Hydrocarbons 1.2

We will begin our study of organic families with a review of **hydrocarbons**, many of which contain multiple bonds between carbon atoms, a functional group with characteristic properties.

Fossil fuels (**Figure 1**) contain mainly hydrocarbons: simple molecules of hydrogen and carbon that are the result of the breakdown of living organisms from long ago. These compounds include the natural gas that is piped to our homes, the propane in tanks for barbecues, and the gasoline for our cars. Hydrocarbons are classified by the kinds of carbon−carbon bonds in their molecules. In **alkanes**, all carbons are bonded to other atoms by single bonds, resulting in the maximum number of hydrogen atoms bonded to each carbon atom. These molecules are thus called *saturated hydrocarbons*. **Alkenes** are hydrocarbons that contain one or more carbon−carbon double bonds, and **alkynes** contain one or more carbon–carbon triple bonds. These two groups are called *unsaturated hydrocarbons* because they contain fewer than the maximum possible number of hydrogen atoms. Because alkenes and alkynes have multiple bonds, they react in characteristic ways. The multiple bond is the functional group of these two chemical families.

In all of these hydrocarbons, the carbon−carbon backbone may form a straight chain, one or more branched chains, or a **cyclic** (ring) structure (**Table 1**). All of these molecules are included in a group called **aliphatic hydrocarbons**.

A hydrocarbon branch that is attached to the main structure of the molecule is called an **alkyl group**. When meth*ane* is attached to the main chain of a molecule, it is called a meth*yl* group, $-CH_3$. An eth*yl* group is CH_3CH_2, the branch formed when eth*ane* links to another chain.

Table 1 Examples of Hydrocarbons

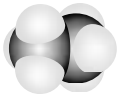
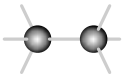
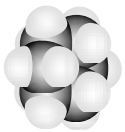
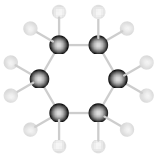
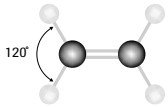
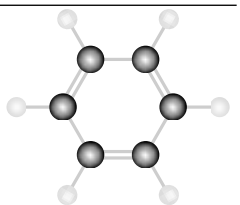
Hydrocarbon group	Example	Formula	Spacefill diagram	Bond and angles diagram
Aliphatic				
alkane	ethane	CH_3CH_3		
	cyclohexane	C_6H_{12}		
alkene	ethene	CH_2CH_2		
alkyne	ethyne	CHCH		
Aromatic				
	benzene	C_6H_6		

Figure 1
Crude oil is made up of a variety of potentially useful hydrocarbons.

hydrocarbon an organic compound that contains only carbon and hydrogen atoms in its molecular structure

alkane a hydrocarbon with only single bonds between carbon atoms

alkene a hydrocarbon that contains at least one carbon−carbon double bond; general formula, C_nH_{2n}

alkyne a hydrocarbon that contains at least one carbon−carbon triple bond; general formula, C_nH_{2n-2}

cyclic hydrocarbon a hydrocarbon whose molecules have a closed ring structure

aliphatic hydrocarbon a compound that has a structure based on straight or branched chains or rings of carbon atoms; does not include aromatic compounds such as benzene

alkyl group a hydrocarbon group derived from an alkane by the removal of a hydrogen atom; often a substitution group or branch on an organic molecule

aromatic hydrocarbon a compound with a structure based on benzene: a ring of six carbon atoms

IUPAC International Union of Pure and Applied Chemistry; the organization that establishes the conventions used by chemists

A fourth group of hydrocarbons with characteristic properties and structures is called the **aromatic hydrocarbons**. The simplest aromatic hydrocarbon is benzene; all other members of this family are derivatives of benzene. The formula for benzene is C_6H_6, and the six carbon atoms form a unique ring structure. Unlike cyclohexane, C_6H_{12}, the benzene ring has a planar (flat) structure, and is unsaturated (**Table 1**). As we will learn later in this chapter and in Chapter 10, the bonds in the benzene ring have properties intermediate between single bonds and double bonds; the common structural diagram for benzene shows a hexagon with an inscribed circle, symbolizing the presence of double bonds in unspecified locations within the six-carbon ring (**Figure 2**). The unique structure and properties of compounds containing benzene rings have prompted their classification as a broad organic family of their own. Named historically for the pleasant aromas of compounds such as oil of wintergreen, aromatic compounds include all organic molecules that contain the benzene ring. All other hydrocarbons and their oxygen or nitrogen derivatives that are not aromatic are called aliphatic compounds.

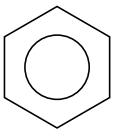


Figure 2
Benzene, C_6H_6, is colourless, flammable, toxic, and carcinogenic, and has a pleasant odour. Its melting point is 5.5°C and its boiling point 80.1°C. It is widely used in the manufacture of plastics, dyes, synthetic rubber, and drugs.

Nomenclature of Hydrocarbons

Because there are so many organic compounds, a systematic method of naming them is essential. In this book, we will use the **IUPAC** system of nomenclature, with additional nonsystematic names that you may encounter in common usage. It is especially important to have a good grasp of the nomenclature of hydrocarbons, as the names of many organic molecules are based on those of hydrocarbon parent molecules.

Alkanes

All alkanes are named with the suffix *-ane*. The prefix in the name indicates the number of carbon atoms in the *longest straight chain* in the molecule (**Table 2**). Thus a 5-C straight-chained alkane would be named pentane.

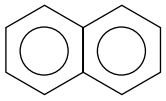
Any alkyl branches in the carbon chain are named with the prefix for the branch, followed by the suffix *-yl*. Thus, a branch that contains a 2-C chain is called an ethyl group. The name of a branched alkane must also indicate the point of attachment of the branch. This is accomplished by assigning numbers to each C atom of the parent alkane, and pointing out the location of the branch chain by the numeral of the C atom where the branching occurs. The naming system always uses the lowest numbers possible to denote a position on the chain. Finally, all numerals are separated by commas; numerals and letters are separated by hyphens; and names of branches and parent chains are not separated.

DID YOU KNOW?

Joined Benzene Rings

Like other hydrocarbons, benzene rings can link together to form a wide variety of compounds (**Figure 3**), many of which are quite smelly!

(a)



(b)

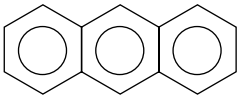


Figure 3
(a) Naphthalene, $C_{10}H_8$, is a colourless solid with a pungent odour. Its melting point is 80°C, and its boiling point 218°C. However, it sublimes on heating. It is the main component of mothballs, and is also used as an insecticide, in solvents, and in the synthesis of dyes.
(b) Anthracene, $C_{14}H_{10}$, is a colourless solid with melting and boiling points of 218°C and 354°C. It is less well known, but is also used in the synthesis of dyes.

Table 2 Alkanes and Related Alkyl Groups

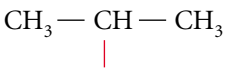
Prefix	IUPAC name	Formula	Alkyl group	Alkyl formula
meth-	methane	$CH_{4(g)}$	methyl-	$-CH_3$
eth-	ethane	$C_2H_{6(g)}$	ethyl-	$-C_2H_5$
prop-	propane	$C_3H_{8(g)}$	propyl-	$-C_3H_7$
but-	butane	$C_4H_{10(g)}$	butyl-	$-C_4H_9$
pent-	pentane	$C_5H_{12(l)}$	pentyl-	$-C_5H_{11}$
hex-	hexane	$C_6H_{14(l)}$	hexyl-	$-C_6H_{13}$
hept-	heptane	$C_7H_{16(l)}$	heptyl-	$-C_7H_{15}$
oct-	octane	$C_8H_{18(l)}$	octyl-	$-C_8H_{17}$
non-	nonane	$C_9H_{20(l)}$	nonyl-	$-C_9H_{19}$
dec-	decane	$C_{10}H_{22(l)}$	decyl-	$-C_{10}H_{21}$

We will take a special look at naming propyl groups and butyl groups. When alkyl groups have three or more C atoms, they may be attached to a parent chain either at their end C atom, or at one of the middle C atoms. For example, **Figure 4** shows two points of attachment for a propyl group. The two arrangements are structural **isomers** of each other, and are commonly known by their nonsystematic names. The prefix *n*- (normal) refers to a straight-chain alkyl group, the point of attachment being at an end C atom. The isomer of the *n*-propyl group is the isopropyl group. **Figure 5** shows the common names for isomers of the butyl group; in this book, we will not concern ourselves with isomers of alkyl groups greater than 4 C atoms.

(a) $CH_3-CH_2-CH_2-$

n-propyl (normal propyl)

(b)



isopropyl

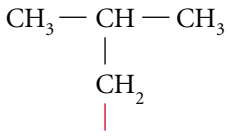
Figure 4
Two isomers of the propyl group. The coloured bond indicates where the group is attached to the larger molecule.

isomer a compound with the same molecular formula as another compound, but a different molecular structure

(a) $CH_3-CH_2-CH_2-CH_2-$

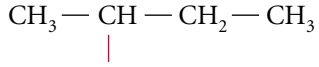
n-butyl (normal butyl)

(b)



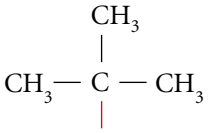
isobutyl

(c)



s-butyl (secondary butyl)

(d)



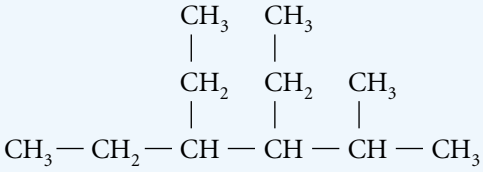
t-butyl (tertiary butyl)

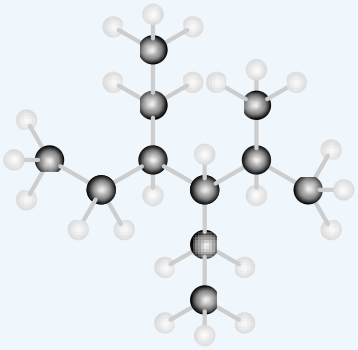
Figure 5
Four isomers of the butyl group

Naming Alkanes

SAMPLE problem

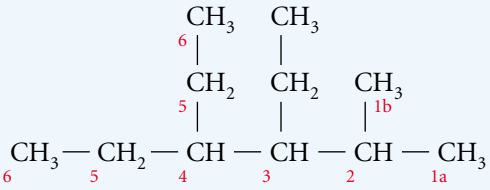
1. Write the IUPAC name for the chemical with the following structural diagram.





First, identify the longest carbon chain. Note that you may have to count along what appear to be branches in the structural diagram to make sure you truly have the longest chain. In this case, the longest carbon chain is 6 C long. So the parent alkane is *hexane*.

Next, number the C atoms as shown.



In this case, there are several possible six-carbon chains. Choose the one that gives the lowest possible total of numbers identifying the location of the branches. Usually it is best to start numbering with the end carbon that is closest to a branch. In this case, the first branch is on C 2. Notice that it makes no difference whether we choose C 1a or C 1b to be the actual C 1.

Name each branch and identify its location on the parent chain. In this example, there is a methyl group on C 2 and an ethyl group on each of C 3 and C 4. Thus the branches are 2-methyl, 3-ethyl, and 4-ethyl.

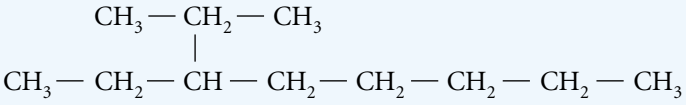
To check that you've got the lowest total, try naming the structure from the other ends of the chain. If we had counted from either of the C 6 ends, we would arrive at 3-ethyl, 4-ethyl, and 5-methyl—a set of numbers with a higher total.

When the same alkyl group (e.g., ethyl) appears more than once, they are grouped as di-, tri-, tetra-, etc. In this compound, the two ethyl groups are combined as 3,4-diethyl.

Finally, write the complete IUPAC name, following this format: (number indicating location)-(branch name)(parent chain). In this book, when more than one branch is present, the branches are listed in alphabetical order. (Note that other sources may list the branches in order of complexity.) Alphabetically, ethyl comes before methyl. So the name begins with the ethyl groups, followed by the methyl group, and ends with the parent alkane. Watch the use of commas and hyphens, and note that no punctuation is used between the alkane name and the alkyl group that precedes it.

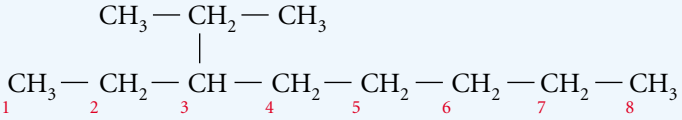
The IUPAC name for this compound is 3,4-diethyl-2-methylhexane.

2. *Write the IUPAC name for the following hydrocarbon.*



First, identify the longest carbon chain: 8 C atoms. So the molecule is an octane.

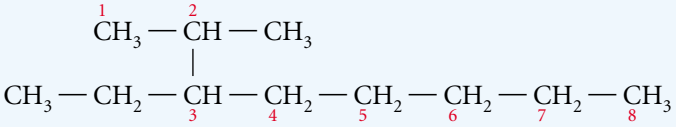
Next, number the C atoms as shown.



If we start counting at C 1, the branch group attached to C 3 contains 3 C atoms, so it is a propyl group. However, the propyl group is attached to the parent chain at its middle C atom, not at an end C atom. This arrangement of the propyl group is called isopropyl (**Figure 4(b)**).

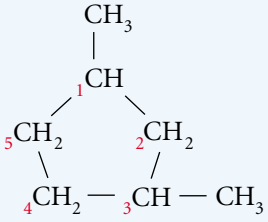
One possible name for this compound is 3-isopropyloctane.

However, a different name results if we number this hydrocarbon from the top branch.



This shows a methyl group on C 2 and an ethyl group on C 3, giving the name 3-ethyl-2-methyloctane. Where more than one name is correct, we use the one that includes the lowest possible numerals.

The correct name of this compound is 3-ethyl-2-methyloctane.



3. *Draw a structural diagram for 1,3-dimethylcyclopentane.*

The parent alkane is cyclopentane. Start by drawing a ring of 5 C atoms single-bonded to each other, in the shape of a pentagon.

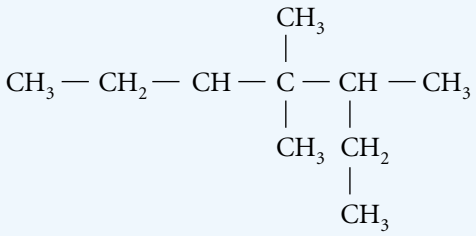
Next, number the C atoms in the ring, starting anywhere in the ring.

Then attach a methyl group to C 1 and another to C 3.

Finally, add H atoms to the C atoms to complete the bonding and the diagram.

Example

Write the IUPAC name for the following hydrocarbon.



Solution

This alkane is 3,4,4-trimethylheptane.

SUMMARY Naming Branched Alkanes

Step 1 Identify the longest carbon chain; note that structural diagrams can be deceiving—the longest chain may travel through one or more "branches" in the diagram.

Step 2 Number the carbon atoms, starting with the end that is closest to the branch(es).

Step 3 Name each branch and identify its location on the parent chain by the number of the carbon at the point of attachment. Note that the name with the lowest numerals for the branches is preferred. (This may require restarting your count from the other end of the longest chain.)

Step 4 Write the complete IUPAC name, following this format: (number of location)-(branch name)(parent chain).

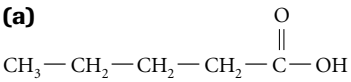
Step 5 When more than one branch is present, the branches are listed either in alphabetical order or in order of complexity; in this book, we will follow the alphabetical order.

Note: When naming cyclic hydrocarbons, the carbon atoms that form the ring structure form the parent chain; the prefix *cyclo-* is added to the parent hydrocarbon name, and the naming of substituted groups is the same as for noncyclic compounds.

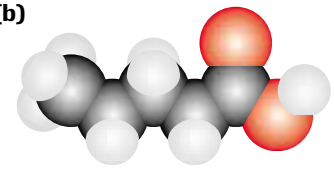
LEARNING TIP

The structure of an organic molecule can be represented in many different ways: some representations give three-dimensional detail; others are simplified to show only the carbon backbone and functional groups. The following structural diagrams all show the same molecule—pentanoic acid—but in slightly different ways.

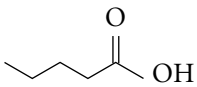
(a)



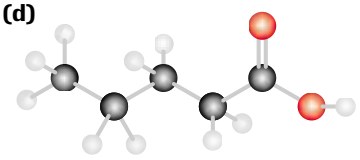
(b)



(c)



(d)

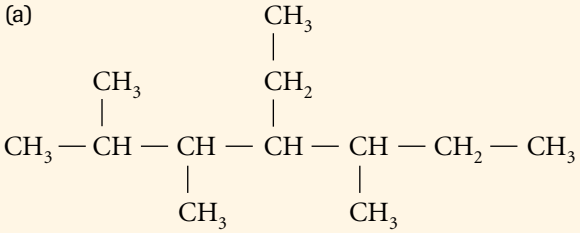


Practice

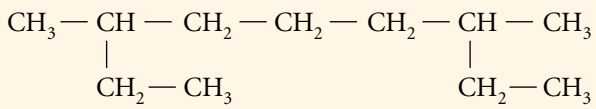
Understanding Concepts

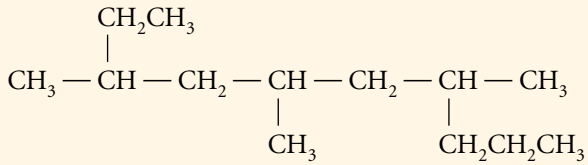
1. Write IUPAC names for the following hydrocarbons.

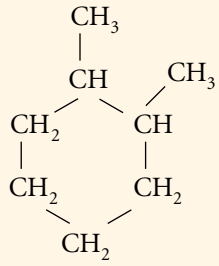
(a)



4-ethyl-2,3,5-trimethylheptane

(b) 

(c) 

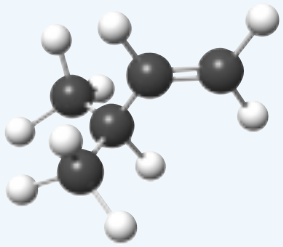
(d) 

2. Draw a structural diagram for each of the following hydrocarbons:
(a) 3,3,5-trimethyloctane
(b) 3,4-dimethyl-4-ethylheptane
(c) 2-methyl-4-isopropylnonane
(d) cyclobutane
(e) 1,1-diethylcyclohexane

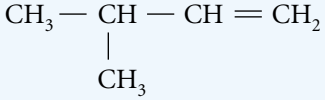
Alkenes and Alkynes

The general rules for naming alkenes and alkynes are similar to those for alkanes, using the alkyl prefixes and ending with *-ene* or *-yne* respectively.

SAMPLE problem — Naming Alkenes and Alkynes



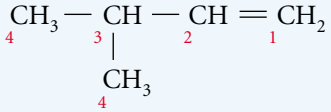
1. Write the IUPAC name for the hydrocarbon whose structural diagram and ball-and-stick model are shown.



First, find the longest C chain that includes the multiple bond. In this case, it is 4 C long, so the alkene is a butene.

Number the C atoms, beginning with the end closest to the double bond.

The double bond is between C 1 and C 2, so the alkene is a 1-butene.

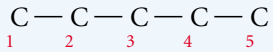


Next, identify any branches: A methyl group is attached to C 3, so the branch is 3-methyl.

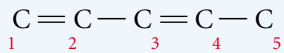
Finally, write the name, following the conventions for hyphenation and punctuation. Since a number precedes the word butene, hyphens are inserted and the alkene is 3-methyl-1-butene.

2. Draw a structural diagram for 2-methyl-1,3-pentadiene.

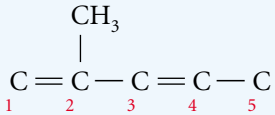
First, draw and number a 5 C chain for the pentadiene.



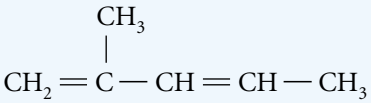
Now insert the double bonds. The name "diene" tells us that there are two double bonds, one starting at C 1 and another starting at C 3.



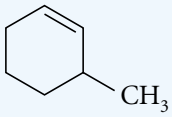
Draw a methyl group attached to C atom 2.

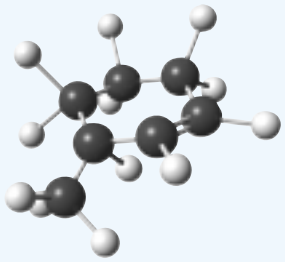


Finally, write in the remaining H atoms.



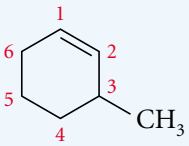
3. Write the IUPAC name for the compound whose structural diagram and ball-and-stick model are shown.





First, identify the ring structure, which contains 6 C atoms with one double bond. The parent alkene is therefore cyclohexene.

Next, number the C atoms beginning with one of the C atoms in the double bond. The numbering system should result in the attached group having the lowest possible number, which places the methyl group at C 3 .

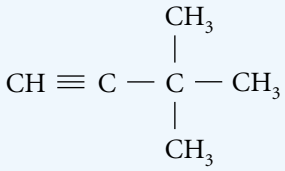


The IUPAC name for this compound is 3-methylcyclohexene.

Example 1

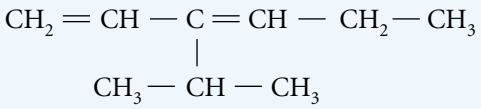
Draw a structural diagram for 3,3-dimethyl-1-butyne.

Solution



Example 2

Write the IUPAC name for the following compound.



Solution

The compound is 3-isopropyl-1,3-hexadiene.

LEARNING TIP

Some alkenes and alkynes have common names.

IUPAC name	Common name
ethene	ethylene
propene	propylene
ethyne	acetylene

SUMMARY Naming Alkenes and Alkynes

Step 1. The parent chain must be an alkene or alkyne, and thus must contain the multiple bond.

Step 2. When numbering the C atoms in the parent chain, begin with the end closest to the multiple bond.

Step 3. The location of the multiple bond is indicated by the number of the C atom that begins the multiple bond; for example, if a double bond is between the second and third C atoms of a pentene, it is named 2-pentene.

Step 4. The presence and location of multiple double bonds or triple bonds is indicated by the prefixes *di-*, *tri-*, etc.; for example, an octene with double bonds at the second, fourth, and sixth C atoms is named 2,4,6-octatriene.

Practice

Understanding Concepts

3. Explain why no number is used in the names ethene and propene.

4. Write the IUPAC name and the common name for the compound in **Figure 6**.

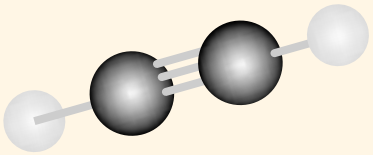
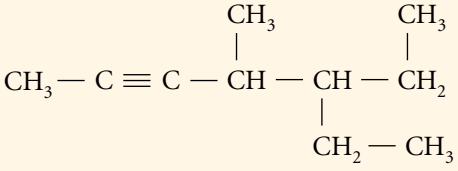
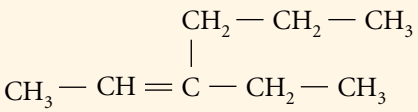


Figure 6
When this compound combusts, it transfers enough heat to melt most metals.

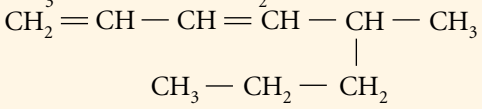
5. Write IUPAC names for the compounds with the following structural diagrams:

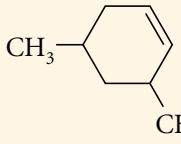
(a)



(b) 

(c) $CH_3CH=CH-CH_2-CH=CH-CH_2-CH=CH_2$

(d) 

(e) 

6. Draw structural diagrams for each of the following compounds:
(a) 2-methyl-5-ethyl-2-heptene
(b) 1,3,5-hexatriene
(c) 3,4-dimethylcyclohexene
(d) 1-butyne
(e) 4-methyl-2-pentyne

Aromatic Hydrocarbons

In naming simple aromatic compounds, we usually consider the benzene ring to be the parent molecule, with alkyl groups named as branches attached to the benzene. For example, if a methyl group is attached to a benzene ring, the molecule is called methylbenzene (**Figure 7**). Since the 6 C atoms of benzene are in a ring, with no beginning or end, we do not need to include a number when naming aromatic compounds that contain only one additional group.

When two or more groups are attached to the benzene ring, we do need to use a numbering system to indicate the locations of the groups. We always number the C atoms so that we have the lowest possible numbers for the points of attachment. Numbering may proceed either clockwise or counterclockwise. As shown in the examples in **Figure 8**, we start numbering with one of the attached ethyl groups, then proceed in the direction that is closest to the next ethyl group.

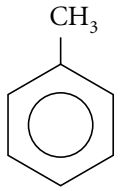
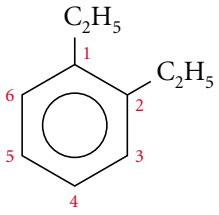
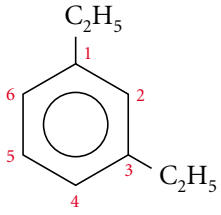


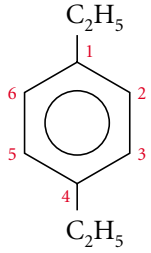
Figure 7
Methylbenzene, commonly called toluene, is a colourless liquid that is insoluble in water, but will dissolve in alcohol and other organic fluids. It is used as a solvent in glues and lacquers and is toxic to humans. Toluene reacts with nitric acid to produce the explosive trinitrotoluene (TNT).



(a) 1,2-diethylbenzene



(b) 1,3-diethylbenzene



(c) 1,4-diethylbenzene

Figure 8
Three isomers of diethylbenzene

Solution

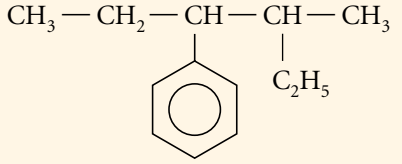
(a) 1-ethyl-2,4-dimethylbenzene
(b) 4-phenyl-3-propyl-1-hexene

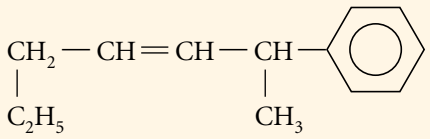
SUMMARY *Naming Aromatic Hydrocarbons*

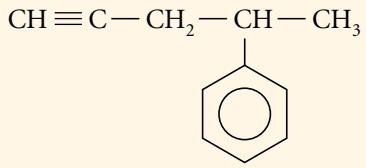
1. If an alkyl group is attached to a benzene ring, the compound is named as an alkylbenzene. Alternatively, the benzene ring may be considered as a branch of a large molecule; in this case, the benzene ring is called a phenyl group.
2. If more than one alkyl group is attached to a benzene ring, the groups are numbered using the lowest numbers possible, starting with one of the added groups.

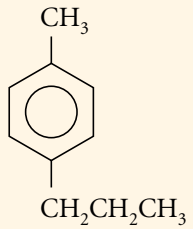
Practice

7. Write IUPAC names for the following hydrocarbons.

(a) 

(b) 

(c) 

(d) 

8. Draw structural diagrams for the following hydrocarbons:

(a) 1,2,4-trimethylbenzene
(b) 1-ethyl-2-methylbenzene
(c) 3-phenylpentane
(d) *o*-diethylbenzene
(e) *p*-ethylmethylbenzene

Physical Properties of Hydrocarbons

Figure 10
The nonpolar hydrocarbons in gasoline are insoluble in water and remain in a separate phase.

Since hydrocarbons contain only C and H atoms, two elements with very similar electronegativities, bonds between C and H are relatively nonpolar. The main intermolecular interaction in hydrocarbons is van der Waals forces: the attraction of the electrons of one molecule for the nuclei of another molecule. Since these intermolecular forces are weak, the molecules are readily separated. The low boiling points and melting points of the smaller molecules are due to the fact that small molecules have fewer electrons and weaker van der Waals forces, compared with large molecules (**Table 3**). These differences in boiling points of the components of petroleum enable the separation of these compounds in a process called **fractional distillation**. Hydrocarbons, being largely nonpolar, generally have very low solubility in polar solvents such as water, which is why gasoline remains separate from water (**Figure 10**). This property of hydrocarbons makes them good solvents for other nonpolar molecules.

fractional distillation the separation of components of petroleum by distillation, using differences in boiling points; also called fractionation

Table 3 Boiling Points of the First 10 Straight Alkanes

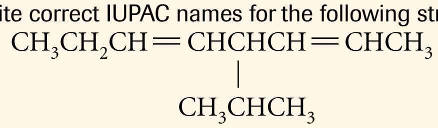
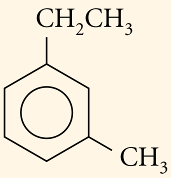
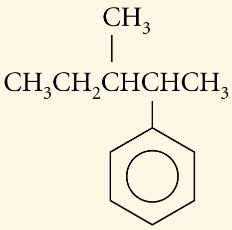
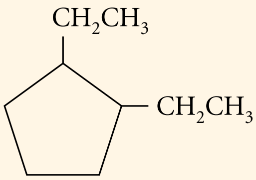
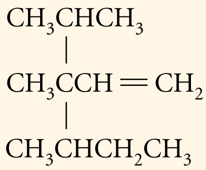
Formula	Name	b.p. (°C)
$CH_{4(g)}$	methane	−161
$C_2H_{6(g)}$	ethane	−89
$C_3H_{8(g)}$	propane	−44
$C_4H_{10(g)}$	butane	−0.5
$C_5H_{12(l)}$	pentane	36
$C_6H_{14(l)}$	hexane	68
$C_7H_{16(l)}$	heptane	98
$C_8H_{18(l)}$	octane	125
$C_9H_{20(l)}$	nonane	151
$C_{10}H_{22(l)}$	decane	174

Section 1.2 Questions

Understanding Concepts

1. Draw a structural diagram for each hydrocarbon:
   (a) 2-ethyloctane
   (b) 2-ethyl-3-*i*sepropylnonane
   (c) methylcyclopentane
   (d) 3-hexyne
   (e) 3-methyl-1,5-heptadiene
   (f) 1,2,4-trimethylbenzene
   (g) 4-*s*-butyloctane
   (h) 2-phenylpropane
   (i) 3-methyl-2-pentene
   (j) *n*-propylbenzene
   (k) *p*-diethylbenzene
   (l) 1, 3-dimethylcyclohexane

2. For each of the following names, determine if it is a correct name for an organic compound. Give reasons for your answer, including a correct name.
   (a) 2-dimethylhexane
   (b) 3-methyl-1-pentyne
   (c) 2,4-dimethylheptene
   (d) 3,3-ethylpentane
   (e) 3,4-dimethylhexane
   (f) 3,3-dimethylcyclohexene
   (g) 2-ethyl-2-methylpropane
   (h) 2,2-dimethyl-1-butene
   (i) 1-methyl-2-ethylpentane
   (j) 2-methylbenzene
   (k) 1,5-dimethylbenzene
   (l) 3,3-dimethylbutane

3. Write correct IUPAC names for the following structures.
   (a) 
   (b) 
   (c) 
   (d) 
   (e) 
4. Draw a structural diagram for each of the following compounds, and write the IUPAC name for each:
   (a) ethylene
   (b) propylene
   (c) acetylene
   (d) toluene, the toxic solvent used in many glues
   (e) the *o*-, *m*-, and *p*- isomers of xylene (dimethylbenzene), used in the synthesis of other organic compounds such as dyes

Making Connections

5. (a) Use the information in **Table 3** to plot a graph showing the relationship between the number of carbon atoms and the boiling points of the alkanes. Describe and propose an explanation for the relationship you discover.
   (b) Research a use for each of the first 10 alkanes, and suggest why each is appropriate for this use.

GO www.science.nelson.com