# 1.3 Aromatic Hydrocarbons

Michael Faraday (1791–1867) was the first person to isolate and identify benzene from a mixture of oils in 1825 (**Figure 1**). Since then, benzene has been used in many commercial products. One of its first uses was as an aftershave in the nineteenth and early twentieth centuries. In 1903, benzene was used to decaffeinate coffee. It was also used as an anti-knock additive in gasoline to control the ignition of the fuel until the 1950s, when it was replaced by tetraethyl lead. Benzene is also widely used in industry as a solvent in chemical reactions. Testing has identified benzene as a carcinogen and implicated it in other health problems. As the hazards of benzene have become known, many of its commercial uses have been discontinued.

**Figure 1** Michael Faraday (left) working in his chemistry lab

## What Is an Aromatic Hydrocarbon?

An **aromatic hydrocarbon** is an unsaturated hydrocarbon that has a ring structure and a bonding arrangement that causes it to be chemically stable. Benzene, $C_6H_6$, is a flat 6-carbon ring with a hydrogen atom bonded to each carbon atom (**Figure 2**). It is the simplest aromatic hydrocarbon. The structural diagram often shows benzene as having three double bonds alternating with three single bonds. Measurements of the bond length between carbon atoms, however, have shown that all six bond lengths are equal. If benzene actually had three double bonds, then those bonds would be shorter than the other three. To indicate that all six bonds are identical, the structure is shown as alternating between two arrangements of double bonds (Figure 2(b)) or as a hexagon with a circle inside (Figure 2(c)). The hexagon with the circle indicates that the electrons in the bonds are shared equally between all 6 carbon atoms.

**aromatic hydrocarbon** an unsaturated cyclic hydrocarbon with a pattern of bonding that makes it chemically stable

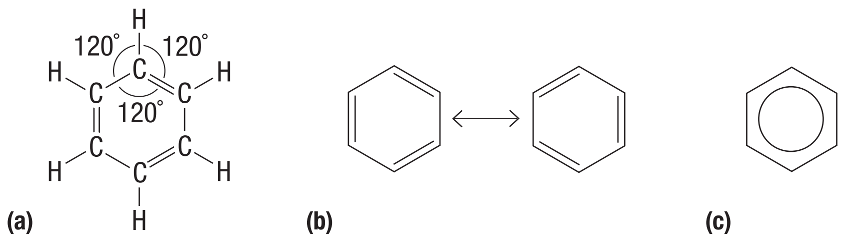
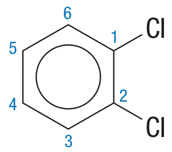
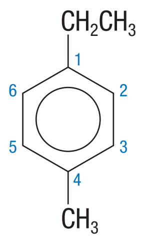



**Figure 2** (a) The structure of benzene, a planar ring system in which all bond angles are 120° (b) Two structural formulas implying that the structure of benzene is a combination of them both together (c) The common representation of benzene




1,2-dichlorobenzene




1-ethyl-4-methylbenzene

**Figure 3** Substituted benzenes

## Naming Aromatic Compounds

There are two conventions for naming compounds that include a benzene ring. Which one we use depends on the structure of the other part of the compound.

We use the first convention when naming aromatic compounds that have non-carbon substituents or a small alkyl group. In this case, the benzene ring is generally considered to be the parent molecule. The attached functional groups are named as substituents to benzene. If a single group is attached to a benzene ring, we put the name of the group before the root *-benzene*. For example, chlorobenzene, $C_6H_5Cl$, has one chlorine atom replacing a hydrogen atom on the benzene ring. Compounds made up of a benzene ring with one or more halogen atoms attached are called aromatic halides.

If two or more substituents are bonded to the benzene ring, we number the carbon atoms of the benzene ring starting with the first substituent (alphabetically) and continue numbering in the direction of the next closest substituent. **Figure 3** shows some examples.

In the second naming convention, the benzene ring is considered to be a substituent on a hydrocarbon chain. A benzene ring that has lost 1 hydrogen atom is called a **phenyl group**, just as a methyl group is like a methane molecule that has lost 1 hydrogen atom. The compound is named using "phenyl" as the substituent (**Figure 4**). WEB LINK

**phenyl group** a benzene ring (minus 1 hydrogen atom) that behaves as a substituent in an organic compound

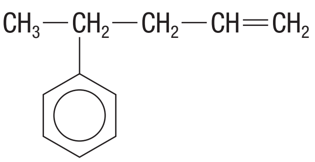



**Figure 4** Benzene as a substituent group in 4-phenylpent-1-ene

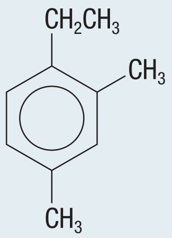
## Tutorial 1 Naming and Drawing Aromatic Compounds

Aromatic hydrocarbons with one or more simple substituents are named by adding the substituent name(s) to the root “benzene.” If the substituent is complex, such as a hydrocarbon chain with a multiple bond, consider this the parent group and the benzene ring the substituent. In this tutorial, you will recognize when to use each convention, and practise naming and drawing compounds using both conventions.

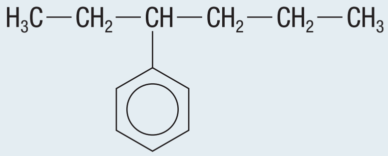
### **Sample Problem 1:** Naming Aromatic Compounds

Name the compounds represented by the following structural formulas:

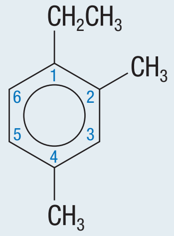
(a)



(b)



### Solution (a)



The structure has three simple substituents, so can be named as a substituted benzene. Number the carbon atoms to give the substituents the lowest numbers.

This compound is 1-ethyl-2,4-dimethylbenzene.

### Solution (b)

Treat the benzene ring as the substituent. The alkane chain is a hexane and the benzene ring is bonded to the third carbon atom in the chain. Therefore, this compound is 3-phenylhexane.

### **Sample Problem 2:** Drawing Aromatic Compounds

Draw the structural formula for each of the following compounds:

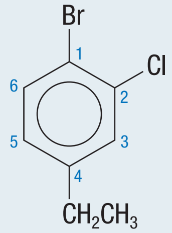
(a) 1-bromo-2-chloro-4-ethylbenzene

(b) 4,6-diphenyloct-2-ene

### Solution (a)

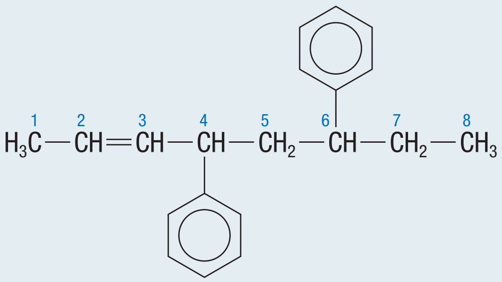
First, draw the benzene ring and number the carbon atoms.

Next, add the substituents as indicated in the name: a bromine atom on carbon 1, a chlorine atom on carbon 2, and an ethyl group on carbon 4.



### Solution (b)

First, draw the parent alkene, oct-2-ene. Next, add the benzene rings to the fourth and sixth carbon atoms.

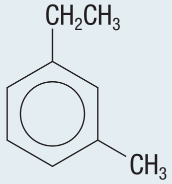
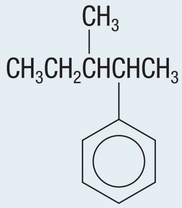


**LEARNING TIP**

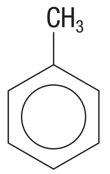
**Traditional Names for Aromatic Hydrocarbons**

An older naming convention for substituted aromatic compounds used the Greek prefixes *ortho*-, *meta*-, and *para*- to indicate the positions of substituents. Ortho substituents are on adjacent carbon atoms in 1,2 positions. Meta substituents are separated by 1 carbon atom in 1,3 positions. Para substituents are located on opposite sides of the 6-carbon ring in 1,4 positions.

## Practice

1. Name each of the following compounds: K/U
   (a) 
   (b) 

2. Draw the structural formulas of the following compounds: T/I C
   (a) 1-fluoro-3-methylbenzene (b) 2-phenylbut-2-ene



toluene

**Figure 5** Toluene (methylbenzene) is a substituted benzene compound with one methyl group substituted for a hydrogen atom.

## Properties of Aromatic Hydrocarbons

Many aromatic hydrocarbons are liquids at room temperature, while others are crystalline solids. Their symmetrical structure causes them to be non-polar unless they contain an electronegative substituent, so they are generally insoluble in water. From its discovery and well into the second half of the twentieth century, benzene was widely used as a solvent in industrial processes and for dry cleaning clothes. Since the discovery that benzene is carcinogenic, other chemicals have replaced benzene in the workplace. One replacement compound is methylbenzene, commonly known as toluene, $C_6H_5CH_3$ (**Figure 5**).

UNIT TASK **BOOKMARK**

Aromatic compounds tend to be quite volatile, which means that they easily evaporate and disperse in the air. You may consider the properties of aromatic compounds as you work on the Unit Task, described on page 116.

## Reactions of Aromatic Compounds

Its unusual bonding makes the benzene ring behave quite differently from an unsaturated hydrocarbon. Unsaturated hydrocarbons easily undergo addition reactions. However, benzene does not because its bonds are not really alternating double and single bonds. Each bond in benzene is identical and they are much more stable than a carbon–carbon double bond. Bond strength is between that of a single and that of a double bond. In general, therefore, aromatic compounds are much less reactive than alkenes. The hydrogenation of benzene to form cyclohexane requires high temperatures and a catalyst. Benzene does undergo substitution reactions in which hydrogen atoms are replaced by other atoms, such as halogens (**Figure 6**).

Substitution reactions are characteristic of saturated hydrocarbons, and addition reactions are characteristic of unsaturated ones. Benzene reacts more like a saturated hydrocarbon because of the specialized bonding in the benzene ring (**Figure 7**).

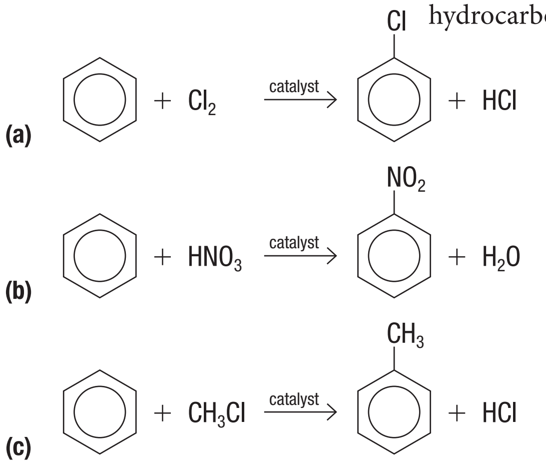


**Figure 6** Substitution reactions of benzene. (a) Reaction with chlorine, $Cl_2$, produces chlorobenzene (an aromatic halide) and hydrogen chloride. (b) Reaction with nitric acid, $HNO_3$, produces nitrobenzene and water. (c) Reaction with chloromethane, $CH_3Cl$, produces toluene and hydrogen chloride.

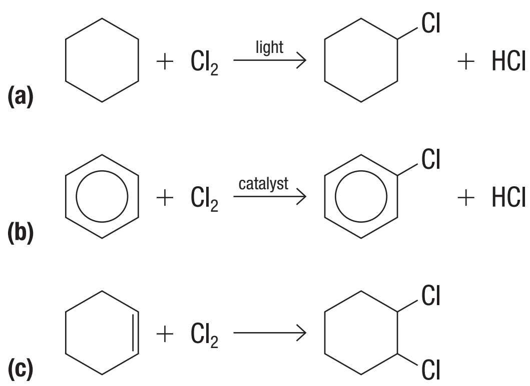


**Figure 7** Reactions of cyclohexane, benzene, and cyclohexene with chlorine. (a) Cyclohexane reacts with chlorine in a substitution reaction. A hydrogen atom is lost as the chlorine atom is gained. (b) Benzene reacts with chlorine in a substitution reaction, like cyclohexane. (c) Cyclohexene reacts with chlorine in an addition reaction: no atoms are lost from the organic compound.

# 1.3 Review

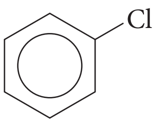
## Summary

- Aromatic hydrocarbons are a class of cyclic unsaturated hydrocarbons that have a ring structure and bonding that causes them to be chemically stable.
- Measurements show that the bonds in a benzene ring are all equal in length.
- Naming aromatic compounds with one or more simple substituents requires just the addition of the substituent group name. Naming aromatic compounds with a more complex substituent requires treating the benzene ring, named "phenyl," as a substituent on a carbon chain.
- Benzene is less reactive than alkenes. Since it participates in substitution reactions, benzene behaves more like an alkane.

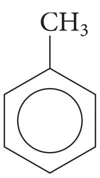
## Questions

1. Name the compounds represented by the following structural formulas: K/U

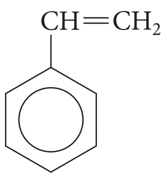
   (a)

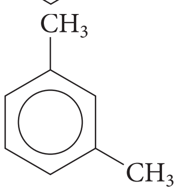
   (b)

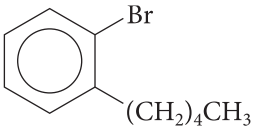
   (c)

   (d)

   (e)

2. Draw the structural formula for each of the following compounds: K/U C
   (a) 1,3-dichloro-4-ethylbenzene
   (b) 1-bromo-3-phenylhept-5-yne
3. (a) Draw the chemical equation for the reaction between benzene and bromine, $Br_2$. Is this reaction likely to occur? Explain why or why not.
   (b) How would your answer to (a) be different if the organic reactant were cyclohexene instead of benzene? T/I
4. Draw structural formulas representing the reaction that produces iodobenzene. Label the reactants and classify the reaction as addition or substitution. K/U T/I C
5. Mothballs are small lumps of pesticide that discourage moths from damaging woollen clothing. The main component of mothballs is paradichlorobenzene. T/I C A
   (a) What is the proper IUPAC name for this compound? (See the Learning Tip on page 29.)
   (b) Draw the structure of paradichlorobenzene.
   (c) When you order this chemical from a company, the label says "paradichlorobenzene" even though that is not the correct IUPAC name. Why do you think the compound is labelled this way? Do you think it is a good idea, or should all products be labelled with their IUPAC name? Explain your reasoning.
6. (a) Predict the products of reactions involving the following reactants:
   (i) cyclohexene and hydrogen bromide
   (ii) benzene and chloroethane
   (b) Explain how these two reactions are different, and the reason for the differences. K/U T/I
7. One aromatic compound that has been the subject of many studies is bisphenol-A. This chemical was used as a hardener in many plastics, but studies have uncovered a possible link to adverse health effects. As a result, Canada has now banned some products, including baby bottles, containing bisphenol-A. Find out more about this substance and the decision to restrict its use. Create a graphic organizer showing the pros and cons of banning products containing bisphenol-A. T/I C A
8. Benzene has, in the past, been used as a solvent in the dry-cleaning industry. Research this use, discover why its use is being phased out, and find out what "greener" alternatives are now used for dry cleaning. Present your findings in an attention-grabbing format for your stated target audience. T/I C A

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