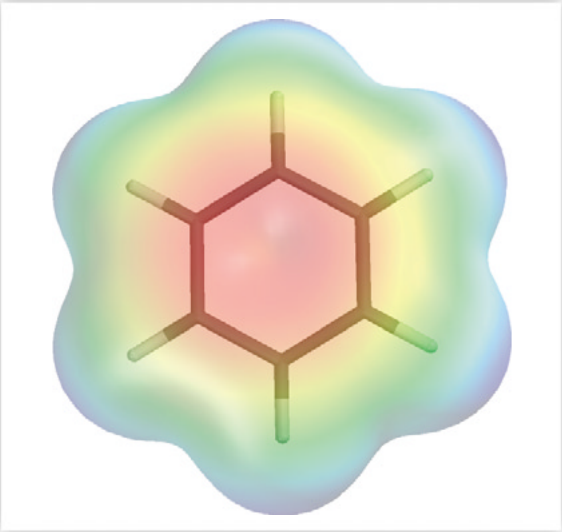
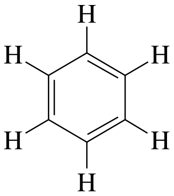


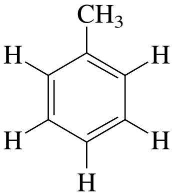
CHAPTER 11

ARENES AND AROMATICITY

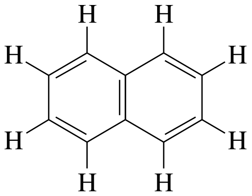
In this chapter and the next we extend our coverage of conjugated systems to include **arenes.** Arenes are hydrocarbons based on the benzene ring as a structural unit. Benzene, toluene, and naphthalene, for example, are arenes.



Benzene



Toluene



Naphthalene

One factor that makes conjugation in arenes special is its cyclic nature. A conjugated system that closes upon itself can have properties that are much different from those of open-chain polyenes. Arenes are also referred to as **aromatic hydrocarbons.** Used in this sense, the word **"aromatic"** has nothing to do with odor but means instead that arenes are much more stable than we expect them to be based on their formulation as conjugated trienes. Our goal in this chapter is to develop an appreciation for the concept of **aromaticity**—to see what are the properties of benzene and its derivatives that reflect its special stability, and to explore the reasons for it. This chapter develops the idea of the benzene ring as a fundamental structural unit and examines the effect of a benzene ring as a substituent. The chapter following this one describes reactions that involve the ring itself.

Let's begin by tracing the history of benzene, its origin, and its structure. Many of the terms we use, including *aromaticity* itself, are of historical origin. We'll begin with the discovery of benzene.

11.1 BENZENE

In 1825, Michael Faraday isolated a new hydrocarbon from illuminating gas, which he called "bicarburet of hydrogen." Nine years later Eilhardt Mitscherlich of the University of Berlin prepared the same substance by heating benzoic acid with lime and found it to be a hydrocarbon having the empirical formula C_nH_n.

Faraday is better known in chemistry for his laws of electrolysis and in physics for proposing the relationship between electric and magnetic fields and for demonstrating the principle of electromagnetic induction.

$$\underset{\text{Benzoic acid}}{C_6H_5CO_2H} + \underset{\text{Calcium oxide}}{CaO} \xrightarrow{\text{heat}} \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Calcium carbonate}}{CaCO_3}$$

Eventually, because of its relationship to benzoic acid, this hydrocarbon came to be named *benzin,* then later *benzene,* the name by which it is known today.

Benzoic acid had been known for several hundred years by the time of Mitscherlich's experiment. Many trees exude resinous materials called *balsams* when cuts are made in their bark. Some of these balsams are very fragrant, which once made them highly prized articles of commerce, especially when the trees that produced them could be found only in exotic, faraway lands. *Gum benzoin* is a balsam obtained from a tree that grows in Java and Sumatra. "Benzoin" is a word derived from the French equivalent, *benjoin,* which in turn comes from the Arabic *luban jawi,* meaning "incense from Java." Benzoic acid is itself odorless but can easily be isolated from gum benzoin.

Compounds related to benzene were obtained from similar plant extracts. For example, a pleasant-smelling resin known as *tolu balsam* was obtained from the South American tolu tree. In the 1840s it was discovered that distillation of tolu balsam gave a methyl derivative of benzene, which, not surprisingly, came to be named *toluene.*

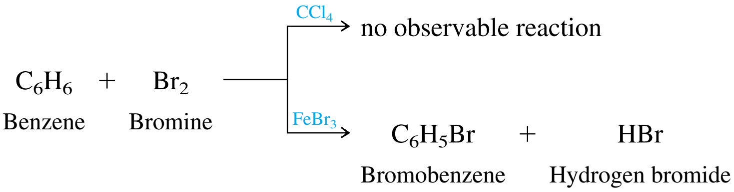
Although benzene and toluene are not particularly fragrant compounds themselves, their origins in aromatic plant extracts led them and compounds related to them to be classified as *aromatic hydrocarbons.* Alkanes, alkenes, and alkynes belong to another class, the **aliphatic hydrocarbons.** The word "aliphatic" comes from the Greek *aleiphar* (meaning "oil" or "unguent") and was given to hydrocarbons that were obtained by the chemical degradation of fats.

Benzene was prepared from coal tar by August W. von Hofmann in 1845. Coal tar remained the primary source for the industrial production of benzene for many years, until petroleum-based technologies became competitive about 1950. Current production is about 6 million tons per year in the United States. A substantial portion of this benzene is converted to styrene for use in the preparation of polystyrene plastics and films.

Toluene is also an important organic chemical. Like benzene, its early industrial production was from coal tar, but most of it now comes from petroleum.

11.2 KEKULÉ AND THE STRUCTURE OF BENZENE

The classification of hydrocarbons as aliphatic or aromatic took place in the 1860s when it was already apparent that there was something special about benzene, toluene, and their derivatives. Their molecular formulas (benzene is C_6H_6, toluene is C_7H_8) indicate that, like alkenes and alkynes, they are unsaturated and should undergo addition reactions. Under conditions in which bromine, for example, reacts rapidly with alkenes and alkynes, however, benzene proved to be inert. Benzene does react with Br_2 in the presence of iron(III) bromide as a catalyst, but even then addition isn't observed. Substitution occurs instead!



Furthermore, only one monobromination product of benzene was ever obtained, which suggests that all the hydrogen atoms of benzene are equivalent. Substitution of one hydrogen by bromine gives the same product as substitution of any of the other hydrogens.

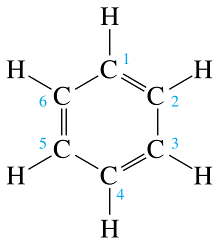
Chemists came to regard the six carbon atoms of benzene as a fundamental structural unit. Reactions could be carried out that altered its substituents, but the integrity of the benzene unit remained undisturbed. There must be something "special" about benzene that makes it inert to many of the reagents that add to alkenes and alkynes.

In 1866, only a few years after publishing his ideas concerning what we now recognize as the structural theory of organic chemistry, August Kekulé applied it to the structure of benzene. He based his reasoning on three premises:

1. Benzene is C_6H_6.
2. All the hydrogens of benzene are equivalent.
3. The structural theory requires that there be four bonds to each carbon.

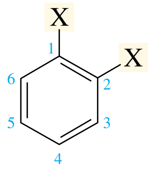
Kekulé advanced the venturesome notion that the six carbon atoms of benzene were joined together in a ring. Four bonds to each carbon could be accommodated by a system of alternating single and double bonds with one hydrogen on each carbon.

In 1861, Johann Josef Loschmidt, who was later to become a professor at the University of Vienna, privately published a book containing a structural formula for benzene similar to that which Kekulé would propose five years later. Loschmidt's book reached few readers, and his ideas were not well known.

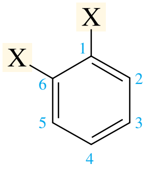


A flaw in Kekulé's structure for benzene was soon discovered. Kekulé's structure requires that 1,2- and 1,6-disubstitution patterns create different compounds (isomers).

How many isomers of C_6H_6 can you write? An article in the March 1994 issue of the *Journal of Chemical Education* (pp. 222–224) claims that there are several hundred and draws structural formulas for 25 of them.



1,2-Disubstituted derivative of benzene



1,6-Disubstituted derivative of benzene

The two substituted carbons are connected by a double bond in one but by a single bond in the other. Since no such cases of isomerism in benzene derivatives were known, and

BENZENE, DREAMS, AND CREATIVE THINKING

At ceremonies in Berlin in 1890 celebrating the twenty-fifth anniversary of his proposed structure of benzene, August Kekulé recalled the thinking that led him to it. He began by noting that the idea of the structural theory came to him during a daydream while on a bus in London. Kekulé went on to describe the origins of his view of the benzene structure.

> There I sat and wrote for my textbook; but things did not go well; my mind was occupied with other matters. I turned the chair towards the fireplace and began to doze. Once again the atoms danced before my eyes. This time smaller groups modestly remained in the background. My mental eye, sharpened by repeated apparitions of similar kind, now distinguished larger units of various shapes. Long rows, frequently joined more densely; everything in motion, twisting and turning like snakes. And behold, what was that? One of the snakes caught hold of its own tail and mockingly whirled round before my eyes. I awoke, as if by lightning; this time, too, I spent the rest of the night working out the consequences of this hypothesis.*

Concluding his remarks, Kekulé merged his advocacy of creative imagination with the rigorous standards of science by reminding his audience:

> Let us learn to dream, then perhaps we shall find the truth. But let us beware of publishing our dreams before they have been put to the proof by the waking understanding.

The imagery of a whirling circle of snakes evokes a vivid picture that engages one's attention when first exposed to Kekulé's model of the benzene structure. Recently, however, the opinion has been expressed that Kekulé might have engaged in some hyperbole during his speech. Professor John Wotiz of Southern Illinois University suggests that discoveries in science are the result of a disciplined analysis of a sufficient body of experimental observations to progress to a higher level of understanding. Wotiz' view that Kekulé's account is more fanciful than accurate has sparked a controversy with ramifications that go beyond the history of organic chemistry. How does creative thought originate? What can we do to become more creative? Because these are questions that have concerned psychologists for decades, the idea of a sleepy Kekulé being more creative than an alert Kekulé becomes more than simply a charming story he once told about himself.

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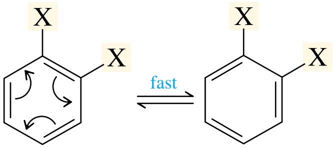
* The Kekulé quotes are taken from the biographical article of K. Hafner published in *Angew. Chem. Internat. ed. Engl.* **18,** 641–651 (1979).

none could be found, Kekulé suggested that two isomeric structures could exist but interconverted too rapidly to be separated.



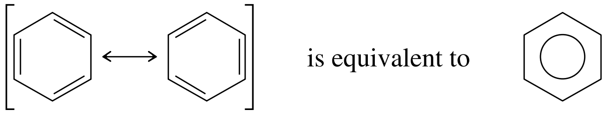
Kekulé's ideas about the structure of benzene left an important question unanswered. What is it about benzene that makes it behave so much differently from other unsaturated compounds? We'll see in this chapter that the answer is a simple one—the low reactivity of benzene and its derivatives reflects their special stability. Kekulé was wrong. *Benzene is not cyclohexatriene, nor is it a pair of rapidly equilibrating cyclohexatriene isomers.* But there was no way that Kekulé could have gotten it right given the state of chemical knowledge at the time. After all, the electron hadn't even been discovered yet. It remained for twentieth-century electronic theories of bonding to provide insight into why benzene is so stable. We'll outline these theories shortly. First, however, let's look at the structure of benzene in more detail.

Benzene is planar and its carbon skeleton has the shape of a regular hexagon. There is no evidence that it has alternating single and double bonds. As shown in Figure 11.1, all the carbon–carbon bonds are the same length (140 pm) and the 120° bond angles correspond to perfect sp^2 hybridization. Interestingly, the 140-pm bond distances in benzene are exactly midway between the typical sp^2–sp^2 single-bond distance of 146 pm and the sp^2–sp^2 double-bond distance of 134 pm. If bond distances are related to bond type, what kind of carbon–carbon bond is it that lies halfway between a single bond and a double bond in length?

11.3 A RESONANCE PICTURE OF BONDING IN BENZENE

Twentieth-century theories of bonding in benzene provide a rather clear picture of aromaticity. We'll start with a resonance description of benzene.

The two Kekulé structures for benzene have the same arrangement of atoms, but differ in the placement of electrons. Thus they are resonance forms, and neither one by itself correctly describes the bonding in the actual molecule. As a hybrid of the two Kekulé structures, benzene is often represented by a hexagon containing an inscribed circle.



The circle-in-a-hexagon symbol was first suggested by the British chemist Sir Robert Robinson to represent what he called the "aromatic sextet"—the six delocalized π electrons of the three double bonds. Robinson's symbol is a convenient time-saving shorthand device, but Kekulé-type formulas are better for counting and keeping track of electrons, especially in chemical reactions.

PROBLEM 11.1 Write structural formulas for toluene ($C_6H_5CH_3$) and for benzoic acid ($C_6H_5CO_2H$) (a) as resonance hybrids of two Kekulé forms and (b) with the Robinson symbol.

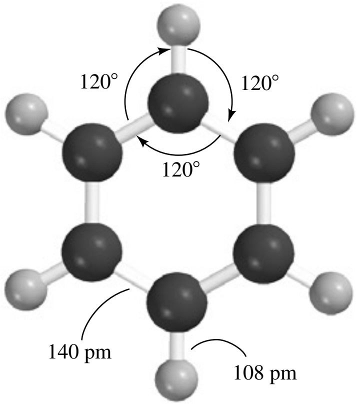


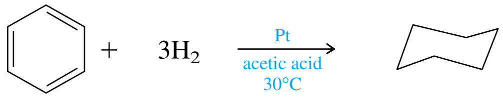
FIGURE 11.1 Bond distances and bond angles of benzene.

Since the carbons that are singly bonded in one resonance form are doubly bonded in the other, the resonance description is consistent with the observed carbon–carbon bond distances in benzene. These distances not only are all identical but also are intermediate between typical single-bond and double-bond lengths.

We have come to associate electron delocalization with increased stability. On that basis alone, benzene ought to be stabilized. It differs from other conjugated systems that we have seen, however, in that its π electrons are delocalized over a *cyclic conjugated* system. Both Kekulé structures of benzene are of equal energy, and one of the principles of resonance theory is that stabilization is greatest when the contributing structures are of similar energy. Cyclic conjugation in benzene, then, leads to a greater stabilization than is observed in noncyclic conjugated trienes. How much greater that stabilization is can be estimated from heats of hydrogenation.

11.4 THE STABILITY OF BENZENE

Hydrogenation of benzene and other arenes is more difficult than hydrogenation of alkenes and alkynes. Two of the more active catalysts are rhodium and platinum, and it is possible to hydrogenate arenes in the presence of these catalysts at room temperature and modest pressure. Benzene consumes three molar equivalents of hydrogen to give cyclohexane.



Benzene Hydrogen (2–3 atm pressure) Cyclohexane (100%)

Nickel catalysts, although less expensive than rhodium and platinum, are also less active. Hydrogenation of arenes in the presence of nickel requires high temperatures (100–200°C) and pressures (100 atm).

The measured heat of hydrogenation of benzene to cyclohexane is, of course, the same regardless of the catalyst and is 208 kJ/mol (49.8 kcal/mol). To put this value into perspective, compare it with the heats of hydrogenation of cyclohexene and 1,3-cyclohexadiene, as shown in Figure 11.2. The most striking feature of Figure 11.2 is that the heat of hydrogenation of benzene, with three "double bonds," is less than the heat of hydrogenation of the two double bonds of 1,3-cyclohexadiene.

Our experience has been that some 125 kJ/mol (30 kcal/mol) is given off whenever a double bond is hydrogenated. When benzene combines with three molecules of hydrogen, the reaction is far less exothermic than we would expect it to be on the basis of a 1,3,5-cyclohexatriene structure for benzene.

How much less? Since 1,3,5-cyclohexatriene does not exist (if it did, it would instantly relax to benzene), we cannot measure its heat of hydrogenation in order to compare it with benzene. We can approximate the heat of hydrogenation of 1,3,5-cyclohexatriene as being equal to three times the heat of hydrogenation of cyclohexene, or a total of 360 kJ/mol (85.8 kcal/mol). The heat of hydrogenation of benzene is 152 kJ/mol (36 kcal/mol) *less* than expected for a hypothetical 1,3,5-cyclohexatriene with noninteracting double bonds. This is the **resonance energy** of benzene. It is a measure of how much more stable benzene is than would be predicted on the basis of its formulation as a pair of rapidly interconverting 1,3,5-cyclohexatrienes.

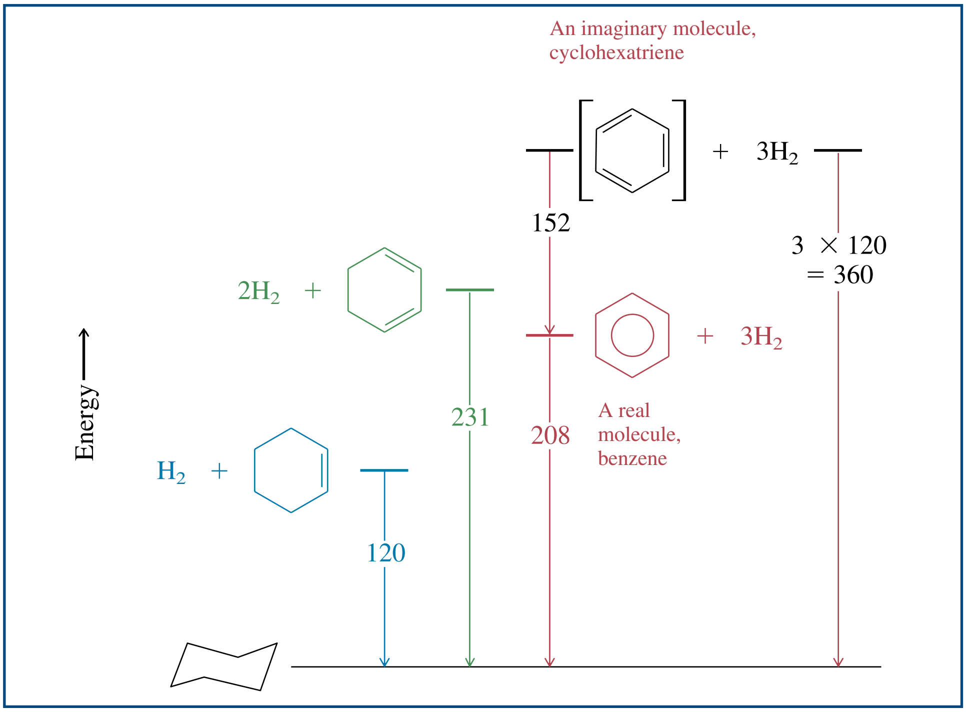
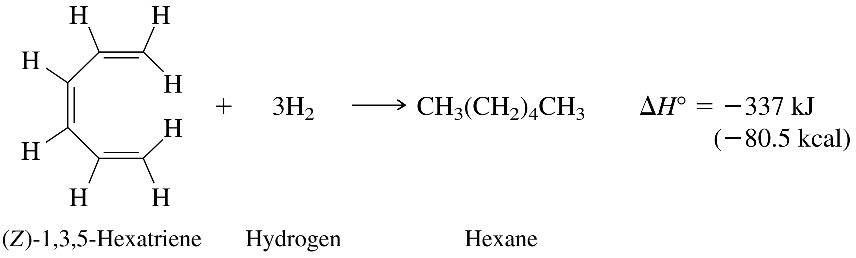


FIGURE 11.2 Heats of hydrogenation of cyclohexene, 1,3-cyclohexadiene, a hypothetical 1,3,5-cyclohexatriene, and benzene. All heats of hydrogenation are in kilojoules per mole.

We reach a similar conclusion when comparing benzene with the open-chain conjugated triene (*Z*)-1,3,5-hexatriene. Here we compare two real molecules, both conjugated trienes, but one is cyclic and the other is not. The heat of hydrogenation of (*Z*)-1,3,5-hexatriene is 337 kJ/mol (80.5 kcal/mol), a value which is 129 kJ/mol (30.7 kcal/mol) greater than that of benzene.

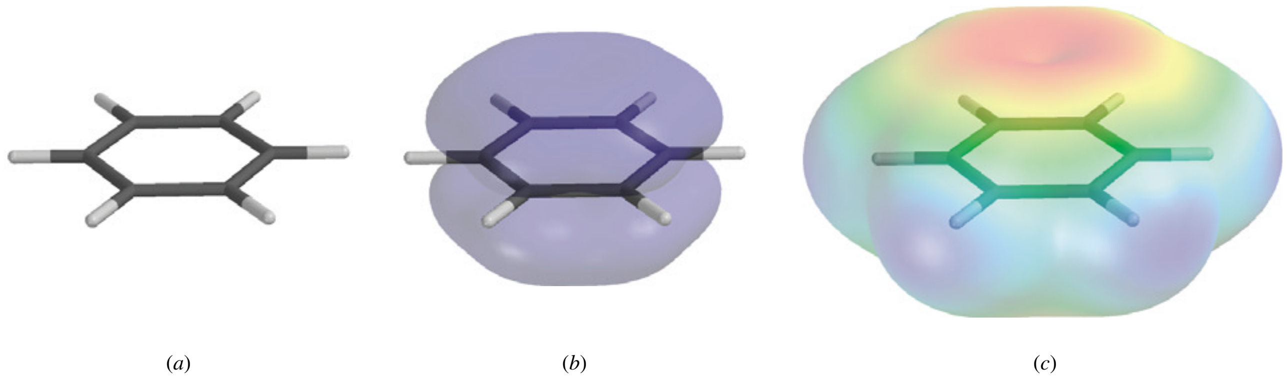


$$+ \quad 3H_2 \longrightarrow CH_3(CH_2)_4CH_3 \qquad \Delta H^\circ = -337\text{ kJ}\ (-80.5\text{ kcal})$$

(*Z*)-1,3,5-Hexatriene Hydrogen Hexane

The precise value of the resonance energy of benzene depends, as comparisons with 1,3,5-cyclohexatriene and (*Z*)-1,3,5-hexatriene illustrate, on the compound chosen as the reference. What is important is that the resonance energy of benzene is quite large, six to ten times that of a conjugated triene. It is this very large increment of resonance energy that places benzene and related compounds in a separate category that we call *aromatic*.

PROBLEM 11.2 The heats of hydrogenation of cycloheptene and 1,3,5-cycloheptatriene are 110 kJ/mol (26.3 kcal/mol) and 305 kJ/mol (73.0 kcal/mol), respectively. In both cases cycloheptane is the product. What is the resonance energy of 1,3,5-cycloheptatriene? How does it compare with the resonance energy of benzene?



(*a*) (*b*) (*c*)

FIGURE 11.3 (*a*) The framework of bonds shown in the tube model of benzene are σ bonds. (*b*) Each carbon is sp^2-hybridized and has a 2*p* orbital perpendicular to the σ framework. Overlap of the 2*p* orbitals generates a π system encompassing the entire ring. (*c*) Electrostatic potential plot of benzene. The red area in the center corresponds to the region above and below the plane of the ring where the π electrons are concentrated.

11.5 AN ORBITAL HYBRIDIZATION VIEW OF BONDING IN BENZENE

The structural facts that benzene is planar, all of the bond angles are 120°, and each carbon is bonded to three other atoms, suggest sp^2 hybridization for carbon and the framework of σ bonds shown in Figure 11.3*a*.

In addition to its three sp^2 hybrid orbitals, each carbon has a half-filled 2*p* orbital that can participate in π bonding. Figure 11.3*b* shows the continuous π system that encompasses all of the carbons that result from overlap of these 2*p* orbitals. The six π electrons of benzene are delocalized over all six carbons.

The electrostatic potential map of benzene (Figure 11.3*c*) shows regions of high electron density above and below the plane of the ring, which is where we expect the most loosely held electrons (the π electrons) to be.

11.6 THE π MOLECULAR ORBITALS OF BENZENE

The picture of benzene as a planar framework of σ bonds with six electrons in a delocalized π orbital is a useful, but superficial, one. Six electrons cannot simultaneously occupy any one orbital, be it an atomic orbital or a molecular orbital. A more rigorous molecular orbital analysis recognizes that overlap of the six 2*p* atomic orbitals of the ring carbons generates six π molecular orbitals. These six π molecular orbitals include three which are bonding and three which are antibonding. The relative energies of these orbitals and the distribution of the π electrons among them are illustrated in Figure 11.4. Benzene is said to have a **closed-shell** π electron configuration. All the bonding orbitals are filled, and there are no electrons in antibonding orbitals.

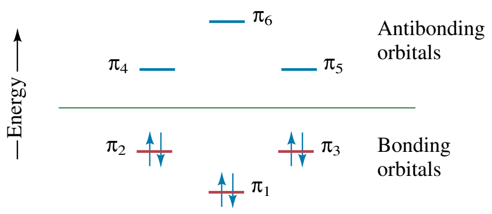


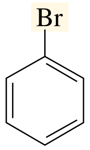
FIGURE 11.4 The π molecular orbitals of benzene arranged in order of increasing energy. The six π electrons of benzene occupy the three lowest energy orbitals, all of which are bonding. The nodal properties of these orbitals may be viewed on *Learning By Modeling.*

Higher level molecular orbital theory can provide quantitative information about orbital energies and how strongly a molecule holds its electrons. When one compares aromatic and nonaromatic species in this way, it is found that cyclic delocalization causes the π electrons of benzene to be more strongly bound (more stable) than they would be if restricted to a system with alternating single and double bonds.

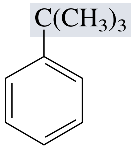
We'll come back to the molecular orbital description of benzene later in this chapter (Section 11.19) to see how other conjugated polyenes compare with benzene.

11.7 SUBSTITUTED DERIVATIVES OF BENZENE AND THEIR NOMENCLATURE

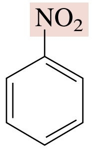
All compounds that contain a benzene ring are aromatic, and substituted derivatives of benzene make up the largest class of aromatic compounds. Many such compounds are named by attaching the name of the substituent as a prefix to *benzene.*



Bromobenzene



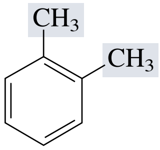
tert-Butylbenzene



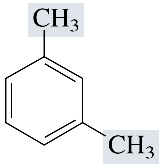
Nitrobenzene

Many simple monosubstituted derivatives of benzene have common names of long standing that have been retained in the IUPAC system. Table 11.1 lists some of the most important ones.

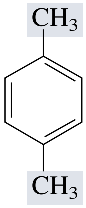
Dimethyl derivatives of benzene are called *xylenes.* There are three xylene isomers, the *ortho* (*o*)-, *meta* (*m*)-, and *para* (*p*)- substituted derivatives.



o-Xylene
(1,2-dimethylbenzene)

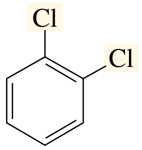


m-Xylene
(1,3-dimethylbenzene)

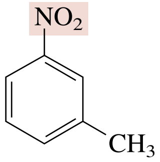


p-Xylene
(1,4-dimethylbenzene)

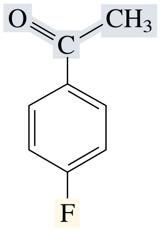
The prefix *ortho* signifies a 1,2-disubstituted benzene ring, *meta* signifies 1,3-disubstitution, and *para* signifies 1,4-disubstitution. The prefixes *o, m,* and *p* can be used when a substance is named as a benzene derivative or when a specific base name (such as acetophenone) is used. For example,



o-Dichlorobenzene
(1,2-dichlorobenzene)

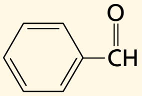
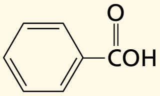
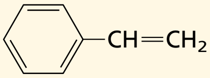
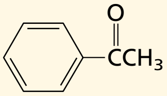
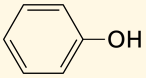
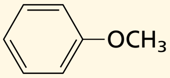
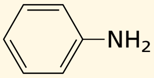


m-Nitrotoluene
(3-nitrotoluene)



p-Fluoroacetophenone
(4-fluoroacetophenone)

TABLE 11.1 Names of Some Frequently Encountered Derivatives of Benzene

Structure	Systematic Name	Common Name*
	Benzenecarbaldehyde	Benzaldehyde
	Benzenecarboxylic acid	Benzoic acid
	Vinylbenzene	Styrene
	Methyl phenyl ketone	Acetophenone
	Benzenol	Phenol
	Methoxybenzene	Anisole
	Benzenamine	Aniline

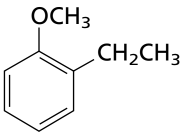
*These common names are acceptable in IUPAC nomenclature and are the names that will be used in this text.

PROBLEM 11.3 Write a structural formula for each of the following compounds:

(a) *o*-Ethylanisole (c) *p*-Nitroaniline

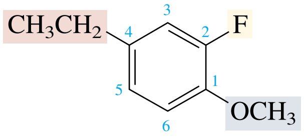
(b) *m*-Chlorostyrene

SAMPLE SOLUTION (a) The parent compound in *o*-ethylanisole is anisole. Anisole, as shown in Table 11.1, has a methoxy (CH_3O—) substituent on the benzene ring. The ethyl group in *o*-ethylanisole is attached to the carbon adjacent to the one that bears the methoxy substituent.

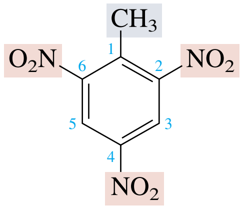


o-Ethylanisole

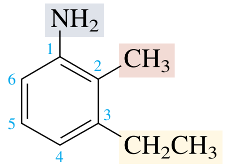
The prefixes *o, m,* and *p* are *not* used when three or more substituents are present on benzene; numerical locants must be used instead.



4-Ethyl-2-fluoroanisole



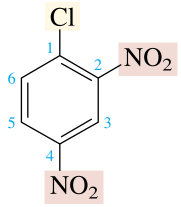
2,4,6-Trinitrotoluene



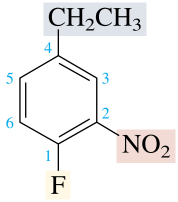
3-Ethyl-2-methylaniline

In these examples the base name of the benzene derivative determines the carbon at which numbering begins: anisole has its methoxy group at C-1, toluene its methyl group at C-1, and aniline its amino group at C-1. The direction of numbering is chosen to give the next substituted position the lowest number irrespective of what substituent it bears. *The order of appearance of substituents in the name is alphabetical.* When no simple base name other than benzene is appropriate, positions are numbered so as to give the lowest locant at the first point of difference. Thus, each of the following examples is named as a 1,2,4-trisubstituted derivative of benzene rather than as a 1,3,4-derivative:

The "first point of difference" rule was introduced in Section 2.11.

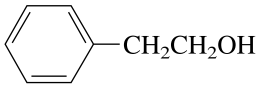


1-Chloro-2,4-dinitrobenzene

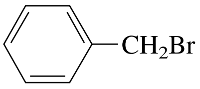


4-Ethyl-1-fluoro-2-nitrobenzene

When the benzene ring is named as a substituent, the word "phenyl" stands for C_6H_5—. Similarly, an arene named as a substituent is called an *aryl* group. A *benzyl* group is $C_6H_5CH_2$—.

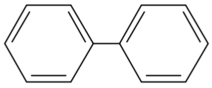


2-Phenylethanol

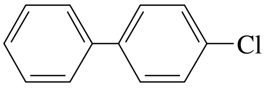


Benzyl bromide

Biphenyl is the accepted IUPAC name for the compound in which two benzene rings are connected by a single bond.



Biphenyl



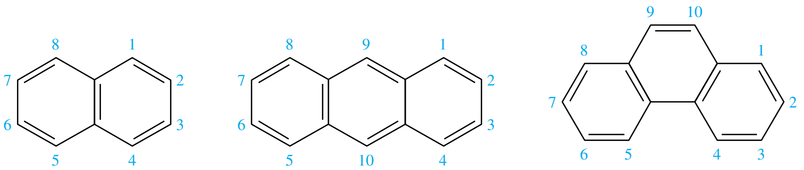
p-Chlorobiphenyl

11.8 POLYCYCLIC AROMATIC HYDROCARBONS

Members of a class of arenes called **polycyclic benzenoid aromatic hydrocarbons** possess substantial resonance energies because each is a collection of benzene rings fused together.

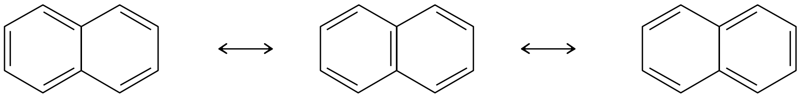
Naphthalene is a white crystalline solid melting at 80°C that sublimes readily. It has a characteristic odor and was formerly used as a moth repellent.

Naphthalene, anthracene, and phenanthrene are the three simplest members of this class. They are all present in **coal tar,** a mixture of organic substances formed when coal is converted to coke by heating at high temperatures (about 1000°C) in the absence of air. Naphthalene is **bicyclic** (has two rings), and its two benzene rings share a common side. Anthracene and phenanthrene are both **tricyclic** aromatic hydrocarbons. Anthracene has three rings fused in a “linear” fashion, and “angular” fusion characterizes phenanthrene. The structural formulas of naphthalene, anthracene, and phenanthrene are shown along with the numbering system used to name their substituted derivatives:



Arene:	Naphthalene	Anthracene	Phenanthrene
Resonance energy:	255 kJ/mol (61 kcal/mol)	347 kJ/mol (83 kcal/mol)	381 kJ/mol (91 kcal/mol)

In general, the most stable resonance structure for a polycyclic aromatic hydrocarbon is the one which has the greatest number of rings that correspond to Kekulé formulations of benzene. Naphthalene provides a fairly typical example:



Most stable resonance form

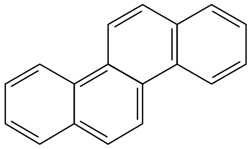
Only left ring corresponds to Kekulé benzene.

Both rings correspond to Kekulé benzene.

Only right ring corresponds to Kekulé benzene.

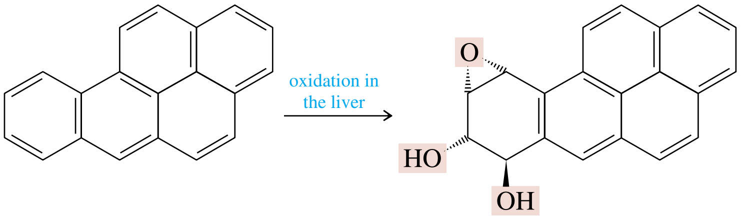
Notice that anthracene cannot be represented by any single Lewis structure in which all three rings correspond to Kekulé formulations of benzene, but phenanthrene can.

PROBLEM 11.4 Chrysene is an aromatic hydrocarbon found in coal tar. The structure shown is not the most stable resonance form. Write the most stable resonance form for chrysene.



A large number of polycyclic benzenoid aromatic hydrocarbons are known. Many have been synthesized in the laboratory, and several of the others are products of combustion. Benzo[a]pyrene, for example, is present in tobacco smoke, contaminates food cooked on barbecue grills, and collects in the soot of chimneys. Benzo[a]pyrene is a **carcinogen** (a cancer-causing substance). It is converted in the liver to an epoxy diol that can induce mutations leading to the uncontrolled growth of certain cells.

In 1775, the British surgeon Sir Percivall Pott suggested that scrotal cancer in chimney sweeps was caused by soot. This was the first proposal that cancer could be caused by chemicals present in the workplace.



Benzo[a]pyrene

7,8-Dihydroxy-9,10-epoxy-7,8,9,10-tetrahydrobenzo[a]pyrene

CARBON CLUSTERS, FULLERENES, AND NANOTUBES

The 1996 Nobel Prize in chemistry was awarded to Professors Harold W. Kroto (University of Sussex), Robert F. Curl, and Richard E. Smalley (both of Rice University) for groundbreaking work involving elemental carbon that opened up a whole new area of chemistry. The work began when Kroto wondered whether polyacetylenes of the type $HC{\equiv}C{-}(C{\equiv}C)_n{-}C{\equiv}CH$ might be present in interstellar space and discussed experiments to test this idea while visiting Curl and Smalley at Rice in the spring of 1984. Smalley had developed a method for the laser-induced evaporation of metals at very low pressure and was able to measure the molecular weights of the various clusters of atoms produced. Kroto, Curl, and Smalley felt that by applying this technique to graphite (Figure 11.5) the vaporized carbon produced might be similar to that produced by a carbon-rich star.

When the experiment was carried out in the fall of 1985, Kroto, Curl, and Smalley found that under certain conditions a species with a molecular formula of C_{60} was present in amounts much greater than any other. On speculating about what C_{60} might be, they concluded that its most likely structure is the spherical cluster of carbon atoms shown in Figure 11.6 and suggested it be called *buckminsterfullerene* because of its similarity to the geodesic domes popularized by the American architect and inventor R. Buckminster Fuller. (It is also often referred to as a "buckyball.") Other carbon clusters, some larger than C_{60} and some smaller, were also formed in the experiment, and the general term *fullerene* refers to such carbon clusters.

All of the carbon atoms in buckminsterfullerene are equivalent and are sp^2-hybridized; each one simultaneously belongs to one five-membered ring and two benzene-like six-membered rings. The strain caused by distortion of the rings from coplanarity is equally distributed among all of the carbons.

Confirmation of the structure proposed for C_{60} required isolation of enough material to allow the arsenal of modern techniques of structure determination to be applied. A quantum leap in fullerene research came in 1990 when a team led by Wolfgang Krätschmer of the Max Planck Institute for Nuclear Physics in Heidelberg and Donald Huffman of the University of Arizona successfully prepared buckminsterfullerene in amounts sufficient for its isolation, purification and detailed study. Not only was the buckminsterfullerene structure shown to be correct, but academic and industrial scientists around the world seized the opportunity afforded by the availability of C_{60} in quantity to study its properties.

Speculation about the stability of C_{60} centered on the extent to which the aromaticity associated with its 20 benzene rings is degraded by their non-

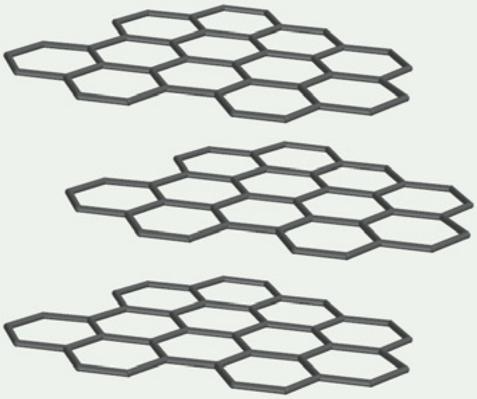


FIGURE 11.5 Graphite is a form of elemental carbon composed of parallel sheets of fused benzene-like rings.

FIGURE 11.6 Buckminsterfullerene (C_{60}). Note that all carbons are equivalent and that no five-membered rings are adjacent to one another.

—Cont.

planarity and the accompanying angle strain. It is now clear that C_{60} is a relatively reactive substance, reacting with many substances toward which benzene itself is inert. Many of these reactions are characterized by the addition of nucleophilic substances to buckminsterfullerene, converting sp^2-hybridized carbons to sp^3-hybridized ones and reducing the overall strain.

The field of fullerene chemistry expanded in an unexpected direction in 1991 when Sumio Iijima of the NEC Fundamental Research Laboratories in Japan discovered fibrous carbon clusters in one of his fullerene preparations. This led, within a short time, to substances of the type portrayed in Figure 11.7 called *single-walled nanotubes.* The best way to think about this material is as a "stretched" fullerene. Take a molecule of C_{60}, cut it in half, and place a cylindrical tube of fused six-membered carbon rings between the two halves.

Thus far, the importance of carbon cluster chemistry has been in the discovery of new knowledge. Many scientists feel that the earliest industrial applications of the fullerenes will be based on their novel electrical properties. Buckminsterfullerene is an insulator, but has a high electron affinity and is a superconductor in its reduced form. Nanotubes have aroused a great deal of interest for their electrical properties and as potential sources of carbon fibers of great strength.

Although the question that began the fullerene story, the possibility that carbon clusters are formed in stars, still remains unanswered, the attempt to answer that question has opened the door to novel structures and materials.

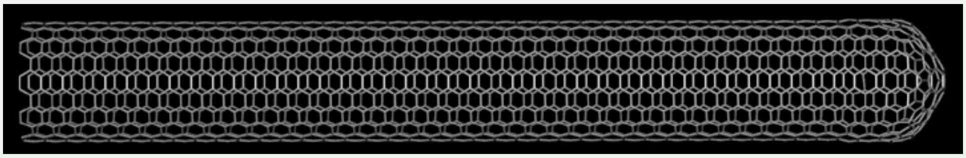


FIGURE 11.7 A portion of a nanotube. The closed end is approximately one half of a buckyball. The main length cannot close as long as all of the rings are hexagons.

11.9 PHYSICAL PROPERTIES OF ARENES

In general, arenes resemble other hydrocarbons in their physical properties. They are nonpolar, insoluble in water, and less dense than water. In the absence of polar substituents, intermolecular forces are weak and limited to van der Waals attractions of the induced-dipole/induced-dipole type.

Selected physical properties for a number of arenes are listed in Appendix 1.

At one time, benzene was widely used as a solvent. This use virtually disappeared when statistical studies revealed an increased incidence of leukemia among workers exposed to atmospheric levels of benzene as low as 1 ppm. Toluene has replaced benzene as an inexpensive organic solvent, because it has similar solvent properties but has not been determined to be carcinogenic in the cell systems and at the dose levels that benzene is.

11.10 REACTIONS OF ARENES: A PREVIEW

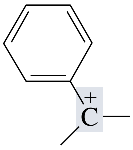
We'll examine the chemical properties of aromatic compounds from two different perspectives:

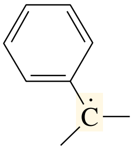
1. *One mode of chemical reactivity involves the ring itself as a functional group and includes*
   (a) Reduction
   (b) Electrophilic aromatic substitution

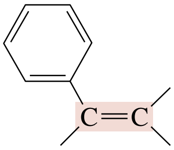
Reduction of arenes by catalytic hydrogenation was described in Section 11.4. A different method using Group I metals as reducing agents, which gives 1,4-cyclohexadiene derivatives, will be presented in Section 11.11. **Electrophilic aromatic substitution** is the most important reaction type exhibited by benzene and its derivatives and constitutes the entire subject matter of Chapter 12.

2. *The second family of reactions are those in which the aryl group acts as a substituent and affects the reactivity of a functional unit to which it is attached.*

A carbon atom that is directly attached to a benzene ring is called **a benzylic** carbon (analogous to the allylic carbon of C=C—**C**). A phenyl group (C_6H_5—) is an even better conjugating substituent than a vinyl group (CH_2=CH—), and benzylic carbocations and radicals are more highly stabilized than their allylic counterparts. The double bond of an alkenylbenzene is stabilized to about the same extent as that of a conjugated diene.


Benzylic carbocation

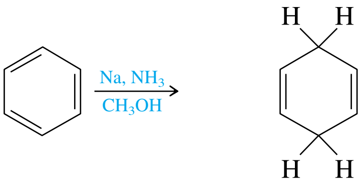

Benzylic radical


Alkenylbenzene

Reactions involving benzylic cations, benzylic radicals, and alkenylbenzenes will be discussed in Sections 11.12 through 11.17.

11.11 THE BIRCH REDUCTION

We saw in Section 9.10 that the combination of a Group I metal and liquid ammonia is a powerful reducing system capable of reducing alkynes to trans alkenes. In the presence of an alcohol, this same combination reduces arenes to *nonconjugated dienes.* Thus, treatment of benzene with sodium and methanol or ethanol in liquid ammonia converts it to 1,4-cyclohexadiene.



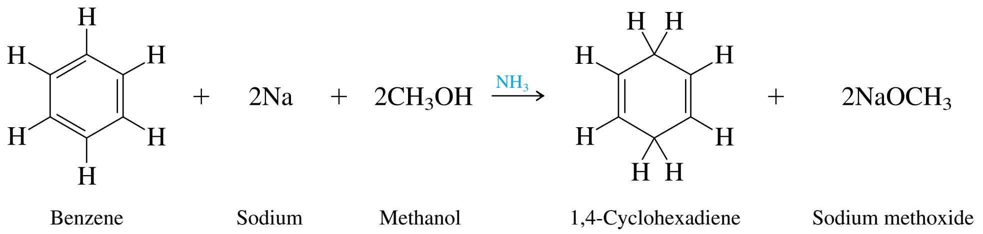
Benzene 1,4-Cyclohexadiene (80%)

Metal–ammonia–alcohol reductions of aromatic rings are known as **Birch reductions,** after the Australian chemist Arthur J. Birch, who demonstrated their usefulness beginning in the 1940s.

The mechanism by which the Birch reduction of benzene takes place is analogous to the mechanism for the metal–ammonia reduction of alkynes (Figure 11.8). It involves a sequence of four steps in which steps 1 and 3 are single-electron transfers from the metal and steps 2 and 4 are proton transfers from the alcohol.

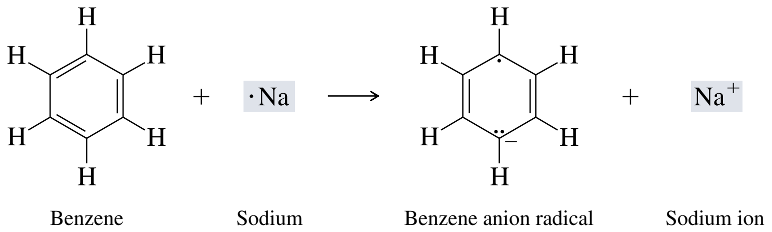
The Birch reduction not only provides a method to prepare dienes from arenes, which cannot be accomplished by catalytic hydrogenation, but also gives a nonconjugated diene system rather than the more stable conjugated one.

The overall reaction:

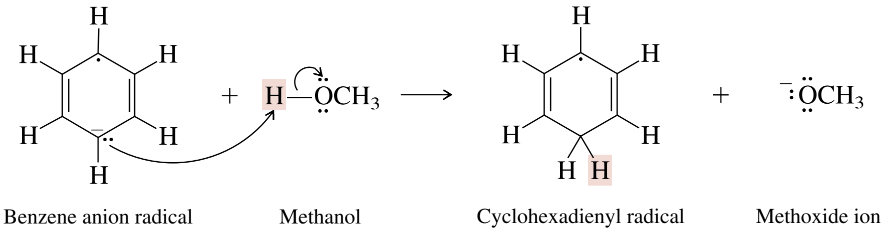


The mechanism:

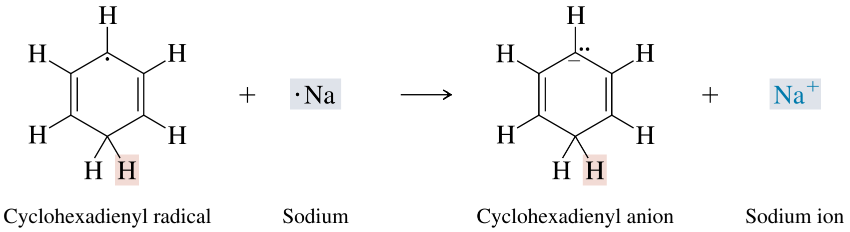
Step 1: An electron is transferred from sodium (the reducing agent) to the π system of the aromatic ring. The product is an anion radical.



Step 2: The anion radical is a strong base and abstracts a proton from methanol.



Step 3: The cyclohexadienyl radical produced in step 2 is converted to an anion by electron transfer from sodium.



Step 4: Proton transfer from methanol to the anion gives 1,4-cyclohexadiene.

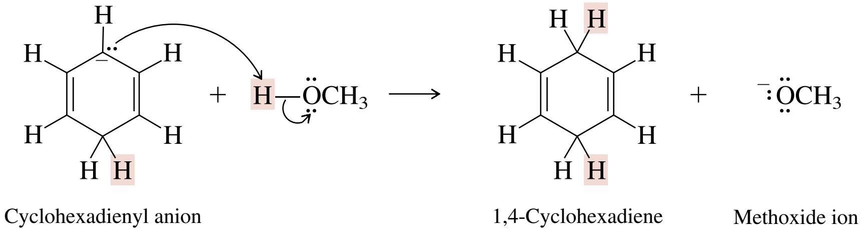
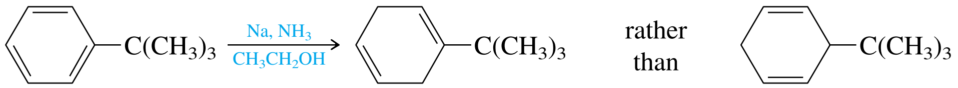


FIGURE 11.8 Mechanism of the Birch reduction.

Alkyl-substituted arenes give 1,4-cyclohexadienes in which the alkyl group is a substituent on the double bond.



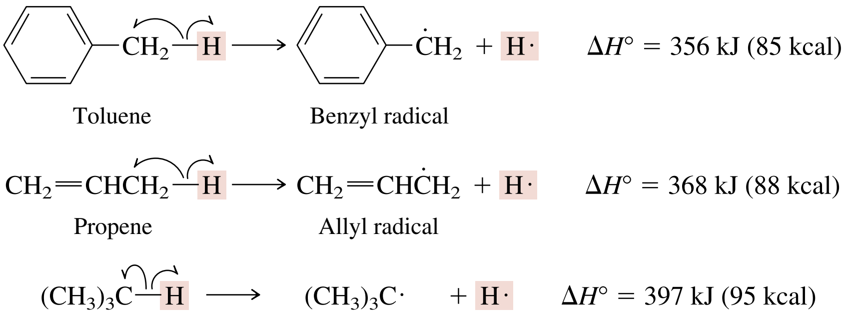
tert-Butylbenzene — 1-*tert*-Butyl-1,4-cyclohexadiene (86%) — 3-*tert*-Butyl-1,4-cyclohexadiene

PROBLEM 11.5 A single organic product was isolated after Birch reduction of *p*-xylene. Suggest a reasonable structure for this substance.

Substituents other than alkyl groups may also be present on the aromatic ring, but their reduction is beyond the scope of the present discussion.

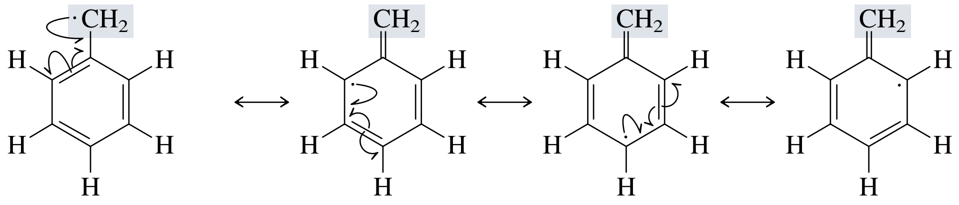
11.12 FREE-RADICAL HALOGENATION OF ALKYLBENZENES

The benzylic position in alkylbenzenes is analogous to the allylic position in alkenes. Thus a benzylic C—H bond, like an allylic one, is weaker than a C—H bond of an alkane, as the bond dissociation energies of toluene, propene, and 2-methylpropane attest:



2-Methylpropane — *tert*-Butyl radical

We attributed the decreased bond dissociation energy in propene to stabilization of allyl radical by electron delocalization. Similarly, electron delocalization stabilizes benzyl radical and weakens the benzylic C—H bond. The unpaired electron is shared by the benzylic carbon and by the ring carbons that are ortho and para to it.



Most stable Lewis structure of benzyl radical

In orbital terms, as represented in Figure 11.9, benzyl radical is stabilized by delocalization of electrons throughout the extended π system formed by overlap of the *p* orbital of the benzylic carbon with the π system of the ring.

The comparative ease with which a benzylic hydrogen is abstracted leads to high selectivity in free-radical halogenations of alkylbenzenes. Thus, chlorination of toluene

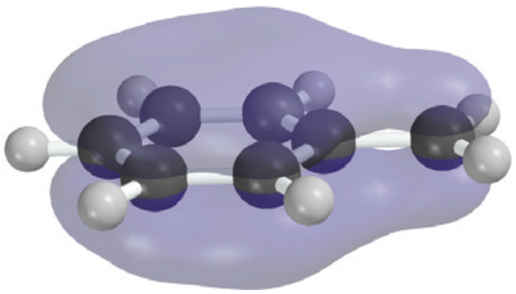
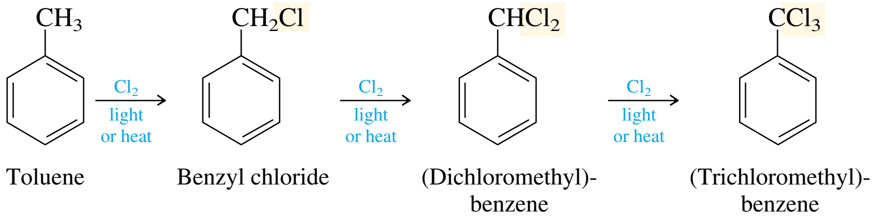


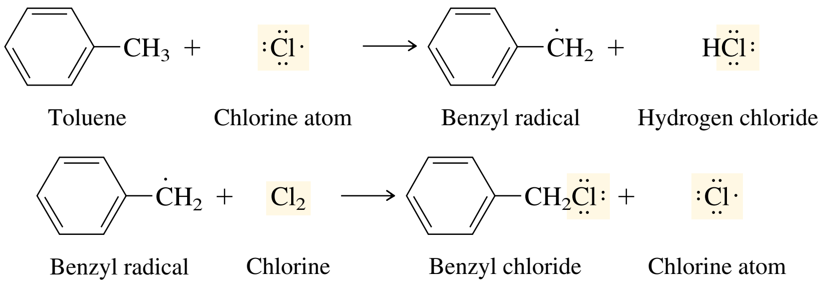
FIGURE 11.9 The benzyl radical is stabilized by overlap of its half-filled *p* orbital with the π system of the aromatic ring.

takes place exclusively at the benzylic carbon and is an industrial process for the preparation of the compounds shown.



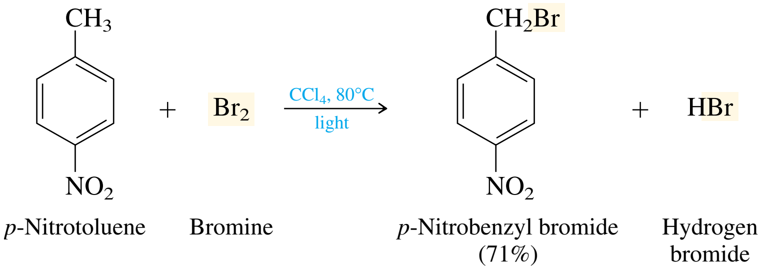
The common names of (dichloromethyl)benzene and (trichloromethyl)benzene are benzal chloride and benzotrichloride, respectively.

The propagation steps in the formation of benzyl chloride involve benzyl radical as an intermediate.



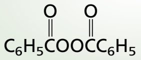
(Dichloromethyl)benzene and (trichloromethyl)benzene arise by further side-chain chlorination of benzyl chloride.

Benzylic bromination is a more commonly used laboratory procedure than chlorination and is typically carried out under conditions of photochemical initiation.

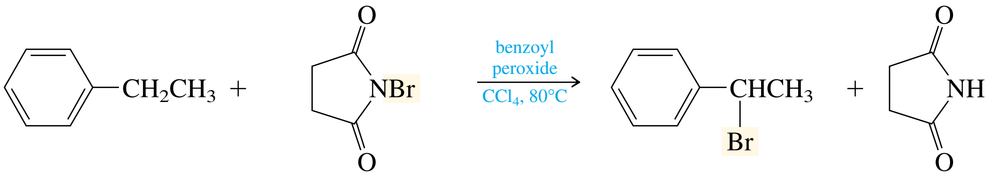


As we saw when discussing allylic bromination in Section 10.4, *N*-bromosuccinimide (NBS) is a convenient free-radical brominating agent. Benzylic brominations with NBS are normally performed in carbon tetrachloride as the solvent in the presence of peroxides, which are added as initiators. As the example illustrates, free-radical bromination is selective for substitution of benzylic hydrogens.

Benzoyl peroxide is a commonly used free-radical initiator. It has the formula



$$C_6H_5\overset{O}{\overset{\|}{C}}O O\overset{O}{\overset{\|}{C}}C_6H_5$$

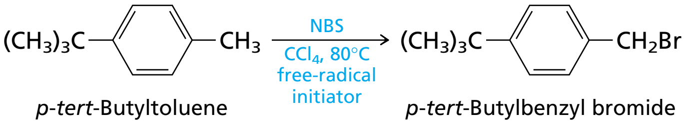


Ethylbenzene   *N*-Bromosuccinimide (NBS)   1-Bromo-1-phenylethane (87%)   Succinimide

PROBLEM 11.6 The reaction of *N*-bromosuccinimide with the following compounds has been reported in the chemical literature. Each compound yields a single product in 95% yield. Identify the product formed from each starting material.

(a) *p-tert*-Butyltoluene   (b) 4-Methyl-3-nitroanisole

SAMPLE SOLUTION (a) The only benzylic hydrogens in *p-tert*-butyltoluene are those of the methyl group that is attached directly to the ring. Substitution occurs there to give *p-tert*-butylbenzyl bromide.



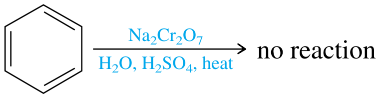
p-tert-Butyltoluene   *p-tert*-Butylbenzyl bromide

11.13 OXIDATION OF ALKYLBENZENES

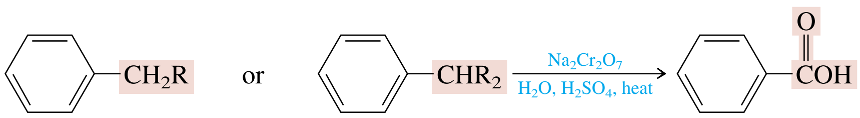
A striking example of the activating effect that a benzene ring has on reactions that take place at benzylic positions may be found in the reactions of alkylbenzenes with oxidizing agents. Chromic acid, for example, prepared by adding sulfuric acid to aqueous sodium dichromate, is a strong oxidizing agent but does not react either with benzene or with alkanes.

An alternative oxidizing agent, similar to chromic acid in its reactions with organic compounds, is potassium permanganate ($KMnO_4$).

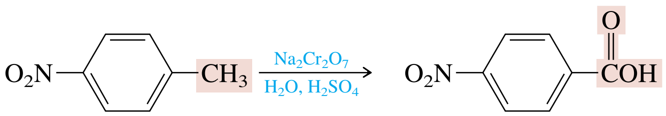
$$RCH_2CH_2R' \xrightarrow[H_2O,\ H_2SO_4,\ heat]{Na_2Cr_2O_7} \text{no reaction}$$



On the other hand, an alkyl side chain on a benzene ring is oxidized on being heated with chromic acid. The product is benzoic acid or a substituted derivative of benzoic acid.

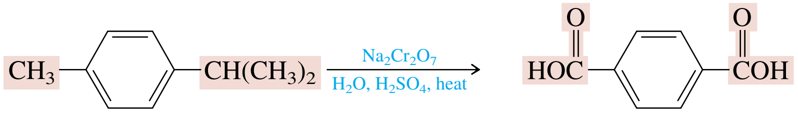


Alkylbenzene   Benzoic acid



p-Nitrotoluene   *p*-Nitrobenzoic acid (82–86%)

When two alkyl groups are present on the ring, both are oxidized.

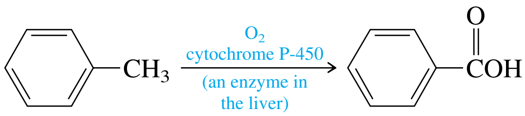


p-Isopropyltoluene *p*-Benzenedicarboxylic acid (45%)

Note that alkyl groups, regardless of their chain length, are converted to carboxyl groups (—CO_2H) attached directly to the ring. An exception is a *tert*-alkyl substituent. Because it lacks benzylic hydrogens, a *tert*-alkyl group is not susceptible to oxidation under these conditions.

PROBLEM 11.7 Chromic acid oxidation of 4-*tert*-butyl-1,2-dimethylbenzene yielded a single compound having the molecular formula $C_{12}H_{14}O_4$. What was this compound?

Side-chain oxidation of alkylbenzenes is important in certain metabolic processes. One way in which the body rids itself of foreign substances is by oxidation in the liver to compounds more easily excreted in the urine. Toluene, for example, is oxidized to benzoic acid by this process and is eliminated rather readily.

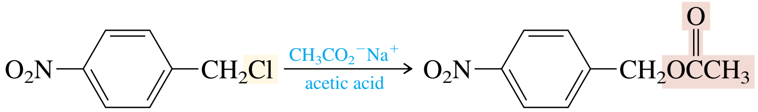


Toluene Benzoic acid

Benzene, with no alkyl side chain, undergoes a different reaction in the presence of these enzymes, which convert it to a substance capable of inducing mutations in DNA. This difference in chemical behavior seems to be responsible for the fact that benzene is carcinogenic but toluene is not.

11.14 NUCLEOPHILIC SUBSTITUTION IN BENZYLIC HALIDES

Primary benzylic halides are ideal substrates for S_N2 reactions, since they are very reactive toward good nucleophiles and cannot undergo competing elimination.



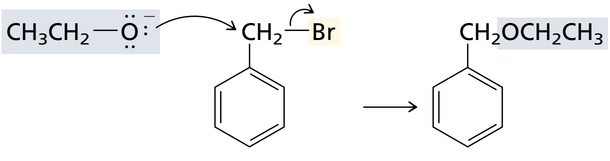
p-Nitrobenzyl chloride *p*-Nitrobenzyl acetate (78–82%)

Benzylic halides that are secondary resemble secondary alkyl halides in that they undergo substitution only when the nucleophile is weakly basic. If the nucleophile is a strong base such as sodium ethoxide, elimination by the E2 mechanism is faster than substitution.

PROBLEM 11.8 Give the structure of the principal organic product formed on reaction of benzyl bromide with each of the following reagents:

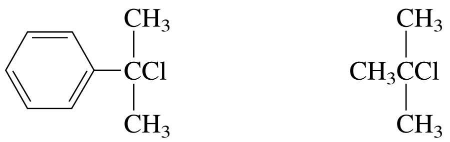
(a) Sodium ethoxide
(b) Potassium *tert*-butoxide
(c) Sodium azide
(d) Sodium hydrogen sulfide
(e) Sodium iodide (in acetone)

SAMPLE SOLUTION (a) Benzyl bromide is a primary bromide and undergoes S_N2 reactions readily. It has no hydrogens β to the leaving group and so cannot undergo elimination. Ethoxide ion acts as a nucleophile, displacing bromide and forming benzyl ethyl ether.



Ethoxide ion Benzyl bromide Benzyl ethyl ether

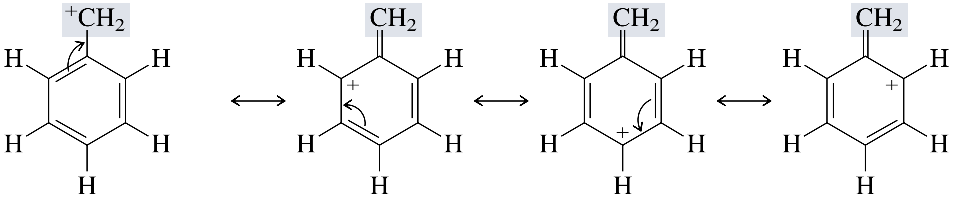
Benzylic halides resemble allylic halides in the readiness with which they form carbocations. On comparing the rate of S_N1 hydrolysis in aqueous acetone of the following two tertiary chlorides, we find that the benzylic chloride reacts over 600 times faster than does *tert*-butyl chloride.



2-Chloro-2-phenylpropane 2-Chloro-2-methylpropane

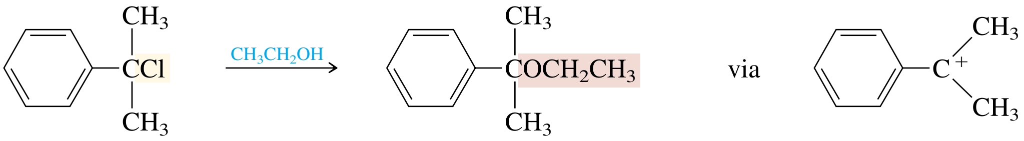
Just as the odd electron in benzyl radical is shared by the carbons ortho and para to the benzylic carbon, the positive charge in benzyl cation is shared by these same positions.

See *Learning By Modeling* for an electrostatic potential map of benzyl cation.



Most stable Lewis structure of benzyl cation

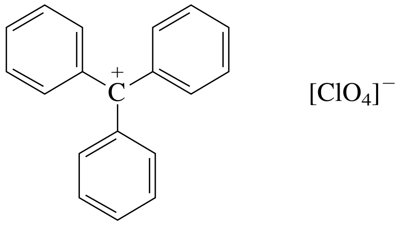
Unlike the case with allylic carbocations, however, dispersal of the positive charge does not result in nucleophilic attack at more than one carbon. There is no "benzylic rearrangement" analogous to allylic rearrangement (Section 10.2), because the aromatic stabilization would be lost if the nucleophile became bonded to one of the ring carbons. Thus, when conditions are chosen that favor S_N1 substitution over E2 elimination (solvolysis, weakly basic nucleophile), benzylic halides give a single substitution product in high yield.



2-Chloro-2-phenylpropane 2-Ethoxy-2-phenylpropane (87%)

The triphenylmethyl group is often referred to as a *trityl* group.

Additional phenyl substituents stabilize carbocations even more. Triphenylmethyl cation is particularly stable. Its perchlorate salt is ionic and stable enough to be isolated and stored indefinitely.

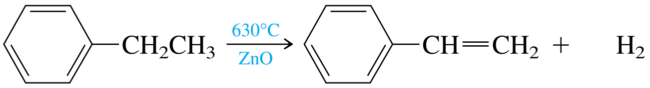


Triphenylmethyl perchlorate

11.15 PREPARATION OF ALKENYLBENZENES

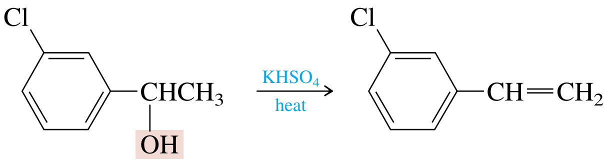
Alkenylbenzenes are prepared by the various methods described in Chapter 5 for the preparation of alkenes: *dehydrogenation, dehydration,* and *dehydrohalogenation.*

Dehydrogenation of alkylbenzenes is not a convenient laboratory method but is used industrially to convert ethylbenzene to styrene.

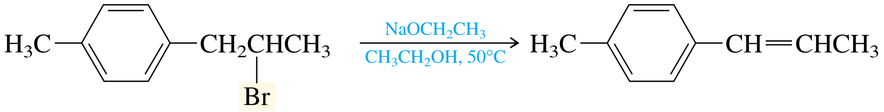


Ethylbenzene Styrene Hydrogen

Acid-catalyzed dehydration of benzylic alcohols is a useful route to alkenylbenzenes, as is dehydrohalogenation under E2 conditions.



1-(*m*-Chlorophenyl)ethanol *m*-Chlorostyrene (80–82%)

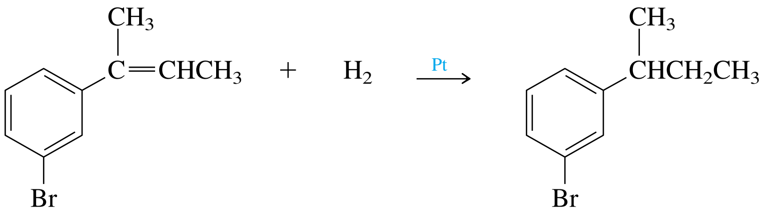


2-Bromo-1-(*p*-methylphenyl)propane 1-(*p*-Methylphenyl)propene (99%)

11.16 ADDITION REACTIONS OF ALKENYLBENZENES

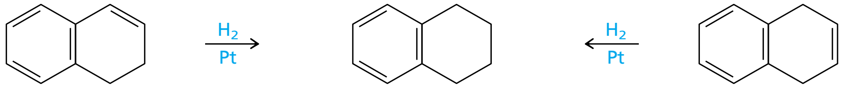
Most of the reactions of alkenes that were discussed in Chapter 6 find a parallel in the reactions of alkenylbenzenes.

Hydrogenation of the side-chain double bond of an alkenylbenzene is much easier than hydrogenation of the aromatic ring and can be achieved with high selectivity, leaving the ring unaffected.



2-(*m*-Bromophenyl)-2-butene Hydrogen 2-(*m*-Bromophenyl)butane (92%)

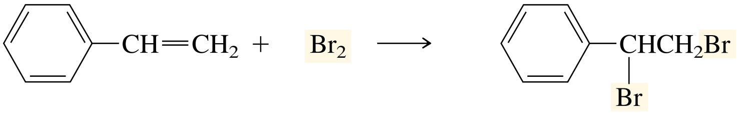
PROBLEM 11.9 Both 1,2-dihydronaphthalene and 1,4-dihydronaphthalene may be selectively hydrogenated to 1,2,3,4-tetrahydronaphthalene.



1,2-Dihydronaphthalene 1,2,3,4-Tetrahydronaphthalene 1,4-Dihydronaphthalene

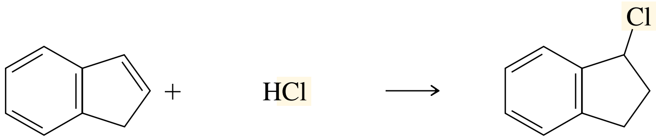
One of these isomers has a heat of hydrogenation of 101 kJ/mol (24.1 kcal/mol), and the heat of hydrogenation of the other is 113 kJ/mol (27.1 kcal/mol). Match the heat of hydrogenation with the appropriate dihydronaphthalene.

The double bond in the alkenyl side chain undergoes addition reactions that are typical of alkenes when treated with electrophilic reagents.



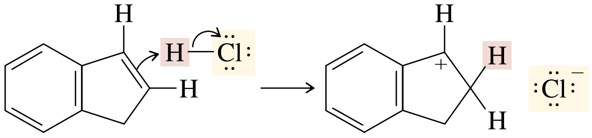
Styrene Bromine 1,2-Dibromo-1-phenylethane (82%)

The regioselectivity of electrophilic addition is governed by the ability of an aromatic ring to stabilize an adjacent carbocation. This is clearly seen in the addition of hydrogen chloride to indene. Only a single chloride is formed.



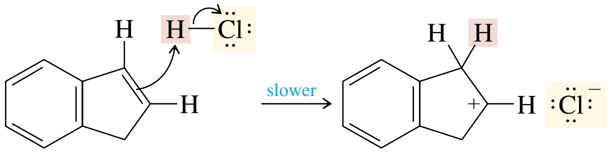
Indene Hydrogen chloride 1-Chloroindane (75–84%)

Only the benzylic chloride is formed, because protonation of the double bond occurs in the direction that gives a carbocation that is both secondary and benzylic.



Carbocation that leads to observed product

Protonation in the opposite direction also gives a secondary carbocation, but it is not benzylic.



Less stable carbocation

This carbocation does not receive the extra increment of stabilization that its benzylic isomer does and so is formed more slowly. The orientation of addition is controlled by the rate of carbocation formation; the more stable benzylic carbocation is formed faster and is the one that determines the reaction product.

PROBLEM 11.10 Each of the following reactions has been reported in the chemical literature and gives a single organic product in high yield. Write the structure of the product for each reaction.

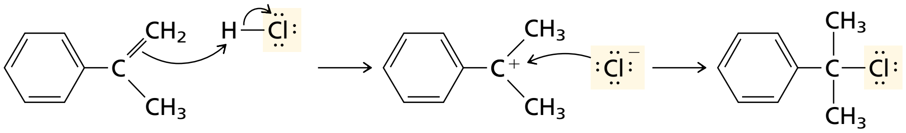
(a) 2-Phenylpropene + hydrogen chloride

(b) 2-Phenylpropene treated with diborane in tetrahydrofuran followed by oxidation with basic hydrogen peroxide

(c) Styrene + bromine in aqueous solution

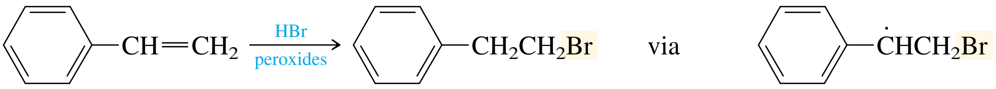
(d) Styrene + peroxybenzoic acid (two organic products in this reaction; identify both by writing a balanced equation.)

SAMPLE SOLUTION (a) Addition of hydrogen chloride to the double bond takes place by way of a tertiary benzylic carbocation.



2-Phenylpropene Hydrogen chloride 2-Chloro-2-phenylpropane

In the presence of peroxides, hydrogen bromide adds to the double bond of styrene with a regioselectivity opposite to Markovnikov's rule. The reaction is a free-radical addition, and the regiochemistry is governed by preferential formation of the more stable radical.



Styrene 1-Bromo-2-phenylethane (major product) 2-Bromo-1-phenylethyl radical (secondary; benzylic)

11.17 POLYMERIZATION OF STYRENE

The annual production of styrene in the United States is on the order of 8×10^9 lb, with about 65% of this output used to prepare polystyrene plastics and films. Styrofoam coffee cups are made from polystyrene. Polystyrene can also be produced in a form that is very strong and impact-resistant and is used widely in luggage, television and radio cabinets, and furniture.

As described in the box "Diene Polymers" in Chapter 10, most synthetic rubber is a copolymer of styrene and 1,3-butadiene.

Polymerization of styrene is carried out under free-radical conditions, often with benzoyl peroxide as the initiator. Figure 11.10 illustrates a step in the growth of a polystyrene chain by a mechanism analogous to that of the polymerization of ethylene (Section 6.21).

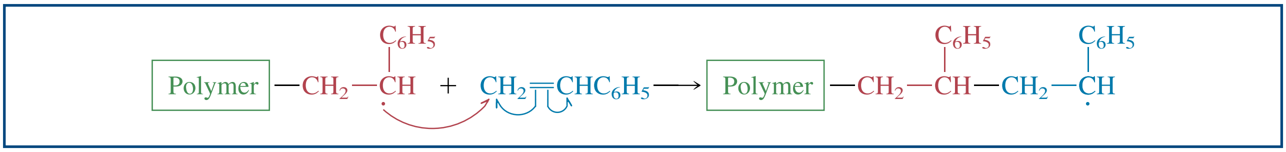
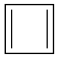


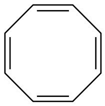
FIGURE 11.10 Chain propagation step in polymerization of styrene. The growing polymer chain has a free-radical site at the benzylic carbon. It adds to a molecule of styrene to extend the chain by one styrene unit. The new polymer chain is also a benzylic radical; it attacks another molecule of styrene, and the process repeats over and over again.

11.18 CYCLOBUTADIENE AND CYCLOOCTATETRAENE

During our discussion of benzene and its derivatives, it may have occurred to you that cyclobutadiene and cyclooctatetraene might be stabilized by π electron delocalization in a manner analogous to that of benzene.



Cyclobutadiene

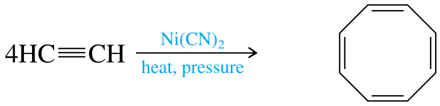


Cyclooctatetraene

The same thought occurred to early chemists. However, the complete absence of naturally occurring compounds based on cyclobutadiene and cyclooctatetraene contrasted starkly with the abundance of compounds based on the benzene nucleus. Attempts to synthesize cyclobutadiene and cyclooctatetraene met with failure and reinforced the growing conviction that these compounds would prove to be quite unlike benzene if, in fact, they could be isolated at all.

The first breakthrough came in 1911 when Richard Willstätter prepared cyclooctatetraene by a lengthy degradation of *pseudopelletierine,* a natural product obtained from the bark of the pomegranate tree. Nowadays, cyclooctatetraene is prepared from acetylene in a reaction catalyzed by nickel cyanide.

Willstätter's most important work, for which he won the 1915 Nobel Prize in chemistry, was directed toward determining the structure of chlorophyll.



Acetylene Cyclooctatetraene (70%)

Thermochemical measurements suggest a value of only about 20 kJ/mol (about 5 kcal/mol) for the resonance energy of cyclooctatetraene, far less than the aromatic stabilization of benzene (152 kJ/mol; 36 kcal/mol).

PROBLEM 11.11 Both cyclooctatetraene and styrene have the molecular formula C_8H_8 and undergo combustion according to the equation

$$C_8H_8 + 10O_2 \longrightarrow 8CO_2 + 4H_2O$$

The measured heats of combustion are 4393 and 4543 kJ/mol (1050 and 1086 kcal/mol). Which heat of combustion belongs to which compound?

Structural studies confirm the absence of appreciable π electron delocalization in cyclooctatetraene. Its structure is as pictured in Figure 11.11—a *nonplanar* hydrocarbon with four short carbon–carbon bond distances and four long carbon–carbon bond distances. Cyclooctatetraene is satisfactorily represented by a single Lewis structure having alternating single and double bonds in a tub-shaped eight-membered ring.

All the evidence indicates that cyclooctatetraene lacks the "special stability" of benzene, and is more appropriately considered as a conjugated polyene than as an aromatic hydrocarbon.

Cyclobutadiene escaped chemical characterization for more than 100 years. Despite numerous attempts, all synthetic efforts met with failure. It became apparent not only that cyclobutadiene was not aromatic but that it was exceedingly unstable. Beginning in the 1950s, a variety of novel techniques succeeded in generating cyclobutadiene as a transient, reactive intermediate.

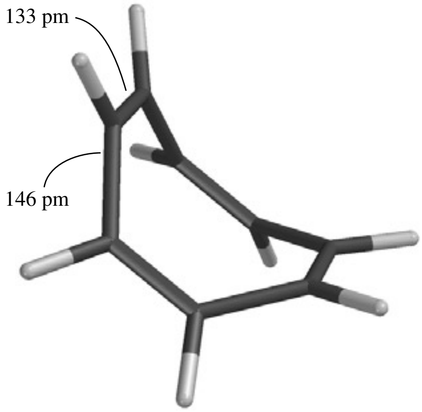
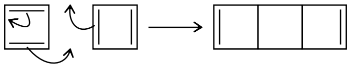


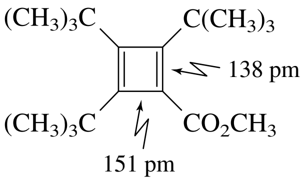
FIGURE 11.11 Molecular geometry of cyclooctatetraene. The ring is not planar, and the bond distances alternate between short double bonds and long single bonds.

PROBLEM 11.12 One of the chemical properties that make cyclobutadiene difficult to isolate is that it reacts readily with itself to give a dimer:



What reaction of dienes does this resemble?

Structural studies of cyclobutadiene and some of its derivatives reveal a pattern of alternating single and double bonds and a rectangular, rather than a square, shape. Bond distances in a stable, highly substituted derivative of cyclobutadiene illustrate this pattern of alternating short and long ring bonds.



Methyl 2,3,4-tri-*tert*-butylcyclobutadiene-1-carboxylate

Thus cyclobutadiene, like cyclooctatetraene, is not aromatic. *Cyclic conjugation, although necessary for aromaticity, is not sufficient for it.* Some other factor or factors must contribute to the special stability of benzene and its derivatives. To understand these factors, let's return to the molecular orbital description of benzene.

11.19 HÜCKEL'S RULE: ANNULENES

One of the early successes of molecular orbital theory occurred in 1931 when Erich Hückel discovered an interesting pattern in the π orbital energy levels of benzene, cyclobutadiene, and cyclooctatetraene. By limiting his analysis to monocyclic conjugated polyenes and restricting the structures to planar geometries, Hückel found that such hydrocarbons are characterized by a set of π molecular orbitals in which one orbital is lowest in energy, another is highest in energy, and the rest are distributed in pairs between them.

Hückel was a German physical chemist. Before his theoretical studies of aromaticity, Hückel collaborated with Peter Debye in developing what remains the most widely accepted theory of electrolyte solutions.

The arrangements of π orbitals for cyclobutadiene, benzene, and cyclooctatetraene as determined by Hückel are presented in Figure 11.12. Their interpretation can be summarized as follows:

Cyclobutadiene	According to the molecular orbital picture, square planar cyclobutadiene should be a diradical (have two unpaired electrons). The four π electrons are distributed so that two are in the lowest energy orbital and, in accordance with Hund's rule, each of the two equal-energy nonbonding orbitals is half-filled. (Remember, Hund's rule tells us that when two orbitals have the same energy, each one is half-filled before either of them reaches its full complement of two electrons.)
Benzene	As seen earlier in Figure 11.4 (Section 11.6), the six π electrons of benzene are distributed in pairs among its three bonding orbitals. All the bonding orbitals are occupied, and all the electron spins are paired.
Cyclooctatetraene	Six of the eight π electrons of cyclooctatetraene occupy three bonding orbitals. The remaining two π electrons occupy, one each, the two equal-energy nonbonding orbitals. Planar cyclooctatetraene should, like square cyclobutadiene, be a diradical.

As it turns out, neither cyclobutadiene nor cyclooctatetraene is a diradical in its most stable electron configuration. The Hückel approach treats them as planar regular polygons. Because the electron configurations associated with these geometries are not particularly stable, cyclobutadiene and cyclooctatetraene adopt structures other than planar regular polygons. Cyclobutadiene, rather than possessing a square shape with two unpaired electron spins, is a spin-paired rectangular molecule. Cyclooctatetraene is nonplanar, with all its π electrons paired in alternating single and double bonds.

On the basis of his analysis Hückel proposed that only certain numbers of π electrons could lead to aromatic stabilization. Only when the number of π electrons is 2, 6, 10, 14, and so on, can a closed-shell electron configuration be realized. These results are summarized in **Hückel's rule: Among planar, monocyclic, fully conjugated polyenes, only those possessing $(4n + 2)$ π electrons, where *n* is an integer, will have special aromatic stability.**

Hückel's rule should not be applied to polycyclic aromatic hydrocarbons (Section 11.8). Hückel's analysis is limited to monocyclic systems.

The general term **annulene** has been coined to apply to completely conjugated monocyclic hydrocarbons. A numerical prefix specifies the number of carbon atoms. Cyclobutadiene is [4]-annulene, benzene is [6]-annulene, and cyclooctatetraene is [8]-annulene.

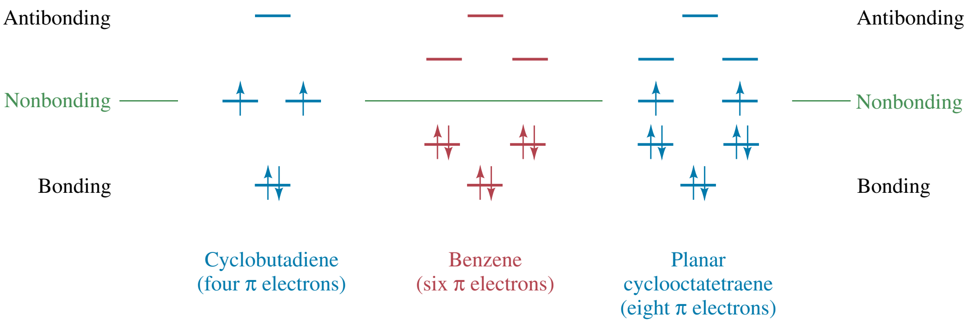
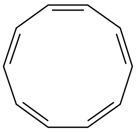


FIGURE 11.12 Distribution of π molecular orbitals and π electrons in cyclobutadiene, benzene, and planar cyclooctatetraene.

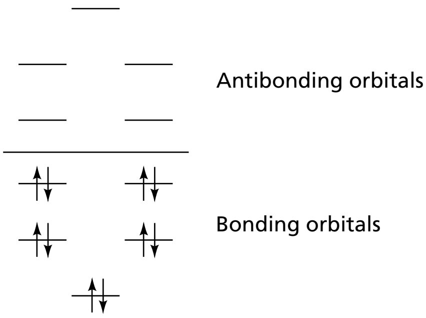
PROBLEM 11.13 Represent the π electron distribution among the π orbitals in

(a) [10]-Annulene (b) [12]-Annulene

SAMPLE SOLUTION (a) [10]-Annulene has ten carbons: ten π orbitals and ten π electrons. Like benzene, it should have a closed-shell electron configuration with all its bonding orbitals doubly occupied.



[10]-Annulene

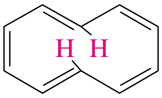


The prospect of observing aromatic character in conjugated polyenes having 10, 14, 18, and so on π electrons spurred efforts toward the synthesis of higher annulenes. A problem immediately arises in the case of the all-cis isomer of [10]-annulene, the structure of which is shown in the preceding problem. Geometry requires a ten-sided regular polygon to have 144° bond angles; sp^2 hybridization at carbon requires 120° bond angles. Therefore, aromatic stabilization due to conjugation in all-*cis*-[10]-annulene is opposed by the destabilizing effect of 24° of angle strain at each of its carbon atoms. All-*cis*-[10]-annulene has been prepared. It is not very stable and is highly reactive.

The size of each angle of a regular polygon is given by the expression

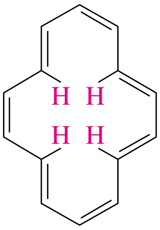
$$180° \times \frac{\text{(number of sides)} - 2}{\text{(number of sides)}}$$

A second isomer of [10]-annulene (the cis, trans, cis, cis, trans stereoisomer) can have bond angles close to 120° but is destabilized by a close contact between two hydrogens directed toward the interior of the ring. In order to minimize the van der Waals strain between these hydrogens, the ring adopts a nonplanar geometry, which limits its ability to be stabilized by π electron delocalization. It, too, has been prepared and is not very stable. Similarly, the next higher $(4n + 2)$ system, [14]-annulene, is also somewhat destabilized by van der Waals strain and is nonplanar.



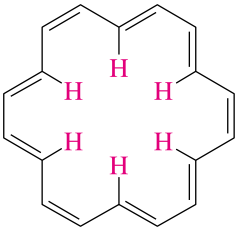
cis,trans,cis,cis,trans-
[10]-Annulene

Planar geometry required for aromaticity destabilized by van der Waals repulsions between indicated hydrogens



[14]-Annulene

When the ring contains 18 carbon atoms, it is large enough to be planar while still allowing its interior hydrogens to be far enough apart that they do not interfere with one another. The [18]-annulene shown is planar or nearly so and has all its carbon–carbon bond distances in the range 137–143 pm—very much like those of benzene. Its resonance energy is estimated to be about 418 kJ/mol (100 kcal/mol). Although its structure and resonance energy attest to the validity of Hückel's rule, which predicts "special stability" for [18]-annulene, its chemical reactivity does not. [18]-Annulene behaves more like a polyene than like benzene in that it is hydrogenated readily, undergoes addition rather than substitution with bromine, and forms a Diels–Alder adduct with maleic anhydride.

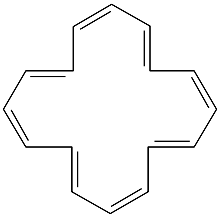


No serious repulsions among six interior hydrogens; molecule is planar and aromatic.

[18]-Annulene

Molecular models of [10]-, [14]-, [16]-, and [18]-annulene can be inspected on *Learning By Modeling.*

According to Hückel's rule, annulenes with $4n$ π electrons are not aromatic. Cyclobutadiene and cyclooctatetraene are [$4n$]-annulenes, and their properties are more in accord with their classification as cyclic polyenes than as aromatic hydrocarbons. Among higher [$4n$]-annulenes, [16]-annulene has been prepared. [16]-Annulene is not planar and shows a pattern of alternating short (average 134 pm) and long (average 146 pm) bonds typical of a nonaromatic cyclic polyene.



[16]-Annulene

PROBLEM 11.14 What does a comparison of the heats of combustion of benzene (3265 kJ/mol; 781 kcal/mol), cyclooctatetraene (4543 kJ/mol; 1086 kcal/mol), [16]-annulene (9121 kJ/mol; 2182 kcal/mol), and [18]-annulene (9806 kJ/mol; 2346 kcal/mol) reveal?

Most of the synthetic work directed toward the higher annulenes was carried out by Franz Sondheimer and his students, first at Israel's Weizmann Institute and later at the University of London. Sondheimer's research systematically explored the chemistry of these hydrocarbons and provided experimental verification of Hückel's rule.

11.20 AROMATIC IONS

Hückel realized that his molecular orbital analysis of conjugated systems could be extended beyond the realm of neutral hydrocarbons. He pointed out that cycloheptatrienyl cation contained a π system with a closed-shell electron configuration similar to that of benzene (Figure 11.13). Cycloheptatrienyl cation has a set of seven π molecular orbitals. Three of these are bonding and contain the six π electrons of the cation. These six π electrons are delocalized over seven carbon atoms, each of which contributes one $2p$ orbital to a planar, monocyclic, completely conjugated π system. Therefore, cycloheptatrienyl cation should be aromatic. It should be appreciably more stable than expected on the basis of any Lewis structure written for it.

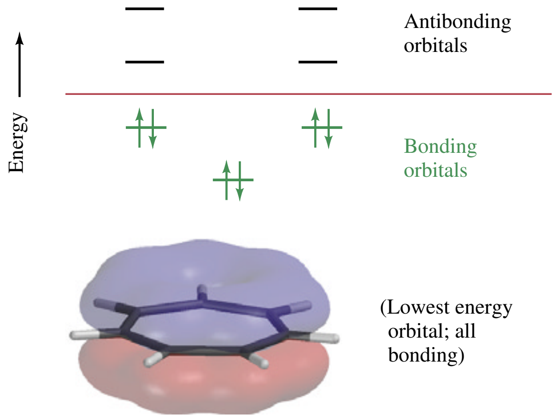
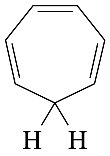
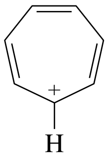


FIGURE 11.13 The π molecular orbitals of cycloheptatrienyl (tropylium) cation.

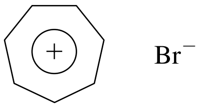


Cycloheptatriene



Cycloheptatrienyl cation (commonly referred to as *tropylium* cation)

It's important to recognize the difference between the hydrocarbon cycloheptatriene and cycloheptatrienyl (tropylium) cation. The carbocation, as we have just stated, is aromatic, whereas cycloheptatriene is not. Cycloheptatriene has six π electrons in a conjugated system, but its π system does not close upon itself. The ends of the triene system are joined by an sp^3-hybridized carbon, which prevents continuous electron delocalization. The ends of the triene system in the carbocation are joined by an sp^2-hybridized carbon, which contributes an empty *p* orbital, and allows continuous delocalization of the six π electrons. When we say cycloheptatriene is not aromatic but tropylium cation is, we are not comparing the stability of the two to each other. Cycloheptatriene is a stable hydrocarbon but does not possess the *special stability* required to be called *aromatic*. Tropylium cation, although aromatic, is still a carbocation and reasonably reactive toward nucleophiles. Its special stability does not imply a rocklike passivity but rather a much greater ease of formation than expected on the basis of the Lewis structure drawn for it. A number of observations indicate that tropylium cation is far more stable than most other carbocations. To emphasize the aromatic nature of tropylium cation, it is sometimes written in the Robinson manner, representing the aromatic sextet with a circle in the ring and including a positive charge within the circle.

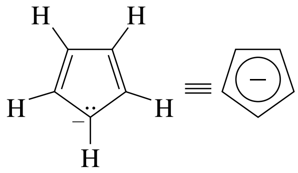


Tropylium bromide

Tropylium bromide was first prepared, but not recognized as such, in 1891. The work was repeated in 1954, and the ionic properties of tropylium bromide were demonstrated. The ionic properties of tropylium bromide are apparent in its unusually high melting point (203°C), its solubility in water, and its complete lack of solubility in diethyl ether.

PROBLEM 11.15 Write resonance structures for tropylium cation sufficient to show the delocalization of the positive charge over all seven carbons.

Cyclopentadienide anion is an *aromatic anion.* It has six π electrons delocalized over a completely conjugated planar monocyclic array of five sp^2-hybridized carbon atoms.

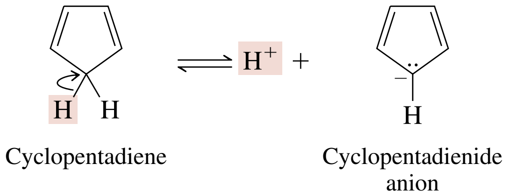


Cyclopentadienide anion

PROBLEM 11.16 Write resonance structures for cyclopentadienide anion sufficient to show the delocalization of the negative charge over all five carbons.

Figure 11.14 presents Hückel's depiction of the molecular orbitals of cyclopentadienide anion. Like benzene and tropylium cation, cyclopentadienide anion has a closed-shell configuration of six π electrons.

A convincing demonstration of the stability of cyclopentadienide anion can be found in the acidity of cyclopentadiene.

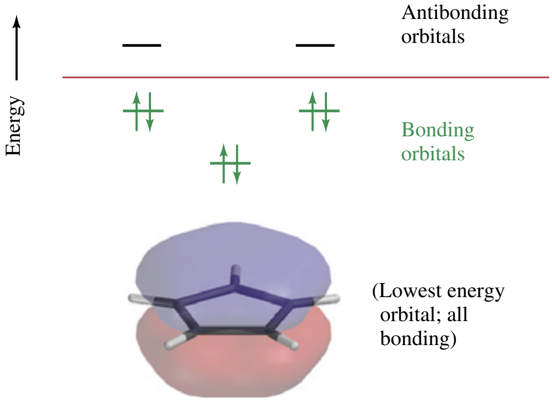


Cyclopentadiene

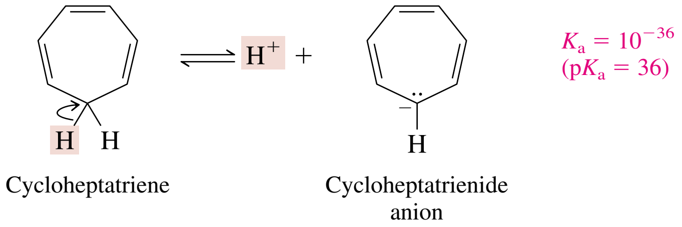
Cyclopentadienide anion

$K_a = 10^{-16}$
($pK_a = 16$)

FIGURE 11.14 The π molecular orbitals of cyclopentadienide anion.



Cyclopentadiene is only a slightly weaker acid than water. The equilibrium for its deprotonation is more favorable than for other hydrocarbons because cyclopentadienide anion is aromatic. The contrast is striking when we compare this equilibrium with that for loss of a proton from cycloheptatriene.

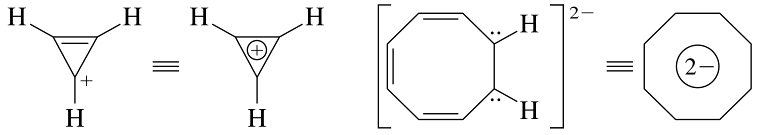


Resonance structures can be written that show delocalization of the negative charge over all of its seven carbons; nevertheless, because cycloheptatrienide anion contains *eight π electrons,* it is not aromatic. The equilibrium constant for formation from the parent hydrocarbon is more favorable by 10^{20} (20 pK_a units) for the aromatic cyclopentadienide anion than for the nonaromatic cycloheptatrienide anion.

PROBLEM 11.17 A standard method for the preparation of sodium cyclopentadienide (C_5H_5Na) is by reaction of cyclopentadiene with a solution of sodium amide in liquid ammonia. Write a balanced equation for this reaction.

Hückel's rule is now taken to apply to planar, monocyclic, completely conjugated systems generally, not just to neutral hydrocarbons. **A planar, monocyclic, continuous system of *p* orbitals possesses aromatic stability when it contains (4*n* + 2) π electrons.**

Other aromatic ions include cyclopropenyl cation (two π electrons) and cyclooctatetraene dianion (ten π electrons).



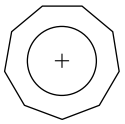
Cyclopropenyl cation

Cyclooctatetraene dianion

Here, liberties have been taken with the Robinson symbol. Instead of restricting its use to a sextet of electrons, organic chemists have come to adopt it as an all-purpose symbol for cyclic electron delocalization.

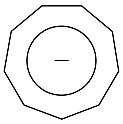
PROBLEM 11.18 Is either of the following ions aromatic?

(a)



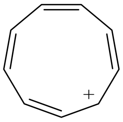
Cyclononatetraenyl cation

(b)



Cyclononatetraenide anion

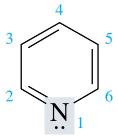
SAMPLE SOLUTION (a) The crucial point is the number of π electrons in a cyclic conjugated system. If there are (4*n* + 2) π electrons, the ion is aromatic. Electron counting is easiest if we write the ion as a single Lewis structure and remember that each double bond contributes two π electrons, a negatively charged carbon contributes two, and a positively charged carbon contributes none.



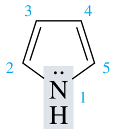
Cyclononatetraenyl cation has eight π electrons; it is *not aromatic.*

11.21 HETEROCYCLIC AROMATIC COMPOUNDS

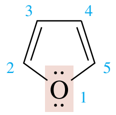
Cyclic compounds that contain at least one atom other than carbon within their ring are called **heterocyclic compounds,** and those that possess aromatic stability are called **heterocyclic aromatic compounds.** Some representative heterocyclic aromatic compounds are *pyridine, pyrrole, furan,* and *thiophene.* The structures and the IUPAC numbering system used in naming their derivatives are shown. In their stability and chemical behavior, all these compounds resemble benzene more than they resemble alkenes.



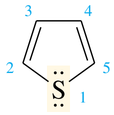
Pyridine



Pyrrole



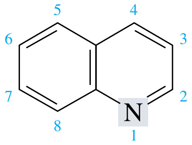
Furan



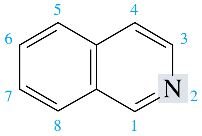
Thiophene

Pyridine, pyrrole, and thiophene, like benzene, are present in coal tar. Furan is prepared from a substance called *furfural* obtained from corncobs.

Heterocyclic aromatic compounds can be polycyclic as well. A benzene ring and a pyridine ring, for example, can share a common side in two different ways. One way gives a compound called *quinoline;* the other gives *isoquinoline.*

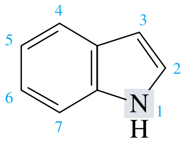


Quinoline

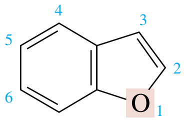


Isoquinoline

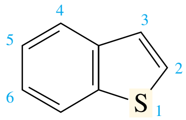
Analogous compounds derived by fusion of a benzene ring to a pyrrole, furan, or thiophene nucleus are called *indole, benzofuran,* and *benzothiophene.*



Indole

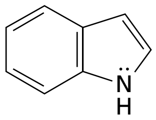


Benzofuran

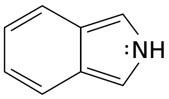


Benzothiophene

PROBLEM 11.19 Unlike quinoline and isoquinoline, which are of comparable stability, the compounds indole and isoindole are quite different from each other. Which one is more stable? Explain the reason for your choice.

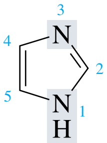


Indole

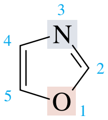


Isoindole

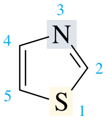
A large group of heterocyclic aromatic compounds are related to pyrrole by replacement of one of the ring carbons β to nitrogen by a second heteroatom. Compounds of this type are called *azoles.*



Imidazole

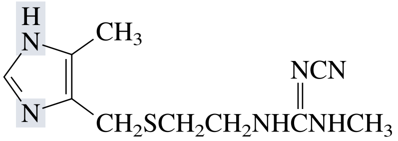


Oxazole

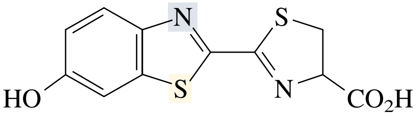


Thiazole

A widely prescribed drug for the treatment of gastric ulcers has the generic name *cimetidine* and is a synthetic imidazole derivative. *Firefly luciferin* is a thiazole derivative that is the naturally occurring light-emitting substance present in fireflies.

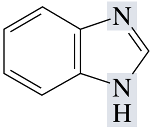


Cimetidine

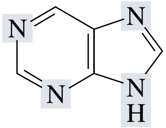


Firefly luciferin

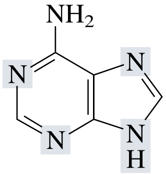
Firefly luciferin is an example of an azole that contains a benzene ring fused to the five-membered ring. Such structures are fairly common. Another example is *benzimidazole,* present as a structural unit in vitamin B_{12}. Some compounds related to benzimidazole include *purine* and its amino-substituted derivative *adenine,* one of the so-called heterocyclic bases found in DNA and RNA (Chapter 27).



Benzimidazole



Purine



Adenine

PROBLEM 11.20 Can you deduce the structural formulas of *benzoxazole* and *benzothiazole?*

The structural types described in this section are but a tiny fraction of those possible. The chemistry of heterocyclic aromatic compounds is a rich and varied field with numerous applications.

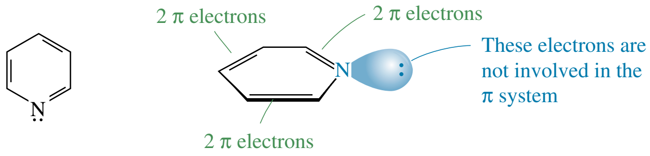
11.22 HETEROCYCLIC AROMATIC COMPOUNDS AND HÜCKEL'S RULE

Hückel's rule can be extended to heterocyclic aromatic compounds. A single heteroatom can contribute either 0 or 2 of its lone-pair electrons as needed to the π system so as to satisfy the $(4n + 2)$ π electron requirement. The lone pair in pyridine, for example, is associated entirely with nitrogen and is not delocalized into the aromatic π system. As shown in Figure 11.15*a,* pyridine is simply a benzene ring in which a nitrogen atom has replaced a CH group. The nitrogen is sp^2-hybridized, and the three double bonds of the ring contribute the necessary six π electrons to make pyridine a heterocyclic aromatic compound. The unshared electron pair of nitrogen occupies an sp^2 orbital in the plane of the ring, not a *p* orbital aligned with the π system.

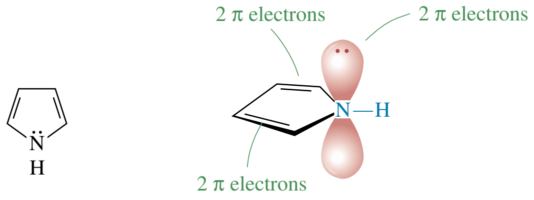
In pyrrole, on the other hand, the unshared pair belonging to nitrogen must be added to the four π electrons of the two double bonds in order to meet the six-π-electron requirement. As shown in Figure 11.15*b,* the nitrogen of pyrrole is sp^2-hybridized and the pair of electrons occupies a *p* orbital where both electrons can participate in the aromatic π system.

Pyridine and pyrrole are both weak bases, but pyridine is much more basic than pyrrole. When pyridine is protonated, its unshared pair is used to bond to a proton and, since the unshared pair is not involved in the π system, the aromatic character of the ring is little affected. When pyrrole acts as a base, the two electrons used to form a bond to hydrogen must come from the π system, and the aromaticity of the molecule is sacrificed on protonation.

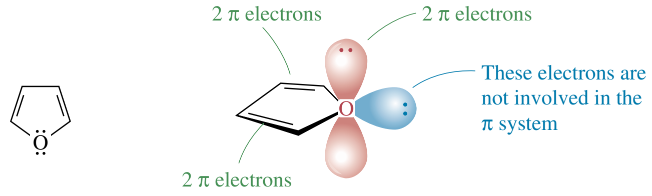
FIGURE 11.15 (*a*) Pyridine has six π electrons plus an unshared pair in a nitrogen sp^2 orbital. (*b*) Pyrrole has six π electrons. (*c*) Furan has six π electrons plus an unshared pair in an oxygen sp^2 orbital, which is perpendicular to the π system and does not interact with it.



(*a*) Pyridine

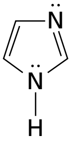


(*b*) Pyrrole



(*c*) Furan

PROBLEM 11.21 Imidazole is a much stronger base than pyrrole. Predict which nitrogen is protonated when imidazole reacts with an acid, and write a structural formula for the species formed.



Imidazole

The oxygen in furan has two unshared electron pairs (Figure 11.15*c*). One pair is like the pair in pyrrole, occupying a *p* orbital and contributing two electrons to complete the six-π-electron requirement for aromatic stabilization. The other electron pair in furan is an "extra" pair, not needed to satisfy the $4n + 2$ rule for aromaticity, and occupies an sp^2-hybridized orbital like the unshared pair in pyridine.

The bonding in thiophene is similar to that of furan.

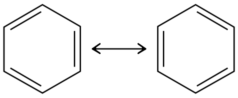
11.23 SUMMARY

The article "A History of the Structural Theory of Benzene—The Aromatic Sextet and Hückel's Rule" in the February 1997 issue of the *Journal of Chemical Education* (pp. 194–201) is a rich source of additional information about this topic.

Section 11.1 Benzene is the parent of a class of hydrocarbons called **arenes,** or **aromatic hydrocarbons.**

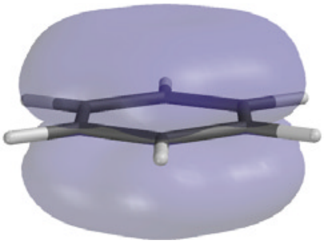
Section 11.2 An important property of aromatic hydrocarbons is that they are much more stable and less reactive than other unsaturated compounds. Benzene, for example, does not react with many of the reagents that react rapidly with alkenes. When reaction does take place, substitution rather than addition is observed. The Kekulé formulas for benzene seem inconsistent with its low reactivity and with the fact that all of the C—C bonds in benzene are the same length (140 pm).

Section 11.3 One explanation for the structure and stability of benzene and other arenes is based on resonance, according to which benzene is regarded as a hybrid of the two Kekulé structures.



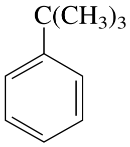
Section 11.4 The extent to which benzene is more stable than either of the Kekulé structures is its **resonance energy,** which is estimated to be 125–150 kJ/mol (30–36 kcal/mol) from heats of hydrogenation data.

Section 11.5 According to the orbital hybridization model, benzene has six π electrons, which are shared by all six sp^2-hybridized carbons. Regions of high π electron density are located above and below the plane of the ring.

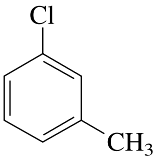


Section 11.6 A molecular orbital description of benzene has three π orbitals that are bonding and three that are antibonding. Each of the bonding orbitals is fully occupied (two electrons each), and the antibonding orbitals are vacant.

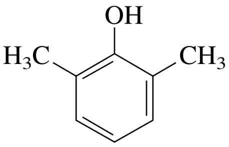
Section 11.7 Many aromatic compounds are simply substituted derivatives of benzene and are named accordingly. Many others have names based on some other parent aromatic compound.



tert-Butylbenzene

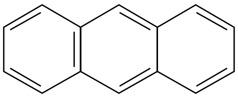


m-Chlorotoluene



2,6-Dimethylphenol

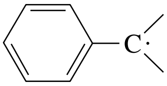
Section 11.8 **Polycyclic aromatic hydrocarbons,** of which anthracene is an example, contain two or more benzene rings fused together.



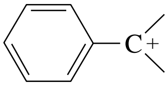
Anthracene

Section 11.9 The physical properties of arenes resemble those of other hydrocarbons.

Section 11.10 Chemical reactions of arenes can take place on the ring itself, or on a side chain. Reactions that take place on the side chain are strongly influenced by the stability of **benzylic radicals** and **benzylic carbocations.**

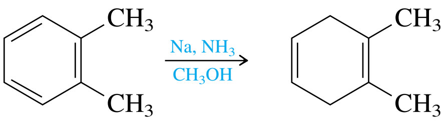


Benzylic free radical



Benzylic carbocation

Section 11.11 An example of a reaction in which the ring itself reacts is the **Birch reduction.** The ring of an arene is reduced to a nonconjugated diene by treatment with a Group I metal (usually sodium) in liquid ammonia in the presence of an alcohol.

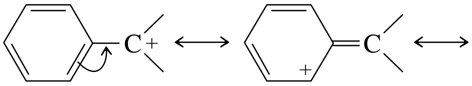


o-Xylene

1,2-Dimethyl-1,4-cyclohexadiene (92%)

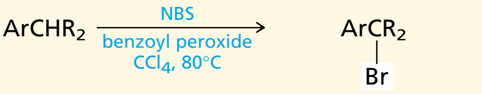
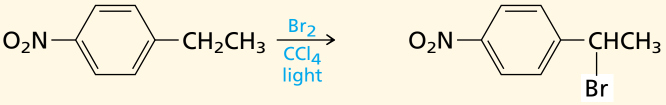
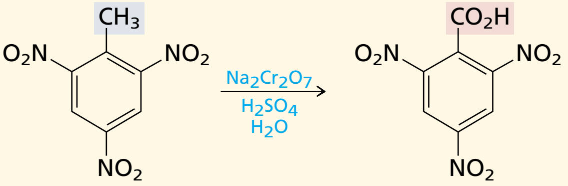
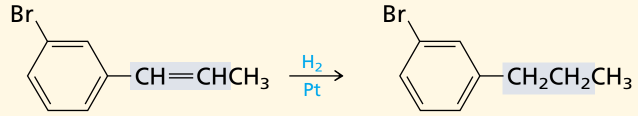
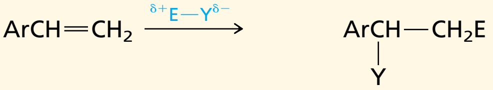
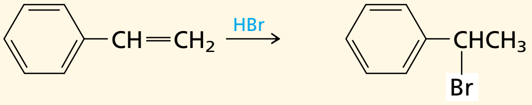
Sections 11.12–11.13 Free-radical halogenation and oxidation involve reactions at the benzylic carbon. See Table 11.2.

Section 11.14 Benzylic carbocations are intermediates in S_N1 reactions of benzylic halides and are stabilized by electron delocalization.

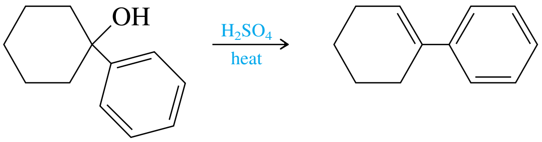


and so on

TABLE 11.2 Reactions Involving Alkyl and Alkenyl Side Chains in Arenes and Arene Derivatives

Reaction (section) and comments	General equation and specific example
Halogenation (Section 11.12) Free-radical halogenation of alkylbenzenes is highly selective for substitution at the benzylic position. In the example shown, elemental bromine was used. Alternatively, *N*-bromosuccinimide is a convenient reagent for benzylic bromination.	 $ArCHR_2 \xrightarrow[\text{benzoyl peroxide}\ CCl_4,\ 80°C]{\text{NBS}} ArCR_2(Br)$ Arene 1-Arylalkyl bromide  *p*-Ethylnitrobenzene 1-(*p*-Nitrophenyl)ethyl bromide (77%)
Oxidation (Section 11.13) Oxidation of alkylbenzenes occurs at the benzylic position of the alkyl group and gives a benzoic acid derivative. Oxidizing agents include sodium or potassium dichromate in aqueous sulfuric acid. Potassium permanganate ($KMnO_4$) is also an effective oxidant.	$ArCHR_2 \xrightarrow{\text{oxidize}} ArCO_2H$ Arene Arenecarboxylic acid  2,4,6-Trinitrotoluene 2,4,6-Trinitrobenzoic acid (57–69%)
Hydrogenation (Section 11.16) Hydrogenation of aromatic rings is somewhat slower than hydrogenation of alkenes, and it is a simple matter to reduce the double bond of an unsaturated side chain in an arene while leaving the ring intact.	$ArCH{=}CR_2 + H_2 \xrightarrow{Pt} ArCH_2CHR_2$ Alkenylarene Hydrogen Alkylarene  1-(*m*-Bromophenyl)propene *m*-Bromopropylbenzene (85%)
Electrophilic addition (Section 11.16) An aryl group stabilizes a benzylic carbocation and controls the regioselectivity of addition to a double bond involving the benzylic carbon. Markovnikov's rule is obeyed.	 $ArCH{=}CH_2 \xrightarrow{\delta+E{-}Y\delta-} ArCH(Y){-}CH_2E$ Alkenylarene Product of electrophilic addition  Styrene 1-Phenylethyl bromide (85%)

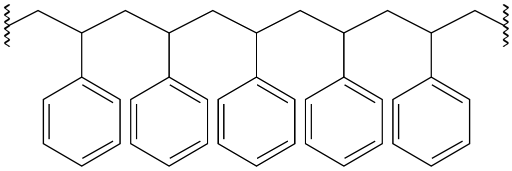
Section 11.15 The simplest alkenylbenzene is styrene ($C_6H_5CH{=}CH_2$). An aryl group stabilizes a double bond to which it is attached. Alkenylbenzenes are usually prepared by dehydration of benzylic alcohols or dehydrohalogenation of benzylic halides.



1-Phenylcyclohexanol 1-Phenylcyclohexene (83%)

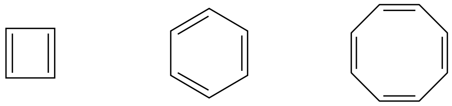
Section 11.16 Addition reactions to alkenylbenzenes occur at the double bond of the alkenyl substituent, and the regioselectivity of electrophilic addition is governed by carbocation formation at the benzylic carbon. See Table 11.2.

Section 11.17 Polystyrene is a widely used vinyl polymer prepared by the free-radical polymerization of styrene.



Polystyrene

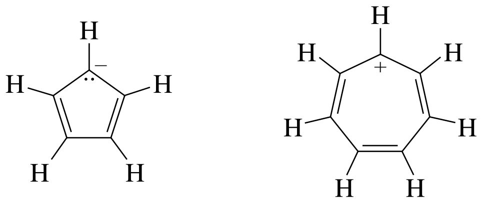
Section 11.18 Although cyclic conjugation is a necessary requirement for aromaticity, this alone is not sufficient. If it were, cyclobutadiene and cyclooctatetraene would be aromatic. They are not.



Cyclobutadiene (not aromatic) Benzene (aromatic) Cyclooctatetraene (not aromatic)

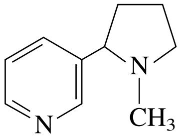
Section 11.19 An additional requirement for aromaticity is that the number of π electrons in conjugated, planar, monocyclic species must be equal to $4n + 2$, where n is an integer. This is called **Hückel's rule.** Benzene, with six π electrons, satisfies Hückel's rule for $n = 1$. Cyclobutadiene (four π electrons) and cyclooctatetraene (eight π electrons) do not. Planar, monocyclic, completely conjugated polyenes are called **annulenes.**

Section 11.20 Species with six π electrons that possess "special stability" include certain ions, such as *cyclopentadienide* anion and *cycloheptatrienyl* cation.



Cyclopentadienide anion (six π electrons) Cycloheptatrienyl cation (six π electrons)

Section 11.21 **Heterocyclic aromatic compounds** are compounds that contain at least one atom other than carbon within an aromatic ring.



Nicotine

Section 11.22 Hückel's rule can be extended to heterocyclic aromatic compounds. Unshared electron pairs of the heteroatom may be used as π electrons as necessary to satisfy the $4n + 2$ rule.

PROBLEMS

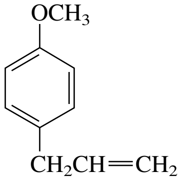
11.22 Write structural formulas and give the IUPAC names for all the isomers of $C_6H_5C_4H_9$ that contain a monosubstituted benzene ring.

11.23 Write a structural formula corresponding to each of the following:

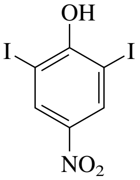
(a) Allylbenzene
(b) (*E*)-1-Phenyl-1-butene
(c) (*Z*)-2-Phenyl-2-butene
(d) (*R*)-1-Phenylethanol
(e) *o*-Chlorobenzyl alcohol
(f) *p*-Chlorophenol
(g) 2-Nitrobenzenecarboxylic acid
(h) *p*-Diisopropylbenzene
(i) 2,4,6-Tribromoaniline
(j) *m*-Nitroacetophenone
(k) 4-Bromo-3-ethylstyrene

11.24 Using numerical locants and the names in Table 11.1 as a guide, give an acceptable IUPAC name for each of the following compounds:

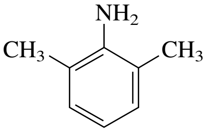
(a) Estragole (principal component of wormwood oil)



(b) Diosphenol (used in veterinary medicine to control parasites in animals)



(c) *m*-Xylidine (used in synthesis of lidocaine, a local anesthetic)



11.25 Write structural formulas and give acceptable names for all the isomeric

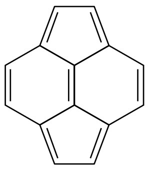
(a) Nitrotoluenes
(b) Dichlorobenzoic acids
(c) Tribromophenols
(d) Tetrafluorobenzenes
(e) Naphthalenecarboxylic acids
(f) Bromoanthracenes

11.26 Mesitylene (1,3,5-trimethylbenzene) is the most stable of the trimethylbenzene isomers. Can you think of a reason why? Which isomer do you think is the least stable? Make a molecular model of each isomer and compare their calculated strain energies with your predictions. Do space-filling models support your explanation?

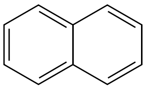
11.27 Which one of the dichlorobenzene isomers does not have a dipole moment? Which one has the largest dipole moment? Compare your answers with the dipole moments calculated using the molecular-modeling software in *Learning By Modeling*.

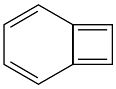
11.28 Identify the longest and the shortest carbon–carbon bonds in styrene. Make reasonable estimates of their bond distances and compare them to the distances in a molecular model.

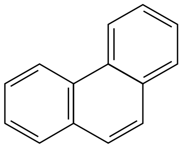
11.29 The resonance form shown is not the most stable one for the compound indicated. Write the most stable resonance form.

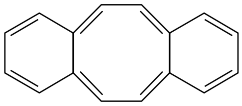


11.30 Each of the following may be represented by at least one alternative resonance structure in which all the six-membered rings correspond to Kekulé forms of benzene. Write such a resonance form for each.

(a)


(b)


(c)


(d)


The common name of isopropylbenzene is *cumene.*

11.31 Give the structure of the expected product from the reaction of isopropylbenzene with

(a) Hydrogen (3 mol), Pt

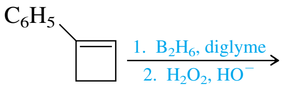
(b) Sodium and ethanol in liquid ammonia

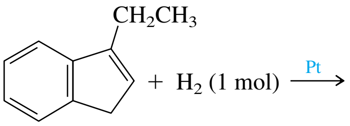
(c) Sodium dichromate, water, sulfuric acid, heat

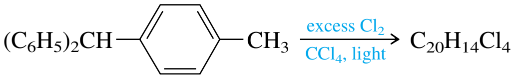
(d) *N*-Bromosuccinimide in CCl_4, heat, benzoyl peroxide

(e) The product of part (d) treated with sodium ethoxide in ethanol

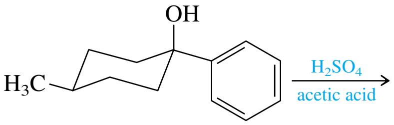
11.32 Each of the following reactions has been described in the chemical literature and gives a single organic product in good yield. Identify the product of each reaction.

(a)


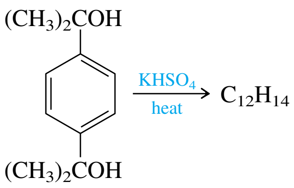
(b)


(c)


(d) $(E)\text{-}C_6H_5CH{=}CHC_6H_5 \xrightarrow[\text{acetic acid}]{CH_3CO_2OH}$

(e)


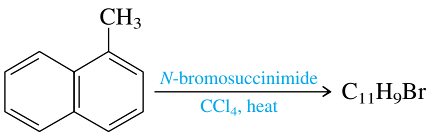
(f)



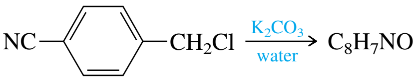
(g)

(DDT)

(h)



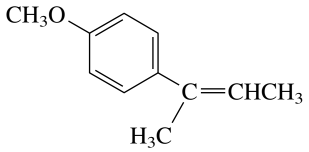
(i)



11.33 A certain compound A, when treated with *N*-bromosuccinimide and benzoyl peroxide under photochemical conditions in refluxing carbon tetrachloride, gave 3,4,5-tribromobenzyl bromide in excellent yield. Deduce the structure of compound A.

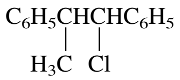
11.34 A compound was obtained from a natural product and had the molecular formula $C_{14}H_{20}O_3$. It contained three methoxy ($—OCH_3$) groups and a $—CH_2CH{=}C(CH_3)_2$ substituent. Oxidation with either chromic acid or potassium permanganate gave 2,3,5-trimethoxybenzoic acid. What is the structure of the compound?

11.35 Hydroboration–oxidation of (*E*)-2-(*p*-anisyl)-2-butene yielded an alcohol A, mp 60°C, in 72% yield. When the same reaction was performed on the *Z* alkene, an isomeric liquid alcohol B was obtained in 77% yield. Suggest reasonable structures for A and B, and describe the relationship between them.



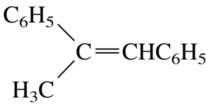
2-(*p*-Anisyl)-2-butene

11.36 Dehydrohalogenation of the diastereomeric forms of 1-chloro-1,2-diphenylpropane is stereospecific. One diastereomer yields (*E*)-1,2-diphenylpropene, and the other yields the *Z* isomer. Which diastereomer yields which alkene? Why?



$C_6H_5\underset{\substack{|\\ H_3C}}{C}H\underset{\substack{|\\ Cl}}{C}HC_6H_5$

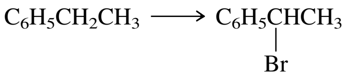
1-Chloro-1,2-diphenylpropane



1,2-Diphenylpropene

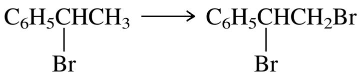
11.37 Suggest reagents suitable for carrying out each of the following conversions. In most cases more than one synthetic operation will be necessary.

(a)



$C_6H_5CH_2CH_3 \longrightarrow C_6H_5\underset{\substack{|\\ Br}}{C}HCH_3$

(b)

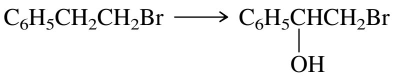


$C_6H_5\underset{\substack{|\\ Br}}{C}HCH_3 \longrightarrow C_6H_5\underset{\substack{|\\ Br}}{C}HCH_2Br$

(c) $C_6H_5CH{=}CH_2 \longrightarrow C_6H_5C{\equiv}CH$

(d) $C_6H_5C{\equiv}CH \longrightarrow C_6H_5CH_2CH_2CH_2CH_3$

(e) $C_6H_5CH_2CH_2OH \longrightarrow C_6H_5CH_2CH_2C{\equiv}CH$

(f) 

$C_6H_5CH_2CH_2Br \longrightarrow C_6H_5\underset{\displaystyle OH}{\underset{|}{C}}HCH_2Br$

11.38 The relative rates of reaction of ethane, toluene, and ethylbenzene with bromine atoms have been measured. The most reactive hydrocarbon undergoes hydrogen atom abstraction a million times faster than does the least reactive one. Arrange these hydrocarbons in order of decreasing reactivity.

11.39 Write the principal resonance structures of *o*-methylbenzyl cation and *m*-methylbenzyl cation. Which one has a tertiary carbocation as a contributing resonance form?

11.40 The same anion is formed by loss of the most acidic proton from 1-methyl-1,3-cyclopentadiene as from 5-methyl-1,3-cyclopentadiene. Explain.

11.41 There are two different tetramethyl derivatives of cyclooctatetraene that have methyl groups on four adjacent carbon atoms. They are both completely conjugated and are not stereoisomers. Write their structures.

11.42 Evaluate each of the following processes applied to cyclooctatetraene, and decide whether the species formed is aromatic or not.

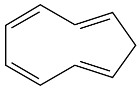
(a) Addition of one more π electron, to give $C_8H_8^{-}$

(b) Addition of two more π electrons, to give $C_8H_8^{2-}$

(c) Removal of one π electron, to give $C_8H_8^{+}$

(d) Removal of two π electrons, to give $C_8H_8^{2+}$

11.43 Evaluate each of the following processes applied to cyclononatetraene, and decide whether the species formed is aromatic or not:



Cyclononatetraene

(a) Addition of one more π electron, to give $C_9H_{10}^{-}$

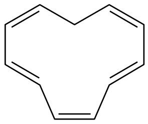
(b) Addition of two more π electrons, to give $C_9H_{10}^{2-}$

(c) Loss of H^+ from the sp^3-hybridized carbon

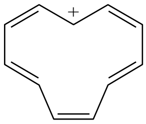
(d) Loss of H^+ from one of the sp^2-hybridized carbons

11.44 From among the molecules and ions shown, all of which are based on cycloundecapentaene, identify those which satisfy the criteria for aromaticity as prescribed by Hückel's rule.

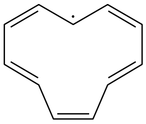
(a) Cycloundecapentaene



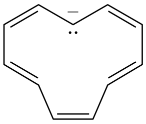
(c) Cycloundecapentaenyl cation



(b) Cycloundecapentaenyl radical



(d) Cycloundecapentaenide anion



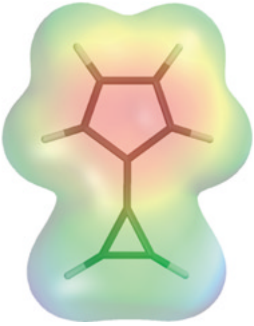
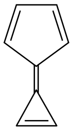
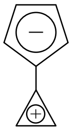


FIGURE 11.16 Electrostatic potential map of calicene (problem 11.45).

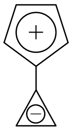
11.45 (a) Figure 11.16 is an electrostatic potential map of *calicene,* so named because its shape resembles a chalice (*calix* is the Latin word for "cup"). Both the electrostatic potential map and its calculated dipole moment ($\mu = 4.3$ D) indicate that calicene is an unusually polar hydrocarbon. Which of the dipolar resonance forms, A or B, better corresponds to the electron distribution in the molecule? Why is this resonance form more important than the other?



Calicene

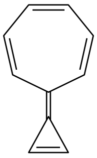


A



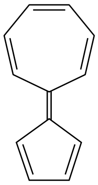
B

(b) Which one of the following should be stabilized by resonance to a greater extent? (*Hint:* Consider the reasonableness of dipolar resonance forms.)



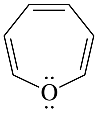
C

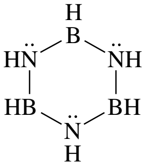
or

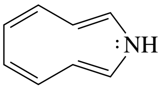


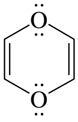
D

11.46 Classify each of the following heterocyclic molecules as aromatic or not, according to Hückel's rule:

(a) 

(c) 

(b) 

(d) 

11.47 Pellagra is a disease caused by a deficiency of *niacin* ($C_6H_5NO_2$) in the diet. Niacin can be synthesized in the laboratory by the side-chain oxidation of 3-methylpyridine with chromic acid or potassium permanganate. Suggest a reasonable structure for niacin.

11.48 *Nitroxoline* is the generic name by which 5-nitro-8-hydroxyquinoline is sold as an antibacterial drug. Write its structural formula.

11.49 *Acridine* is a heterocyclic aromatic compound obtained from coal tar that is used in the synthesis of dyes. The molecular formula of acridine is $C_{13}H_9N$, and its ring system is analogous to that of anthracene except that one CH group has been replaced by N. The two most stable resonance structures of acridine are equivalent to each other, and both contain a pyridine-like structural unit. Write a structural formula for acridine.

11.50 Make molecular models of the two chair conformations of *cis*-1-*tert*-butyl-4-phenylcyclohexane. What is the strain energy calculated for each conformation by molecular mechanics? Which has a greater preference for the equatorial orientation, phenyl or *tert*-butyl?