circle-in-a-hexagon" drawing often used to represent benzene.
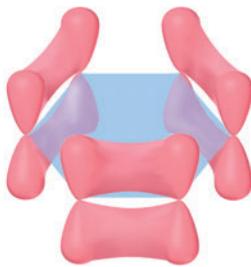

(a) σ-bonds

(b) $2p$ atomic orbitals
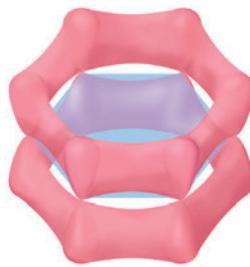
◀ Figure 30.2 **The σ- and π-bond networks in benzene, C_6H_6.** (a) The C—C and C—H σ-bonds all lie in the plane of the molecule and are formed by using carbon sp^2 hybrid orbitals. (b) Each carbon atom has an unhybridized $2p$ orbital that lies perpendicular to the molecular plane. These six $2p$ orbitals form the π-orbitals of benzene.


(a) Localized π-bonds
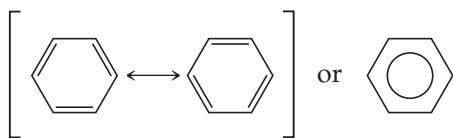
(b) Localized π-bonds

(c) Delocalized π-bonds

◀ Figure 30.3 **Delocalized π-bonds in benzene.** (a) The six $2p$ orbitals of benzene, shown in Figure 30.2(b), can be used to make three C—C π-bonds. (a) and (b) show two equivalent ways to make localized π-bonds. These π-bonds correspond to the two resonance structures for benzene. (c) A representation of the delocalization of the three C—C π-bonds among the six C atoms.
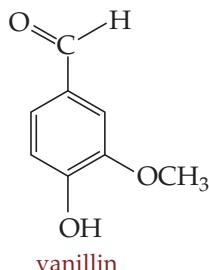
The model described in Figure 30.3(c) leads to the description of each carbon–carbon bond as having an identical bond length, which is between the length of a carbon–carbon single bond (154 pm) and the length of a carbon–carbon double bond (134 pm). This is consistent with the observed bond lengths in benzene (139 pm).

Since we cannot describe the π-bonds in benzene as individual electron-pair bonds between neighboring atoms, we say that the π-bonds are *delocalized* among the six carbon atoms. In Section 30.3 we investigate the effects of delocalization on reactivity and the concept of *aromaticity*. **Figure 30.4** shows the structures of some common aromatic compounds.
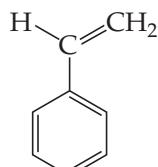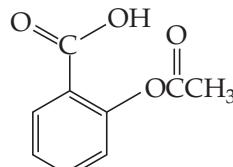
Go Figure   Identify the functional groups attached to benzene in these examples.

vanillin
(from vanilla beans)
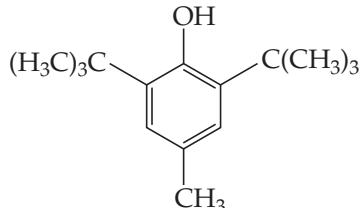
styrene
(used to make polystyrene)
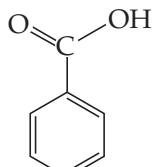
acetylsalicylic acid
(aspirin)

terephthalic acid
(used in forming sails for windsurfers)

2,6-di-*tert*-butyl-4-methylphenol
(BHT—a widely used antioxidant)

benzoic acid
(a fungicide)

▲ Figure 30.4 **Important aromatic compounds.** A small sample of common aromatic compounds containing benzene. These compounds are important in biochemistry, as pharmaceuticals, and in the production of modern materials.
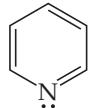
Self-Assessment Exercise

30.1 Naphthalene, $C_{10}H_8$, has two benzene rings fused together along a common edge. How many π-electrons are there in naphthalene?

(a) 6

(b) 8

(c) 10

(d) 12

Exercises

30.2 Pyridine is an analog of benzene in which one of the sp^2 carbon atoms is replaced by nitrogen. **(a)** Does this molecule have delocalized π-bonds? **(b)** Draw a representation for pyridine that illustrates how this delocalization comes about.

(c) How might the lone pair on nitrogen orientate itself within pyridine?

30.3 What structural features help us identify a compound as an aromatic hydrocarbon?

30.4 Name another compound that has the same empirical formula as benzene.

30.2 | Isomerism and Nomenclature in Aromatic Compounds

Benzene and its derivatives play an important role in much of society. For example, when polymerized styrene forms polystyrene, a substance used for insulation and as a building material; tyrosine and phenylalanine are important naturally occurring amino acids that are benzene derivatives; phenols, the hydroxylated form of benzene, are the principal components of the tannins and are responsible for the antioxidant capacity of red wine; vanillin is the compound responsible for the very pleasant sweet, buttery smell associated with the extract of the vanilla plant. Finally, many drugs are composed around a benzene core, including aspirin and paracetamol.

Aspirin, for example, is the common name of acetylsalicylic acid, a benzene-containing compound used commonly as an analgesic for pain relief. Aspirin was developed by Bayer in 1853 though salicylic acid present in willow bark had been known to relieve headaches since around 450 BCE.

Many other compounds isolated during the 19th century were related to benzene. For example, toluene was extracted by distillation from the balsam of the tolu tree in the 1840s. Each of these compounds had a low C : H ratio and many, such as vanillin, had pleasant rather than pungent aromas. As a result, this group of compounds were called aromatic compounds. We will see in Section 30.3 that, as the unusual properties of aromatic compounds were investigated, the term "aromatic" came to be applied to compounds with an unusual stability, regardless of their odor.

By the end of this section, you should:

• Know the names of simple aromatic compounds

Aromatic compounds or *arenes* are a large and important class of organic compounds. The simplest member of the series is benzene (C_6H_6) and further arenes are formed essentially by fusing another C_6 skeleton to benzene. Each aromatic ring
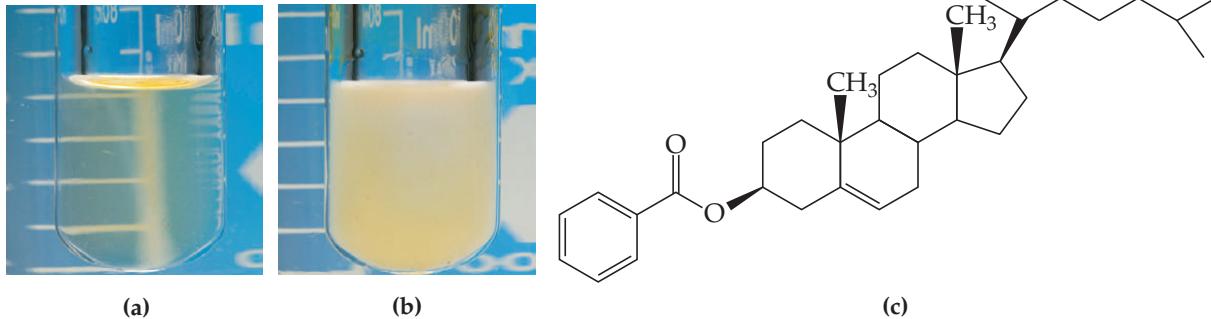
CHEMISTRY AND LIFE The Discovery of Liquid Crystals

In 1888 Frederick Reinitzer (1857–1927), an Austrian botanist, discovered that an organic compound he was studying, cholesteryl benzoate, had interesting and unusual properties. When heated, the substance melts at 145 °C to form a viscous milky liquid; at 179 °C the milky liquid suddenly becomes clear. When the substance is cooled, the reverse process occurs. Reinitzer's work represents the first systematic report of what we now call a *liquid crystal* (**Figure 30.5**).
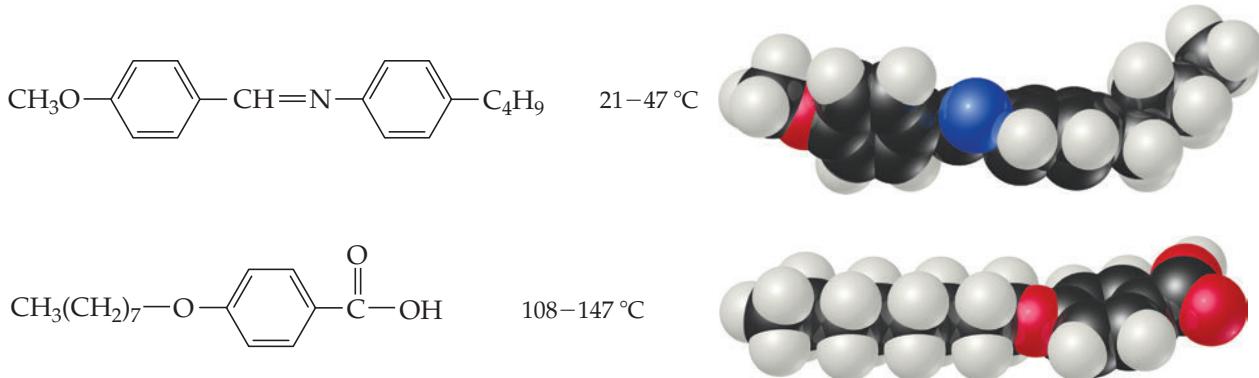
Instead of passing directly from a solid to the liquid phase when heated, some substances, such as cholesteryl benzoate, pass through an intermediate liquid crystalline phase that has some of the structure of solids and some of the freedom of motion possessed by liquids. Because of partial ordering, liquid crystals may be very viscous and possess properties between that of a solid and a liquid. The region in which they exhibit these properties is marked by sharp transition temperatures, as in Reinitzer's example of cholesteryl benzoate.

From the time of their discovery in 1888 until about 30 years ago, liquid crystals were largely a laboratory curiosity. However, researchers found that the weak intermolecular forces that hold the molecules together in a liquid crystal are easily affected by changes in temperature, pressure and electric fields. As a result, liquid crystals are now widely used as temperature and pressure sensors and in the displays of electrical devices such as digital watches, calculators, mobile phones and laptop and hand-held calculators.
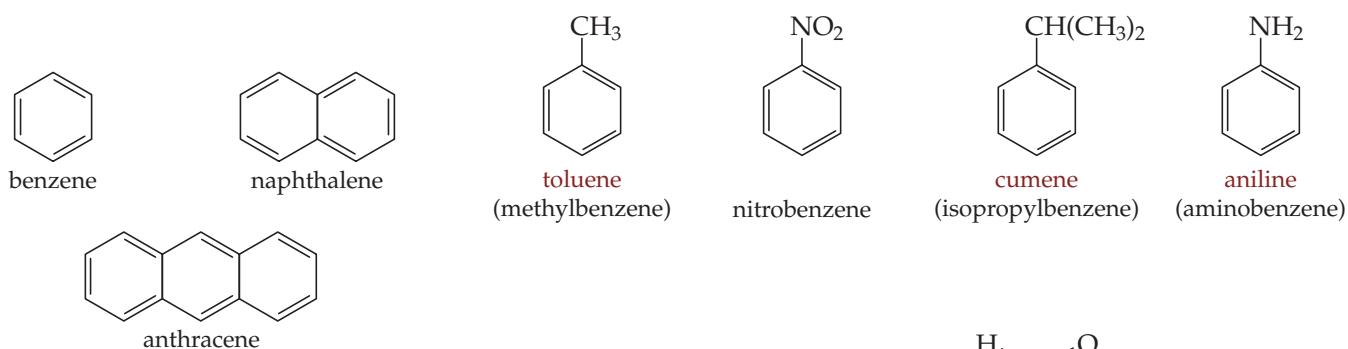
Substances that form liquid crystals are often composed of long, rod-like molecules. They usually contain a long-chain alkane component (minimum chain length of five carbons) linked to an aromatic group such as benzene (**Figure 30.6**). The liquid crystalline properties they exhibit are in fact due to the ordered interplay of London dispersion forces and aromatic–aromatic interactions, also called π–π interactions.

(a)   (b)   (c)
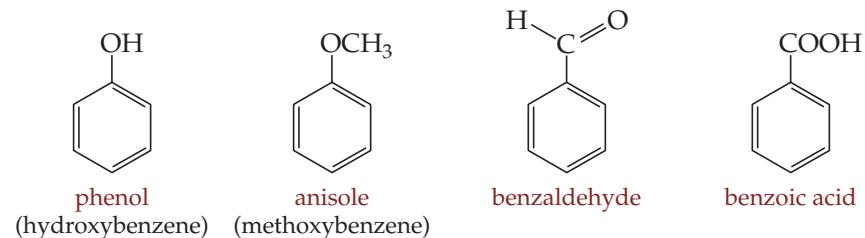
▲ **Figure 30.5 Liquid and liquid crystal.** (a) Molten cholesteryl benzoate at a temperature above 179 °C. In this temperature region the substance is a clear liquid. Note that the printing on the surface of the beaker behind the sample test tube is readable. (b) Cholesteryl benzoate at a temperature between 179 °C and its melting point, 145 °C. In this temperature interval, cholesteryl benzoate exists as a milky liquid crystalline phase. (c) The structure of cholesteryl benzoate.

▲ **Figure 30.6 Structures and liquid crystal temperature intervals of two typical liquid crystalline materials.** The temperature interval indicates the temperature range in which the substance exhibits liquid crystalline behavior.

benzene naphthalene

anthracene
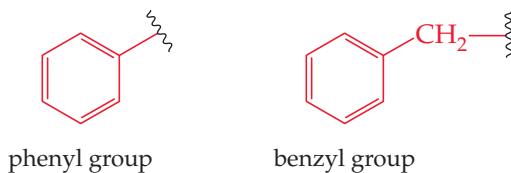
▲ **Figure 30.7 Condensed structural formulas and common names of several aromatic compounds.** The aromatic rings are represented by hexagons with a circle inscribed inside to denote aromatic character. Each corner represents a carbon atom. Each carbon is bound to three other atoms—either three carbons or two carbons and a hydrogen. The hydrogen atoms are not shown.

CH_3

NO_2

$CH(CH_3)_2$

NH_2

toluene
(methylbenzene) nitrobenzene cumene
(isopropylbenzene) aniline
(aminobenzene)

OH

OCH_3

H—C=O

COOH

phenol
(hydroxybenzene) anisole
(methoxybenzene) benzaldehyde benzoic acid
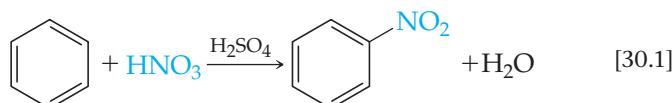
▲ **Figure 30.8 Benzene derivatives containing a single functional group.** The eight most common monosubstituted benzenes are listed together with their systematic and common names.

system is given a common name, as shown in **Figure 30.7**. The systematic names of monosubstituted benzenes are usually derived from benzene, although some common names are still used. For example, methylbenzene is known more commonly as toluene. The common names phenol, anisole, benzaldehyde, benzoic acid and aniline are also retained. **Figure 30.8** illustrates some systematic and common names.
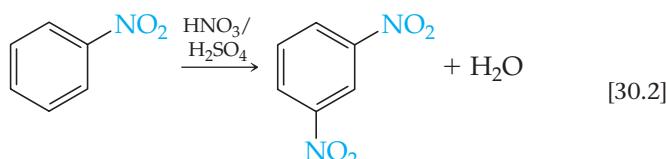
The substituent group C_6H_5 formed by the loss of a hydrogen atom from benzene is called a **phenyl group**. The loss of a hydrogen atom from toluene leads to a **benzyl group**.

phenyl group benzyl group

When a benzene ring has two substituents, they can form three possible constitutional isomers—*ortho*, *meta* and *para* (**Figure 30.9**). When benzene is warmed in a mixture of nitric and sulfuric acids, for example, hydrogen is substituted by the nitro group, NO_2:

$$\text{benzene} + HNO_3 \xrightarrow{H_2SO_4} \text{nitrobenzene } NO_2 + H_2O \qquad [30.1]$$
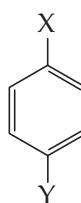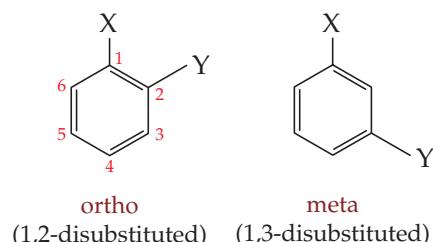
More vigorous treatment results in substitution of a second nitro group into the molecule:

$$NO_2 \xrightarrow[H_2SO_4]{HNO_3/} NO_2 \; NO_2 + H_2O \qquad [30.2]$$
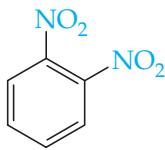
Go Figure How many *ortho*, *meta* and *para* positions exist in a monosubstituted benzene?

ortho
(1,2-disubstituted) meta
(1,3-disubstituted)

para
(1,4-disubstituted)
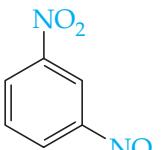
▲ **Figure 30.9 Substitution on benzene.** There are three ways of arranging two substituents on benzene—as *ortho*, *meta* and *para* substitution. Each isomer has different physical and chemical properties.
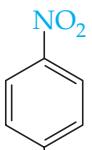
The three possible isomers of benzene with two nitro groups attached are *ortho-*, *meta-* and *para-*dinitrobenzene:

|		
ortho-dinitrobenzene	*meta*-dinitrobenzene	*para*-dinitrobenzene
mp 118 °C	mp 90 °C	mp 174 °C

The *meta* isomer is formed as the major product of the reaction of nitric acid with nitrobenzene. We will explore the reason for this further in Section 30.5.
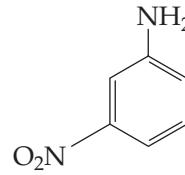
When one of the two substituents on the ring is able to impart a common name (for example, aniline, toluene, phenol), the compound is named based on that parent molecule. The substituent that imparts the common name occupies position number 1. When neither group imparts a common name, the two substituents are listed alphabetically (with the lowest position numbers possible) before ending in *benzene*. The same rules apply to three or more substituents.
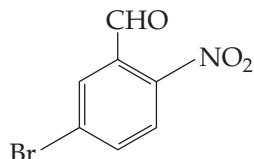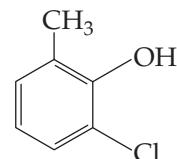
2-ethyltoluene or	4-chlorophenol or	3-nitroaniline or
o-ethyltoluene	*p*-chlorophenol	*m*-nitroaniline

|	
5-bromo-2-nitrobenzaldehyde	2-chloro-6-methylphenol
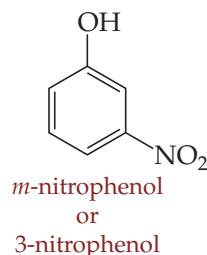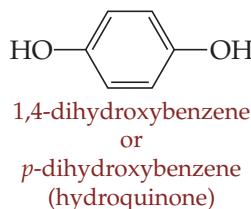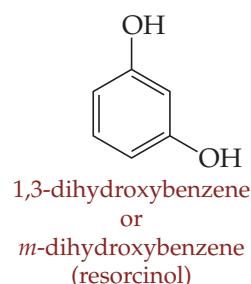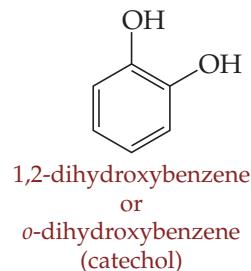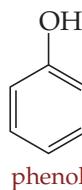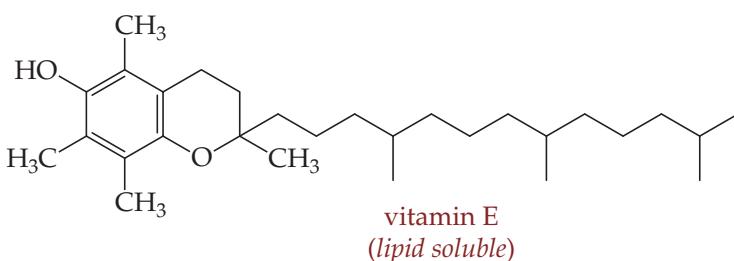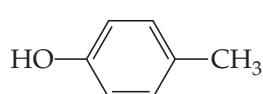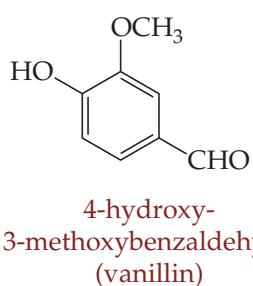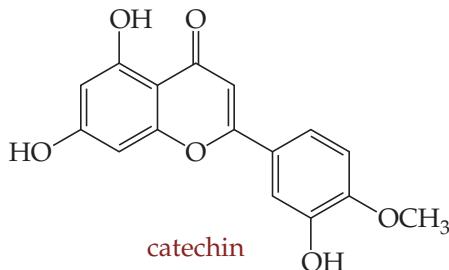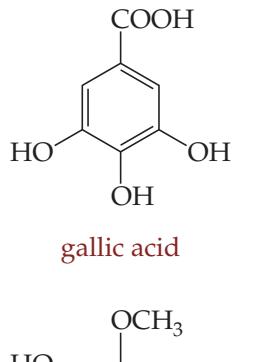
In naming disubstituted benzenes, either position numbers or the use of *o* for *ortho*, *m* for *meta* and *p* for *para* is acceptable. For the more substituted benzenes, only position numbers are used. As with other nomenclature we have studied, these position numbers need to be made as small as possible while maintaining the parent molecule group at position 1. Where a choice of parent group exists, there is a hierarchy similar to that used for multifunctional alkanes. For example, 2-chloro-6-methylphenol is named as such and not as 3-chloro-2-hydroxytoluene. This hierarchical method of naming is based on which functional group is of higher order. A useful, though not exhaustive, order is:

toluene < aniline < phenol < benzaldehyde < benzoic acid

Phenols

Phenols, or hydroxybenzenes, are named after the parent compound, phenol, which was first isolated from coal tar in 1834. The phenol structure is based on the direct attachment of the OH group to a benzene ring. This connectivity confers unique properties on phenols. Some phenol derivatives are named as substituted phenols, others as hydroxy compounds, depending on which other functional groups are present. Many have trivial names.

Phenols are an important class of natural product, widely distributed throughout nature. Several examples of naturally occurring phenols are shown here and in **Figure 30.10**. Gallic acid and catechin are phenols found in wines. One of their properties is to act as an antioxidant. Compare their structure with another phenolic antioxidant, vitamin E. Vanillin is the compound responsible for the odour produced by vanilla beans. The cresols, of which *p*-cresol is shown, are isolated from coal tar. They found use in the 1960s–1980s as a wood preservative. There is evidence to suggest that due to their anti-oxidant properties, the polyphenols in fruit and vegetable juice, and in wine, may play an important role in delaying the onset of colds and in more specific conditions such as Alzheimer's disease.

gallic acid

catechin

4-hydroxy-3-methoxybenzaldehyde
(vanillin)

p-cresol or
4-methylphenol

vitamin E
(*lipid soluble*)

The largest single use of phenol is as an intermediate in the production of low-cost thermoset resins (called *phenolic resins*), used in the production of plywood adhesive as well as in the construction and car industries. Medicinally, phenol and its derivatives have been used in the past as a disinfectant and as a topical anesthetic in preparations such as ointments, ear and nose drops, cold sore lotions, throat lozenges and antiseptic lotions.

phenol

1,2-dihydroxybenzene
or
o-dihydroxybenzene
(catechol)

1,3-dihydroxybenzene
or
m-dihydroxybenzene
(resorcinol)

1,4-dihydroxybenzene
or
p-dihydroxybenzene
(hydroquinone)

m-nitrophenol
or
3-nitrophenol

▲ Figure 30.10 Common phenols.

Self-Assessment Exercise
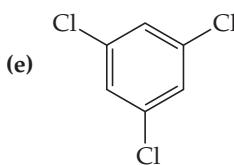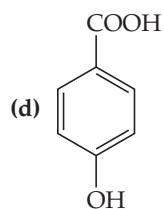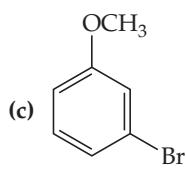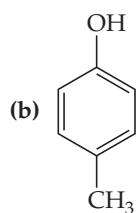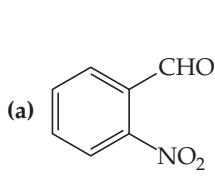
30.5 Dimethylbenzene is usually called xylene. Which name unambiguously describes the following structure?

(a) o-xylene

(b) m-xylene

(c) p-xylene

Exercises

30.6 Name the following structures.

(a) *(structure: benzene ring with CHO and NO$_2$ groups)*

(b) *(structure: benzene ring with OH and CH$_3$ groups)*

(c) *(structure: benzene ring with OCH$_3$ and Br groups)*

(d) *(structure: benzene ring with COOH and OH groups)*

(e) *(structure: benzene ring with three Cl groups)*
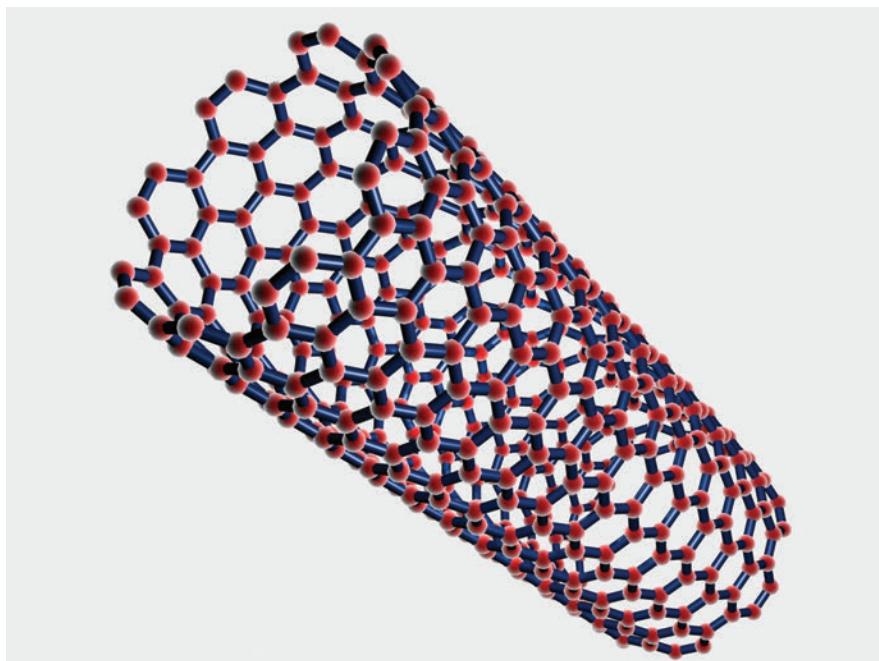
30.7 When naphthalene is reacted with nitric and sulfuric acids, two compounds containing one nitro group are formed. Draw the structures of these two compounds.

30.3 | Aromaticity

The illustration portrays an atomic model of a carbon nanotube. The fact that carbon nanotubes can be made either semiconducting or metallic is unique among all solid-state materials. Because the basic elements of the transistor are semiconductors and metals, there is great interest in building nanoscale electronic circuits using only carbon nanotubes. Carbon nanotubes are also being explored for their mechanical properties. Experiments on individual carbon nanotubes suggest that they are stronger than steel of the same dimensions. Carbon nanotubes have also been spun into fibres with polymers, adding great strength and toughness to the composite material.
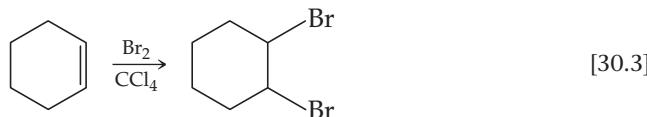
By the end of this section, you should be able to:

• Recognize an aromatic compound based on three criteria

The planar, highly symmetrical structure of benzene, with its 120° bond angles, suggests a high degree of unsaturation. You might therefore expect benzene to resemble the unsaturated hydrocarbons and be highly reactive. The chemical behavior of benzene, however, is unlike that of alkenes or alkynes. Benzene and the other aromatic hydrocarbons are much more stable than alkenes and alkynes because the π-electrons are delocalized in the unhybridized p orbitals (Section 30.1).

Let's consider two molecules, cyclohexene and benzene, and their reactions with bromine. Although cyclohexene reacts readily with bromine at room temperature, benzene does not react with bromine at all under these conditions.

The systematic and common names are listed.

[30.3]

[30.4]

FIGURE 30.12 illustrates the structure of cyclohexatriene and its difference from benzene. This difference is due to the property of **resonance**. Resonance is an extremely important concept in describing the bonding in and stability of organic molecules, particularly aromatic and other highly conjugated molecules. For many molecules and ions, no single Lewis structure provides a truly accurate representation, so a set of **resonance structures** is often used to describe a molecule or ion. For example, there are two equivalent Lewis structures for benzene, each of which satisfies the octet rule. These two structures are in resonance, each resonance structure showing three C—C single bonds and three C—C double bonds, but the double bonds are in different places in the two structures. The actual structure is neither of these two but somewhere intermediate to both.

In the case of benzene, curved arrows can also be used to interconvert the two canonical structures as shown in **FIGURE 30.13**.
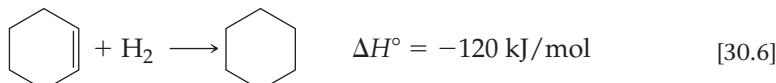
So far we have discussed benzene as an aromatic compound, but what is aromaticity? Originally, molecules derived from benzene were called aromatic purely because of their smell. Later, however, the German chemist Eric Hückel (1896–1980) defined what an aromatic compound is through a set of criteria. It must:

1. be cyclic and planar;

2. have at least one unhybridized p orbital on each atom of the ring; and

3. have $[4n + 2]$ π-electrons, where n is an integer $n = 0, 1, 2, 3 \ldots$
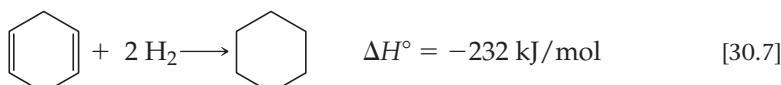
Aromatic molecules resist any move to break that aromaticity. This resistance is quantified as aromatic stabilization or **resonance energy**. We can estimate the stabilization of the π-electrons in benzene by comparing the energy released when hydrogen gas reacts with benzene (a reaction known as *hydrogenation*) to form a saturated compound, with the energy required to hydrogenate certain alkenes. The hydrogenation of benzene to form cyclohexane can be represented as

$\Delta H° = -208 \text{ kJ/mol}$
[30.5]

The enthalpy change in this reaction is -208 kJ/mol. The heat of hydrogenation of the cyclic alkene cyclohexene is -120 kJ/mol:

$\Delta H° = -120 \text{ kJ/mol}$
[30.6]

Similarly, the heat released on hydrogenating 1,4-cyclohexadiene is -232 kJ/mol^{-1}:

$\Delta H° = -232 \text{ kJ/mol}$
[30.7]
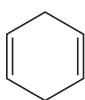
From these last two reactions, it appears that the heat of hydrogenating each double bond is roughly -116 kJ/mol. Since benzene has the equivalent of three double bonds, we might expect that the heat of hydrogenating benzene would be about three times -116 kJ/mol (or -348 kJ/mol). Instead, the heat released is 140 kJ less, indicating that benzene is more stable than would be expected for three double bonds. The difference of 140 kJ/mol^{-1} between the "expected" heat of hydrogenation, -348 kJ/mol, and the

observed heat of hydrogenation, -208 kJ/mol, is due to stabilization of the π-electrons through delocalization.
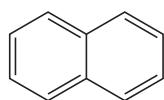
Many other molecules apart from aromatic hydrocarbons show aromaticity. These molecules typically contain one or more **heteroatoms** (for example, O, N, S). Such compounds, called **heterocyclic compounds**, tend to be biologically active and are dealt with in more detail in Chapter 31.

Self-Assessment Exercise

**30.8** Which of the following compounds is aromatic?
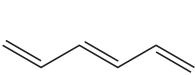
(a)   (b)   (c)   (d)

Exercises

30.9 **(a)** Use the concept of resonance to explain why all six C—C bonds in benzene are equal in length. **(b)** The C—C bond lengths in benzene are longer than C—C single bonds but shorter than C—C double bonds. Use the resonance model to explain this observation.
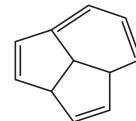
30.10 **(a)** Briefly discuss some of the evidence that has been used to demonstrate the phenomenon of aromaticity. **(b)** Briefly discuss the valence-bond model of aromaticity.

30.11 **(a)** What *two* experimental results prove that cyclohexatriene is a poor representation of the real structure of benzene? **(b)** Benzene has six sp^2-hybridized carbons. How many electrons are left in each of the six p orbitals of benzene? How many electrons in the π-system of benzene? **(c)** With the aid of resonance structures, describe how the structure of benzene and the hypothetical cyclohexatriene differ.

30.12 **(a)** Draw a benzylic cation. **(b)** Use arrow notation to describe why this intermediate is more stable than that for the corresponding methylcyclohexane primary carbocation.

30.13 List the criteria that compounds must meet in order to be considered aromatic.

30.14 **(a)** How many π-electrons should an aromatic molecule contain? **(b)** Is the following molecule aromatic?

30.4 | Acidity of Phenols
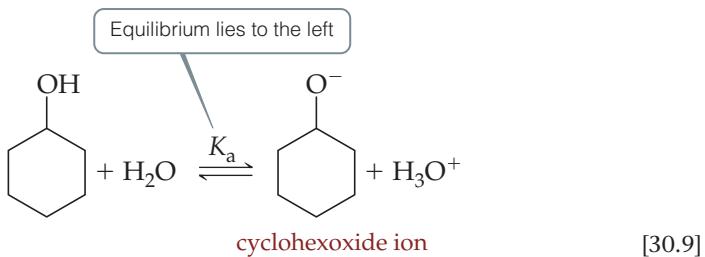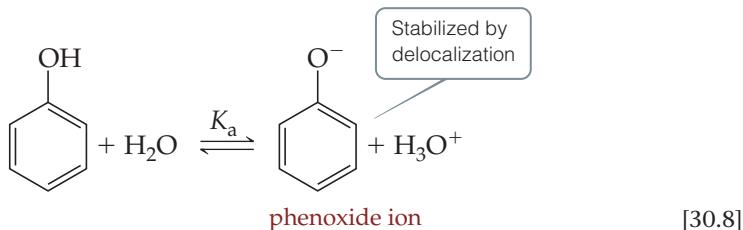
In 1907, the New York–based chemist Leo Baekeland invented the first plastic to be made from synthetic components. He named it Bakelite, after himself, and was granted a patent two years later. It is a thermosetting plastic, which means that, once made, it cannot be melted and reshaped. It is made from phenol and formaldehyde in the presence of a catalyst and a filler such as wood dust or asbestos fibers to form a rigid, highly cross-linked polymer resin. The components can be mixed and even formulated into a powder with the final stage of the curing process being conducted in a mold involving both heat and pressure. Only a couple of minutes were required for the resin to set into a hard, durable, solvent resistant, slightly shiny material which could be turned from the mold while still hot. This made production rapid and the electrical insulating properties of Bakelite meant it was quickly adopted for casings of electrical equipment such as telephones, radios, and light switches. This was expanded to include a lot of household items, toys and games, equipment, and jewelry.

In this section, we look at phenol and, in particular, the acidity of phenol and its derivatives. By the end of the section, you should be able to
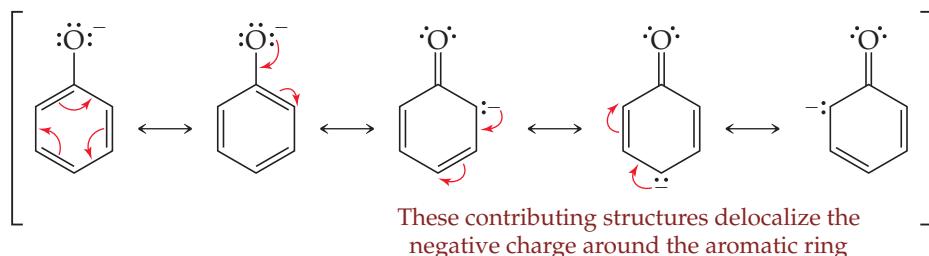
- Understand the factors that affect the acidity of a phenol.

Phenols are approximately 10^6 times stronger acids than alcohols. Phenol was originally named carbolic acid, due to its unusually high acidity for an alcohol. To illustrate the difference in acidity of alcohols and phenols, let us consider two molecules: phenol and cyclohexanol. The chemical equations for their acid-dissociation constants are:

$$\text{phenol} + H_2O \xrightleftharpoons{K_a} \text{phenoxide ion} + H_3O^+ \qquad [30.8]$$

Stabilized by delocalization

phenoxide ion

Equilibrium lies to the left

$$\text{cyclohexanol} + H_2O \xrightleftharpoons{K_a} \text{cyclohexoxide ion} + H_3O^+ \qquad [30.9]$$

cyclohexoxide ion

The pK_a of phenol is about 10, while that for cyclohexanol is about 16 (recall that $pK_a = -\log_{10}K_a$). The difference in acidity between phenol and cyclohexanol is due to the stability of the corresponding anion products. Phenols are more acidic because of the **resonance-stabilized** nature of the anion formed upon deprotonation relative to the alkoxide. This delocalization can be seen in the contributing structures illustrated in **Figure 30.11**.

The stability of the phenoxide ion arises from resonance. The last three structures on the right in Figure 30.11 illustrate, using curved arrow notation, how the charge is

These contributing structures delocalize the negative charge around the aromatic ring

▲ **Figure 30.11 Resonance stabilization.** Phenoxide ions are stabilized relative to alkoxide ions because phenoxide ions are able to resonance stabilize the negative charge around the aromatic ring.

TABLE 30.1   Relative pK$_a$ values for selected alcohols and phenols*

Compound	Structural formula	pK$_a$	
Hydrogen chloride	HCl	−7	**Stronger acid**
Picric acid		0.5	
2,4-Dinitrophenol		4	
4-Nitrophenol		7	
4-Chlorophenol		9	
p-Cresol		10	
Phenol		10	
Water	H$_2$O	15.7	
1-Propanol	CH$_3$CH$_2$CH$_2$OH	16	**Weaker acid**

* Error in measurement ±0.2.

distributed to the *ortho* and *para* positions of the aromatic ring. This charge distribution through resonance is important to the reactivity of aromatic compounds.

In contrast to phenoxide, the cyclohexoxide ion doesn't allow for charge delocalization; the charge is localized on oxygen. Although arrow notation and the use of contributing structures allow us to rationalize why phenols are more acidic, they do not give us quantitative information on how strong an acid they might be. The pK$_a$ value needs to be determined experimentally.

Table 30.1 compares the pK$_a$ of several alcohols and phenols. Electron-withdrawing groups on the phenyl ring of phenol increase the acidity through **inductive effects**. **Electron-withdrawing groups** are those that are more electronegative than carbon. They can be atoms (for example, F, Cl, Br) or a collection of atoms such as the *nitro group*, NO$_2$, which, combined, are electron deficient. Each of these groups is able partially to withdraw electron density out of the O—H bond, making this bond weaker and hence the phenol more acidic. They can also contribute to the charge delocalization of the resulting phenoxide ion.

Sample Exercise 30.1
Utilizing the acidity difference
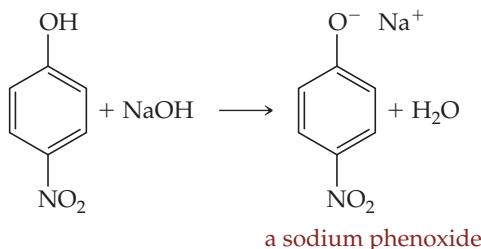
Suggest a method of separating 4-nitrophenol (pK$_a$ = 7) and cyclohexanol (pK$_a$ = 16) in a solution of diethyl ether.

SOLUTION

Analyze We are asked to find a way of separating a phenol and alcohol in an organic solution.

Plan Take advantage of the difference in pK_a between the two compounds and use the extraction method to remove one from the ether. Sodium phenoxides are salts, and many salts (including organic salts) are soluble in water. Cyclohexanol is not soluble in water because of the large cyclohexyl ring, which makes this compound more hydrophobic. The result is that the phenol can be separated into the water layer while the cyclohexanol stays in the diethyl ether layer.

Solve The pK_a of phenols is such that an aqueous 1 M sodium hydroxide (NaOH) solution is basic enough to deprotonate the phenol, but not the cyclohexanol, by the following chemical equation:


a sodium phenoxide
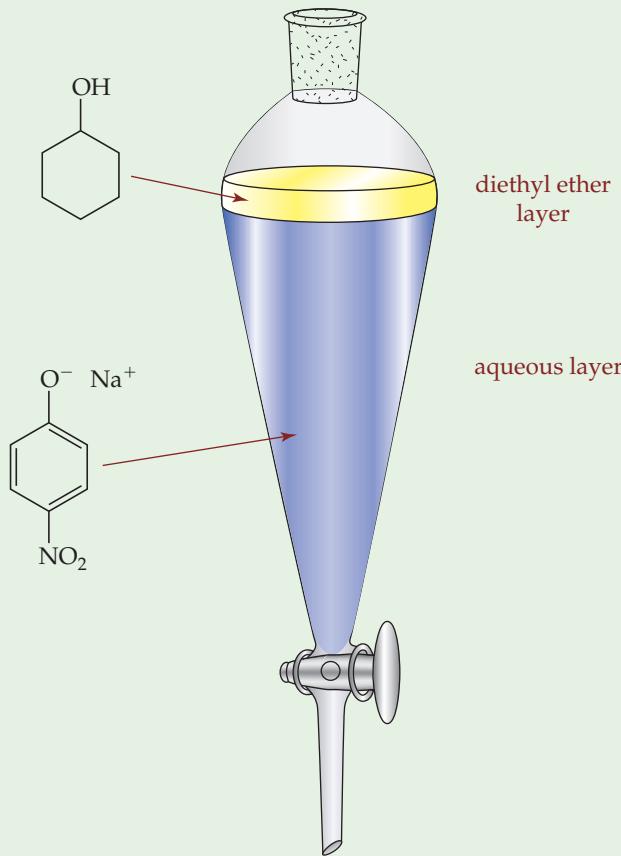
Once reaction has occurred, two layers are formed—an diethyl ether layer and an aqueous layer. The layers are then separated using a separating funnel.
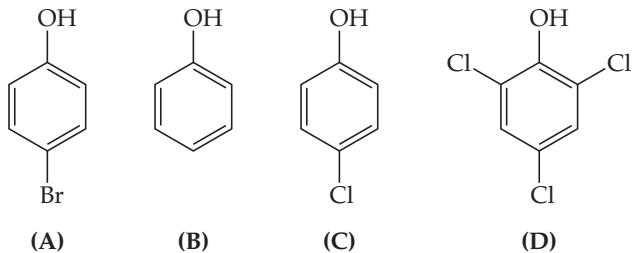
Once the two solutions are separated, the diethyl ether can be distilled off (bp 35 °C) to leave the pure cyclohexanol. Acidification of the aqueous layer using 1 M HCl yields 4-nitrophenol as a solid, which can be filtered off and dried.

▶ **Practice Exercise**
Arrange these compounds in increasing order of acidity: 2,4-dichlorophenol, phenol, 2,6-dinitrophenol and 4-nitro-2-chlorophenol, using the trends in Table 30.1.

diethyl ether layer

aqueous layer

Self-Assessment Exercise

30.15 Order the following in terms of increasing acidity.

(A)   (B)   (C)   (D)

(a) A < B < C < D
(b) B < A < C < D
(c) B < C < D < A
(d) D < C < A < B

Exercises

30.16 The phenolate ion gains stability through contributing resonance structures unlike the alkoxides ion. What does this tell you about the relative basicity of the alkoxide and phenolate ions?

30.17 The acidity of the chlorophenols increases in the order *p*-chlorophenol < *m*-chlorophenol < *o*-chlorophenol. Explain this effect.

30.18 Draw a flow diagram to show how you could separate *p*-chlorophenol from *p*-chlorotoluene.

<div style="text-align:right">

30.5 | **Electrophilic Aromatic Substitution (EAS) Reactions**

</div>
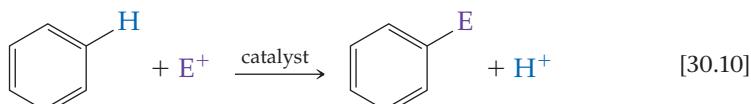
In the mid-1939s, Louis Hammett conducted pioneering work on what became known as linear free-energy relationships. His starting point was to look at how the acidity of benzoic acid changed when substituents were placed in either the *meta* or *para* positions. He then examined different reactions of aromatic compounds and determined how their rates compared for a particular substituent. This enabled him to construct a set of constants, one of which depended on the substituent present and the other on the type of reaction conducted. In this way, he was able to quantify, and understand better, the effect that a substituent has on the reaction of an aromatic compound. He coined the term "physical organic chemistry" to describe this area of the physical measurements of organic reactions.

In this section, we look at the substitution reactions of aromatic compounds and see that they are influenced by what is already attached to the ring. A patten emerges! By the end of this section, you should:

- Have a basic knowledge of the scope of the substitution reactions of aromatic compounds
- Be able to predict the effect a substituent has on the rate and position of substitution in EAS reactions

Although aromatic hydrocarbons are unsaturated, they do not readily undergo addition reactions. The delocalized π-bonding causes aromatic compounds to behave quite differently from alkenes and alkynes.

Benzene, for example, does not react with Cl_2 or Br_2 under ordinary conditions. In contrast, aromatic hydrocarbons undergo substitution reactions relatively easily. Such a reaction is called an **electrophilic aromatic substitution (EAS)** reaction. In a substitution reaction, one atom of a molecule is replaced (substituted) by another atom or group of atoms. These reactions occur in the presence of an electrophile, usually given the symbol E^+. A catalyst is usually needed to generate the electrophile.

$$\text{C}_6\text{H}_5\text{—H} + E^+ \xrightarrow{\text{catalyst}} \text{C}_6\text{H}_5\text{—E} + H^+ \qquad [30.10]$$

Table 30.2 illustrates the four most common EAS reactions, their names and the nature of the electrophile used. Halogenation, employing either the *bromonium ion* (Br^+)

TABLE 30.2   The four most common forms of electrophilic aromatic substitution reaction
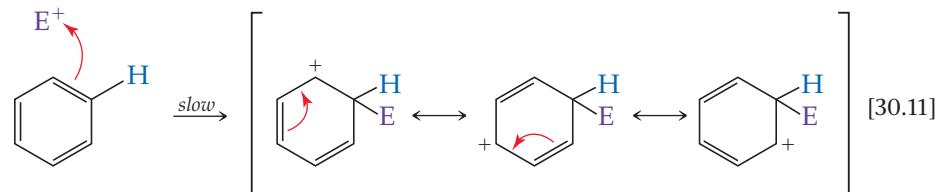
Reaction name	E⁺	Reagent	Catalyst	Products
Halogenation	Cl^+ chloronium	+ Cl_2	$FeCl_3$	+ HCl
Nitration	NO_2^+ nitronium	+ HNO_3	H_2SO_4	+ H_2O
Friedel–Crafts alkylation	R^+ alkyl carbocation	+ RX	$AlCl_3$	+ HX
Friedel–Crafts acylation	RC^+ (with O double bond) acylium ion	+ RCX (with O double bond)	$AlCl_3$	+ HX

Note: The R group represents a general group (for example, alkyl, aryl).
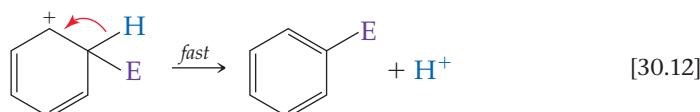
or *chloronium ion* (Cl^+), and nitration, employing the *nitronium ion* (NO_2^+), are useful ways of introducing new functionality to the benzene ring.

The Friedel-Crafts alkylation and acylation reactions generate new C—C bonds. Discovered in the late 1870s, they are two of the most important methods in forming new C—C bonds to the aromatic ring. The alkylation reaction uses carbocations to accomplish the substitution reaction. Tertiary carbocations react more cleanly and more efficiently than 2° or 1° carbocations. The *acylium ion* is formed from an activated carboxylic acid as the electrophile in a Friedel-Crafts acylation. This reaction generates aromatic ketones in high yields.

The mechanism of an electrophilic aromatic substitution reaction involves two steps. The initial step is rate-determining and leads to the formation of a resonance-stabilized carbocation intermediate, sometimes called a Wheland intermediate or sigma complex.

[30.11]

This resonance stabilized intermediate is able to lose H⁺ to regain aromaticity—the driving force in making this reaction a substitution rather than an addition reaction.

[30.12]

Sample Exercise 30.2
Electrophilic aromatic substitution

Draw the structural formula for the major product formed when *p*-xylene (1,4-dimethylbenzene) is reacted with HNO_3/H_2SO_4. Justify your choice for the major product.
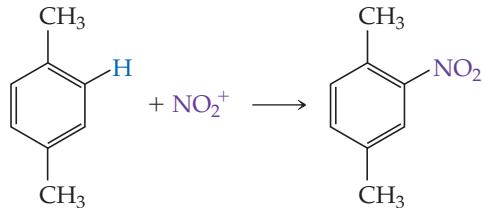
SOLUTION

Analyze We are asked to determine the major product of the reaction of 1,4-dimethylbenzene with a mixture of nitric and sulfuric acid.

Plan The reaction of nitric acid with sulfuric acid yields the nitronium ion, NO_2^+, which is a useful electrophile. We will use this electrophile in a reaction with 1,4-dimethylbenzene.

Solve The major product is identified through the following reaction:

Because of the symmetry of *p*-xylene, substitution occurs in one of four equivalent positions.

▶ **Practice Exercise**
Addition of iodomethane to an aromatic compound, in the presence of $AlCl_3$, yields significant amounts of 4-chlorotoluene. What is the aromatic compound?
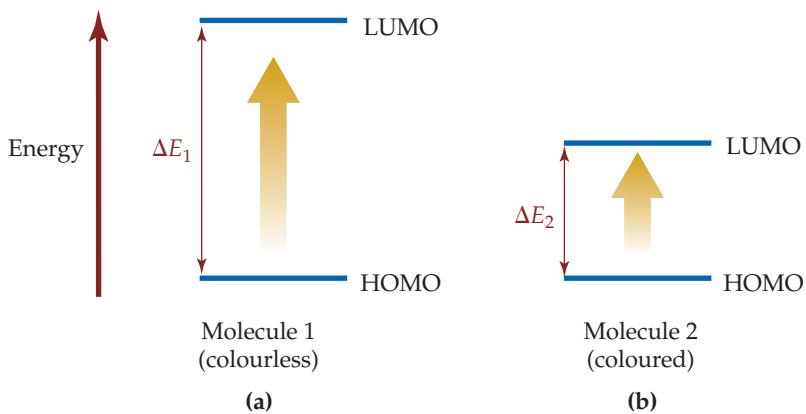
A CLOSER LOOK | Organic Dyes

Light excites electrons in molecules. In a molecular orbital picture, we can envisage light exciting an electron from a filled molecular orbital (MO) to an empty one at higher energy. Because the MOs have definite energies, only light of the proper wavelength can excite electrons. The situation is analogous to that of atomic line spectra. If the appropriate wavelength for exciting electrons is in the visible portion of the electromagnetic spectrum, the substance will appear colored as certain wavelengths of white light are absorbed, whereas others are not.

In using MO theory to discuss the absorption of light by molecules, we focus on two MOs in particular. The *highest occupied molecular orbital* (HOMO) is the MO of highest energy that has electrons in it. The *lowest unoccupied molecular orbital* (LUMO) is the MO of lowest energy that does not have electrons in it. The energy difference between the HOMO and the LUMO—known as the HOMO–LUMO gap—is related to the minimum energy needed to excite an electron in the molecule. Colorless or white substances usually have such a large HOMO–LUMO gap that visible light is not energetic enough to excite an electron to the higher level (**Figure 30.12**). For example, the typical energy needed to excite an electron in naphthalene corresponds to light with a wavelength of 200–300 nm, which is far into the ultraviolet part of the spectrum. As a result, naphthalene cannot absorb any visible light and is therefore colorless.

Many of nature's rich colors, such as the green of plants and the bright hues of flowers, and the colors found in an ink-jet printer, are due to *organic dyes* **Figure 30.13**, organic molecules that strongly absorb selected wavelengths of visible light. Organic dyes contain extensively delocalized π-electrons as a result of *conjugation*. The HOMO–LUMO gap in such molecules decreases as the number of conjugated double bonds increases, making it easier to excite the molecule with lower-energy (longer-wavelength) radiation (Figure 30.12). Generally, then, the more conjugated a compound is, the more colored that compound will be.

▲ **Figure 30.12 Molecules absorbing light.** The smaller the energy gap between the HOMO and LUMO within a molecule, the greater the likelihood that the molecule is colored. This is because a light of longer wavelength (lower energy) can be absorbed by the molecule to allow the excitation.
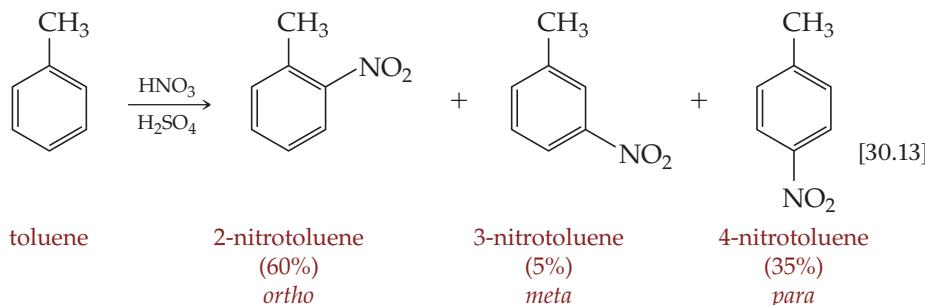

▲ **Figure 30.13 Organic dyes.** Many of the bright colors we see in our lives are a result of aromatic compounds.

Directing Groups and Substitution Effects

So far we have only considered benzene as the starting material for an electrophilic aromatic substitution reaction. Now we ask, what effects will other functional groups have on electrophilic aromatic substitution?

Let us begin to answer this question by looking at the nitration of toluene. In this case, three products, corresponding to the three possible isomers, are formed.

toluene   2-nitrotoluene   3-nitrotoluene   4-nitrotoluene
            (60%)   (5%)   (35%)
            ortho   *meta*   *para*

[30.13]
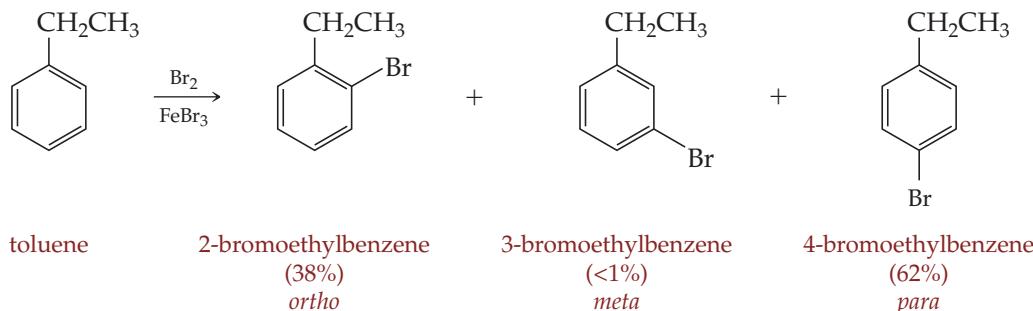
Two things are to be noted here:

1. The nitration of toluene is approximately 25 times faster than that of benzene. In this case we say that toluene is **activated** towards electrophilic aromatic substitution. Therefore the methyl group can be classed as an **activating group**. The fact that nitration only occurs once (dinitration does not happen easily under these conditions) suggests that the nitro group is a **deactivating group**. Further nitration is possible under forcing conditions to give 2,4,6-trinitrotoluene (TNT) (**Figure 30.14**).

2. The product ratio strongly favors both *ortho* and *para* substitution. If all positions on the phenyl ring of toluene were equally reactive, the ratio of nitration at *ortho : meta : para* should be statistical at 40 : 40 : 20 (there are two *ortho* and *meta* positions to one *para* position). This is not the case, so this means that the methyl group is an ***ortho*, *para*-director**. In other words, the methyl group directs a second substituent to the *ortho* and *para* positions, but not to the *meta* position.

Both the activation and product distribution can be rationalized by looking at the intermediates formed after the addition of the electrophile and their relative stabilities, and then comparing this to the nitration of benzene (**Figure 30.15**). We can look at these intermediates because the rate-determining step in this reaction is the addition of the electrophile rather than the re-aromatization leading to the nitrobenzene product.

In both *ortho*- and *para*-attack, an intermediate resonance contributor can be drawn that form a 3° carbocation. As we saw in previous chapters, tertiary carbocations are more stable than either primary or secondary carbocations. In the case of benzene (shown) and for *meta*-attack, only 2° carbocation intermediates are formed. As a result, the overall stability of the intermediates for *ortho*- and *para*-attack are both favored and lower in energy.
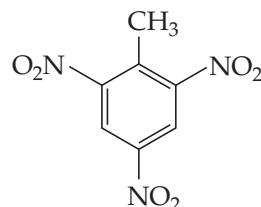
Bromination of ethylbenzene using bromine and iron(III) tribromide (ferric bromide) also follows the same trend, with *ortho*- and *para*-substituted isomers favored. Here, because of steric effects around the ethyl group, the *para*-isomer is favored over the *ortho*-isomer.

<table>
<tr><td>Go Figure</td><td>Why might TNT be explosive?</td></tr>
</table>

▲ **Figure 30.14** **TNT.** Actually TNT is an acronym for 2,4,6-trinitrotoluene, a highly unstable and explosive compound if a force is applied to it.

toluene   2-bromoethylbenzene   3-bromoethylbenzene   4-bromoethylbenzene
            (38%)   (<1%)   (62%)
   *ortho*   *meta*   *para*
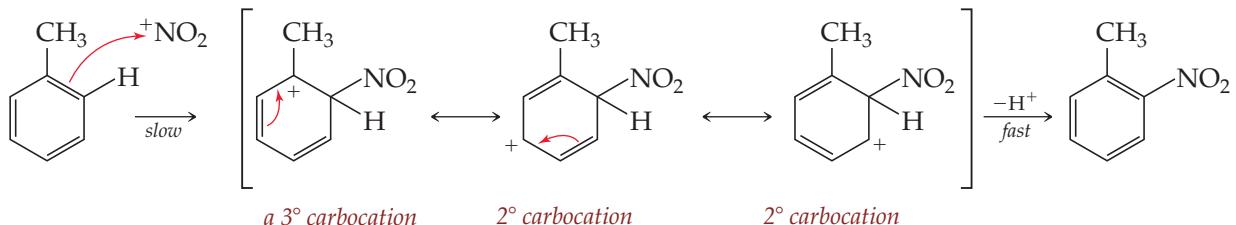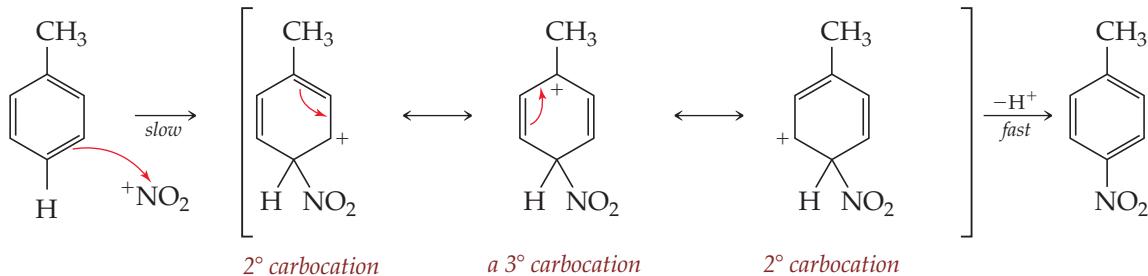
The methyl group in toluene or the ethyl group in ethylbenzene are slightly electron donating, stabilizing the intermediates formed upon the first step of an EAS reaction.

ortho attack

para attack
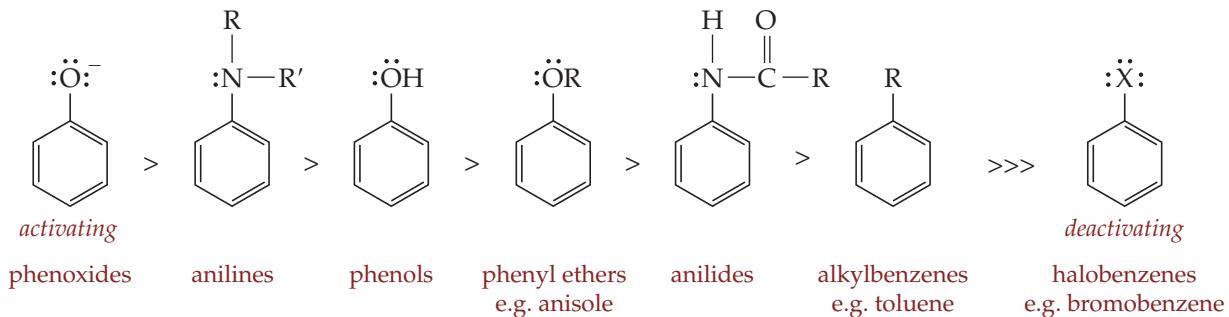
benzene

▲ **Figure 30.15** **Intermediates of nitrating toluene and benzene.** The intermediates of electrophilic aromatic substitution reactions reveal information about which isomer dominates in a reaction.

Generally speaking, *electron-donating groups are ortho, para-directors and activating towards electrophilic aromatic substitution.*

Ortho-, *para*-directing groups and their relative activation for EAS are:

| phenoxides | anilines | phenols | phenyl ethers e.g. anisole | anilides | alkylbenzenes e.g. toluene | halobenzenes e.g. bromobenzene |
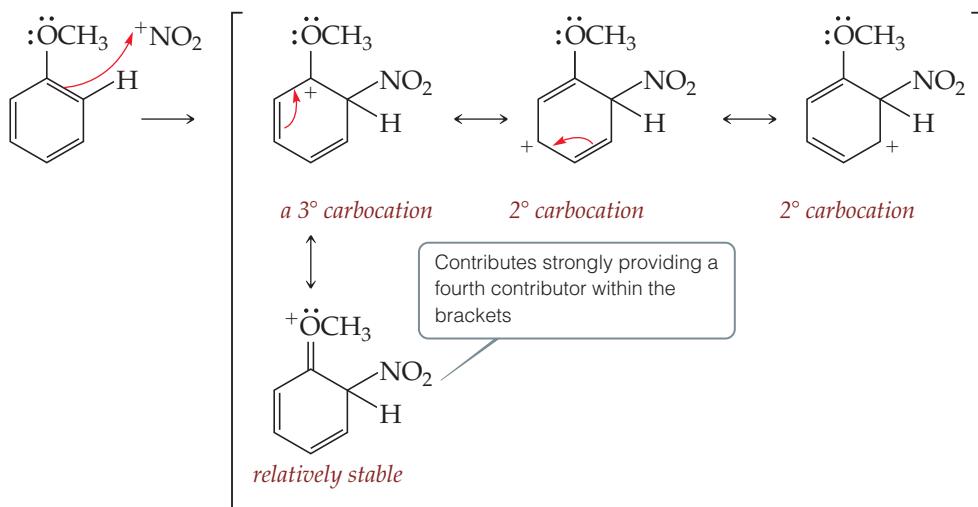
Notice that in many of these cases, the functional group contains a lone pair capable of playing a stabilizing role in the intermediates of an EAS reaction. This effect, which occurs in the first five examples and halobenzenes, is called *resonance stabilization*. In the case of alkylbenzenes, the donation of electron density into the ring is called *inductive stabilization*. In each case, however, some electron density is donated into the ring to stabilize the positive charge generated in the intermediates.
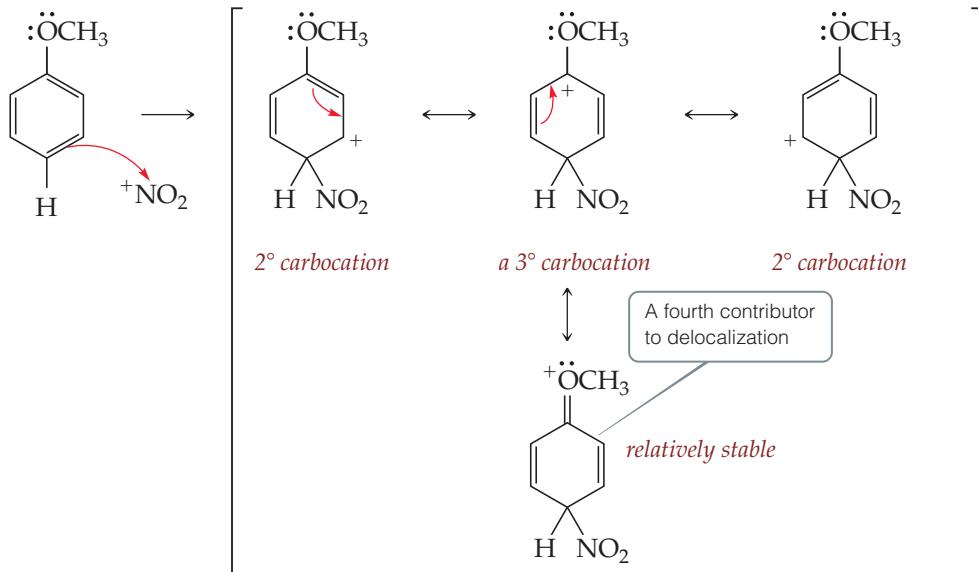
Although the halobenzenes (F, Cl, Br, I) are weakly deactivating by virtue of their inductive electron-withdrawing effects, they are still *o,p*-directing because of their ability to resonance stabilize the cationic intermediates.

To help with your understanding of resonance stabilization, let's look at the intermediates of the nitration of anisole. Here, the alkoxy group ($-OR$) is able to use its non-bonding lone pair to participate in resonance stabilization, forming a very stable fourth contributor in both *ortho*- and *para*-intermediates that is not available in the *meta* case. This difference in the number of contributors is used to rationalize the product distribution. The effect of the methoxy group's activation is such that anisole nitrates 10 000 times faster than benzene.

ortho-attack

a 3° carbocation   2° carbocation   2° carbocation

Contributes strongly providing a fourth contributor within the brackets

$^{+}\ddot{O}CH_3$

relatively stable

para-attack

2° carbocation   a 3° carbocation   2° carbocation

A fourth contributor to delocalization

$^{+}\ddot{O}CH_3$

relatively stable

meta-attack

Only three contributors here, all of which are 2° carbocations
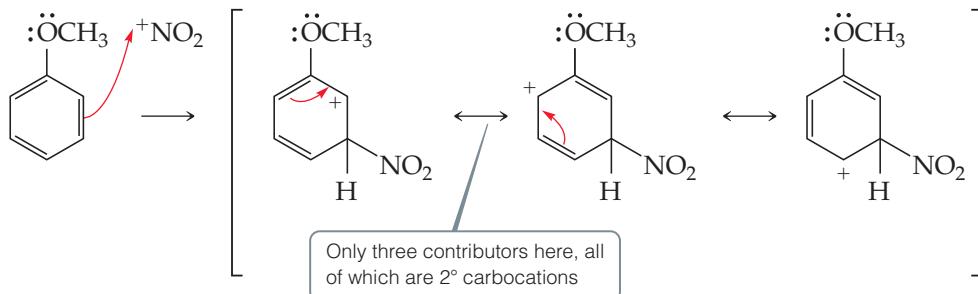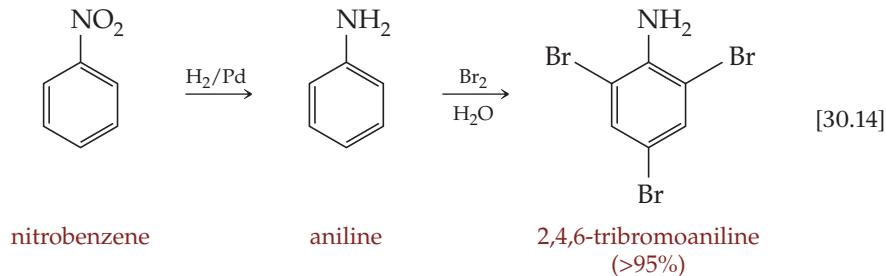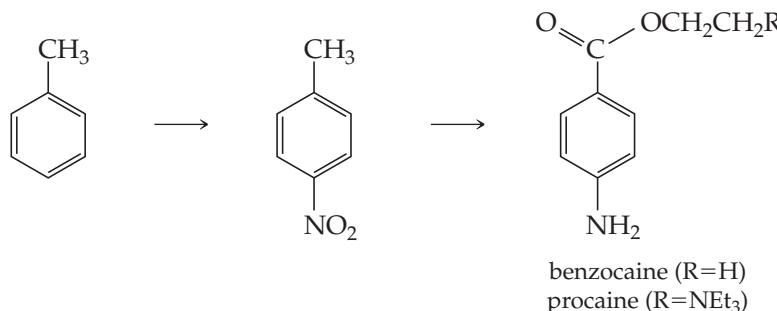
Anilines are very reactive towards EAS and are highly activated *ortho-*, *para*-directors. For example, the bromination of aniline occurs rapidly and without the addition of a catalyst to give the tribromoaniline in excellent yield:

nitrobenzene   aniline   2,4,6-tribromoaniline
(>95%)

[30.14]

Sample Exercise 30.3
EAS reaction

4-Nitrotoluene is the starting material for the synthesis of the local anaesthetics benzocaine and procaine. Describe a synthesis of 4-nitrotoluene starting from toluene.

benzocaine (R=H)
procaine (R=NEt$_3$)
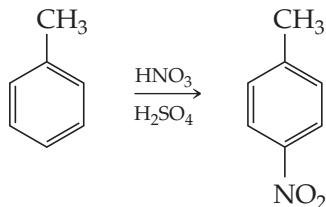
SOLUTION

Analyze We are asked to synthesize 4-nitrotoluene from toluene.

Plan To begin this exercise we look at the functional group differences between starting materials and products. In this reaction, the introduction of a *para*-nitro substituent is made, which can be achieved by EAS.
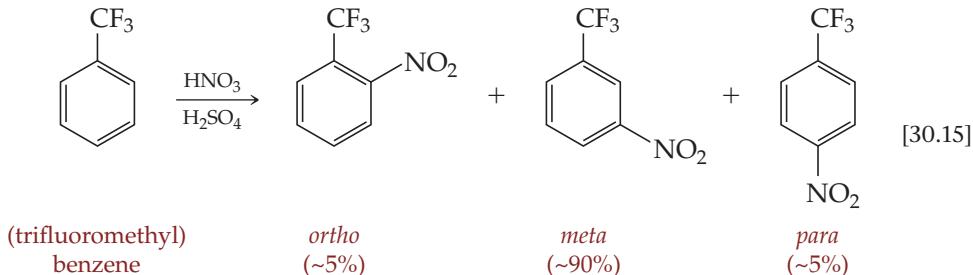
Solve Since methyl groups are *ortho-*, *para*-directing, 4-nitrotoluene can be formed by nitration of toluene and separation of the *ortho-* and *para*-isomers:
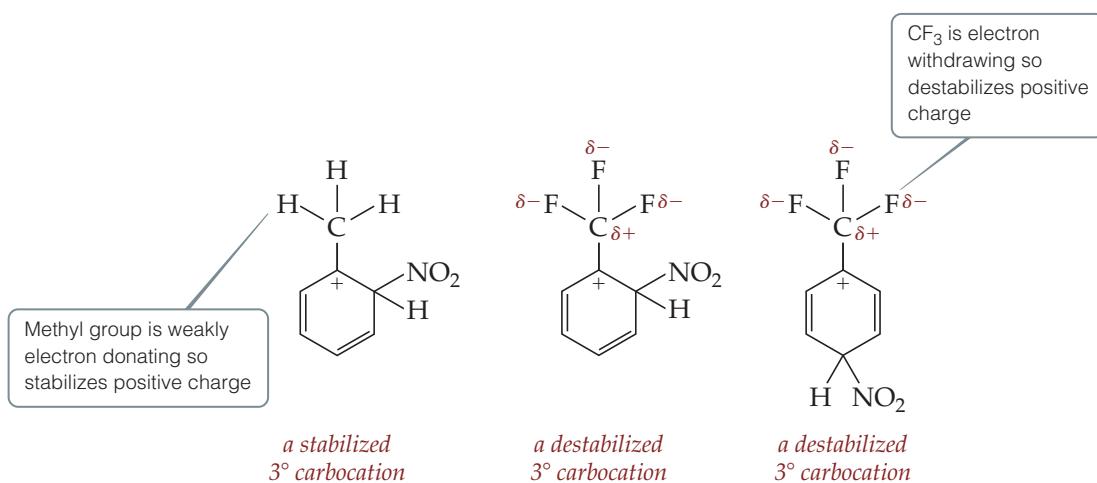
▶ **Practice Exercise**
(a) Would *tert*-butylbenzene (2-methyl-2-phenylpropane) be more or less reactive than benzene towards nitration?
(b) Comment on which position would be favored and why.

So far we have dealt with electron-donating substituents. Now let's see what happens with the nitration of (trifluoromethyl)benzene, an analogue of toluene where each of the methyl hydrogens is replaced with fluorine. In this case, the *meta* product 3-nitro(trifluoromethyl)benzene is almost exclusively formed (~90% yield).

(trifluoromethyl)   *ortho*   *meta*   *para*
benzene   (~5%)   (~90%)   (~5%)

[30.15]
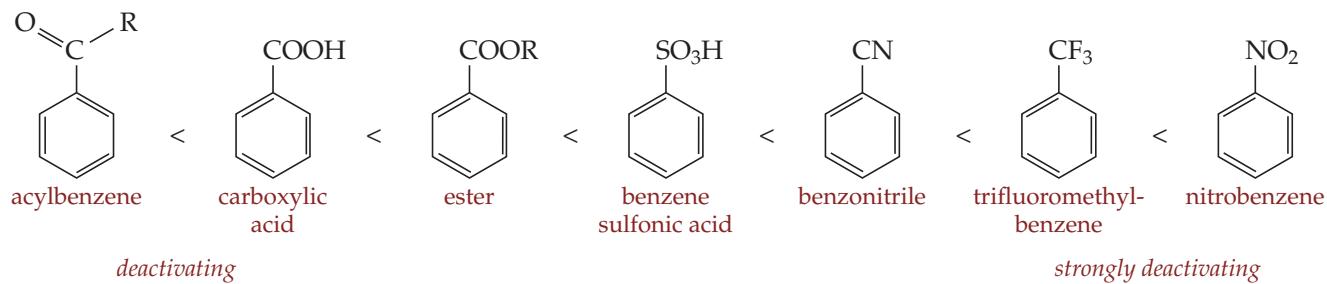
The near exclusive formation of the *meta* isomer means that the trifluoromethyl group is a **meta-director**. Though similar in size, there is a marked difference between the inductive properties of methyl and trifluoromethyl groups. The electronegativity of F compared to H means that inductively the trifluoromethyl group is electron withdrawing. This has two implications.

1. The electron-withdrawing nature means that attack on the electrophile by the electrons of the aromatic ring is impeded. This leads to deactivation.

2. The second is that in the case of *ortho*- and *para*-attack, the once favorable 3° carbocation of toluene is now significantly destabilized by the CF_3 group. This makes the *meta* substitution pathway more favorable. The instability relates to the neighboring location of the carbocation with the electropositive carbon bearing the three fluoro groups. This situation is analogous to that for carbonyl compounds attached to an aromatic ring where the carbonyl carbon is also $\delta+$.

> CF$_3$ is electron withdrawing so destabilizes positive charge

> Methyl group is weakly electron donating so stabilizes positive charge

| *a stabilized* 3° carbocation | *a destabilized* 3° carbocation | *a destabilized* 3° carbocation |
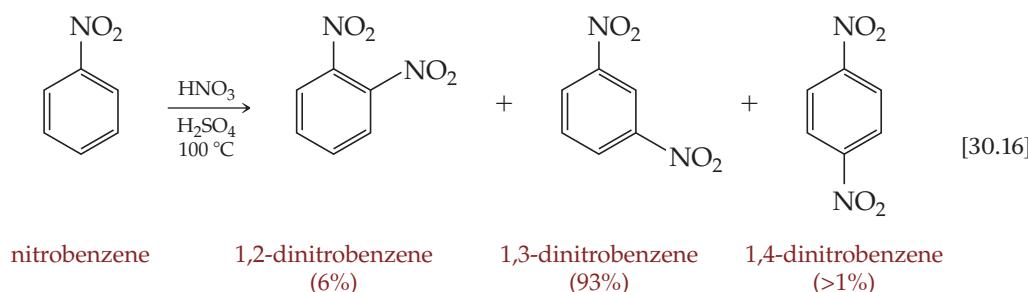
Many groups are *meta*-directing and deactivating. A series of mono-substituted benzenes and their relative deactivation for EAS include:

| acylbenzene | < | carboxylic acid | < | ester | < | benzene sulfonic acid | < | benzonitrile | < | trifluoromethyl-benzene | < | nitrobenzene |

deactivating   *strongly deactivating*
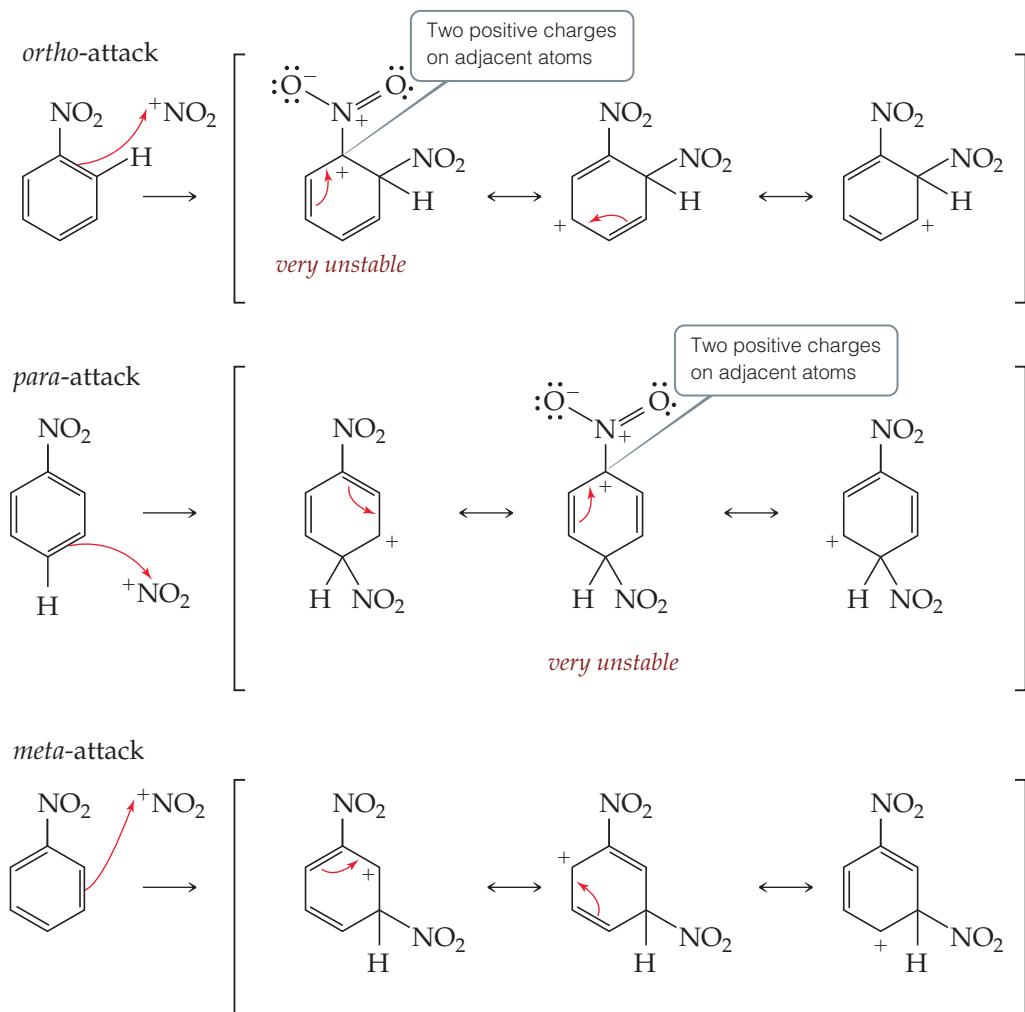
Generally speaking, electron-withdrawing groups are *meta*-directors and deactivating towards electrophilic aromatic substitution.

Let us complete our appreciation of directing groups by studying the nitration of nitrobenzene. The nitration of nitrobenzene is approximately 100 000 times slower than the nitration of benzene. In this case, the nitro group is said to be *strongly deactivating* and more forcing conditions are required to nitrate. This is due to the inductive electron-withdrawing effects of the nitro group, weakening the attack of the aromatic ring on the electrophile.

[30.16]

| nitrobenzene | 1,2-dinitrobenzene (6%) | 1,3-dinitrobenzene (93%) | 1,4-dinitrobenzene (>1%) |
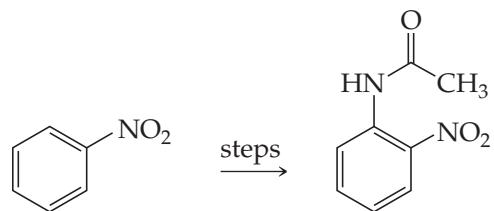
The reason why nitro groups are *meta*-directors becomes more obvious when investigating the resonance forms of the intermediates upon nitration. The proximity of the two positive charges in one resonance form of the *ortho* and *para* cases, in which they are on adjacent atoms, severely destabilizes this group of intermediates, disfavoring *ortho*-, *para*-attack in favor of *meta*-attack.

ortho-attack

para-attack

meta-attack

Sample Exercise 30.4
Directing groups

Determine a suitable pathway for forming 2-nitrophenylacetamide from nitrobenzene.

SOLUTION
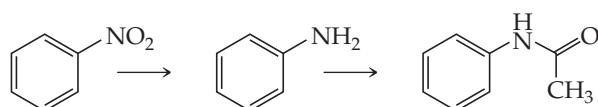
Analyze We are asked to form 2-nitrophenylacetamide from nitrobenzene.

Plan Identify the differences in structure to determine what functionality needs to be added. Our knowledge of directing groups will also play a significant role in the pathway we follow. We also need to have some idea of synthetic transformations.
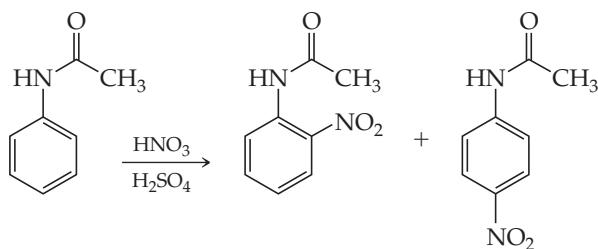
Solve The acetamide group can be formed in two steps from the nitro group by reduction, using catalytic hydrogenation or $SnCl_2$ forming the amine (aniline in this case). Acetylation using acetic anhydride or acetyl chloride leads to the acetamide:

Continued

Acetamides and anilines are *o-*, *p*-directing and activating but nitro groups are *m*-directing and deactivating. Hence it makes sense to nitrate either the aniline or acetamide to give the desired product. You will need to separate the *o-* from *p*-isomer, however.
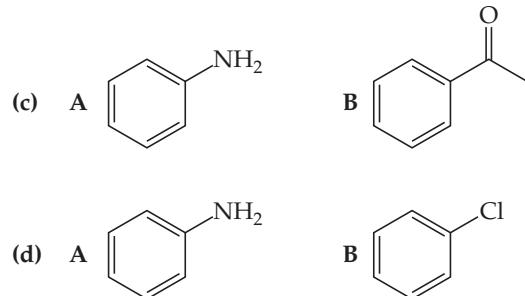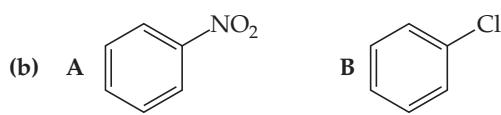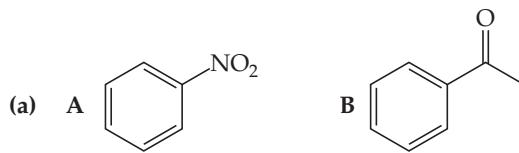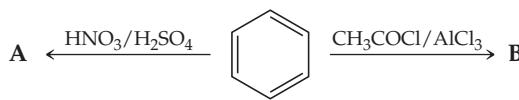

Trying to elaborate a synthesis from the nitrobenzene will undoubtedly lead to *meta* substitution, so this pathway should not be followed in this case.

▶ **Practice Exercise**
Which reacts more rapidly with HNO_3/H_2SO_4: anisole, toluene or nitrobenzene?

Self-Assessment Exercise

30.19 What product is formed in each of the following reactions?

(a) A B

(b) A B

(c) A B

(d) A B

30.20 What is the major product of the nitration of benzonitrile (cyanobenzene)?
(a) *ortho*-nitrobenzonitrile
(b) *meta*-nitrobenzonitrile
(c) *para*-nitrobenzonitrile
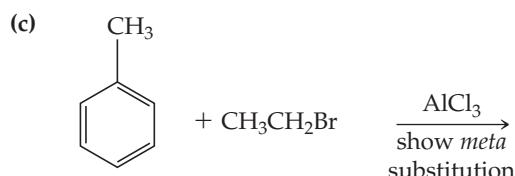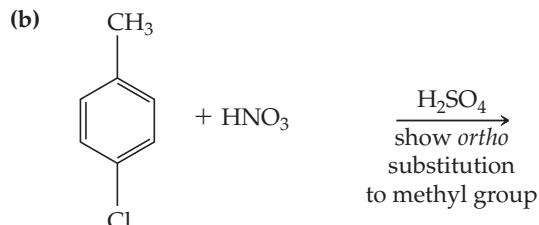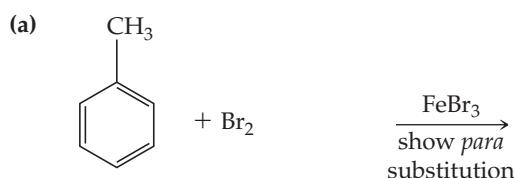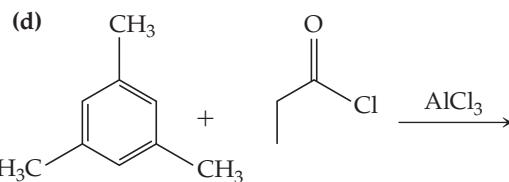
Exercises

30.21 (a) What is the difference between a substitution and an addition reaction? Which one is commonly observed with alkenes and which one with aromatic hydrocarbons? (b) Using condensed structural formulas, write the balanced equation for the addition reaction of 2,4-dimethyl-2-pentene with Br_2. (c) Write a balanced equation for the substitution reaction of Cl_2 with *para*-dichlorobenzene in the presence of $FeCl_3$ as a catalyst.
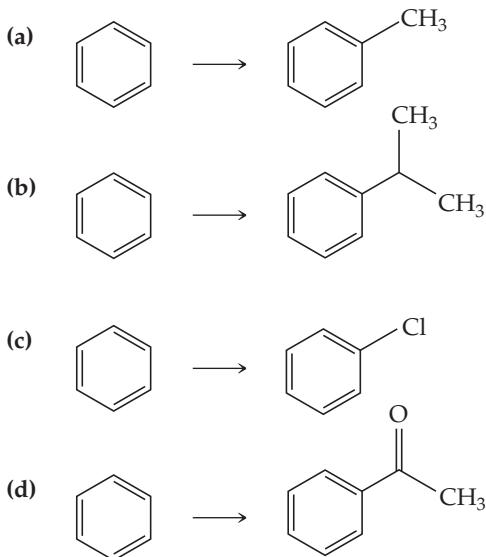
30.22 Write a series of reactions leading to *para*-bromoethylbenzene, beginning with benzene and using other reagents as needed.

30.23 Suggest a suitable product for each of the following transformations. Also, give the name of the reaction type exemplified.

(a)

(b)

(c)

(d)
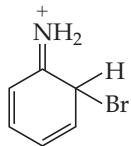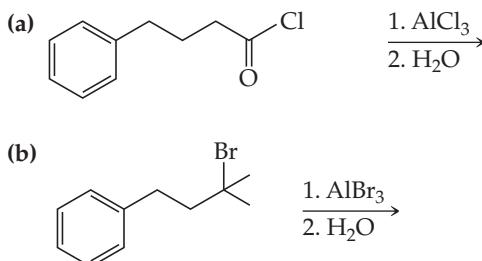
30.24 Suggest ways of conducting the transformations shown here.

(a)

(b)

(c)

(d)

30.25 Draw all the resonance structures of the species shown here.

30.26 Provide the major organic product of the following reactions. [*Hint*: Think intramolecular.]

(a)

1. AlCl₃
2. H₂O

(b)

1. AlBr₃
2. H₂O

30.27 Which of the following functional groups is the most deactivating for EAS? **(a)** methoxy, **(b)** phenol **(c)** ethyl, **(d)** acetamide, **(e)** benzene?
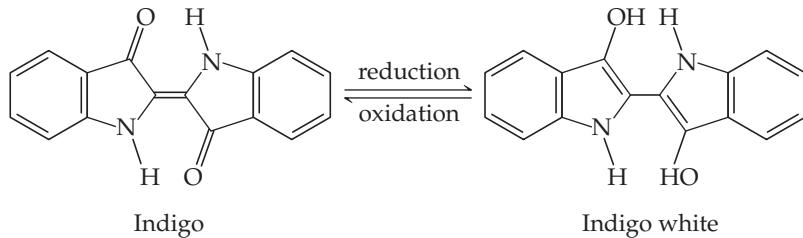
Sample Integrative Exercise
Putting concepts together

Indigo is a dark blue dye with the following structure.

reduction
oxidation

Indigo   Indigo white

(a) Classify the central double bond as either *E* or *Z*. **(b)** Intramolecular hydrogen bonding occurs in indigo but only intermolecular hydrogen bonding occurs in the related diastereoisomer. Explain why this is so. **(c)** The ring containing the nitrogen atom in indigo is planar. What does this suggest about the hybridization of the nitrogen atom? **(d)** Indigo is very insoluble in water. In order for it to be used as a dye, it is first converted to a water-soluble form (indigo white). The cloth is impregnated with solution and, upon oxidation, the blue dye is precipitated in the cloth. What structural feature of indigo white is responsible for the increase in water solubility? **(e)** Is indigo white aromatic?

SOLUTION

Analyze This exercise focuses on the structure of indigo and the effect this has on hydrogen bonding and solubility.
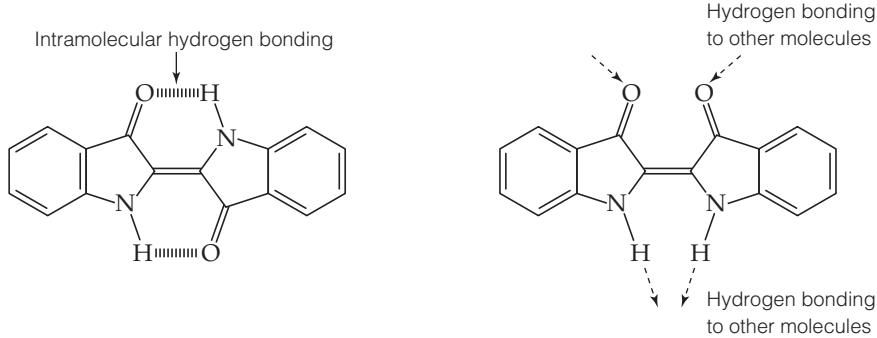
Plan Determine the priority of the groups attached to the central double bond in order to classify it as *E* or *Z* then identify hydrogen bonding sites within the molecule and its isomer. Work out the hybridization of the N atom and examine factors that may influence water solubility.

Continued

Solve

(a) In assigning priorities to the groups at either end of the central double bond, nitrogen has a higher priority than carbon. Consequently indigo has the two high priority groups in an *E* arrangement.

(b) The hydrogen bonding in indigo forms six-member rings which are stable. In the *Z* isomer of this compound the hydrogen bond donor atoms and hydrogen bond acceptor atoms are not matched with each other and consequently can only hydrogen bond to appropriate surrounding molecules.

(c) A planar nitrogen atom with three bonds suggests sp^2 hybridization with the lone pair in a *p* orbital.

(d) Reduction of a ketone to an alcohol group will be accompanied by an increased opportunity for hydrogen bonding and will increase the water solubility of the material.

(e) Yes, it follows the $(4n + 2)$ rule for aromaticity. The lone pair on nitrogen forms part of the aromatic structure.

Chapter Summary and Key Terms

SECTION 30.1 **Aromatic hydrocarbons**, or **arenes**, are compounds containing multiple sp^2-hybridized carbons, most often in a six-membered ring, which we call benzene. They are less reactive than alkenes and undergo very different chemical reactions because of the delocalization of their π-electrons.

SECTION 30.2 Aromatic hydrocarbons larger than benzene that incorporate multiple rings are given trivial names. Simple aromatic hydrocarbons bearing a single substituent are named based on benzene—for example, nitrobenzene. The substituent C_6H_5 is called a **phenyl group**. Loss of a hydrogen from toluene leads to a **benzyl group**. **Phenols** are a benzene derivative bearing a hydroxyl group. Disubstituted benzenes occur as three isomers labelled *ortho*, *meta*, *para*.

SECTION 30.3 Aromatic compounds are stabilized by the contributions of two or more **resonance structures**. **Resonance** is an extremely important concept in describing the bonding and stability of aromatic compounds. The **resonance energy** associated with benzene is the difference in energy between hydrogenating benzene and the theoretical molecule 1,3,5-cyclohexatriene. Compounds are aromatic if they follow Hückel's criteria. The major criterion states that a compound is aromatic if it has $[4n + 2]$ π-electrons and is cyclic.

Heterocyclic compounds contain a **heteroatom**—that is, an atom other than carbon.

SECTION 30.4 Phenols are an unusual class of compound prevalent in nature. Their acidity differs greatly from another common and closely related class, the alcohols, because of the relative stability of the phenoxide ion. The anion is **resonance-stabilized** as a result of the phenolate's ability to distribute the electron density around the aromatic ring. **Electron-withdrawing groups** on the phenyl ring of phenol increase the acidity through **inductive effects**.

SECTION 30.5 Addition reactions are difficult to carry out with aromatic hydrocarbons, but **electrophilic aromatic substitution (EAS) reactions** are easily accomplished in the presence of a catalyst. Two general reactions are halogenation, which substitutes hydrogen for a single halogen (typically Cl or Br), and nitration, which substitutes a hydrogen for NO_2. Two new types of reactions discussed are the **Friedel–Crafts alkylation** and **acylation reactions**. Each of these reaction types is useful as they produce new C—C bonds. Substituted benzenes also undergo EAS, though the substituent can act as an **activating** or **deactivating** depending on whether it is electron donating or electron withdrawing. Generally, electron-donating groups are *ortho-*, *para-directing* whereas electron-deficient groups are *meta-directing*.

Key Skills
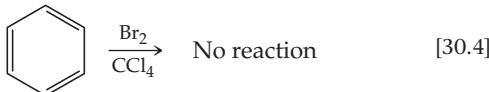
- Know how to derive the name of simple mono- and disubstituted aromatic compounds by positional numbering, for example 1,2-dibromobenzene, as well as by *ortho*, *meta* and *para* nomenclature, for example *o*-dibromobenzene. (Section 30.2)

- Learn the common names such as toluene, phenol, aniline, etc. and the hierarchy of functional groups. (Section 30.2)

- Be able to use the curved arrow notation introduced in Chapter 26 to understand the stability and directive properties of different functional groups on the aromatic structure. (Section 30.5)

- Be able to draw Wheland intermediates to show the directive influences of substituents on benzene in EAS. (Section 30.5)
- Understand why phenols are acidic and be able to describe this through drawing resonance contributors to an intermediate structure. (Section 30.4)
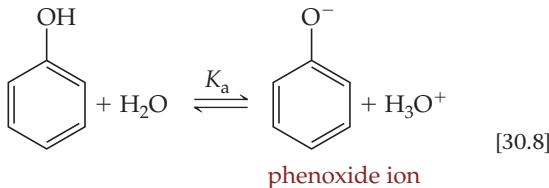
- Be able to identify electrophiles from a given set of reagents, and in the case of substituted benzenes understand qualitatively their directive influences on the product outcome. (Section 30.5)

Key Equations

- Aromaticity

$$\xrightarrow[\text{CCl}_4]{\text{Br}_2} \text{No reaction} \qquad [30.4]$$

- Electrophilic aromatic substitution

$$\xrightarrow{\text{E}^+} \qquad + \text{H}^+ \qquad [30.10]$$

- Acidity

$$+ \text{H}_2\text{O} \underset{}{\overset{K_a}{\rightleftharpoons}} \qquad + \text{H}_3\text{O}^+ \qquad [30.8]$$
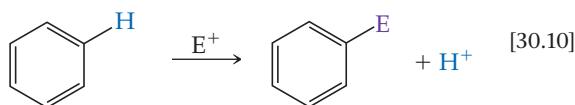
phenoxide ion
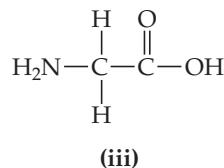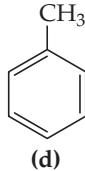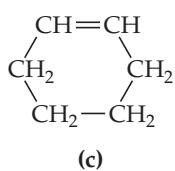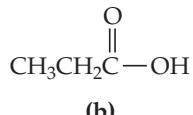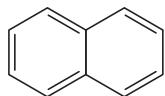
Exercises
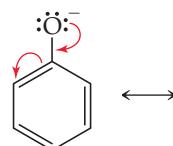
Visualizing Concepts

30.28 **(a)** Draw a six-membered ring as a line drawing and demonstrate how sp^2 hybrid orbitals interact, as in benzene. **(b)** Illustrate how the p orbitals overlap to form a stable aromatic structure. [Section 30.1]
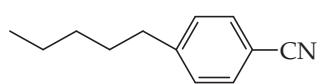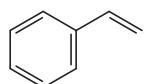
**30.29** Which of the following molecules will readily undergo an electrophilic substitution reaction? [Section 30.5]

(a)

$$\text{CH}_3\text{CH}_2\overset{\displaystyle O}{\overset{\displaystyle \|}{\text{C}}}-\text{OH}$$

(b)

(c)

(d)

**30.30** Consider the following molecules. Which of these would be most likely to exhibit liquid crystalline behavior? [Section 30.3]


(i)


(ii)

$$\text{H}_2\text{N}-\overset{\displaystyle H}{\underset{\displaystyle H}{\text{C}}}-\overset{\displaystyle O}{\overset{\displaystyle \|}{\text{C}}}-\text{OH}$$

(iii)
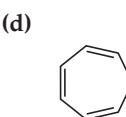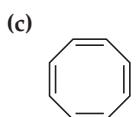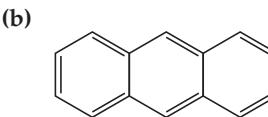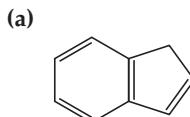
30.31 Draw the product of the following valence electron movements. [Section 30.4]
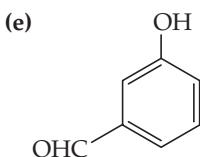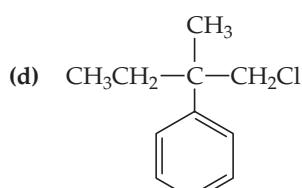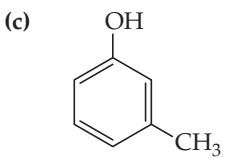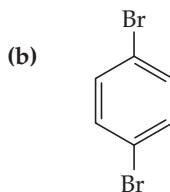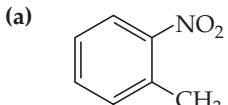
**30.32** Which of the following structures is aromatic? [Section 30.3]

(a)

(b)

(c)

(d)

Benzene Structure and Nomenclature (Sections 30.1 and 30.2)

30.33 Name the following compounds systematically:

(a) [structure: benzene ring with NO₂ and CH₃]

(b) [structure: benzene ring with Br at 1 and 4 positions]

(c) [structure: benzene ring with OH and CH₃]

(d) $CH_3CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle \text{(phenyl)}}{|}}{C}}-CH_2Cl$

(e) [structure: benzene ring with OH and OHC]
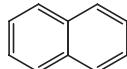
30.34 What observations made by Reinitzer on cholesteryl benzoate suggested that this substance possesses a liquid crystalline phase?

30.35 In contrast to ordinary liquids, liquid crystals are said to possess "order". What does this mean?

Aromaticity (Section 30.3)

30.36 Which hydrogens are more acidic, those of cyclohexane or benzene? Why?
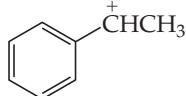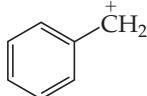
30.37 Mothballs are composed of naphthalene, $C_{10}H_8$, the structure of which consists of two six-membered rings of carbon that are fused along an edge, as shown in the following incomplete Lewis structure:

[structure: naphthalene]
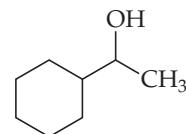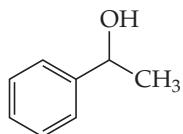
(a) Write two different complete Lewis structures for naphthalene. (b) The observed C—C bond lengths in the molecule are intermediate between C—C single and C—C double bonds. Explain. (c) Represent the resonance in naphthalene in a way analogous to that used to represent it in benzene.

30.38 (a) What is the difference between a localized π-bond and a delocalized one? (b) How can you determine whether a molecule or ion will exhibit delocalized π-bonding? (c) Demonstrate with the aid of a diagram the delocalization in benzene. (d) Is the π-bond in $CH_3CO_2^-$ localized or delocalized?

**30.39** Which of the following compounds is more stable? Explain.

[structure: $\overset{+}{C}H_2$ benzyl cation and $\overset{+}{C}HCH_3$]
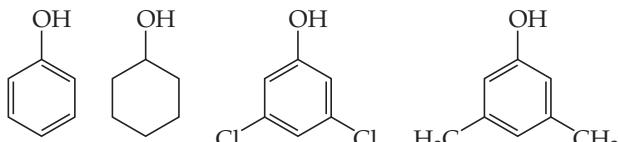
30.40 Which of the following alcohols undergoes dehydration more rapidly when heated with H_2SO_4? Why?

[structures: 1-phenylethanol and 1-cyclohexylethanol]

30.41 (a) One test for the presence of an alkene is to add a small amount of molecular bromine and look for the disappearance of the brown color. This test does not work for detecting the presence of an aromatic hydrocarbon. Explain.
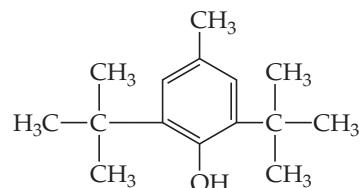
Properties of Phenols (Section 30.4)

30.42 Place the following in decreasing order of acidity:

[structures: phenol; cyclohexanol; 3,5-dichlorophenol; 3,5-dimethylphenol]

30.43 (a) Draw the structure of phenoxide. (b) Use arrow notation to describe why this intermediate is more stable than that for the corresponding cyclohexanol anion.

30.44 Butylated hydroxytoluene (BHT) has the following molecular structure:

[structure: BHT]

BHT
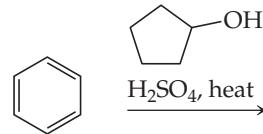
It is widely used as a preservative in a variety of foods, including dried cereals. (a) Based on its structure, would you expect BHT to be more soluble in water or in hexane (C_6H_{14})? Explain. (b) Identify phenol within this structure.

Electrophilic Aromatic Substitution Reactions (Section 30.5)

30.45 Using condensed structural formulas, write a chemical equation for each of the following reactions: (a) hydrogenation of cyclohexatriene; (b) bromination of 1,4-dimethoxybenzene using $FeBr_3$ as a catalyst; (c) reaction of 2-chloropropane with benzene in the presence of $AlCl_3$.

30.46 Suggest a method of preparing ethylbenzene, starting with benzene and ethene as the only organic reagents.
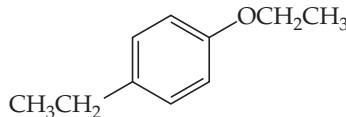
30.47 (a) What would be the electrophile in the following reaction? (b) What is the EAS product?

[structure: benzene + cyclopentanol, H_2SO_4, heat →]

30.48 Rank the following groups in order of increasing activating power in electrophilic aromatic substitution reactions: $-OCH_3$, $-CH_2CH_3$, $-Br$.
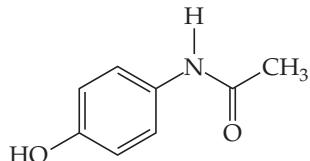
30.49 Draw the most important contributor to the resonance hybrid formed when toluene undergoes *para* nitration.

30.50 What factors affect the *ortho*:*para* ratio in electrophilic aromatic substitution reactions?

30.51 **(a)** What is the effect of a chlorine substituent on EAS? **(b)** What is the effect of a nitro substituent on EAS?

30.52 What is the *major* product (including regioisomer) when ethylbenzene is reacted with $Br_2/FeBr_3$?

30.53 Give a reason why nitrobenzene can be used as a solvent for Friedel-Crafts alkylation.

30.54 Give an explanation why direct nitration of aniline using HNO_3 yields, among other products, *m*-nitroaniline.

30.55 Devise a method for preparing *m*-chloroaniline from benzene.

30.56 Provide a series of synthetic steps by which 2-bromo-4-nitrobenzoic acid can be prepared from toluene.

30.57 What is the *major* product of the bromination of 4-methylphenol by Br_2 in the presence of $FeBr_3$?

30.58 What is the *major* product of the nitration of 4-bromoanisole?

**30.59** What is the major mononitration product of 1-ethoxy-4-ethylbenzene?
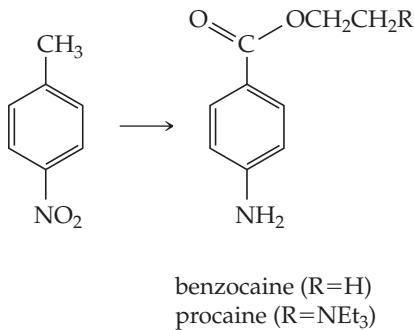
Integrative Exercises

30.60 **(a)** Devise a synthesis of the analgesic acetaminophen (paracetamol) from phenol.

(b) Does the name *paracetamol* tell you anything about the structure of the molecule?

30.61 4-Nitrotoluene is the starting material for the synthesis of the local anaesthetics benzocaine and procaine. Describe a synthesis of benzocaine starting from 4-nitrotoluene.

benzocaine (R=H)
procaine (R=NEt₃)

30.62 The heat of combustion of decahydronaphthalene ($C_{10}H_{18}$) is -6286 kJ mol^{-1}. The heat of combustion of naphthalene ($C_{10}H_8$) is -5157 kJ mol^{-1}. (In both cases, $CO_2(g)$ and $H_2O(l)$ are the products.) Using these data and data in Appendix C, calculate the heat of hydrogenation of naphthalene. Does this value provide any evidence for aromatic character in naphthalene?

30.63 The *cyclopentadienide ion* has the formula $C_5H_5^-$. The ion consists of a regular pentagon of C atoms, each bonded to two C neighbors, with a hydrogen atom bonded to each C atom. All the atoms lie in the same plane. **(a)** Draw a Lewis structure for the ion. According to your structure, do all five C atoms have the same hybridization? Explain. **(b)** Chemists generally view this ion as having sp^2 hybridization at each C atom. Is that view consistent with your answer to part (a)? **(c)** Your Lewis structure should show one non-bonding pair of electrons. Under the assumption of part (b), in what type of orbital must this non-bonding pair reside? **(d)** Are there resonance structures equivalent to the Lewis structure you drew in part (a)? If so, how many? **(e)** The ion is often drawn as a pentagon enclosing a circle. Is this representation consistent with your answer to part (d)? Explain. **(f)** Both benzene and the cyclopentadienide ion are often described as systems containing six π-electrons. What do you think is meant by this description?
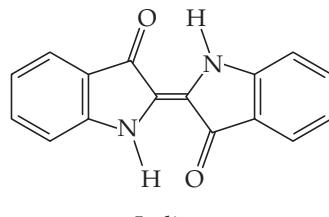
30.64 Both 3-aminobenzoic acid and 4-aminobenzoic acid are precursors to condensation polymers. **(a)** What type of isomers are these molecules? **(b)** Draw the structure of both of these molecules and the repeating unit of the polymer each forms. **(c)** Both compounds may be synthesized from toluene using the following reactions (not given in the correct order).

- Reduction of a nitro group using hydrogen gas and a palladium catalyst.

- Nitration using concentrated nitric acid and concentrated sulfuric acid.

- Oxidation of the aromatic alkyl group with acidified potassium permanganate.

Use your knowledge of the directing effect of a substituent to give the correct sequence of reactions for the synthesis of both compounds.

30.65 The pK_b of methylamine and analine is 3.36 and 9.40 respectively. Which molecule is the stronger base? Explain the reason for this difference.

30.66 Indigo is a blue dye that was originally extracted from plants but now is produced synthetically.

Indigo

(a) List the functional groups present in indigo. **(b)** What is the hybridization of the carbon atoms? **(c)** Explain why the overall shape of indigo is planar. **(d)** The molecule absorbs at 613 nm in the visible region of the spectrum. What energy does this correspond to?

Design an Experiment

There is often more than one way to prepare a compound and a research scientist has to consider the advantages and drawbacks of each route. For example, you are asked to prepare 3-nitrobenzoic acid from benzene. How do you do it? Note the carboxylic acid group cannot be introduced into the ring directly but could be obtained by either a Grignard reaction on a halobenzene or the oxidation of an alkylbenzene. You need to consider the directing effect of a group prior to installing the second substituent onto the ring and whether the group is activating or deactivating. An activating group will give a product under much milder conditions that may have economic advantages. Draw out as many different routes to 3-nitrobenzoic acid as you can and assess each one for its viability. At what point do you purify your compound to remove unused reagents and biproducts? How might you do the purification? If you started with 78 g of benzene, what quantities of reagents do you need for each route?