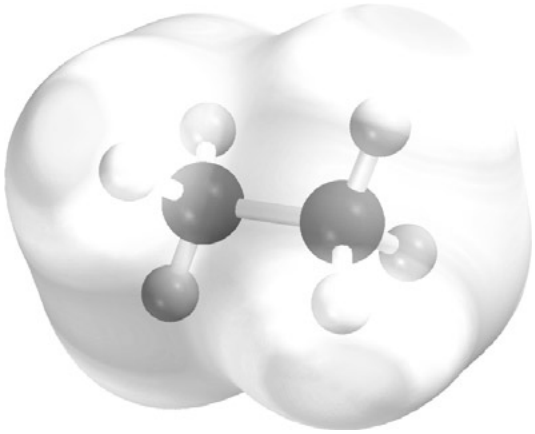
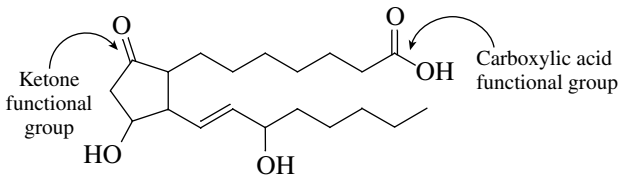


CHAPTER 2

ALKANES

SOLUTIONS TO TEXT PROBLEMS

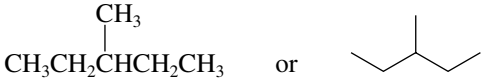
2.1 A carbonyl group is C═O. Of the two carbonyl functions in prostaglandin E_1 one belongs to the ketone family, the other to the carboxylic acids.



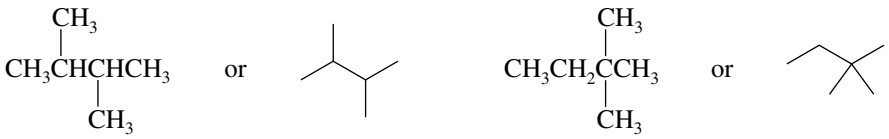
2.2 An unbranched alkane (*n*-alkane) of 28 carbons has 26 methylene (CH_2) groups flanked by a methyl (CH_3) group at each end. The condensed formula is $CH_3(CH_2)_{26}CH_3$.

2.3 The alkane represented by the carbon skeleton formula has 11 carbons. The general formula for an alkane is C_nH_{2n+2}, and thus there are 24 hydrogens. The molecular formula is $C_{11}H_{24}$; the condensed structural formula is $CH_3(CH_2)_9CH_3$.

2.4 In addition to $CH_3(CH_2)_4CH_3$ and $(CH_3)_2CHCH_2CH_2CH_3$, there are three more isomers. One has a five-carbon chain with a one-carbon (methyl) branch:



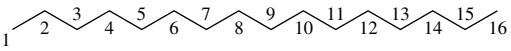
The remaining two isomers have two methyl branches on a four-carbon chain.



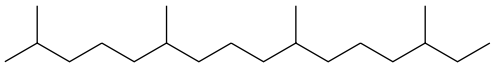
2.5 (*b*) Octacosane is not listed in Table 2.4, but its structure can be deduced from its systematic name. The suffix -cosane pertains to alkanes that contain 20–29 carbons in their longest continuous chain. The prefix octa- means "eight." Octacosane is therefore the unbranched alkane having 28 carbon atoms. It is $CH_3(CH_2)_{26}CH_3$.

(*c*) The alkane has an unbranched chain of 11 carbon atoms and is named **undecane.**

2.6 The ending -hexadecane reveals that the longest continuous carbon chain has 16 carbon atoms.



There are four methyl groups (represented by tetramethyl-), and they are located at carbons 2, 6, 10, and 14.



2,6,10,14-Tetramethylhexadecane
(phytane)

2.7 (*b*) The systematic name of the unbranched C_5H_{12} isomer is **pentane** (Table 2.4).

$$CH_3CH_2CH_2CH_2CH_3$$

IUPAC name: **pentane**
Common name: *n*-pentane

A second isomer, $(CH_3)_2CHCH_2CH_3$, has four carbons in the longest continuous chain and so is named as a derivative of butane. Since it has a methyl group at C-2, it is **2-methylbutane.**

$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$$

IUPAC name: **2-methylbutane**
Common name: isopentane
methyl group at C-2

The remaining isomer, $(CH_3)_4C$, has three carbons in its longest continuous chain and so is named as a derivative of propane. There are two methyl groups at C-2, and so it is a 2,2-dimethyl derivative of propane.

$$\begin{array}{c} CH_3 \\ | \\ CH_3CCH_3 \\ | \\ CH_3 \end{array}$$

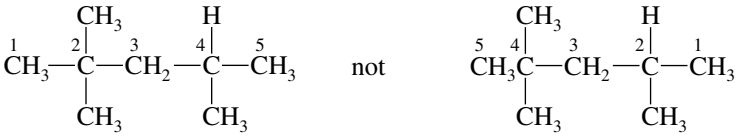
IUPAC name: **2,2-dimethylpropane**
Common name: neopentane

(*c*) First write out the structure in more detail, and identify the longest continuous carbon chain.

$$\begin{array}{ccccccc} & & CH_3 & & H & & \\ & & | & & | & & \\ CH_3- & C & -CH_2- & C & - & CH_3 & \\ & & | & & | & & \\ & & CH_3 & & CH_3 & & \end{array}$$

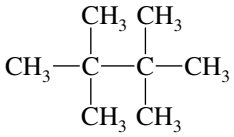
There are five carbon atoms in the longest chain, and so the compound is named as a derivative of pentane. This five-carbon chain has three methyl substituents attached to it, making it

a trimethyl derivative of pentane. Number the chain in the direction that gives the lowest numbers to the substituents at the first point of difference.



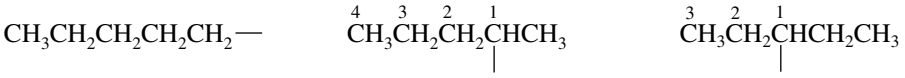
2,2,4-Trimethylpentane (correct) not 2,4,4-Trimethylpentane (incorrect)

(*d*) The longest continuous chain in $(CH_3)_3CC(CH_3)_3$ contains four carbon atoms.



The compound is named as a tetramethyl derivative of butane; it is **2,2,3,3-tetramethylbutane.**

2.8 There are three C_5H_{11} alkyl groups with unbranched carbon chains. One is primary, and two are secondary. The IUPAC name of each group is given beneath the structure. Remember to number the alkyl groups from the point of attachment.



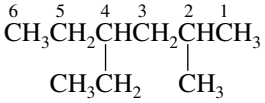
Pentyl group (primary) 1-Methylbutyl group (secondary) 1-Ethylpropyl group (secondary)

Four alkyl groups are derived from $(CH_3)_2CHCH_2CH_3$. Two are primary, one is secondary, and one is tertiary.

3-Methylbutyl group (primary) 2-Methylbutyl group (primary)

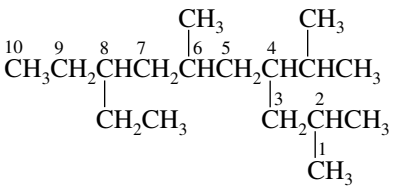
1,1-Dimethylpropyl group (tertiary) 1,2-Dimethylpropyl group (secondary)

2.9 (*b*) Begin by writing the structure in more detail, showing each of the groups written in parentheses. The compound is named as a derivative of hexane, because it has six carbons in its longest continuous chain.



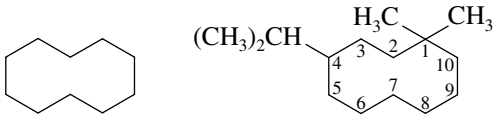
The chain is numbered so as to give the lowest number to the substituent that appears closest to the end of the chain. In this case it is numbered so that the substituents are located at C-2 and C-4 rather than at C-3 and C-5. In alphabetical order the groups are ethyl and methyl; they are listed in alphabetical order in the name. The compound is 4-ethyl-2-methylhexane.

(*c*) The longest continuous chain is shown in the structure; it contains ten carbon atoms. The structure also shows the numbering scheme that gives the lowest number to the substituent at the first point of difference.



In alphabetical order, the substituents are ethyl (at C-8), isopropyl at (C-4), and two methyl groups (at C-2 and C-6). The alkane is 8-ethyl-4-isopropyl-2,6-dimethyldecane. The systematic name for the isopropyl group (1-methylethyl) may also be used, and the name becomes 8-ethyl-2,6-dimethyl-4-(1-methylethyl)decane.

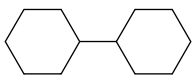
2.10 (*b*) There are ten carbon atoms in the ring in this cycloalkane, thus it is named as a derivative of cyclodecane.



Cyclodecane

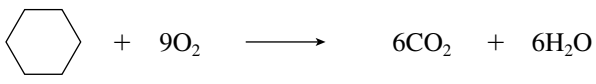
The numbering pattern of the ring is chosen so as to give the lowest number to the substituent at the first point of difference between them. Thus, the carbon bearing two methyl groups is C-1, and the ring is numbered counterclockwise, placing the isopropyl group on C-4 (numbering clockwise would place the isopropyl on C-8). Listing the substituent groups in alphabetical order, the correct name is 4-isopropyl-1,1-dimethylcyclodecane. Alternatively, the systematic name for isopropyl (1-methylethyl) could be used, and the name would become 1,1-dimethyl-4-(1-methylethyl)cyclodecane.

(*c*) When two cycloalkyl groups are attached by a single bond, the compound is named as a cycloalkyl-substituted cycloalkane. This compound is cyclohexylcyclohexane.



2.11 The alkane that has the most carbons (nonane) has the highest boiling point (151°C). Among the others, all of which have eight carbons, the unbranched isomer (octane) has the highest boiling point (126°C) and the most branched one (2,2,3,3-tetramethylbutane) the lowest (106°C). The remaining alkane, 2-methylheptane, boils at 116°C.

2.12 All hydrocarbons burn in air to give carbon dioxide and water. To balance the equation for the combustion of cyclohexane (C_6H_{12}), first balance the carbons and the hydrogens on the right side. Then balance the oxygens on the left side.



Cyclohexane Oxygen Carbon dioxide Water

2.13 (*b*) Icosane (Table 2.4) is $C_{20}H_{42}$. It has four more methylene (CH_2) groups than hexadecane, the last unbranched alkane in Table 2.5. Its calculated heat of combustion is therefore (4×653 kJ/mol) higher.

$$\begin{aligned}\text{Heat of combustion of icosane} &= \text{heat of combustion of hexadecane} + 4 \times 653 \text{ kJ/mol} \\ &= 10{,}701 \text{ kJ/mol} + 2612 \text{ kJ/mol} \\ &= 13{,}313 \text{ kJ/mol}\end{aligned}$$

2.14 Two factors that influence the heats of combustion of alkanes are, in order of decreasing importance, (1) the number of carbon atoms and (2) the extent of chain branching. Pentane, isopentane, and neopentane are all C_5H_{12}; hexane is C_6H_{14}. Hexane has the largest heat of combustion. Branching leads to a lower heat of combustion; neopentane is the most branched and has the lowest heat of combustion.

Hexane	$CH_3(CH_2)_4CH_3$	Heat of combustion 4163 kJ/mol (995.0 kcal/mol)
Pentane	$CH_3CH_2CH_2CH_2CH_3$	Heat of combustion 3527 kJ/mol (845.3 kcal/mol)
Isopentane	$(CH_3)_2CHCH_2CH_3$	Heat of combustion 3529 kJ/mol (843.4 kcal/mol)
Neopentane	$(CH_3)_4C$	Heat of combustion 3514 kJ/mol (839.9 kcal/mol)

2.15 (*b*) In the reaction

$$CH_2{=}CH_2 + Br_2 \longrightarrow BrCH_2CH_2Br$$

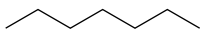
carbon becomes bonded to an atom (Br) that is more electronegative than itself. Carbon is *oxidized.*

(*c*) In the reaction

$$6CH_2{=}CH_2 + B_2H_6 \longrightarrow 2(CH_3CH_2)_3B$$

one carbon becomes bonded to hydrogen and is, therefore, *reduced.* The other carbon is also reduced, because it becomes bonded to boron, which is less electronegative than carbon.

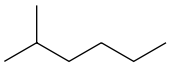
2.16 It is best to approach problems of this type systematically. Since the problem requires all the isomers of C_7H_{16} to be written, begin with the unbranched isomer heptane.



$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$

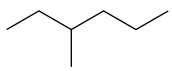
Heptane

Two isomers have six carbons in their longest continuous chain. One bears a methyl substituent at C-2, the other a methyl substituent at C-3.



$(CH_3)_2CHCH_2CH_2CH_2CH_3$

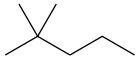
2-Methylhexane



$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2CH_3$

3-Methylhexane

Now consider all the isomers that have two methyl groups as substituents on a five-carbon continuous chain.

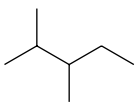


$(CH_3)_3CCH_2CH_2CH_3$

2,2-Dimethylpentane

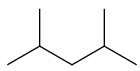
$(CH_3CH_2)_2C(CH_3)_2$

3,3-Dimethylpentane



$(CH_3)_2CH\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$

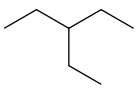
2,3-Dimethylpentane



$(CH_3)_2CHCH_2CH(CH_3)_2$

2,4-Dimethylpentane

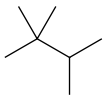
There is one isomer characterized by an ethyl substituent on a five-carbon chain:



$(CH_3CH_2)_3CH$

3-Ethylpentane

The remaining isomer has three methyl substituents attached to a four-carbon chain.

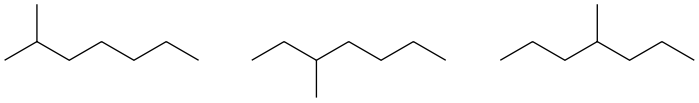


$(CH_3)_3CCH(CH_3)_2$

2,2,3-Trimethylbutane

2.17 In the course of doing this problem, you will write and name the 17 alkanes that, in addition to octane, $CH_3(CH_2)_6CH_3$, comprise the 18 constitutional isomers of C_8H_{18}.

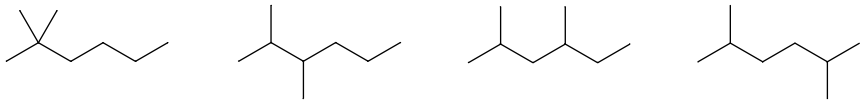
(*a*) The easiest way to attack this part of the exercise is to draw a bond-line depiction of heptane and add a methyl branch to the various positions.



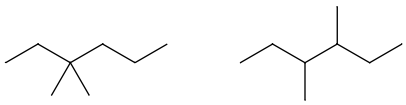
2-Methylheptane 3-Methylheptane 4-Methylheptane

Other structures bearing a continuous chain of seven carbons would be duplicates of these isomers rather than unique isomers. "5-Methylheptane," for example, is an incorrect name for 3-methylheptane, and "6-methylheptane" is an incorrect name for 2-methylheptane.

(*b*) Six of the isomers named as derivatives of hexane contain two methyl branches on a continuous chain of six carbons.

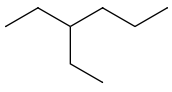


2,2-Dimethylhexane 2,3-Dimethylhexane 2,4-Dimethylhexane 2,5-Dimethylhexane



3,3-Dimethylhexane 3,4-Dimethylhexane

One isomer bears an ethyl substituent:



3-Ethylhexane

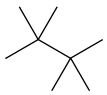
(*c*) Four isomers are trimethyl-substituted derivatives of pentane:

2,2,3-Trimethylpentane 2,3,3-Trimethylpentane 2,2,4-Trimethylpentane 2,3,4-Trimethylpentane

Two bear an ethyl group and a methyl group on a continuous chain of five carbons:

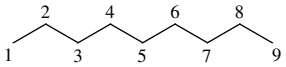
3-Ethyl-2-methylpentane 3-Ethyl-3-methylpentane

(*d*) Only one isomer is named as a derivative of butane:

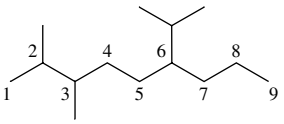


2,2,3,3-Tetramethylbutane

2.18 (*a*) The longest continuous chain contains nine carbon atoms. Begin the problem by writing and numbering the carbon skeleton of nonane.



Now add two methyl groups (one to C-2 and the other to C-3) and an isopropyl group (to C-6) to give a structural formula for 6-isopropyl-2,3-dimethylnonane.



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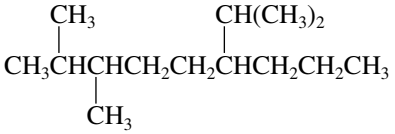
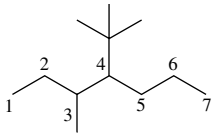


(*b*) To the carbon skeleton of heptane (seven carbons) add a *tert*-butyl group to C-4 and a methyl group to C-3 to give 4-*tert*-butyl-3-methylheptane.



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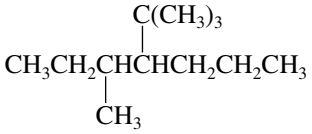
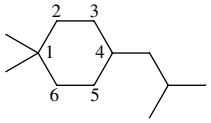


(*c*) An isobutyl group is —$CH_2CH(CH_3)_2$. The structure of 4-isobutyl-1,1-dimethylcyclohexane is as shown.



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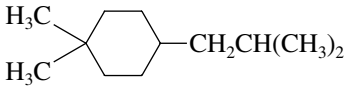
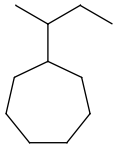
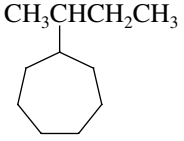


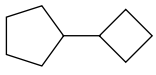
(*d*) A *sec*-butyl group is $CH_3\underset{|}{C}HCH_2CH_3$. *sec*-Butylcycloheptane has a *sec*-butyl group on a seven-membered ring.



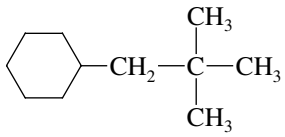
or



(*e*) A cyclobutyl group is a substituent on a five-membered ring in cyclobutylcyclopentane.

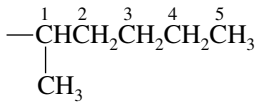


(*f*) Recall that an alkyl group is numbered from the point of attachment. The structure of (2,2-dimethylpropyl)cyclohexane is

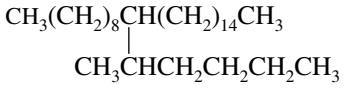


(*g*) The name "pentacosane" contains no numerical locants or suffixes indicating the presence of alkyl groups. It must therefore be an unbranched alkane. Table 2.4 in the text indicates that the suffix -cosane refers to alkanes with 20–29 carbons. The prefix penta- stands for "five," and so pentacosane must be the unbranched alkane with 25 carbons. Its condensed structural formula is $CH_3(CH_2)_{23}CH_3$.

(*h*) We need to add a 1-methylpentyl group to C-10 of pentacosane. A 1-methylpentyl group is:



It has five carbons in the longest continuous chain counting from the point of attachment and bears a methyl group at C-1. 10-(1-Methylpentyl)pentacosane is therefore:

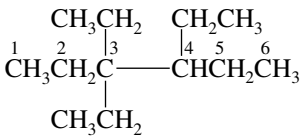


2.19 (*a*) This compound is an unbranched alkane with 27 carbons. As noted in part (*g*) of the preceding problem, alkanes with 20–29 carbons have names ending in -cosane. Thus, we add the prefix hepta- ("seven") to -cosane to name the alkane $CH_3(CH_2)_{25}CH_3$ as **heptacosane.**

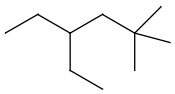
(*b*) The alkane $(CH_3)_2CHCH_2(CH_2)_{14}CH_3$ has 18 carbons in its longest continuous chain. It is named as a derivative of **octadecane.** There is a single substituent, a methyl group at C-2. The compound is **2-methyloctadecane.**

(*c*) Write the structure out in more detail to reveal that it is **3,3,4-triethylhexane.**

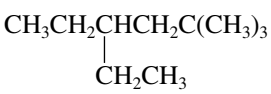
$(CH_3CH_2)_3CCH(CH_2CH_3)_2$ is rewritten as



(*d*) Each line of a bond-line formula represents a bond between two carbon atoms. Hydrogens are added so that the number of bonds to each carbon atom totals four.

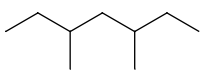


is the same as

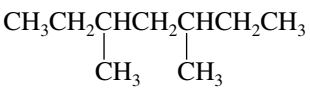


The IUPAC name is **4-ethyl-2,2-dimethylhexane.**

(*e*)

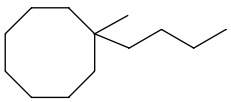


is the same as

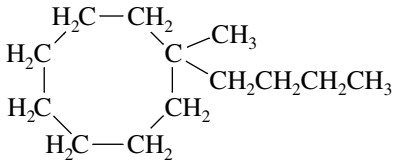


The IUPAC name is **3,5-dimethylheptane.**

(*f*)

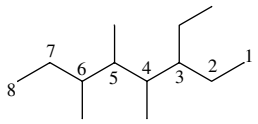


is the same as



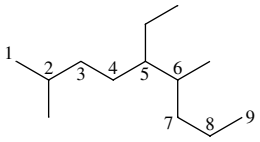
The IUPAC name is **1-butyl-1-methylcyclooctane.**

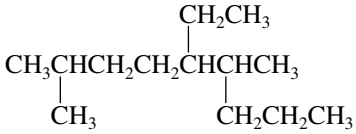
(*g*) Number the chain in the direction shown to give **3-ethyl-4,5,6-trimethyloctane.** When numbered in the opposite direction, the locants are also 3, 4, 5, and 6. In the case of ties, however, choose the direction that gives the lower number to the substituent that appears first in the name. "Ethyl" precedes "methyl" alphabetically.



2.20 (*a*) The alkane contains 13 carbons. Since all alkanes have the molecular formula C_nH_{2n+2}, the molecular formula must be $C_{13}H_{28}$.

(*b*) The longest continuous chain is indicated and numbered as shown.





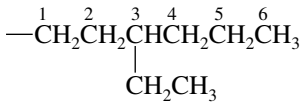
In alphabetical order, the substituents are ethyl (at C-5), methyl (at C-2), methyl (at C-6). The IUPAC name is **5-ethyl-2,6-dimethylnonane.**

(*c*) Fill in the hydrogens in the alkane to identify the various kinds of groups present. There are five **methyl** (CH_3) groups, five **methylene** (CH_2) groups, and three **methine** (CH) groups in the molecule.

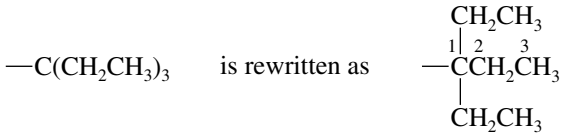
(*d*) A primary carbon is attached to one other carbon. There are five primary carbons (the carbons of the five CH_3 groups). A secondary carbon is attached to two other carbons, and there are five of these (the carbons of the five CH_2 groups). A tertiary carbon is attached to three other carbons, and there are three of these (the carbons of the three methine groups). A quaternary carbon is attached to four other carbons. None of the carbons is a quaternary carbon.

2.21 (*a*) The group $CH_3(CH_2)_{10}CH_2$— is an unbranched alkyl group with 12 carbons. It is a **dodecyl group.** The carbon at the point of attachment is directly attached to only one other carbon. It is a primary alkyl group.

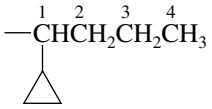
(*b*) The longest continuous chain from the point of attachment is six carbons; it is a hexyl group bearing an ethyl substituent at C-3. The group is a **3-ethylhexyl group.** It is a primary alkyl group.



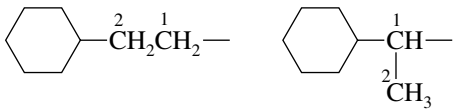
(*c*) By writing the structural formula of this alkyl group in more detail, we see that the longest continuous chain from the point of attachment contains three carbons. It is a **1,1-diethylpropyl** group. Because the carbon at the point of attachment is directly bonded to three other carbons, it is a tertiary alkyl group.



(*d*) This group contains four carbons in its longest continuous chain. It is named as a butyl group with a cyclopropyl substituent at C-1. It is a **1-cyclopropylbutyl** group and is a secondary alkyl group.



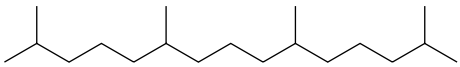
(*e*, *f*) A two-carbon group that bears a cyclohexyl substituent is a **cyclohexylethyl** group. Number from the point of attachment when assigning a locant to the cyclohexyl group.



2-Cyclohexylethyl (primary)

1-Cyclohexylethyl (secondary)

2.22 The IUPAC name for pristane reveals that the longest chain contains 15 carbon atoms (as indicated by -pentadecane). The chain is substituted with four methyl groups at the positions indicated in the name.



Pristane (2,6,10,14-tetramethylpentadecane)

2.23 (*a*) An alkane having 100 carbon atoms has 2(100) + 2 = 202 hydrogens. The molecular formula of hectane is $C_{100}H_{202}$ and the condensed structural formula is $CH_3(CH_2)_{98}CH_3$. The 100 carbon atoms are connected by 99 σ bonds. The total number of σ bonds is 301 (99 C—C bonds + 202 C—H bonds).

(*b*) Unique compounds are formed by methyl substitution at carbons 2 through 50 on the 100-carbon chain (C-51 is identical to C-50, and so on). There are 49 *x*-methylhectanes.

(*c*) Compounds of the type 2,*x*-dimethylhectane can be formed by substitution at carbons 2 through 99. There are 98 of these compounds.

2.24 Isomers are different compounds that have the same molecular formula. In all these problems the safest approach is to write a structural formula and then count the number of carbons and hydrogens.

(*a*) Among this group of compounds, only butane and isobutane have the same molecular formula; only these two are isomers.

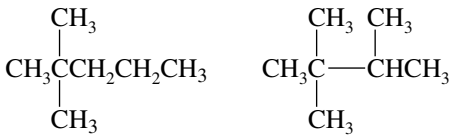
Butane C_4H_{10}

Cyclobutane C_4H_8

Isobutane C_4H_{10}

2-Methylbutane C_5H_{12}

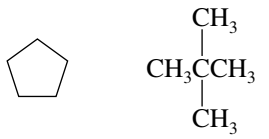
(*b*) The two compounds that are isomers, that is, those that have the same molecular formula, are 2,2-dimethylpentane and 2,2,3-trimethylbutane.



2,2-Dimethylpentane C_7H_{16}

2,2,3-Trimethylbutane C_7H_{16}

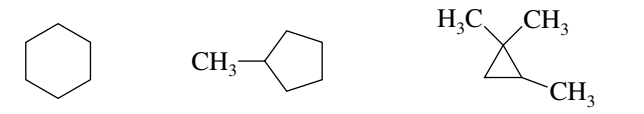
Cyclopentane and neopentane are not isomers of these two compounds, nor are they isomers of each other.



Cyclopentane
C_5H_{10}

Neopentane
C_5H_{12}

(*c*) The compounds that are isomers are cyclohexane, methylcyclopentane, and 1,1,2-trimethylcyclopropane.



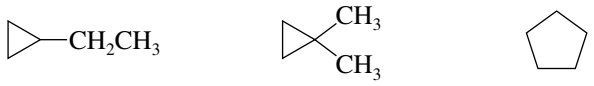
Cyclohexane
C_6H_{12}

Methylcyclopentane
C_6H_{12}

1,1,2-Trimethylcyclopropane
C_6H_{12}

Hexane, $CH_3CH_2CH_2CH_2CH_2CH_3$, has the molecular formula C_6H_{14}; it is not an isomer of the others.

(*d*) The three that are isomers all have the molecular formula C_5H_{10}.

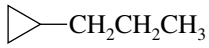


Ethylcyclopropane
C_5H_{10}

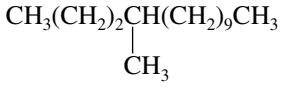
1,1-Dimethylcyclopropane
C_5H_{10}

Cyclopentane
C_5H_{10}

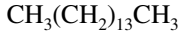
Propylcyclopropane is not an isomer of the others. Its molecular formula is C_6H_{12}.



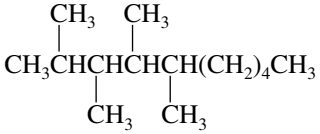
(*e*) Only 4-methyltetradecane and pentadecane are isomers. Both have the molecular formula $C_{15}H_{32}$.



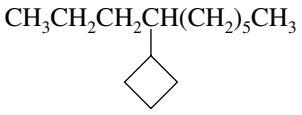
4-Methyltetradecane
$C_{15}H_{32}$



Pentadecane
$C_{15}H_{32}$



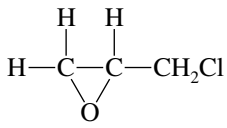
2,3,4,5-Tetramethyldecane
$C_{14}H_{30}$



4-Cyclobutyldecane
$C_{14}H_{28}$

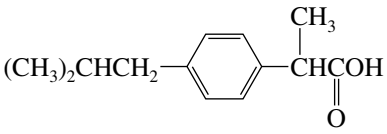
2.25 The oxygen and two of the carbons of C_3H_5ClO are part of the structural unit that characterizes epoxides. The problem specifies that a methyl group (CH_3) is *not* present; therefore, add the

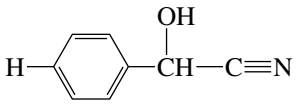
remaining carbon and the chlorine as a —CH_2Cl unit, and fill in the remaining bonds with hydrogen substituents.



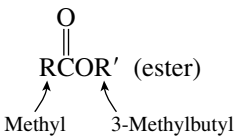
Epichlorohydrin

2.26 (*a*) Ibuprofen is (*b*) Mandelonitrile is

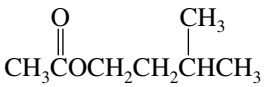




2.27 Isoamyl acetate is

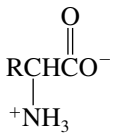


which is

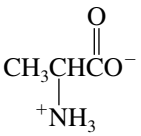


2.28 Thiols are characterized by the —SH group. *n*-Butyl mercaptan is $CH_3CH_2CH_2CH_2SH$.

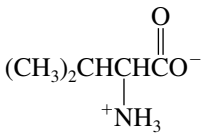
2.29 α-Amino acids have the general formula



The individual amino acids in the problem have the structures shown:



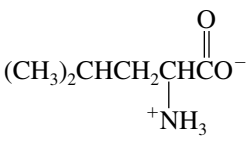
(*a*) Alanine



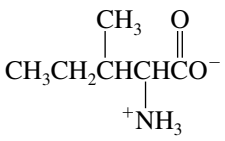
(*b*) Valine

(*c*, *d*) An isobutyl group is $(CH_3)_2CHCH_2$—, and a *sec*-butyl group is

The structures of leucine and isoleucine are:

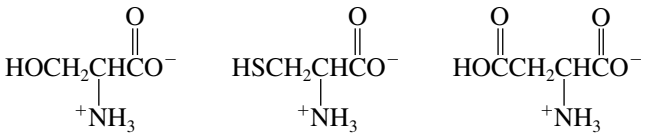


Leucine



Isoleucine

(*e*–*g*) The functional groups that characterize alcohols, thiols, and carboxylic acids are —OH, —SH, and —CO_2H, respectively. The structures of serine, cysteine, and aspartic acid are:



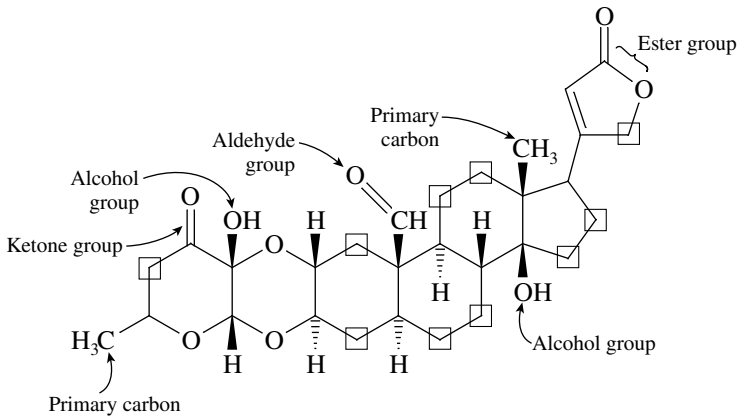
Serine Cysteine Aspartic acid

2.30 Uscharidin has the structure shown.

(*a*) There are two alcohol groups, one aldehyde group, one ketone group, and one ester functionality.

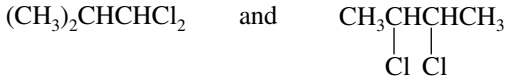
(*b*) Uscharidin contains ten methylene groups (CH_2). They are indicated in the structure by small squares.

(*c*) The primary carbons in uscharidin are the carbons of the two methyl groups.



2.31 (*a*) Methylene groups are —CH_2—. $ClCH_2CH_2CH_2CH_2Cl$ is therefore the $C_4H_8Cl_2$ isomer in which all the carbons belong to methylene groups.

(*b*) The $C_4H_8Cl_2$ isomers that lack methylene groups are



2.32 Since it is an alkane, the sex attractant of the tiger moth has a molecular formula of C_nH_{2n+2}. The number of carbons and hydrogens may be calculated from its molecular weight.

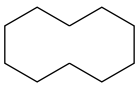
$$12n + 1(2n + 2) = 254$$
$$14n = 252$$
$$n = 18$$

The molecular formula of the alkane is $C_{18}H_{38}$. In the problem it is stated that the sex attractant is a 2-methyl-branched alkane. It is therefore 2-methylheptadecane, $(CH_3)_2CHCH_2(CH_2)_{13}CH_3$.

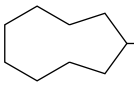
2.33 When any hydrocarbon is burned in air, the products of combustion are carbon dioxide and water.

(*a*) $CH_3(CH_2)_8CH_3 + \frac{31}{2}O_2 \longrightarrow 10CO_2 + 11H_2O$

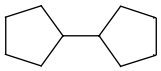
Decane ($C_{10}H_{22}$) Oxygen Carbon dioxide Water

(*b*)  + $15O_2$ ⟶ $10CO_2 + 10H_2O$

Cyclodecane ($C_{10}H_{20}$) Oxygen — Carbon dioxide — Water

(*c*)  $CH_3 + 15O_2$ ⟶ $10CO_2 + 10H_2O$

Methylcyclononane ($C_{10}H_{20}$) Oxygen — Carbon dioxide — Water

(*d*)  + $\frac{29}{2}O_2$ ⟶ $10CO_2 + 9H_2O$

Cyclopentylcyclopentane ($C_{10}H_{18}$) Oxygen — Carbon dioxide — Water

2.34 To determine the quantity of heat evolved per unit mass of material, divide the heat of combustion by the molecular weight.

Methane	Heat of combustion = 890 kJ/mol (212.8 kcal/mol)
	Molecular weight = 16.0 g/mol
	Heat evolved per gram = 55.6 kJ/g (13.3 kcal/g)
Butane	Heat of combustion = 2876 kJ/mol (687.4 kcal/mol)
	Molecular weight = 58.0 g/mol
	Heat evolved per gram = 49.6 kJ/g (11.8 kcal/g)

When equal masses of methane and butane are compared, methane evolves more heat when it is burned.

Equal volumes of gases contain an equal number of moles, so that when equal volumes of methane and butane are compared, the one with the greater heat of combustion in kilojoules (or kilocalories) per mole gives off more heat. Butane evolves more heat when it is burned than does an equal volume of methane.

2.35 When comparing heats of combustion of alkanes, two factors are of importance:

1. The heats of combustion of alkanes increase as the number of carbon atoms increases.
2. An unbranched alkane has a greater heat of combustion than a branched isomer.

(*a*) In the group hexane, heptane, and octane, three unbranched alkanes are being compared. Octane (C_8H_{18}) has the most carbons and has the greatest heat of combustion. Hexane (C_6H_{14}) has the fewest carbons and the lowest heat of combustion. The measured values in this group are as follows:

Hexane	Heat of combustion 4163 kJ/mol (995.0 kcal/mol)
Heptane	Heat of combustion 4817 kJ/mol (1151.3 kcal/mol)
Octane	Heat of combustion 5471 kJ/mol (1307.5 kcal/mol)

(*b*) Isobutane has fewer carbons than either pentane or isopentane and so is the member of the group with the lowest heat of combustion. Isopentane is a 2-methyl-branched isomer of pentane and so has a lower heat of combustion. Pentane has the highest heat of combustion among these compounds.

Isobutane	$(CH_3)_3CH$	Heat of combustion 2868 kJ/mol (685.4 kcal/mol)
Isopentane	$(CH_3)_2CHCH_2CH_3$	Heat of combustion 3529 kJ/mol (843.4 kcal/mol)
Pentane	$CH_3CH_2CH_2CH_2CH_3$	Heat of combustion 3527 kJ/mol (845.3 kcal/mol)

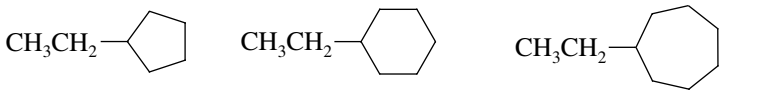
(*c*) Isopentane and neopentane each have fewer carbons than 2-methylpentane, which therefore has the greatest heat of combustion. Neopentane is more highly branched than isopentane; neopentane has the lowest heat of combustion.

Neopentane	$(CH_3)_4C$	Heat of combustion 3514 kJ/mol (839.9 kcal/mol)
Isopentane	$(CH_3)_2CHCH_2CH_3$	Heat of combustion 3529 kJ/mol (843.4 kcal/mol)
2-Methylpentane	$(CH_3)_2CHCH_2CH_2CH_3$	Heat of combustion 4157 kJ/mol (993.6 kcal/mol)

(*d*) Chain branching has a small effect on heat of combustion; the number of carbons has a much larger effect. The alkane with the most carbons in this group is 3,3-dimethylpentane; it has the greatest heat of combustion. Pentane has the fewest carbons in this group and has the smallest heat of combustion.

Pentane	$CH_3CH_2CH_2CH_2CH_3$	Heat of combustion 3527 kJ/mol (845.3 kcal/mol)
3-Methylpentane	$(CH_3CH_2)_2CHCH_3$	Heat of combustion 4159 kJ/mol (994.1 kcal/mol)
3,3-Dimethylpentane	$(CH_3CH_2)_2C(CH_3)_2$	Heat of combustion 4804 kJ/mol (1148.3 kcal/mol)

(*e*) In this series the heat of combustion increases with increasing number of carbons. Ethylcyclopentane has the lowest heat of combustion; ethylcycloheptane has the greatest.



Ethylcyclopentane
4592 kJ/mol
(1097.5 kcal/mol)

Ethylcyclohexane
5222 kJ/mol
(1248.2 kcal/mol)

Ethylcycloheptane
(combustion data not available)

2.36 (*a*) The equation for the hydrogenation of ethylene is given by the sum of the following three reactions:

(1) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\quad \Delta H^\circ = -286$ kJ $(-68.4$ kcal$)$

(2) $H_2C{=}CH_2(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$ $\quad \Delta H^\circ = -1410$ kJ $(-337.0$ kcal$)$

(3) $3H_2O(l) + 2CO_2(g) \longrightarrow CH_3CH_3(g) + \frac{7}{2}O_2(g)$ $\quad \Delta H^\circ = +1560$ kJ $(+372.8$ kcal$)$

Sum: $H_2C{=}CH_2(g) + H_2(g) \longrightarrow CH_3CH_3(g)$ $\quad \Delta H^\circ = -136$ kJ $(-32.6$ kcal$)$

Equations (1) and (2) are the combustion of hydrogen and ethylene, respectively, and ΔH° values for these reactions are given in the statement of the problem. Equation (3) is the reverse of the combustion of ethane, and its value of ΔH° is the negative of the heat of combustion of ethane.

(*b*) Again we need to collect equations of reactions for which the ΔH° values are known.

(1) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\quad \Delta H^\circ = -286$ kJ $(-68.4$ kcal$)$

(2) $HC{\equiv}CH(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$ $\quad \Delta H^\circ = -1300$ kJ $(-310.7$ kcal$)$

(3) $2CO_2(g) + 2H_2O(l) \longrightarrow CH_2{=}CH_2(g) + 3O_2(g)$ $\quad \Delta H^\circ = +1410$ kJ $(+337.0$ kcal$)$

Sum: $HC{\equiv}CH(g) + H_2(g) \longrightarrow CH_2{=}CH_2(g)$ $\quad \Delta H^\circ = -176$ kJ $(-42.1$ kcal$)$

Equations (1) and (2) are the combustion of hydrogen and acetylene, respectively. Equation (3) is the reverse of the combustion of ethylene, and its value of ΔH° is the negative of the heat of combustion of ethylene.

The value of ΔH° for the hydrogenation of acetylene to ethane is equal to the sum of the two reactions just calculated:

$$HC{\equiv}CH(g) + H_2(g) \longrightarrow H_2C{=}CH_2(g) \qquad \Delta H^\circ = -176 \text{ kJ } (-42.1 \text{ kcal})$$

$$H_2C{=}CH_2(g) + H_2(g) \longrightarrow CH_3CH_3(g) \qquad \Delta H^\circ = -136 \text{ kJ } (-32.6 \text{ kcal})$$

Sum: $HC{\equiv}CH(g) + 2H_2(g) \longrightarrow CH_3CH_3(g) \qquad \Delta H^\circ = -312 \text{ kJ } (-74.7 \text{ kcal})$

(*c*) We use the equations for the combustion of ethane, ethylene, and acetylene as shown.

(1) $2CH_2{=}CH_2(g) + 6O_2(g) \longrightarrow 4CO_2(g) + 4H_2O(l) \qquad \Delta H^\circ = -2820 \text{ kJ } (-674.0 \text{ kcal})$

(2) $2CO_2(g) + H_2O(l) \longrightarrow HC{\equiv}CH(g) + \frac{5}{2}O_2(g) \qquad \Delta H^\circ = +1300 \text{ kJ } (+310.7 \text{ kcal})$

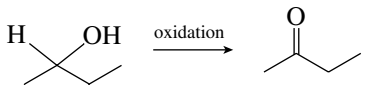
(3) $3H_2O(l) + 2CO_2(g) \longrightarrow CH_3CH_3(g) + \frac{7}{2}O_2(g) \qquad \Delta H^\circ = +1560 \text{ kJ } (+372.8 \text{ kcal})$

Sum: $2CH_2{=}CH_2(g) \longrightarrow CH_3CH_3(g) + HC{\equiv}CH(g) \qquad \Delta H^\circ = +40 \text{ kJ } (+9.5 \text{ kcal})$

The value of ΔH° for reaction (1) is twice that for the combustion of ethylene because 2 mol of ethylene are involved.

2.37 (*a*) The hydrogen content increases in going from $CH_3C{\equiv}CH$ to $CH_3CH{=}CH_2$. The organic compound $CH_3C{\equiv}CH$ is *reduced.*

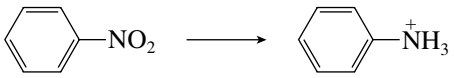
(*b*) *Oxidation* occurs because a C—O bond has replaced a C—H bond in going from starting material to product.



(*c*) There are two carbon–oxygen bonds in the starting material and four carbon–oxygen bonds in the products. *Oxidation* occurs.

$$\underset{\text{Two C—O bonds}}{HO{-}CH_2CH_2{-}OH} \longrightarrow \underset{\text{Four C—O bonds}}{2H_2C{=}O}$$

(*d*) Although the oxidation state of carbon is unchanged in the process



overall, *reduction* of the organic compound has occurred. Its hydrogen content has increased and its oxygen content has decreased.

2.38 In the reaction

$$2CH_3Cl + Si \longrightarrow (CH_3)_2SiCl_2$$

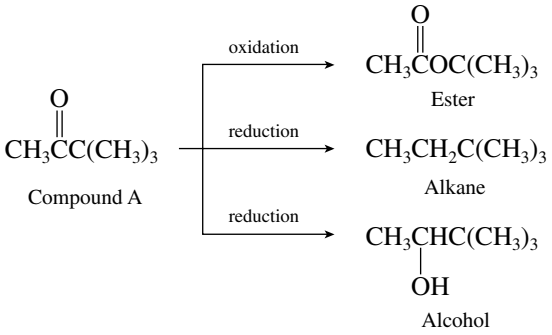
bonds between carbon and an atom more electronegative than itself (chlorine) are replaced by bonds between carbon and an atom less electronegative than itself (silicon). Carbon is reduced; silicon is oxidized.

2.39 (*a*) Compound A has the structural unit $\overset{\overset{O}{\|}}{CCC}$; compound A is a ketone.

(*b*) Converting a ketone to an ester increases the oxygen content of carbon and requires an oxidizing agent.

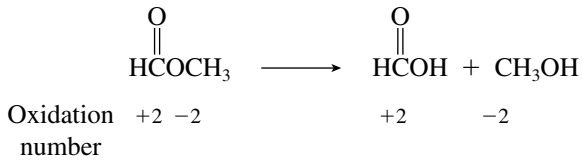
(*c*) Reduction occurs when the hydrogen content increases, as in the conversion of a ketone to an alkane or to an alcohol. Reductions are carried out by using reagents that are reducing agents.

(*d*)



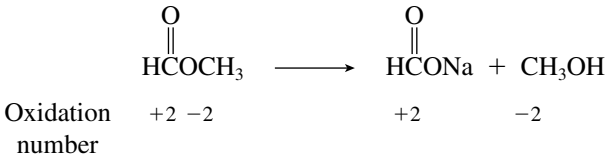
2.40 Methyl formate is an *ester*.

(*a*) The oxidation numbers of the two carbon atoms in methyl formate and the carbon atoms in the reaction products can be determined by comparison with the entries in text Table 2.6.

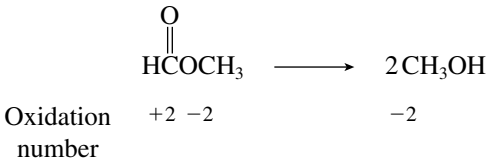


There has been no change in oxidation state in going from reactants to products, and the reaction is neither oxidation nor reduction. The number of carbon–oxygen bonds does not change in this reaction.

(*b*) As in part (*a*), the oxidation states of the carbon atoms in both the reactant and the products do not change in this reaction. The reaction is neither oxidation nor reduction.

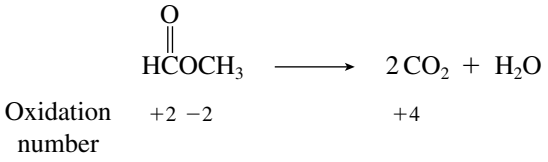


(*c*) The oxidation number of one carbon of methyl formate has decreased in this reaction.



This reaction is a reduction and requires a reagent that is a reducing agent.

(*d*) The oxidation number of both carbon atoms of methyl formate has increased. This reaction is an oxidation and requires use of a reagent that is an oxidizing agent.



(*e*) Once again the formation of carbon dioxide is an example of an oxidation, and the reaction requires use of an oxidizing agent.

$$\underset{\text{Oxidation number}}{\overset{\overset{+2}{\overset{\overset{O}{\|}}{H\overset{-2}{C}OCH_3}}}{}} \longrightarrow \underset{+4}{CO_2} + \underset{-2}{CH_3OH}$$

2.41 Two atoms appear in their elementary state: Na on the left and H_2 on the right. The oxidation state of an atom in its elementary state is 0. Assign an oxidation state of +1 to the hydrogen in the OH group of CH_3CH_2OH. H goes from +1 on the left to 0 on the right; it is reduced. Na goes from 0 on the left to +1 on the right; it is oxidized.

$$2\overset{+1}{C}H_3CH_2\overset{+1}{O}H + 2\overset{0}{N}a \longrightarrow 2CH_3CH_2O\overset{+1}{N}a + \overset{0}{H_2}$$

2.42 Combustion of an organic compound to yield CO_2 and H_2O involves oxidation. Heat is given off in each oxidation step. The least oxidized compound (CH_3CH_2OH) gives off the most heat. The most oxidized compound HO_2CCO_2H gives off the least. The measured values are:

	CH_3CH_2OH	$HOCH_2CH_2OH$	HO_2CCO_2H
kJ/mol	1371	1179	252
kcal/mol	327.6	281.9	60.2

2.43–2.45 Solutions to molecular modeling exercises are not provided in this *Study Guide and Solutions Manual*. You should use *Learning By Modeling* for these exercises.

SELF-TEST

PART A

A-1. Write the structure of each of the four-carbon alkyl groups. Give the common name and the systematic name for each.

A-2. How many σ bonds are present in each of the following?
(*a*) Nonane
(*b*) Cyclononane

A-3. Classify each of the following reactions according to whether the organic substrate is oxidized, reduced, or neither.

(*a*) $CH_3CH_3 + Br_2 \xrightarrow{\text{light}} CH_3CH_2Br + HBr$

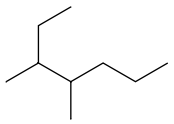
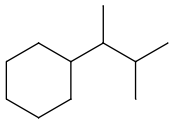
(*b*) $CH_3CH_2Br + HO^- \longrightarrow CH_3CH_2OH + Br^-$

(*c*) $CH_3CH_2OH \xrightarrow[\text{heat}]{H_2SO_4} H_2C{=}CH_2$

(*d*) $H_2C{=}CH_2 + H_2 \xrightarrow{Pt} CH_3CH_3$

A-4. (*a*) Write a structural formula for 3-isopropyl-2,4-dimethylpentane.
(*b*) How many methyl groups are there in this compound? How many isopropyl groups?

A-5. Give the IUPAC name for each of the following substances:

(*a*)  (*b*) 

A-6. The compounds in each part of the previous question contain _____ primary carbon(s), _____ secondary carbon(s), and _____ tertiary carbon(s).

A-7. Give the IUPAC name for each of the following alkyl groups, and classify each one as primary, secondary, or tertiary.

(*a*) $(CH_3)_2CHCH_2\underset{|}{C}HCH_3$

(*b*) $(CH_3CH_2)_3C—$

(*c*) $(CH_3CH_2)_3CCH_2—$

A-8. Write a balanced chemical equation for the complete combustion of 2,3-dimethylpentane.

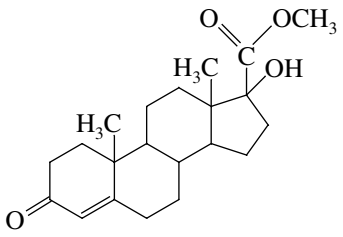
A-9. Write structural formulas, and give the names of all the constitutional isomers of C_5H_{10} that contain a ring.

A-10. Each of the following names is incorrect. Give the correct name for each compound.
(*a*) 2,3-Diethylhexane
(*b*) (2-Ethylpropyl)cyclohexane
(*c*) 2,3-Dimethyl-3-propylpentane

A-11. Which C_8H_{18} isomer
(*a*) Has the highest boiling point?
(*b*) Has the lowest boiling point?
(*c*) Has the greatest number of tertiary carbons?
(*d*) Has only primary and quaternary carbons?

A-12. Draw the constitutional isomers of C_7H_{16} that have five carbons in their longest chain, and give an IUPAC name for each of them.

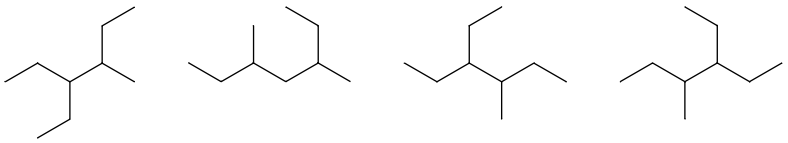
A-13. The compound shown is an example of the broad class of organic compounds known as **steroids.** What functional groups does the molecule contain?



A-14. Given the following heats of combustion (in kilojoules per mole) for the homologous series of unbranched alkanes: hexane (4163), heptane (4817), octane (5471), nonane (6125), estimate the heat of combustion (in kilojoules per mole) for **pentadecane.**

PART B

B-1. Choose the response that best describes the following compounds:



1 2 3 4

(*a*) 1, 3, and 4 represent the same compound.
(*b*) 1 and 3 are isomers of 2 and 4.
(*c*) 1 and 4 are isomers of 2 and 3.
(*d*) All the structures represent the same compound.

B-2. Which of the following is a correct name according to the IUPAC rules?
(*a*) 2-Methylcyclohexane
(*b*) 3,4-Dimethylpentane
(*c*) 2-Ethyl-2-methylpentane
(*d*) 3-Ethyl-2-methylpentane

B-3. Following are the structures of four isomers of hexane. Which of the names given correctly identifies a fifth isomer?

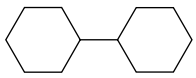
$CH_3CH_2CH_2CH_2CH_2CH_3$ $(CH_3)_3CCH_2CH_3$
$(CH_3)_2CHCH_2CH_2CH_3$ $(CH_3)_2CHCH(CH_3)_2$

(*a*) 2-Methylpentane
(*b*) 2,3-Dimethylbutane
(*c*) 2-Ethylbutane
(*d*) 3-Methylpentane

B-4. Which of the following is cyclohexylcyclohexane?

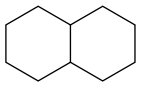
(*a*) $CH_2CH_2CH_2CH_2CH_2CH_3$

(*c*)



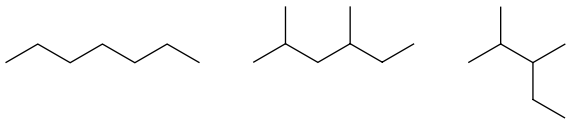
(*b*)

(*d*)



B-5. Which of the following structures is a 3-methylbutyl group?
(*a*) $CH_3CH_2CH_2CH_2CH_2$—
(*b*) $(CH_3)_2CHCH_2CH_2$—
(*c*) $(CH_3CH_2)_2CH$—
(*d*) $(CH_3)_3CCH_2$—

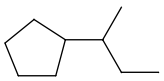
B-6. Rank the following substances in decreasing order of heats of combustion (most exothermic → least exothermic).



1 2 3

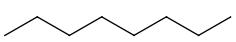
(*a*) 2 > 1 > 3
(*b*) 2 > 3 > 1
(*c*) 3 > 1 > 2
(*d*) 3 > 2 > 1

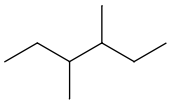
B-7. What is the total number of σ bonds present in the molecule shown?

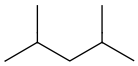


(*a*) 18 (*b*) 26 (*c*) 27 (*d*) 30

B-8. Which of the following substances is *not* an isomer of 3-ethyl-2-methylpentane?

(*a*) 

(*b*) 

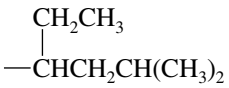
(*c*) 

(*d*) None of these (all are isomers)

B-9. Which alkane has the highest boiling point?

(*a*) Hexane
(*b*) 2,2-Dimethylbutane
(*c*) 2-Methylpentane
(*d*) 2,3-Dimethylbutane
(*e*) 3-Methylpentane

B-10. What is the correct IUPAC name of the alkyl group shown?

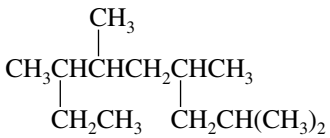


(*a*) 1-Ethyl-3-methylbutyl
(*b*) 1-Ethyl-3,3-dimethylpropyl
(*c*) 4-Ethyl-2-methylbutyl
(*d*) 5-Methylhexyl

B-11. Which of the following compounds is *not* a constitutional isomer of the others?

(*a*) Methylcyclohexane
(*b*) Cyclopropylcyclobutane
(*c*) Ethylcyclopentane
(*d*) 1,1,2-Trimethylcyclobutane
(*e*) Cycloheptane

B-12. The correct IUPAC name for the compound shown is



(*a*) 2-Ethyl-5-isobutyl-3-methylhexane
(*b*) 5-*sec*-Butyl-2-ethyl-3-methylhexane
(*c*) 2-Isobutyl-4,5-dimethylheptane
(*d*) 2-Ethyl-3,5,7-trimethyloctane
(*e*) 2,4,6,7-Tetramethylnonane

B-13. The heats of combustion of two isomers, A and B, are 4817 kJ/mol and 4812 kJ/mol, respectively. From this information it may be determined that

(*a*) Isomer A is 5 kJ/mol more stable
(*b*) Isomer B is 5 kJ/mol less stable
(*c*) Isomer B has 5 kJ/mol more potential energy
(*d*) Isomer A is 5 kJ/mol less stable

B-14. Which of the following reactions requires an *oxidizing agent?*

(*a*) $RCH_2OH \longrightarrow RCH_2Cl$
(*b*) $RCH{=}CH_2 \longrightarrow RCH_2CH_3$
(*c*) $RCH_2Cl \longrightarrow RCH_3$
(*d*) $RCH_2OH \longrightarrow RCH{=}O$
(*e*) None of these