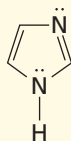


because the unshared pair is not involved in the π system, the aromatic character of the ring is little affected. When pyrrole acts as a base, the two electrons used to form a bond to hydrogen must come from the π system, and the aromaticity of the molecule is sacrificed on protonation.

PROBLEM 11.25 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 11.16c). 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.

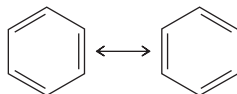
The bonding in thiophene is similar to that of furan.

11.24 SUMMARY

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).

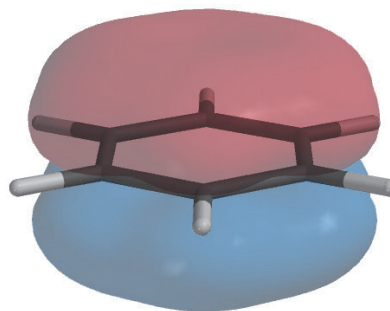
Section 11.3 One explanation for the structure and stability of benzene and other arenes is based on resonance, according to which benzene is regarded as a hybrid of the two Kekulé structures.



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.

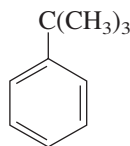
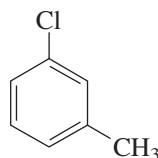
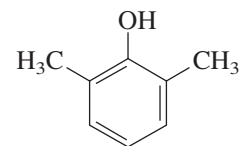
Section 11.5 According to the orbital hybridization model, benzene has six π electrons, which are shared by all six sp^2 -hybridized carbons. Regions of high π electron density are located above and below the plane of the ring.

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.



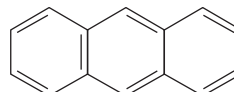
Section 11.6 A molecular orbital description of benzene has three π orbitals that are bonding and three that are antibonding. Each of the bonding orbitals is fully occupied (two electrons each), and the antibonding orbitals are vacant.

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

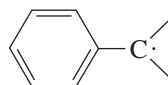
Section 11.8 **Polycyclic aromatic hydrocarbons**, of which anthracene is an example, contain two or more benzene rings fused together.



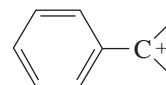
Anthracene

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**.

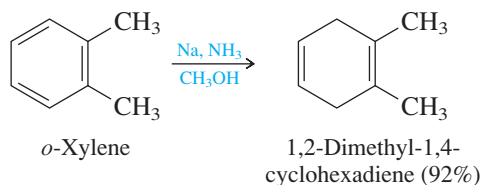


Benzylic free radical



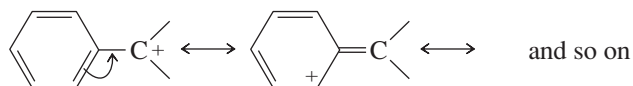
Benzylic carbocation

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.

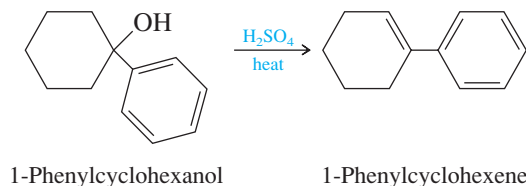


Sections 11.12–11.13 Free-radical halogenation and oxidation involve reactions at the benzylic carbon. See Table 11.2.

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

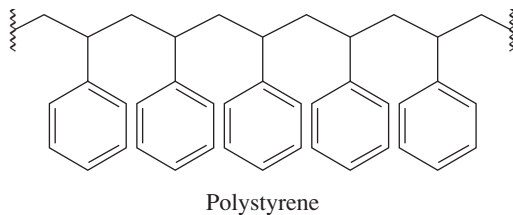


Section 11.15 The simplest alkenylbenzene is styrene ($C_6H_5CH=CH_2$). An aryl group stabilizes a double bond to which it is attached. Alkenylbenzenes are usually prepared by dehydration of benzylic alcohols or dehydrohalogenation of benzylic halides.



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.



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.

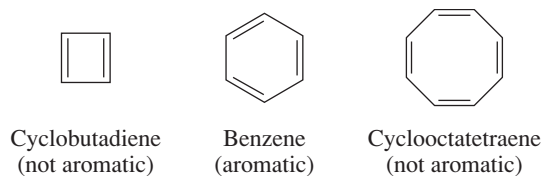
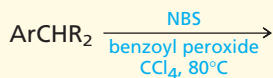


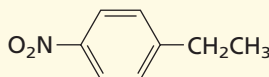
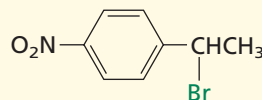
TABLE 11.2 Reactions Involving Alkyl and Alkenyl Side Chains in Arenes and Arene Derivatives**Reaction (section) and comments****General equation and specific example**

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.



Arene

1-Arylalkyl bromide

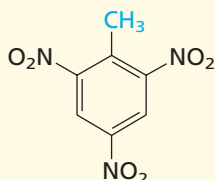
*p*-Ethylnitrobenzene1-(*p*-Nitrophenyl)ethyl bromide (77%)

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.

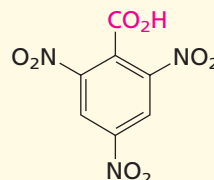


Arene

Arenecarboxylic acid

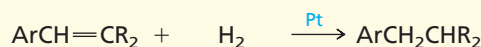


2,4,6-Trinitrotoluene



2,4,6-Trinitrobenzoic acid (57–69%)

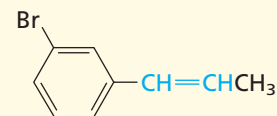
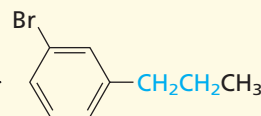
Hydrogenation (Section 11.16) Hydrogenation of aromatic rings is somewhat slower than hydrogenation of alkenes, and it is a simple matter to reduce the double bond of an unsaturated side chain in an arene while leaving the ring intact.



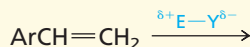
Alkenylarene

Hydrogen

Alkylarene

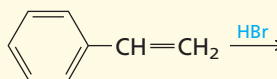
1-(*m*-Bromophenyl)propene*m*-Bromopropylbenzene (85%)

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.

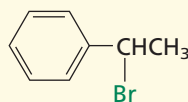


Alkenylarene

Product of electrophilic addition



Styrene

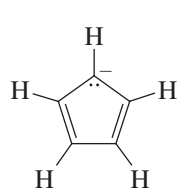


1-Phenylethyl bromide (85%)

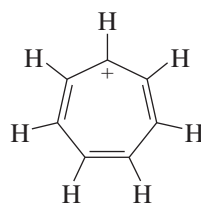
Section 11.19 An additional requirement for aromaticity is that the number of π electrons in conjugated, planar, monocyclic species must be equal to $4n + 2$, where n is an integer. This is called **Hückel's rule**. Benzene, with six π electrons, satisfies Hückel's rule for $n = 1$. Square cyclobutadiene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

Section 11.20 **Annulenes** are monocyclic, completely conjugated polyenes synthesized for the purpose of testing Hückel's rule. They are named by using a bracketed numerical prefix to indicate the number of carbons, followed by the word *annulene*. $[4n]$ Annulenes are characterized by rings with alternating short (double) and long (single) bonds and are *antiaromatic*. The expected aromaticity of $[4n + 2]$ annulenes is diminished by angle and van der Waals strain unless the ring contains approximately 18 carbons.

Section 11.21 Species with six π electrons that possess "special stability" include certain ions, such as *cyclopentadienide* anion and *cycloheptatrienyl* cation.

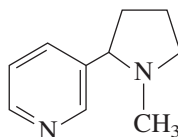


Cyclopentadienide anion
(six π electrons)



Cycloheptatrienyl cation
(six π electrons)

Section 11.22 **Heterocyclic aromatic compounds** are compounds that contain at least one atom other than carbon within an aromatic ring.



Nicotine

Section 11.23 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

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

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

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