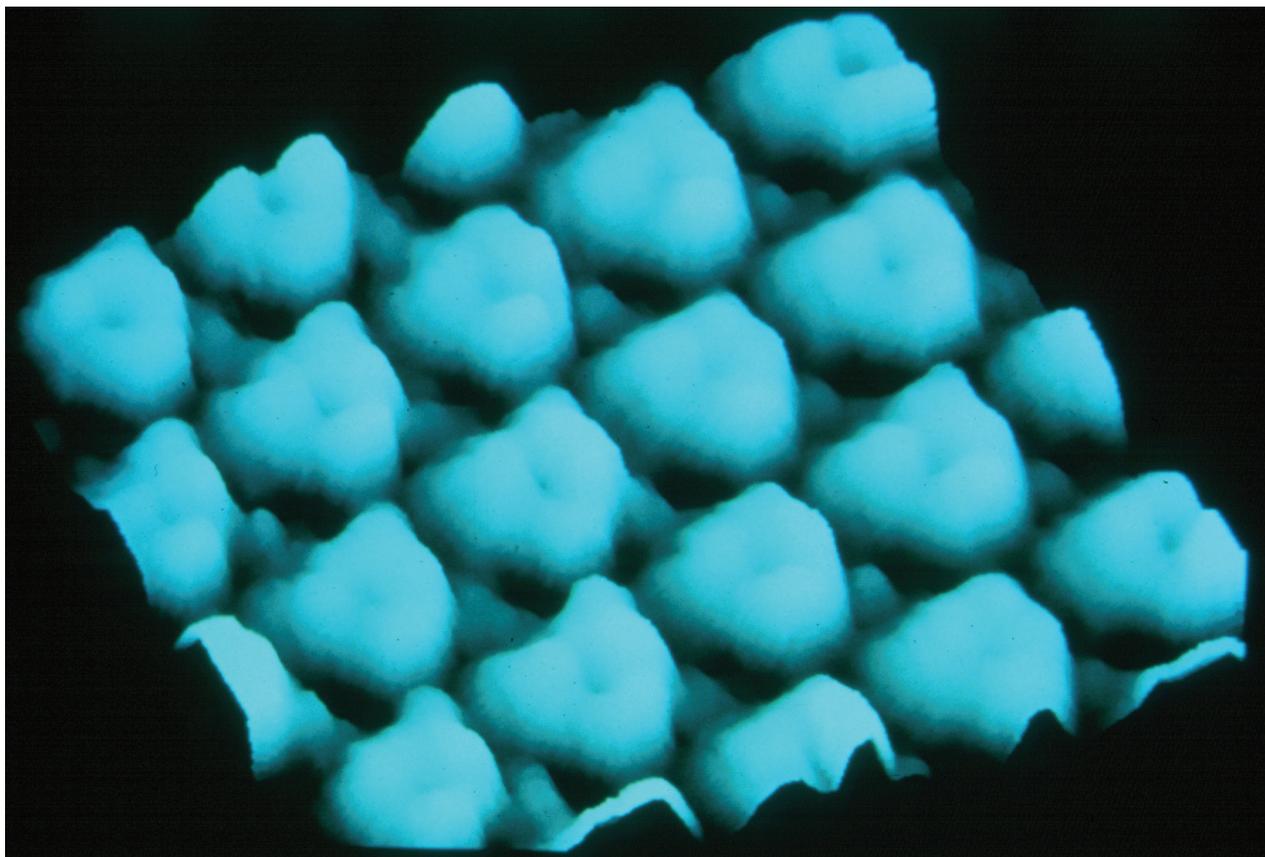


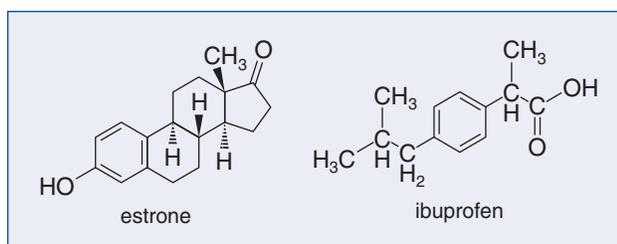
## INTERCHAPTER H

# Aromatic Hydrocarbons



Scanning tunneling micrograph of benzene molecules adsorbed on the surface of a rhodium crystal. The hexagonal shape of the benzene molecules is revealed in this remarkable micrograph.

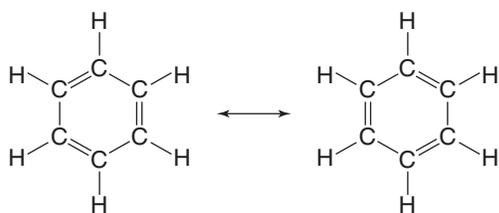
At one time, the term **aromatic** was used to describe a number of substances isolated from coal tar that had characteristic strong fragrances. Many of these substances were subsequently shown to contain benzene rings. Nowadays, we use the term aromatic to refer to the class of compounds that contain benzene-like rings. Many important compounds such as the hormone estrone and the analgesic ibuprofen are aromatic in part of their structure.



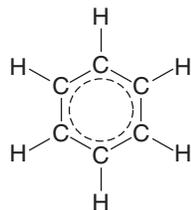
### H-1. Benzene Belongs to a Class of Hydrocarbons Called Aromatic Hydrocarbons

Benzene, which was first identified by Michael Faraday (Chapter 25 Frontispiece) in 1825, is the quintessential example of an aromatic compound. Benzene is a colorless, carcinogenic, flammable liquid with a characteristic odor. A benzene ring is relatively stable because of  $\pi$ -electron delocalization (Section 9-13). Benzene and many other aromatic hydrocarbons are obtained from petroleum and coal tar. About eight million metric tons of benzene are produced annually in the United States.

We noted in Sections 7-6 and 9-13 that benzene is a planar, perfectly hexagonal molecule and that the two principal resonance forms are



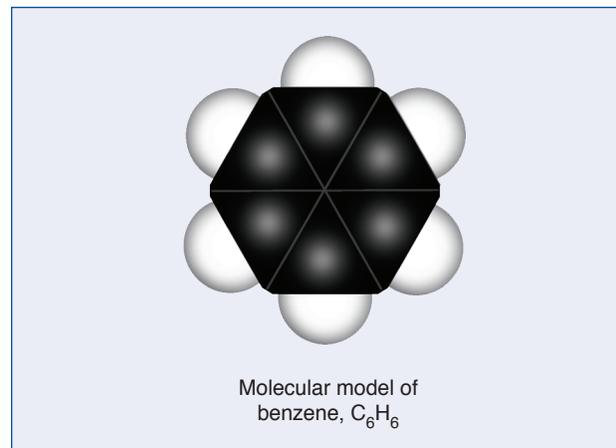
The resonance hybrid is



or, more compactly,

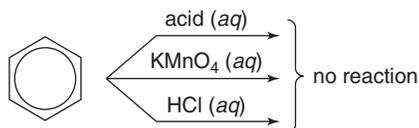


where a hydrogen atom is understood to be bonded to the carbon atom at each vertex in the benzene ring. Although each resonance form of benzene shows localized double bonds, the resonance hybrid does not (Section 9-13).

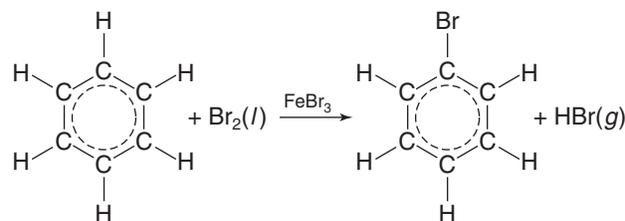


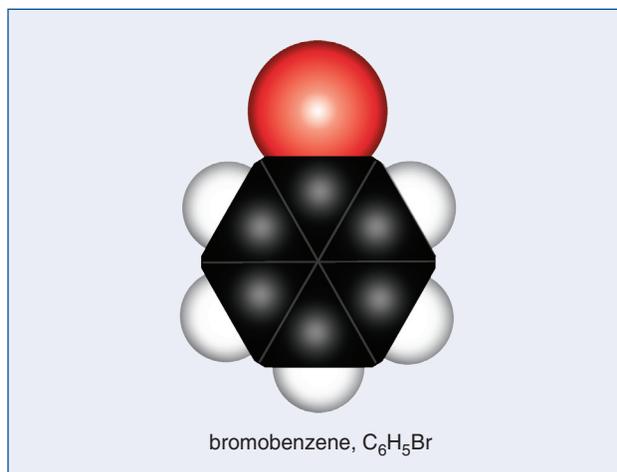
### H-2. Most Reactions of Benzene Are Substitution Reactions

The benzene molecule does not have localized double bonds and does *not* react as an unsaturated hydrocarbon. In fact, the  $\pi$ -electron delocalization causes the ring to be so stable that many of the reactions that unsaturated hydrocarbons undergo do not occur with benzene. For example,

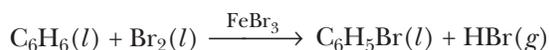


Most of the reactions that benzene undergoes are substitution reactions in which the hydrogen atoms on the ring are replaced by other atoms or groups. For example, the usual reaction of benzene with bromine is a substitution reaction (*not* an addition reaction), as given by

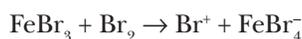




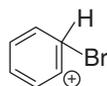
or more succinctly,



The fact that only one kind of monobromobenzene has ever been isolated indicates that all the hydrogen atoms in benzene are equivalent, as you should expect from the hexagonal symmetry of a benzene ring. The hexagonal geometry of the benzene molecule has been confirmed by X-ray and spectroscopic data. This reaction requires  $FeBr_3$ . The  $FeBr_3$  acts as a facilitator by reacting with  $Br_2(l)$  according to



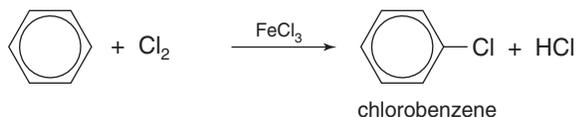
Even though the benzene ring is stable to most reactants, the positively charged  $Br^+$  ions attack the electron-rich ring of the benzene molecule to form an adduct, such as



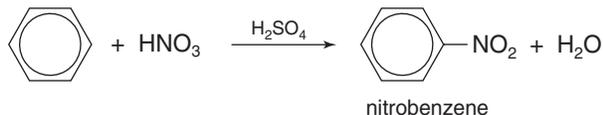
that can then eliminate an  $H^+$  ion to form bromobenzene.

Some other types of substitution reactions that benzene undergoes are given by the equations below.

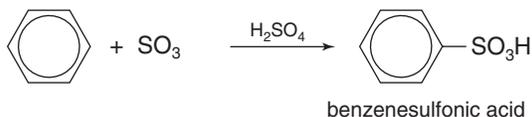
#### Chlorination



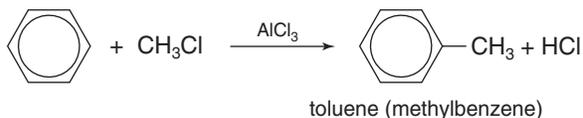
#### Nitration



#### Sulfonation



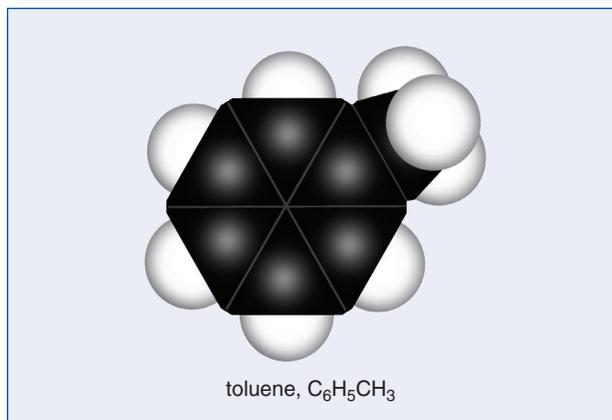
#### Alkylation



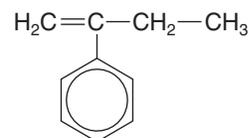
In each case above, the primary reactant also requires a facilitator such as  $H_2SO_4$ , which reacts with the primary reactant to produce  $NO_2^+$  in the case of nitration and  $HSO_3^+$  in the case of sulfonation.

### H-3. Substituted Benzene Rings Are Named According to IUPAC Rules

Many aromatic hydrocarbons have widely used common names. Although the aromatic product in the alkylation reaction above should, strictly speaking, be called methylbenzene, its common name **toluene** is an IUPAC accepted name. Toluene is a widely used industrial solvent often used in paints and thinners (Figure H.1). Toluene, like benzene, is a carcinogen, but it is significantly less toxic than benzene because the methyl group allows it to be more readily broken down by the body.

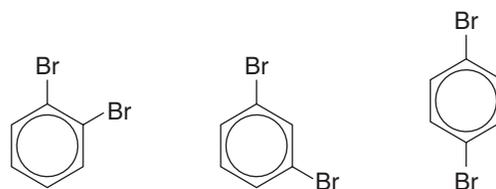


When a benzene ring is a substituent in a molecule, it is called a **phenyl group**. For example, the compound





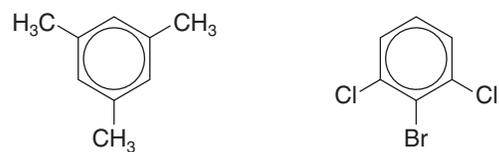
**Figure H.1** Many brands of nail polish use toluene as a solvent. Because toluene is a known carcinogen, some manufacturers now offer toluene-free products. Nail polishes containing toluene or other volatile solvents should always be applied outdoors or in a well-ventilated room.



1,2-dibromobenzene    1,3-dibromobenzene    1,4-dibromobenzene

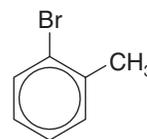
These names result from numbering the six positions around the benzene ring. One of the substituents on the ring is always placed at the number 1 position and the numbers assigned so as to give the lowest numbers to each of the other substituents.

Some other examples of substituted benzenes are



1,3,5-trimethylbenzene

2-bromo-1,3-dichlorobenzene

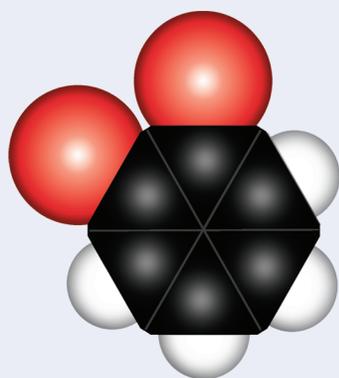


2-bromotoluene

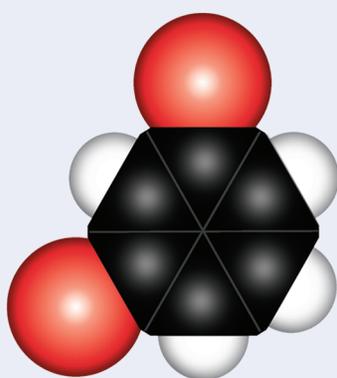
is systematically named 2-phenyl-1-butene. Because the main carbon chain must include the double bond, the benzene ring is a substituent in this case.

The hexagonal symmetry of a benzene ring allows for three different disubstituted benzenes. For example, the formulas for the three isomers of dibromobenzene are

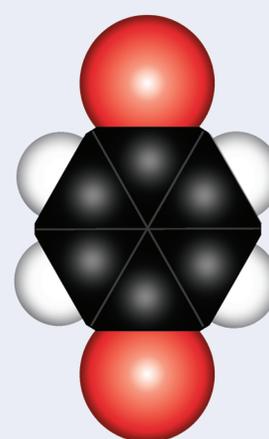
There is a less systematic but more commonly used way to designate the positions of the bromine atoms in the three disubstituted benzene molecules shown above. Substituents at the 1,2 positions are designated **ortho-** (*o*-), those at the 1,3 positions are designated **meta-** (*m*-), and those at the 1,4 positions



1,2-dibromobenzene

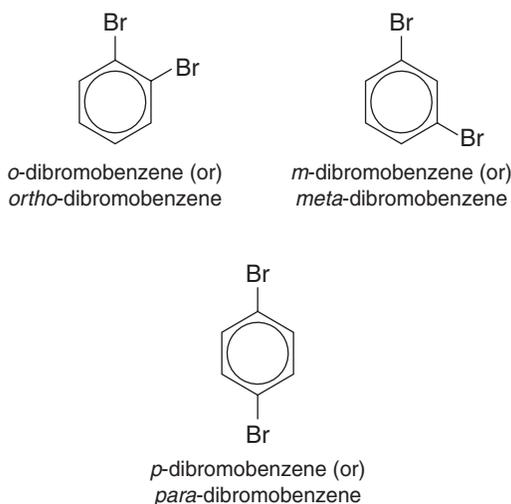


1,3-dibromobenzene

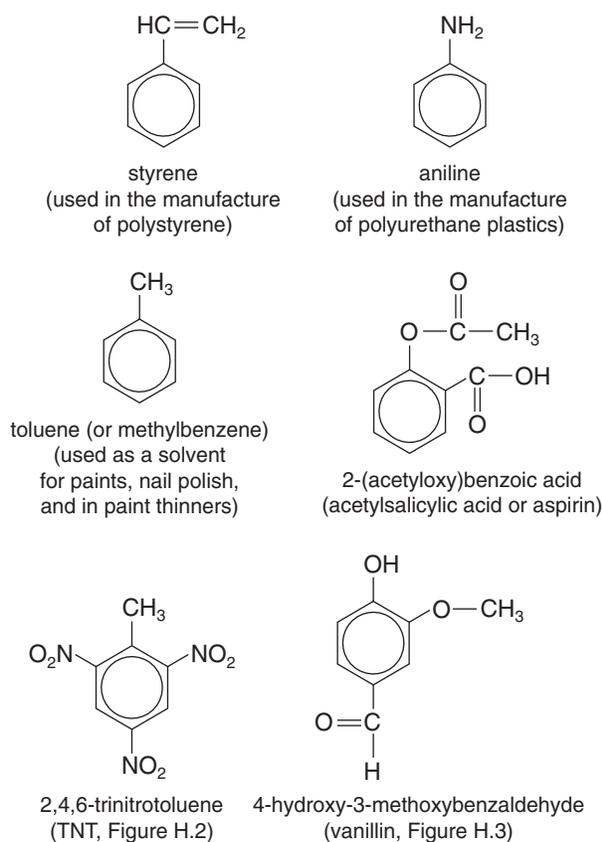


1,4-dibromobenzene

are designated **para-** (*p*-); the letter designations are shorthand for the full prefix. Thus, we write



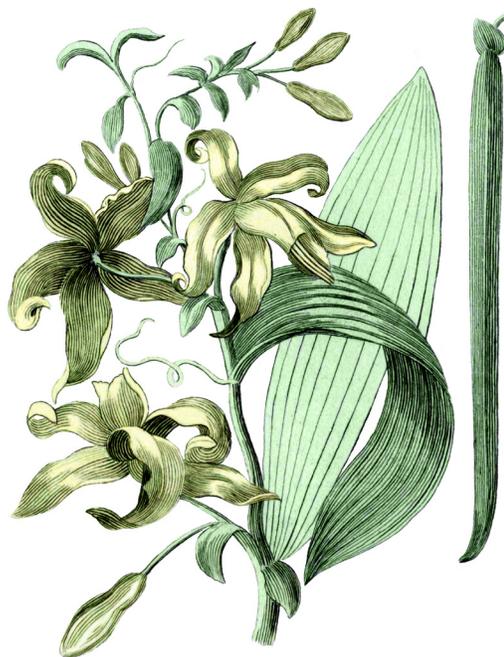
Benzene is used in the manufacture of medicinal chemicals, dyes, plastics, varnishes, lacquers, linoleum, and many other products. Some important derivatives of benzene and their uses are shown below.



We discuss the formation of polymers such as polystyrene and polyurethane in Interchapter S.



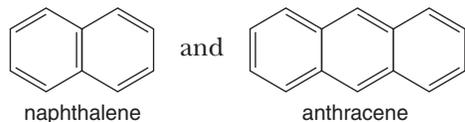
**Figure H.2** The explosive TNT (2,4,6-trinitrotoluene) is a substituted benzene molecule.



**Figure H.3** Vanillin is the chemical responsible for the smell of vanilla and is used as a flavoring, as a scent in perfumes, and as a precursor to the synthesis of various pharmaceuticals. Natural vanillin is extracted from the seed pods of the Mexican orchid *Vanilla planifolia*. The Aztecs used vanillin as a flavoring for chocolate.

### H-4. There Are a Number of Polycyclic Aromatic Compounds

**Polycyclic aromatic molecules** contain regions in which two or more benzene rings are fused together. The two simplest polycyclic aromatic hydrocarbons are



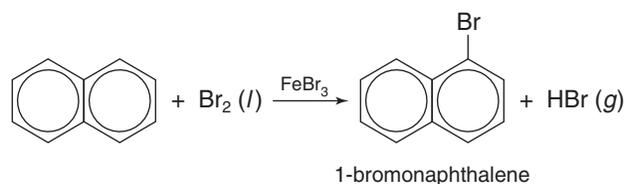
which we could also write even more succinctly as



**Naphthalene** is a solid with a melting point of 80.2°C, but it is very volatile at room temperature. Naphthalene confers the characteristic odor of moth-

balls. **Anthracene** is a solid with a melting point of 218°C. Anthracene is a primary constituent of some coal tars. One of the principal uses of anthracene is in the preparation of alizarin dyes (Figure H.4).

These compounds, as well as other polycyclic aromatic compounds, show many of the characteristics that we associate with aromaticity. Both, for example, react with bromine to yield substituted products instead of addition products, as in

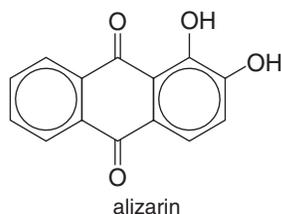


How many isomers of bromonaphthalene do you think exist?

In addition to naphthalene and anthracene, there are a great many more complex polycyclic aromatic

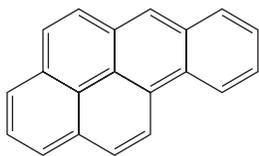


Figure H.4 Alizarin is a substituted anthracene molecule:



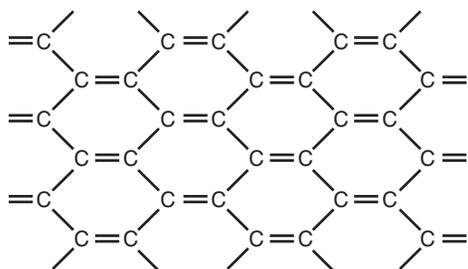
Alizarin was first extracted from the root of the madder plant and used as a dye to produce a deep crimson color. In 1869, it became the first natural pigment to be made synthetically. The fabric swatches shown here have been dyed with alizarin (*left*) and alizarin blend (*right*).

hydrocarbons. Many of these compounds are carcinogens. A noteworthy one is benzo[a]pyrene,



which was the first carcinogen (of many more) discovered in cigarette smoke.

The ultimate polycyclic aromatic hydrocarbon has got to be **graphite**. We'll learn in Chapter 15 that the structure of crystalline graphite consists of essentially unlimited layers of fused benzene rings, as in



The lubricating property of graphite is due to layers like these slipping over one another (Figure H.5).



## TERMS YOU SHOULD KNOW

- aromatic *H1*
- toluene *H2*
- phenyl group *H2*
- ortho- (*o*-) *H3*
- meta- (*m*-) *H3*
- para- (*p*-) *H4*
- polycyclic aromatic molecules *H5*
- naphthalene *H5*
- anthracene *H5*
- graphite *H6*

**Figure H.5** Graphite is used as a solid lubricant in applications where the breakdown of traditional oils could potentially result in catastrophic failure.

## QUESTIONS

**H-1.** Explain why the benzene ring does not readily undergo addition reactions even though its Lewis formula is sometimes written as having several double bonds.

**H-2.** How many isomers are there of bromonaphthalene? What about bromoanthracene?

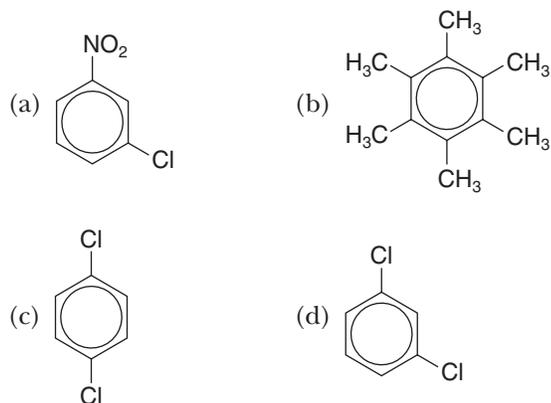
**H-3.** Write the Lewis formula of each of the following benzene derivatives:

- (a) ethylbenzene
- (b) 1,3,5-trichlorobenzene
- (c) 2-chlorotoluene
- (d) *p*-dinitrobenzene

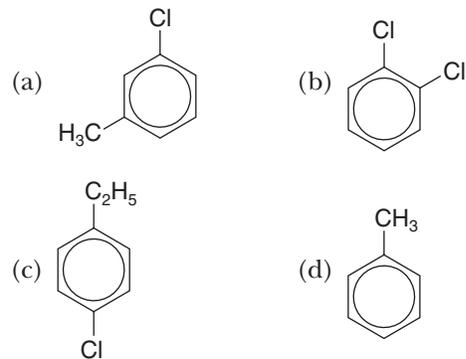
**H-4.** Write the Lewis formula of each of the following molecules containing benzene:

- (a) 2,4-difluorotoluene
- (b) *o*-diethylbenzene
- (c) 3-phenyl-1-butene
- (d) 1-chloro-3-bromobenzene

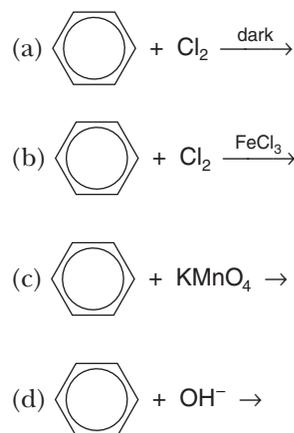
**H-5.** Name the following benzene derivatives:



**H-6.** Name the following benzene derivatives:



**H-7.** Predict the products of the following reactions. If there is no reaction, write N.R.



**H-8.** Predict the products of the following reactions. If there is no reaction, write N.R.

