

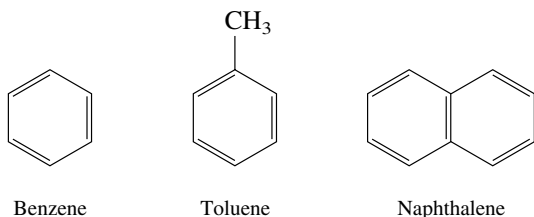
# Functional Groups and Nomenclature II

## CHAPTER 12

**T**HIS CHAPTER BEGINS where Chapter 5 left off and considers the nomenclature, physical properties, natural occurrences, and uses of the principal functional groups that were not discussed in Chapter 5. The nomenclature rules are extensions of those in Chapter 5, with different suffixes for the new functional groups. We will also see how compounds that have more than one functional group are named.

### 12.1 AROMATIC HYDROCARBONS

A complete definition of **aromatic compounds** must wait until Chapter 16. For the present we will define them as benzene and its substituted derivatives. They are also called **arenes**. These aromatic compounds have a six-membered ring with three conjugated double bonds. It is this cycle of conjugated double bonds that makes arenes special. Examples include the following:



If you have spent much time in an organic laboratory, you are well aware that many organic compounds have rather strong (and sometimes disagreeable) odors. Aromatic compounds, however, tend to have more fragrant odors than other compounds. If you have a chance, compare the odor of toluene, for example, with that of cyclohexene. In fact, the term *aromatic* was originally given to

#### MASTERING ORGANIC CHEMISTRY

- ▶ Naming Aromatic Compounds, Phenols, Aldehydes, Ketones, Carboxylic Acids, Acid Chlorides, Anhydrides, Esters, Amides, and Nitriles
- ▶ Drawing Structures of These Compounds from Their Names
- ▶ Recognizing the Common Functional Groups Containing Sulfur or Phosphorus
- ▶ Naming Compounds That Contain More Than One Functional Group
- ▶ Understanding How the Physical Properties of These Compounds Depend on the Functional Group That Is Present

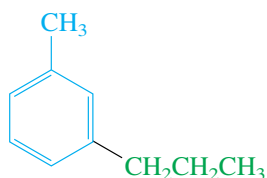
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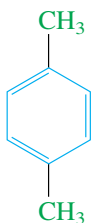
these compounds, even before their structures were known, because of their fragrant odors. Today, however, *aromatic* has evolved to mean something entirely different. To an organic chemist, an **aromatic compound** now means a compound that is especially stable because of its cycle of conjugated *p* orbitals. (The explanation for this special stabilization is provided in Chapter 16.)

Aromatic compounds are named by using benzene as the parent or root and designating the substituents attached to the ring in the same manner that is used to name groups attached to an alkane chain. (Cyclohexatriene is *never* used to name benzene, nor is it used in the names of any aromatic compounds.) Because of their stability, aromatic compounds are very common, and many were isolated in the very early days of organic chemistry. Many of the common names that were originally given to these compounds remain entrenched in the vocabulary of organic chemistry. For example, you will seldom hear methylbenzene referred to by this name; it will invariably be called toluene. Some of the more important of these common names will be introduced as the compounds are encountered.

When several substituents are present on a benzene ring, the ring is numbered in the same manner as the rings of cycloalkanes—that is, so that the numbers for the substituents are as low as possible. In addition, some special terms are used with *disubstituted benzenes only*. Two substituents on adjacent carbons (positions 1 and 2) are said to be *ortho*, or *o*-. Two substituents on positions 1 and 3 are *meta*, or *m*-. And two substituents on positions 1 and 4 are *para*, or *p*-. Finally, if an alkyl group with six or more carbons is attached to a benzene ring, the compound is named as an alkane with a **phenyl** substituent. Some examples are as follows:

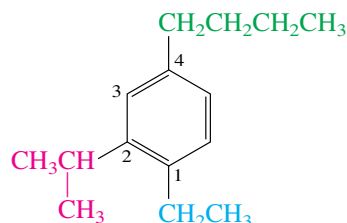


*m*-Propyltoluene  
or 3-propyltoluene



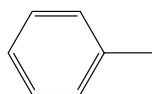
*p*-Dimethylbenzene  
or 1,4-dimethylbenzene

(The common name for the dimethylbenzenes is xylene, so this is also called *p*-xylene.)



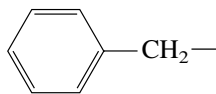
4-Butyl-1-ethyl-2-isopropylbenzene

(The numbering starts with the ethyl, so the numbers are 1, 2, and 4. If numbering started with the butyl, the numbers would be higher—1, 3, and 4.)

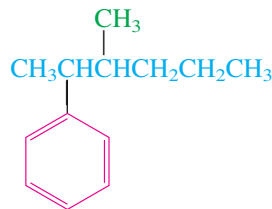


The phenyl group

(Recall that this group can be abbreviated as Ph in drawing structures.)



The benzyl group



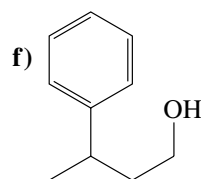
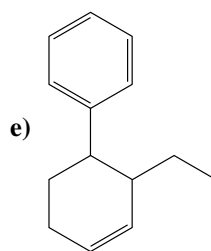
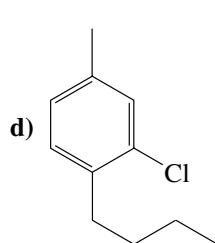
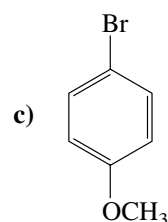
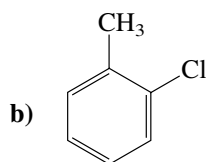
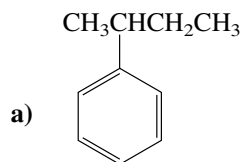
3-Methyl-2-phenylhexane

(The larger or more highly substituted group, the alkyl group in this case, is chosen as the root.)

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**PROBLEM 12.1**

Provide names for these compounds:

**PROBLEM 12.2**

Draw structures for these compounds:

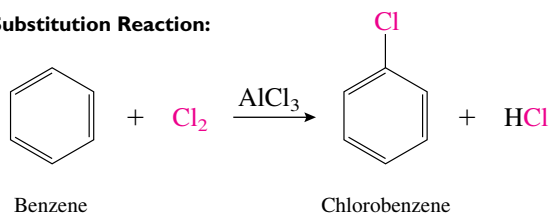
- p*-Ethyltoluene
- m*-Dichlorobenzene
- 2-Phenyl-3-heptyne
- 2-Bromo-1-chloro-3-pentylbenzene
- o*-Xylene
- Benzyl methyl ether

Aromatic hydrocarbons are nonpolar, and their physical properties resemble those of alkanes of similar molecular mass. However, as was the case with cycloalkanes, the symmetrical shapes of many aromatic hydrocarbons often result in higher melting points. For example, the melting and boiling points of benzene are nearly identical to those of cyclohexane. (Recall that cyclohexane melts at considerably higher temperatures than does hexane.) As expected, a mixture of benzene and water forms two layers, with benzene as the upper layer.

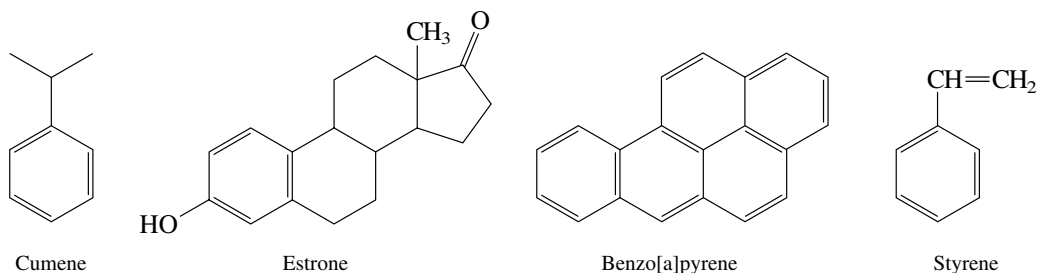
On initial inspection, aromatic compounds might be expected to resemble alkenes in their chemical reactions. However, their reactions are dramatically different. Aromatic compounds are much less reactive than alkenes. The reason for this decrease in reactivity is the large amount of stabilization present in aromatic compounds as a result of their special cycle of conjugated *p* orbitals. This great difference in reactivity is the reason why aromatic compounds are classified separately from the alkenes. As an example of this reactivity difference, the treatment of benzene with  $\text{Cl}_2$  under conditions in which the  $\text{Cl}_2$  would rapidly add to an alkene does not result in any reaction. Under more drastic conditions, in the presence of a Lewis acid catalyst such as  $\text{AlCl}_3$ , a reaction does occur, but the product retains the conjugated system of the aromatic ring. Rather than the addition reaction that would have resulted with an alkene, a chlorine replaces one of the hydrogens on the ring. This reaction, in which one group replaces an-

other, is another type of substitution reaction and is the most important reaction of aromatic compounds.

### Substitution Reaction:



Because of their stability, aromatic compounds are found in a variety of natural sources. Often the aromatic ring occurs in combinations with other functional groups. Benzene itself was first isolated, by Michael Faraday in 1825, from the oily residue that condensed from the gas that was used to light the street lamps of London. A few examples of other naturally occurring compounds that contain aromatic rings are cumene (isopropylbenzene), which occurs in petroleum; estrone, a female sex hormone that has an aromatic ring as part of a complex ring system; and benzo[a]pyrene, which consists of a series of fused aromatic rings. Benzo[a]pyrene is a carcinogenic (cancer-causing) substance produced upon combustion of many materials. It is found in soot and is one of the major carcinogens found in tobacco smoke.



Benzene is one of the major chemicals produced by the petroleum industry. More than 1.6 billion gallons are produced each year by cracking and reforming various petroleum fractions. Most of this is used in the production of styrene, which is then polymerized to polystyrene. Other arenes that are made in large amounts include toluene (830 million gallons), cumene, *o*-xylene, and *p*-xylene. At one time, benzene was an important solvent in the organic laboratory. Recently, however, its use has been phased out because of its potential adverse health effects. Long exposure to benzene has been shown to lead to bone marrow depression and leukemia.

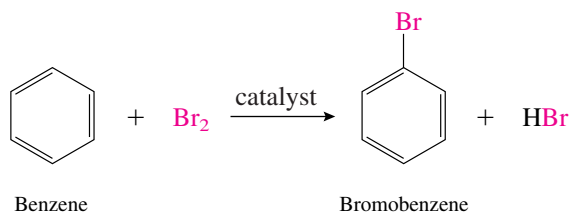
## Focus On

## Structure Proof by the Number of Isomers

How did organic chemists identify the structures of organic compounds before the advent of spectroscopy? Basically, the structure had to be consistent with all the facts known about a compound. Often, these facts included the results of a number of chemical reactions. Let's examine the case of the substitution products that occur on reaction of benzene with bromine.

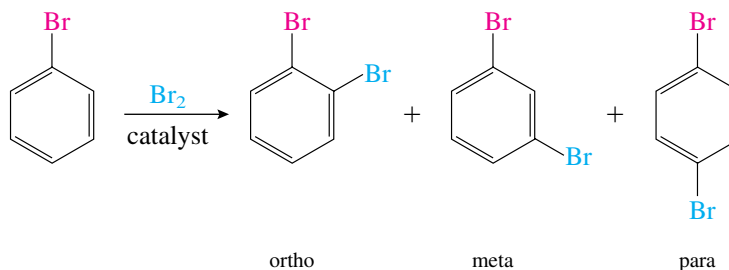
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In 1866, August Kekulé, one of the true pioneers of organic chemistry, proposed a structure for benzene that is remarkably similar to the structure used today. From experiments, he knew that substitution reactions of benzene always gave a single monosubstitution product. For example, the reaction of benzene ( $C_6H_6$ ) with bromine in the presence of aluminum tribromide as a catalyst gave only one monobromide ( $C_6H_5Br$ ). This indicates that all of the hydrogens of benzene must be identical. One of the structures that satisfies the valence rules and this observation is a six-membered ring with three double bonds:

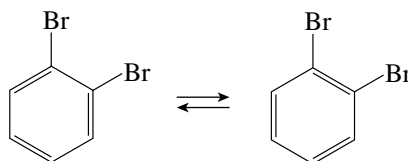


In this structure for benzene, all the carbons are identical, so it does not matter which one bonds to the bromine in the substitution reaction; only one monobromo substitution product is possible.

Kekulé next considered what would happen if bromobenzene were further substituted with a second bromine. From experiment, it was known that reaction of  $C_6H_5Br$  in this same reaction resulted in the formation of three isomers of  $C_6H_4Br_2$ . Today, this reaction would be written as shown in the following equation:



However, to make the results of this reaction consistent with his theory, Kekulé had to make some modifications. To see the problem, it is necessary only to recall that the concept of resonance had not yet been proposed at this point in the development of organic chemistry. Kekulé realized that, according to his structural theory, there should be two products related to the ortho product, one with a single bond between the carbons attached to the bromines and one with a double bond between these carbons.



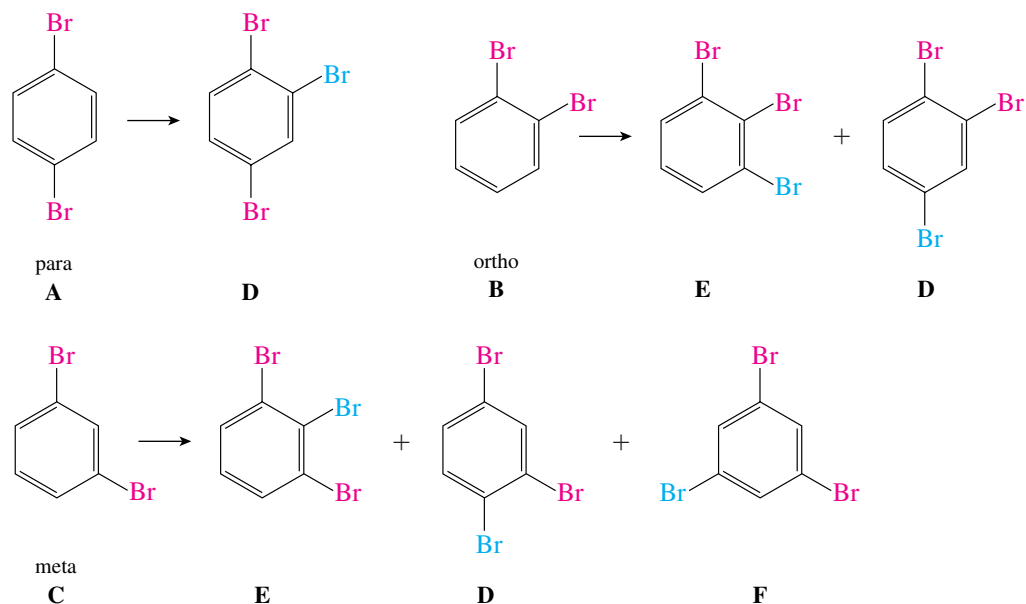
To make his theoretical prediction (four products) consistent with experimental observation (three products), Kekulé proposed that the two “ortho-isomers” were actually in rapid equilibrium and therefore behaved as a single compound. Of course,

today we know that these are two resonance structures of *ortho*-dibromobenzene rather than distinct isomers, but Kekulé's proposal was not too far removed from our current ideas.

Now let's carry our considerations one step further. As we know, bromination of bromobenzene produces three isomers of dibromobenzene. One of these is the *ortho*-isomer, one is the *meta*, and one is the *para*, but which is which? This question was answered by Wilhelm Korner in 1874, who reacted each of the  $C_6H_4Br_2$  isomers under substitution conditions that produced the tribrominated products,  $C_6H_3Br_3$ . By determining the number of isomeric tribromides produced from each dibromide, he was able to assign the structures of all of the compounds. He found that one  $C_6H_4Br_2$  isomer, call it **A**, produced a single isomer of  $C_6H_3Br_3$ , call it **D**. Another isomer of  $C_6H_4Br_2$ , **B**, produced two isomers of  $C_6H_3Br_3$ : **D** (obtained previously) and a new isomer, **E**. The final isomer of  $C_6H_4Br_2$ , **C**, produced three isomers of  $C_6H_3Br_3$ : **D**, **E**, and a new isomer, **F**. These results are summarized in the following equations:

Dibromide		Tribromide	
<b>A</b>	→	<b>D</b>	(one product)
<b>B</b>	→	<b>D</b> + <b>E</b>	(two products)
<b>C</b>	→	<b>D</b> + <b>E</b> + <b>F</b>	(three products)

The products predicted to result from the bromination of the *ortho*-, *meta*-, and *para*-isomers of dibromo benzene are as follows:



The *para*-isomer is predicted to give a single tribromo product. Therefore, the *para*-isomer must be **A**, and its product, 1,2,4-tribromobenzene, must be **D**. The *ortho*-isomer gives two products, so it must be **B**. Its two products are **D** and 1,2,3-tribromobenzene, **E**. Finally, the *meta*-isomer gives three products, so it must be **C**. Its three products are **D**, **E**, and the new product, **F**, which must be 1,3,5-tribromobenzene. Using this logic, Korner was able to assign the structures of not only all of the dibromobenzenes, but also all of the tribromobenzenes!