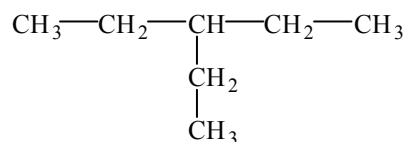
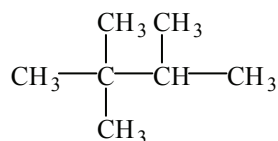
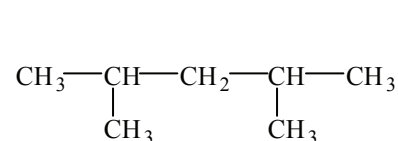
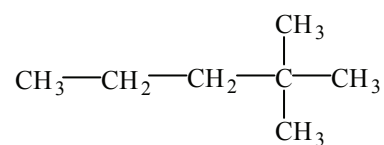
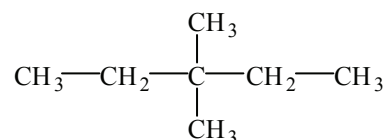
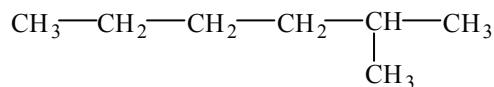
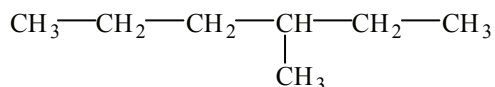
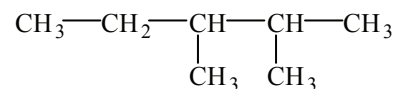


# CHAPTER 24

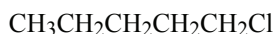
## ORGANIC CHEMISTRY

24.11 The structures are as follows:

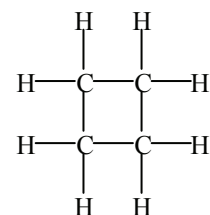
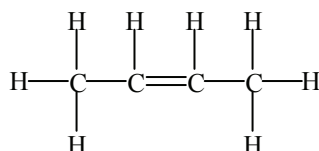
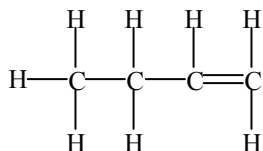


24.12 **Strategy:** For small hydrocarbon molecules (eight or fewer carbons), it is relatively easy to determine the number of structural isomers by trial and error.

**Solution:** We are starting with *n*-pentane, so we do not need to worry about any branched chain structures. In the chlorination reaction, a Cl atom replaces one H atom. There are three different carbons on which the Cl atom can be placed. Hence, *three* structural isomers of chloropentane can be derived from *n*-pentane:

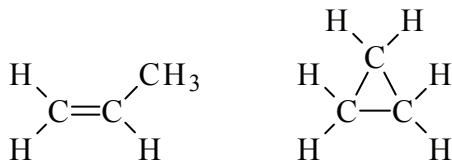


24.13 The molecular formula shows the compound is either an alkene or a cycloalkane. (Why?) You can't tell which from the formula. The possible isomers are:

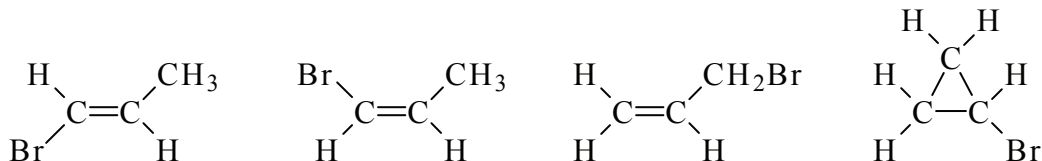


The structure in the middle (2-butene) can exist as *cis* or *trans* isomers. There are two more isomers. Can you find and draw them? Can you have an isomer with a double bond and a ring? What would the molecular formula be like in that case?

- 24.14** Both alkenes and cycloalkanes have the general formula  $C_nH_{2n}$ . Let's start with  $C_3H_6$ . It could be an alkene or a cycloalkane.



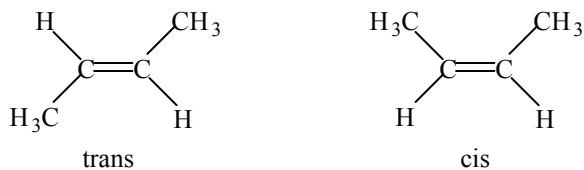
Now, let's replace one H with a Br atom to form  $C_3H_5Br$ . *Four* isomers are possible.



There is only one isomer for the cycloalkane. Note that all three carbons are equivalent in this structure.

- 24.15** The straight chain molecules have the highest boiling points and therefore the strongest intermolecular attractions. These chains can pack together more closely and efficiently than highly branched, cluster structures. This allows intermolecular forces to operate more effectively and cause stronger attractions.
- 24.16** (a) This compound could be an **alkene** or a **cycloalkane**; both have the general formula,  $C_nH_{2n}$ .
- (b) This could be an **alkyne** with general formula,  $C_nH_{2n-2}$ . It could also be a hydrocarbon with two double bonds (a diene). It could be a cyclic hydrocarbon with one double bond (a cycloalkene).
- (c) This must be an **alkane**; the formula is of the  $C_nH_{2n+2}$  type.
- (d) This compound could be an **alkene** or a **cycloalkane**; both have the general formula,  $C_nH_{2n}$ .
- (e) This compound could be an **alkyne** with one triple bond, or it could be a cyclic alkene (unlikely because of ring strain).

- 24.17** The two isomers are:



A simplified method of presenting the structures is:

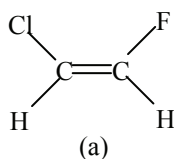


The *cis* structure is more crowded and a little less stable. As a result, slightly more heat (energy) would be released when the alkene adds a molecule of hydrogen to form butane,  $C_4H_{10}$ . Note that butane is the product when either alkene is hydrogenated.

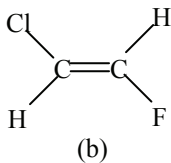
**24.18** If cyclobutadiene were square or rectangular, the C–C–C angles must be 90°. If the molecule is diamond-shaped, two of the C–C–C angles must be less than 90°. Both of these situations result in a great deal of distortion and strain in the molecule. Cyclobutadiene is very unstable for these and other reasons.

**24.19**

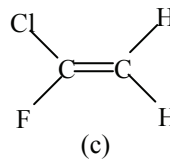
cis-chlorofluoroethylene



trans-chlorofluoroethylene



1,1-chlorofluoroethylene

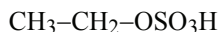


(a) and (b) are geometric isomers.

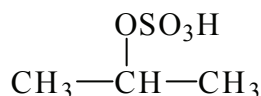
(c) is a structural isomer of both (a) and (b).

**24.20** One compound is an alkane; the other is an alkene. Alkenes characteristically undergo addition reactions with hydrogen, with halogens ( $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ) and with hydrogen halides ( $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ). Alkanes do not react with these substances under ordinary conditions.

**24.21** (a) Ethylene is symmetrical; there is no preference in the addition.



(b) The positive part of the polar reagent adds to the carbon atom that already has the most hydrogen atoms.



**24.22** In this problem you are asked to calculate the standard enthalpy of reaction. This type of problem was covered in Chapter 6.

$$\Delta H_{\text{rxn}}^{\circ} = \Sigma n\Delta H_{\text{f}}^{\circ}(\text{products}) - \Sigma m\Delta H_{\text{f}}^{\circ}(\text{reactants})$$

$$\Delta H_{\text{rxn}}^{\circ} = \Delta H_{\text{f}}^{\circ}(\text{C}_6\text{H}_6) - 3\Delta H_{\text{f}}^{\circ}(\text{C}_2\text{H}_2)$$

You can look up  $\Delta H_{\text{f}}^{\circ}$  values in Appendix 3 of your textbook.

$$\Delta H_{\text{rxn}}^{\circ} = (1)(49.04 \text{ kJ/mol}) - (3)(226.6 \text{ kJ/mol}) = -630.8 \text{ kJ/mol}$$

**24.23** (a)  $\text{CH}_2=\text{CH--CH}_2\text{--CH}_3 + \text{HBr} \rightarrow \text{CH}_3\text{--CHBr--CH}_2\text{--CH}_3$

(b)  $\text{CH}_3\text{--CH}=\text{CH--CH}_3 + \text{HBr} \rightarrow \text{CH}_3\text{--CH}_2\text{--CHBr--CH}_3$

(a) and (b) are the same.

**24.24** In this problem you must distinguish between *cis* and *trans* isomers. Recall that *cis* means that two particular atoms (or groups of atoms) are adjacent to each other, and *trans* means that the atoms (or groups of atoms) are on opposite sides in the structural formula.

In (a), the Cl atoms are adjacent to each other. This is the *cis* isomer. In (b), the Cl atoms are on opposite sides of the structure. This is the *trans* isomer.

The names are: (a) **cis-1,2-dichlorocyclopropane**; and (b) **trans-1,2-dichlorocyclopropane**.

Are any other dichlorocyclopropane isomers possible?

24.25 (a) and (c)

24.26 (a) This is a branched hydrocarbon. The name is based on the longest carbon chain. The name is **2-methylpentane**.

(b) This is also a branched hydrocarbon. The longest chain includes the  $C_2H_5$  group; the name is based on hexane, not pentane. This is an old trick. Carbon chains are flexible and don't have to lie in a straight line. The name is **2,3,4-trimethylhexane**. Why not 3,4,5-trimethylhexane?

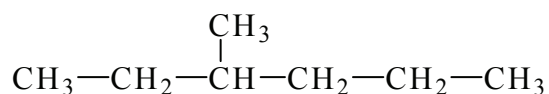
(c) How many carbons in the longest chain? It doesn't have to be straight! The name is **3-ethylhexane**.

(d) An alkene with two double bonds is called a diene. The name is **3-methyl-1,4-pentadiene**.

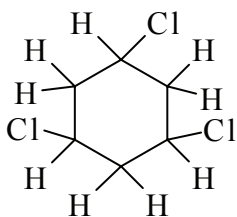
(e) The name is **2-pentyne**.

(f) The name is **3-phenyl-1-pentene**.

24.27 (a) This is a six-carbon chain with a methyl group on the third carbon.

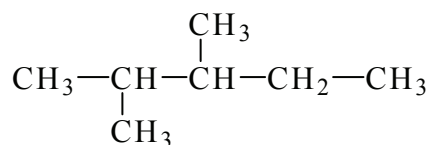


(b) This is a six carbon ring with chlorine atoms on the 1,3, and 5 carbons.

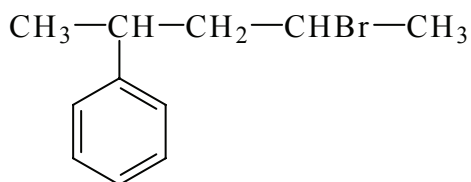


**Note:** The carbon atoms in the ring have been omitted for simplicity.

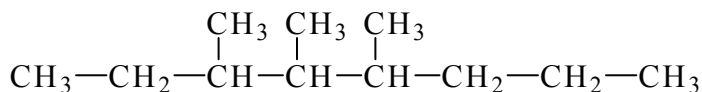
(c) This is a five carbon chain with methyl groups on the 2 and 3 carbons.



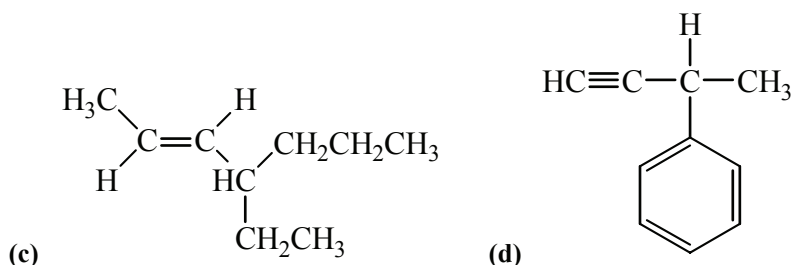
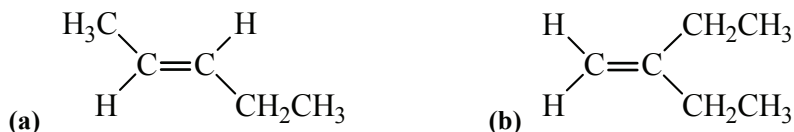
(d) This is a five carbon chain with a bromine atom on the second carbon and a phenyl group (a benzene molecule minus a hydrogen atom,  $C_6H_5$ ) on the fourth carbon.



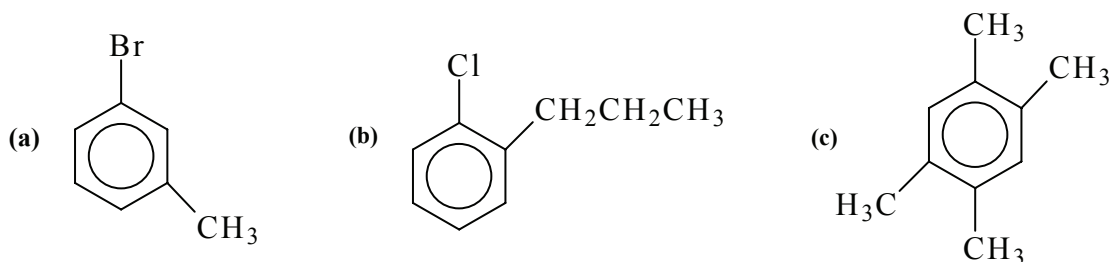
- (e) This is an eight carbon chain with methyl groups on the 3, 4, and 5 carbons.



- 24.28 The hydrogen atoms have been omitted from the skeletal structure for simplicity.



- 24.31



- 24.32 **Strategy:** We follow the IUPAC rules and use the information in Table 24.2 of the text. When a benzene ring has more than *two* substituents, you must specify the location of the substituents with numbers. Remember to number the ring so that you end up with the lowest numbering scheme as possible, giving preference to alphabetical order.

**Solution:**

- (a) Since a chloro group comes alphabetically before a methyl group, let's start by numbering the top carbon of the ring as 1. If we number clockwise, this places the second chloro group on carbon 3 and a methyl group on carbon 4.

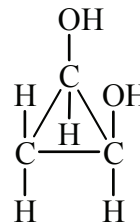
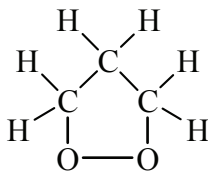
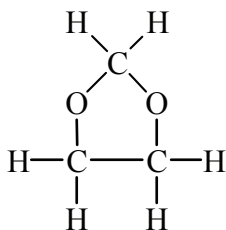
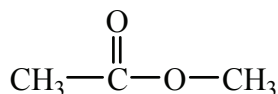
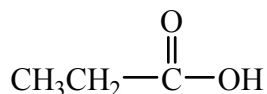
This compound is **1,3-dichloro-4-methylbenzene**.

- (b) If we start numbering counterclockwise from the bottom carbon of the ring, the name is 2-ethyl-1,4-dinitrobenzene. Numbering clockwise from the top carbon gives 3-ethyl-1,4-dinitrobenzene.

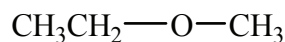
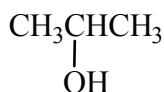
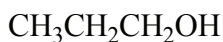
Numbering as low as possible, the correct name is **2-ethyl-1,4-dinitrobenzene**.

- (c) Again, keeping the numbers as low as possible, the correct name for this compound is **1,2,4,5-tetramethylbenzene**. You should number clockwise from the top carbon of the ring.

- 24.35 (a) There is only one isomer:  $\text{CH}_3\text{OH}$
- (b) There are two structures with this molecular formula:  
 $\text{CH}_3\text{-CH}_2\text{-OH}$  and  $\text{CH}_3\text{-O-CH}_3$
- (c) The cyclic di-alcohol has geometric isomers.



- (d) There are two possible alcohols and one ether.

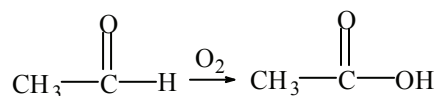


- 24.36 **Strategy:** Learning to recognize functional groups requires memorization of their structural formulas. Table 24.4 of the text shows a number of the important functional groups.

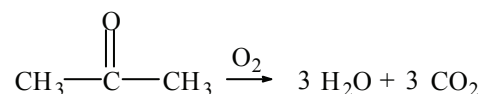
**Solution:**

- (a)  $\text{H}_3\text{C-O-CH}_2\text{-CH}_3$  contains a C-O-C group and is therefore an **ether**.
- (b) This molecule contains an  $\text{RNH}_2$  group and is therefore an **amine**.
- (c) This molecule is an **aldehyde**. It contains a carbonyl group in which one of the atoms bonded to the carbonyl carbon is a hydrogen atom.
- (d) This molecule also contains a carbonyl group. However, in this case there are no hydrogen atoms bonded to the carbonyl carbon. This molecule is a **ketone**.
- (e) This molecule contains a carboxyl group. It is a **carboxylic acid**.
- (f) This molecule contains a hydroxyl group (-OH). It is an **alcohol**.
- (g) This molecule has both an  $\text{RNH}_2$  group and a carboxyl group. It is therefore both an *amine* and a *carboxylic acid*, commonly called an **amino acid**.

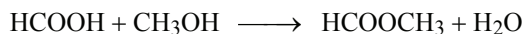
- 24.37 Aldehydes can be oxidized easily to carboxylic acids. The oxidation reaction is:



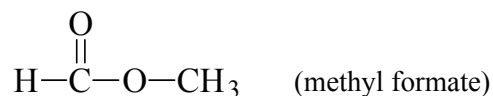
Oxidation of a ketone requires that the carbon chain be broken:



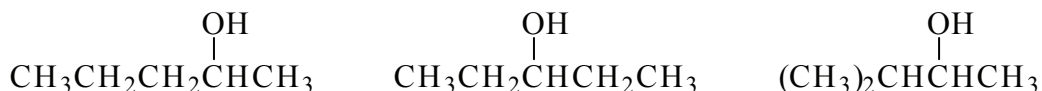
**24.38** Alcohols react with carboxylic acids to form esters. The reaction is:



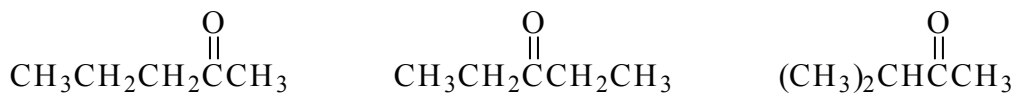
The structure of the product is:



**24.39** Alcohols can be oxidized to ketones under controlled conditions. The possible starting compounds are:

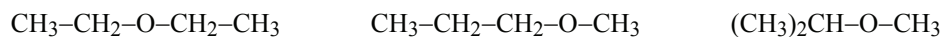


The corresponding products are:



Why isn't the alcohol  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$  a possible starting compound?

**24.40** The fact that the compound does not react with sodium metal eliminates the possibility that the substance is an alcohol. The only other possibility is the ether functional group. There are three ethers possible with this molecular formula:



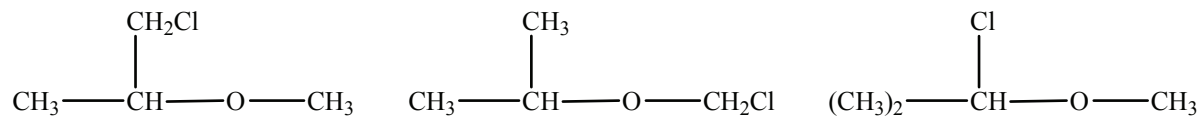
Light-induced reaction with chlorine results in substitution of a chlorine atom for a hydrogen atom (the other product is HCl). For the first ether there are only two possible chloro derivatives:



For the second there are four possible chloro derivatives. Three are shown below. Can you draw the fourth?

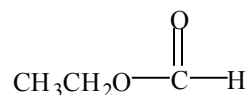


For the third there are three possible chloro derivatives:

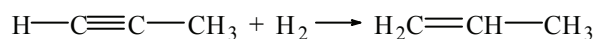


The  $(\text{CH}_3)_2\text{CH}-\text{O}-\text{CH}_3$  choice is the original compound.

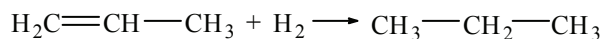
24.41 (a) The product is similar to that in Problem 24.38.



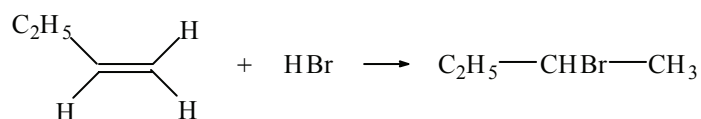
(b) Addition of hydrogen to an alkyne gives an alkene.



The alkene can also add hydrogen to form an alkane.



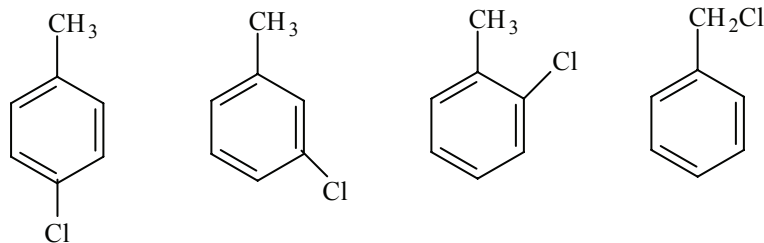
(c) HBr will add to the alkene as shown (Note: the carbon atoms at the double bond have been omitted for simplicity).



How do you know that the hydrogen adds to the CH<sub>2</sub> end of the alkene?

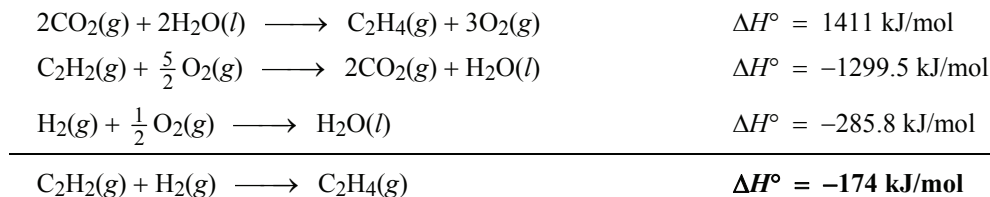
24.42 (a) ketone (b) ester (c) ether

24.43 The four isomers are:



24.44 This is a Hess's Law problem. See Chapter 6.

If we rearrange the equations given and multiply times the necessary factors, we have:



The heat of hydrogenation for acetylene is **-174 kJ/mol**.

- 24.45 (a) Cyclopropane because of the strained bond angles. (The C-C-C angle is 60° instead of 109.5°)  
 (b) Ethylene because of the C=C bond.  
 (c) Acetaldehyde (susceptible to oxidation).



**24.46** To form a hydrogen bond *with water* a molecule must have at least one H–F, H–O, or H–N bond, *or* must contain an O, N, or F atom. The following can form hydrogen bonds with water:

- (a) carboxylic acids      (c) ethers      (d) aldehydes      (f) amines

**24.47** (a) The empirical formula is:

$$\text{H: } 3.2 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 3.17 \text{ mol H}$$

$$\text{C: } 37.5 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 3.12 \text{ mol C}$$

$$\text{F: } 59.3 \text{ g F} \times \frac{1 \text{ mol F}}{19.00 \text{ g F}} = 3.12 \text{ mol F}$$

This gives the formula,  $\text{H}_{3.17}\text{C}_{3.12}\text{F}_{3.12}$ . Dividing by 3.12 gives the empirical formula, **HCF**.

(b) When temperature and amount of gas are constant, the product of pressure times volume is constant (Boyle's law).

$$(2.00 \text{ atm})(0.322 \text{ L}) = 0.664 \text{ atm}\cdot\text{L}$$

$$(1.50 \text{ atm})(0.409 \text{ L}) = 0.614 \text{ atm}\cdot\text{L}$$

$$(1.00 \text{ atm})(0.564 \text{ L}) = 0.564 \text{ atm}\cdot\text{L}$$

$$(0.50 \text{ atm})(1.028 \text{ L}) = 0.514 \text{ atm}\cdot\text{L}$$

The substance does not obey the ideal gas law.

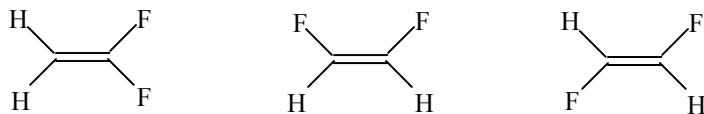
(c) Since the gas does not obey the ideal gas equation exactly, the molar mass will only be approximate. Gases obey the ideal gas law best at lowest pressures. We use the 0.50 atm data.

$$n = \frac{PV}{RT} = \frac{(0.50 \text{ atm})(1.028 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm}/\text{K}\cdot\text{mol})(363 \text{ K})} = 0.0172 \text{ mol}$$

$$\text{Molar mass} = \frac{1.00 \text{ g}}{0.0172 \text{ mol}} = 58.1 \text{ g/mol}$$

This is reasonably close to **C<sub>2</sub>H<sub>2</sub>F<sub>2</sub>** (64 g/mol).

(d) The C<sub>2</sub>H<sub>2</sub>F<sub>2</sub> formula is that of difluoroethylene. Three isomers are possible. The carbon atoms are omitted for simplicity (see Problem 24.17).

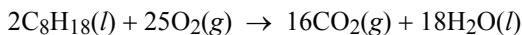


Only the third isomer has no dipole moment.

(e) The name is ***trans*-difluoroethylene**.

- 24.48** (a) rubbing alcohol      (b) vinegar      (c) moth balls      (d) organic synthesis  
 (e) organic synthesis      (f) antifreeze      (g) fuel (natural gas)      (h) synthetic polymers

- 24.49** In any stoichiometry problem, you must start with a balanced equation. The balanced equation for the combustion reaction is:



To find the number of moles of octane in one liter, use density as a conversion factor to find grams of octane, then use the molar mass of octane to convert to moles of octane. The strategy is:

L octane  $\rightarrow$  mL octane  $\rightarrow$  g octane  $\rightarrow$  mol octane

$$1.0 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{0.70 \text{ g C}_8\text{H}_{18}}{1 \text{ mL C}_8\text{H}_{18}} \times \frac{1 \text{ mol C}_8\text{H}_{18}}{114.2 \text{ g C}_8\text{H}_{18}} = 6.13 \text{ mol C}_8\text{H}_{18}$$

Using the mole ratio from the balanced equation, the number of moles of oxygen used is:

$$6.13 \text{ mol C}_8\text{H}_{18} \times \frac{25 \text{ mol O}_2}{2 \text{ mol C}_8\text{H}_{18}} = 76.6 \text{ mol O}_2$$

From the ideal gas equation, we can calculate the volume of oxygen.

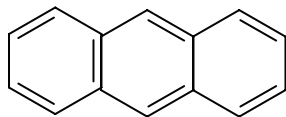
$$V_{\text{O}_2} = \frac{n_{\text{O}_2} RT}{P} = \frac{(76.6 \text{ mol})(293 \text{ K})}{1.00 \text{ atm}} \times \frac{0.0821 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} = 1.84 \times 10^3 \text{ L}$$

Air is only 22% O<sub>2</sub> by volume. Thus, 100 L of air will contain 22 L of O<sub>2</sub>. Setting up the appropriate conversion factor, we find that the volume of air is:

$$\text{? vol of air} = (1.84 \times 10^3 \text{ L O}_2) \times \frac{100 \text{ L air}}{22 \text{ L O}_2} = \mathbf{8.4 \times 10^3 \text{ L air}}$$

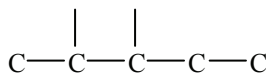
- 24.50 (a)** 2-butyne has **three** C–C sigma bonds.

- (b)** Anthracene is:



There are **sixteen** C–C sigma bonds.

- (c)**

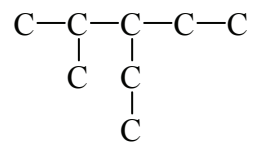


There are **six** C–C sigma bonds.

- 24.51 (a)** A benzene ring has six carbon-carbon bonds; hence, benzene has **six** C–C sigma bonds.

- (b)** Cyclobutane has four carbon-carbon bonds; hence, cyclobutane has **four** sigma bonds.

- (c) Looking at the carbon skeleton of 3-ethyl-2-methylpentane, you should find **seven** C–C sigma bonds.



- 24.52 (a)** The easiest way to calculate the mg of C in CO<sub>2</sub> is by mass ratio. There are 12.01 g of C in 44.01 g CO<sub>2</sub> or 12.01 mg C in 44.01 mg CO<sub>2</sub>.

$$? \text{ mg C} = 57.94 \text{ mg CO}_2 \times \frac{12.01 \text{ mg C}}{44.01 \text{ mg CO}_2} = \mathbf{15.81 \text{ mg C}}$$

Similarly,

$$? \text{ mg H} = 11.85 \text{ mg H}_2\text{O} \times \frac{2.016 \text{ mg H}}{18.02 \text{ mg H}_2\text{O}} = \mathbf{1.326 \text{ mg H}}$$

The mg of oxygen can be found by difference.

$$? \text{ mg O} = 20.63 \text{ mg Y} - 15.81 \text{ mg C} - 1.326 \text{ mg H} = \mathbf{3.49 \text{ mg O}}$$

- (b) Step 1:** Calculate the number of moles of each element present in the sample. Use molar mass as a conversion factor.

$$? \text{ mol C} = (15.81 \times 10^{-3} \text{ g C}) \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 1.316 \times 10^{-3} \text{ mol C}$$

Similarly,

$$? \text{ mol H} = (1.326 \times 10^{-3} \text{ g H}) \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 1.315 \times 10^{-3} \text{ mol H}$$

$$? \text{ mol O} = (3.49 \times 10^{-3} \text{ g O}) \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.18 \times 10^{-4} \text{ mol O}$$

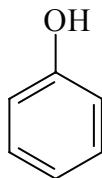
Thus, we arrive at the formula C<sub>1.316×10<sup>-3</sup></sub>H<sub>1.315×10<sup>-3</sup></sub>O<sub>2.18×10<sup>-4</sup></sub>, which gives the identity and the ratios of atoms present. However, chemical formulas are written with whole numbers.

**Step 2:** Try to convert to whole numbers by dividing all the subscripts by the smallest subscript.

$$\text{C: } \frac{1.316 \times 10^{-3}}{2.18 \times 10^{-4}} = 6.04 \approx 6 \quad \text{H: } \frac{1.315 \times 10^{-3}}{2.18 \times 10^{-4}} = 6.03 \approx 6 \quad \text{O: } \frac{2.18 \times 10^{-4}}{2.18 \times 10^{-4}} = 1.00$$

This gives us the empirical formula, **C<sub>6</sub>H<sub>6</sub>O**.

- (c) The presence of six carbons and a corresponding number of hydrogens suggests a benzene derivative. A plausible structure is shown below.

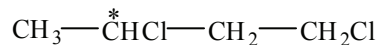


24.53 The structural isomers are:

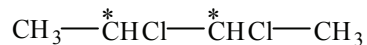
1,2-dichlorobutane



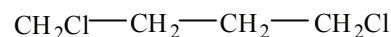
1,3-dichlorobutane



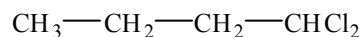
2,3-dichlorobutane



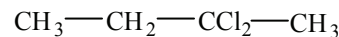
1,4-dichlorobutane



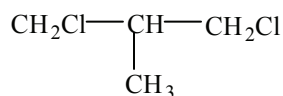
1,1-dichlorobutane



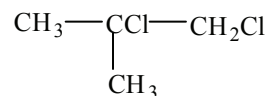
2,2-dichlorobutane



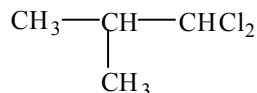
1,3-dichloro-2-methylpropane



1,2-dichloro-2-methylpropane



1,1-dichloro-2-methylpropane



The asterisk identifies the asymmetric carbon atom.

24.54 First, calculate the moles of each element.

$$\text{C: } (9.708 \times 10^{-3} \text{ g CO}_2) \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} = 2.206 \times 10^{-4} \text{ mol C}$$

$$\text{H: } (3.969 \times 10^{-3} \text{ g H}_2\text{O}) \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} = 4.405 \times 10^{-4} \text{ mol H}$$

The mass of oxygen is found by difference:

$$3.795 \text{ mg compound} - (2.649 \text{ mg C} + 0.445 \text{ mg H}) = 0.701 \text{ mg O}$$

$$\text{O: } (0.701 \times 10^{-3} \text{ g O}) \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 4.38 \times 10^{-5} \text{ mol O}$$

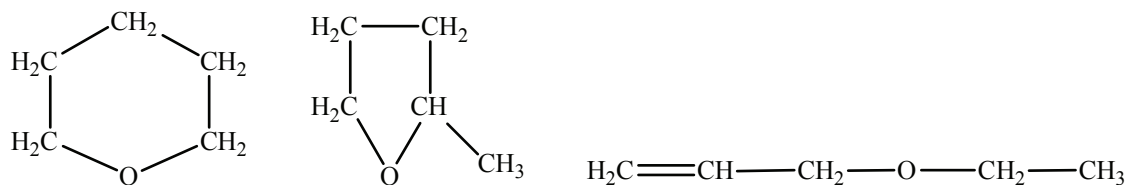
This gives the formula is  $\text{C}_{2.206 \times 10^{-4}}\text{H}_{4.405 \times 10^{-4}}\text{O}_{4.38 \times 10^{-5}}$ . Dividing by the smallest number of moles gives the empirical formula, **C<sub>5</sub>H<sub>10</sub>O**.

We calculate moles using the ideal gas equation, and then calculate the molar mass.

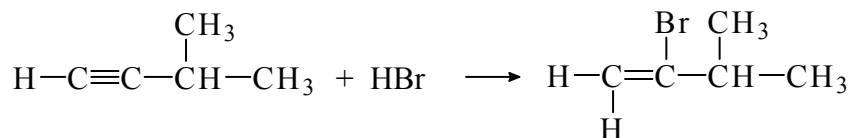
$$n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(0.0898 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(473 \text{ K})} = 0.00231 \text{ mol}$$

$$\text{molar mass} = \frac{\text{g of substance}}{\text{mol of substance}} = \frac{0.205 \text{ g}}{0.00231 \text{ mol}} = \mathbf{88.7 \text{ g/mol}}$$

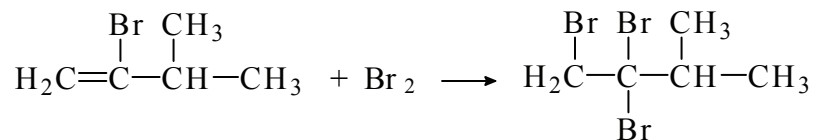
The formula mass of  $C_5H_{10}O$  is 86.13 g, so this is also the molecular formula. Three possible structures are:



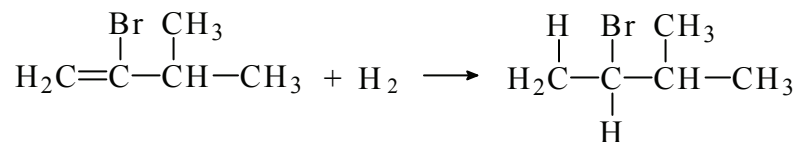
- 24.55 (a)** In comparing the compound in part (a) with the starting alkyne, it is clear that a molecule of HBr has been added to the triple bond. The reaction is:



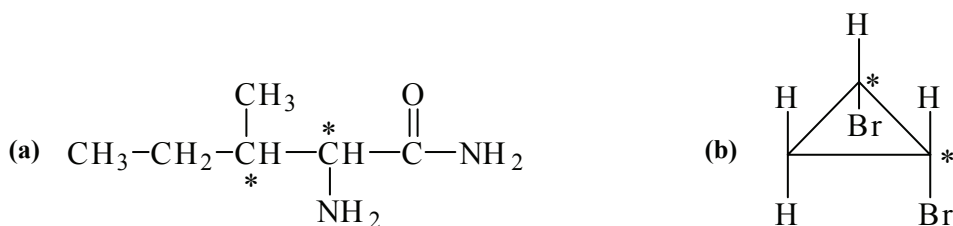
- (b)** This compound can be made from the product formed in part (a) by addition of bromine to the double bond.



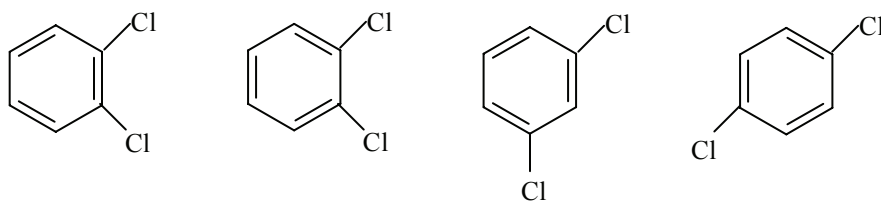
- (c)** This compound can be made from the product of part (a) by addition of hydrogen to the double bond.



- 24.56** A carbon atom is asymmetric if it is bonded to four different atoms or groups. In the given structures the asymmetric carbons are marked with an asterisk (\*).

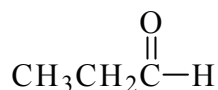


24.57 The isomers are:

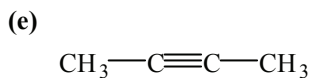
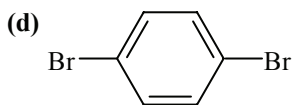
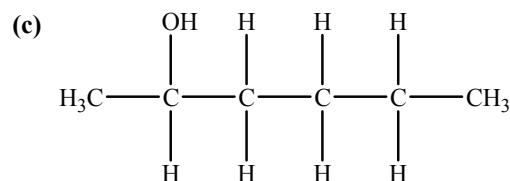
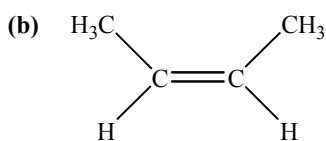
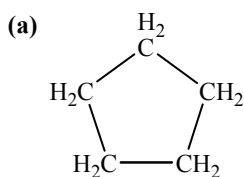


Did you have more isomers? Remember that benzene is a planar molecule; "turning over" a structure does not create a new isomer.

24.58 Acetone is a ketone with the formula,  $\text{CH}_3\text{COCH}_3$ . We must write the structure of an aldehyde that has the same number and types of atoms ( $\text{C}_3\text{H}_6\text{O}$ ). Removing the aldehyde functional group ( $-\text{CHO}$ ) from the formula leaves  $\text{C}_2\text{H}_5$ . This is the formula of an ethyl group. The aldehyde that is a structural isomer of acetone is:



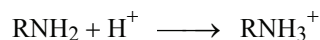
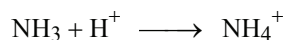
24.59 The structures are:



24.60 (a) alcohol (b) ether (c) aldehyde (d) carboxylic acid (e) amine

24.61 Ethanol has a melting point of  $-117.3^\circ\text{C}$ , a boiling point of  $+78.5^\circ\text{C}$ , and is miscible with water. Dimethyl ether has a melting point of  $-138.5^\circ\text{C}$ , a boiling point of  $-25^\circ\text{C}$  (it is a gas at room temperature), and dissolves in water to the extent of 37 volumes of gas to one volume of water.

24.62 In Chapter 11, we found that salts with their electrostatic intermolecular attractions had low vapor pressures and thus high boiling points. Ammonia and its derivatives (amines) are molecules with dipole-dipole attractions. If the nitrogen has one direct  $\text{N}-\text{H}$  bond, the molecule will have hydrogen bonding. Even so, these molecules will have much weaker intermolecular attractions than ionic species and hence higher vapor pressures. Thus, if we could convert the neutral ammonia-type molecules into salts, their vapor pressures, and thus associated odors, would decrease. Lemon juice contains acids which can react with ammonia-type (amine) molecules to form ammonium salts.



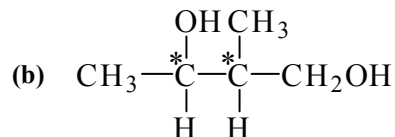
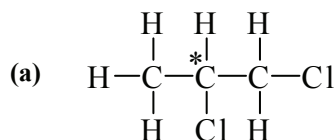
24.63 Cyclohexane readily undergoes halogenation; for example, its reaction with bromine can be monitored by seeing the red color of bromine fading. Benzene does not react with halogens unless a catalyst is present.

24.64 Marsh gas (methane, CH<sub>4</sub>); grain alcohol (ethanol, C<sub>2</sub>H<sub>5</sub>OH); wood alcohol (methanol, CH<sub>3</sub>OH); rubbing alcohol (isopropyl alcohol, (CH<sub>3</sub>)<sub>2</sub>CHOH); antifreeze (ethylene glycol, CH<sub>2</sub>OHCH<sub>2</sub>OH); mothballs (naphthalene, C<sub>10</sub>H<sub>8</sub>); vinegar (acetic acid, CH<sub>3</sub>COOH).

24.65 A mixture of *cis* and *trans* isomers would imply some sort of random addition mechanism in which one hydrogen atom at a time adds to the molecule.

The formation of pure *cis* or pure *trans* isomer indicates a more specific mechanism. For example, a pure *cis* product suggests simultaneous addition of both hydrogen atoms in the form of a hydrogen molecule to one side of the alkene. In practice, the *cis* isomer is formed.

24.66 The asymmetric carbons are shown by asterisks:

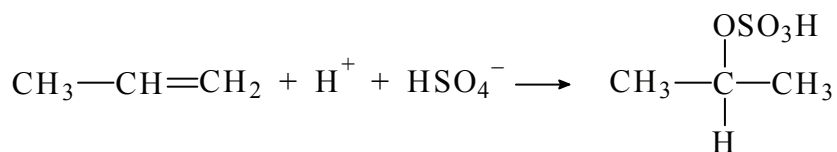


(c) All of the carbon atoms in the ring are asymmetric. Therefore there are **five** asymmetric carbon atoms.

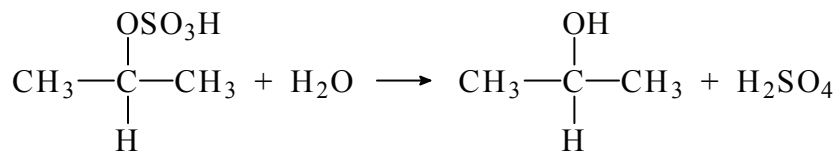
24.67 (a) Sulfuric acid ionizes as follows:



The cation (H<sup>+</sup>) and anion (HSO<sub>4</sub><sup>-</sup>) add to the double bond in propene according to Markovnikov's rule:

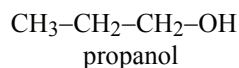


Reaction of the intermediate with water yields isopropanol:



Since sulfuric acid is regenerated, it plays the role of a catalyst.

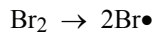
(b) The other structure containing the -OH group is



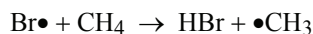
(c) From the structure of isopropanol shown above, we see that the molecule does not have an asymmetric carbon atom. Therefore, isopropanol is achiral.

- (d) Isopropanol is fairly volatile (b.p. = 82.5°C), and the –OH group allows it to form hydrogen bonds with water molecules. Thus, as it evaporates, it produces a cooling and soothing effect on the skin. It is also less toxic than methanol and less expensive than ethanol.

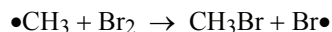
**24.68** The red bromine vapor absorbs photons of blue light and dissociates to form bromine atoms.



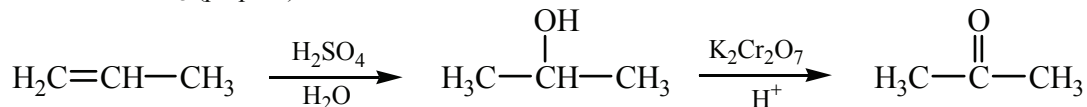
The bromine atoms collide with methane molecules and abstract hydrogen atoms.



The methyl radical then reacts with Br<sub>2</sub>, giving the observed product and regenerating a bromine atom to start the process over again:

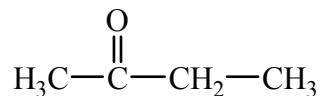


**24.69** From the molar mass of the alkene, we deduce that there can only be 3 carbon atoms. Therefore, the alkene is CH<sub>2</sub>=CH–CH<sub>3</sub> (propene). The reactions are:

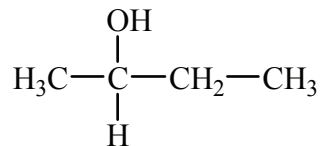


Markovnikov's rule

**24.70** 2-butanone is



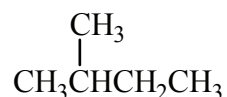
Reduction with LiAlH<sub>4</sub> produces 2-butanol.



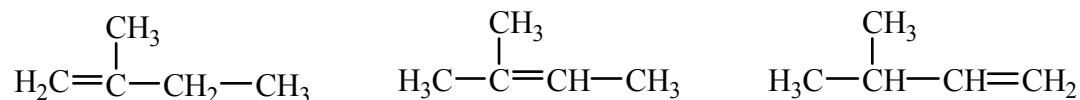
This molecule possesses an asymmetric carbon atom and should be chiral. However, the reduction produces an equimolar *d* and *l* isomers; that is, a racemic mixture (see Section 22.4 of the text). Therefore, the optical rotation as measured in a polarimeter is zero.



24.71 The structures of three alkenes that yield 2-methylbutane



on hydrogenation are:



24.72 To help determine the molecular formula of the alcohol, we can calculate the molar mass of the carboxylic acid, and then determine the molar mass of the alcohol from the molar mass of the acid. Grams of carboxylic acid are given (4.46 g), so we need to determine the moles of acid to calculate its molar mass.

The number of moles in 50.0 mL of 2.27 M NaOH is

$$\frac{2.27 \text{ mol NaOH}}{1000 \text{ mL soln}} \times 50.0 \text{ mL} = 0.1135 \text{ mol NaOH}$$

The number of moles in 28.7 mL of 1.86 M HCl is

$$\frac{1.86 \text{ mol HCl}}{1000 \text{ mL soln}} \times 28.7 \text{ mL} = 0.05338 \text{ mol HCl}$$

The difference between the above two numbers is the number of moles of NaOH reacted with the carboxylic acid.

$$0.1135 \text{ mol} - 0.05338 \text{ mol} = 0.06012 \text{ mol}$$

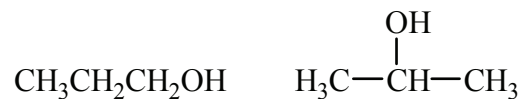
This is the number of moles present in 4.46 g of the carboxylic acid. The molar mass is

$$\mathcal{M} = \frac{4.46 \text{ g}}{0.06012 \text{ mol}} = 74.18 \text{ g/mol}$$

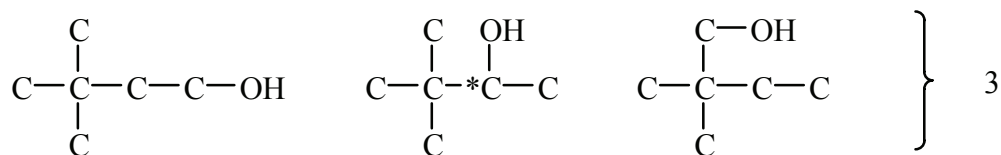
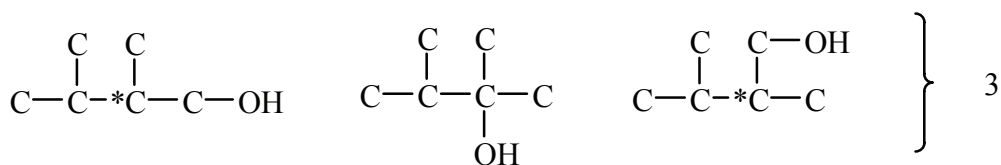
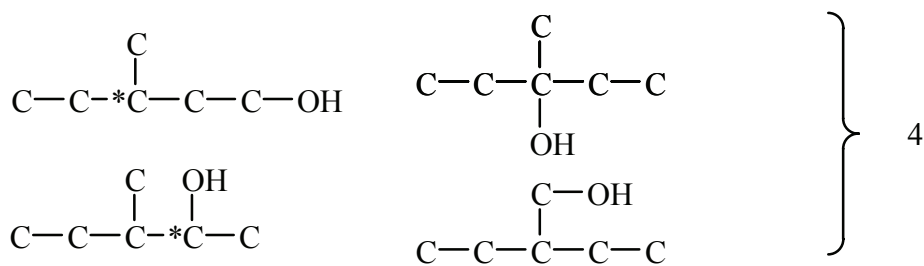
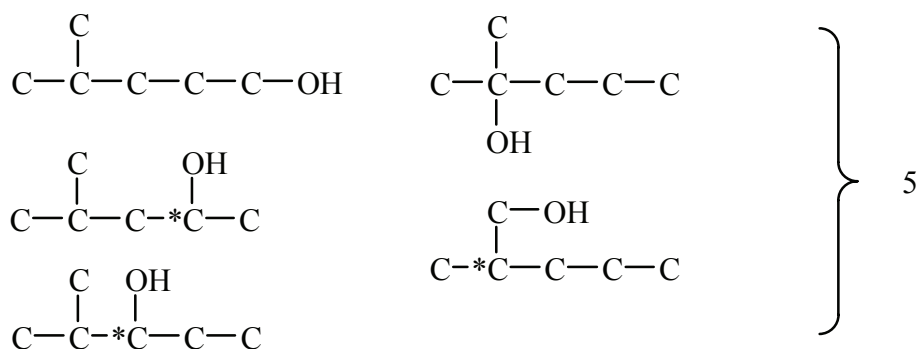
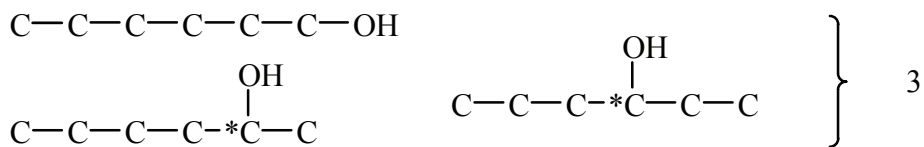
A carboxylic acid contains a  $-\text{COOH}$  group and an alcohol has an  $-\text{OH}$  group. When the alcohol is oxidized to a carboxylic acid, the change is from  $-\text{CH}_2\text{OH}$  to  $-\text{COOH}$ . Therefore, the molar mass of the alcohol is

$$74.18 \text{ g} - 16 \text{ g} + (2)(1.008 \text{ g}) = 60.2 \text{ g/mol}$$

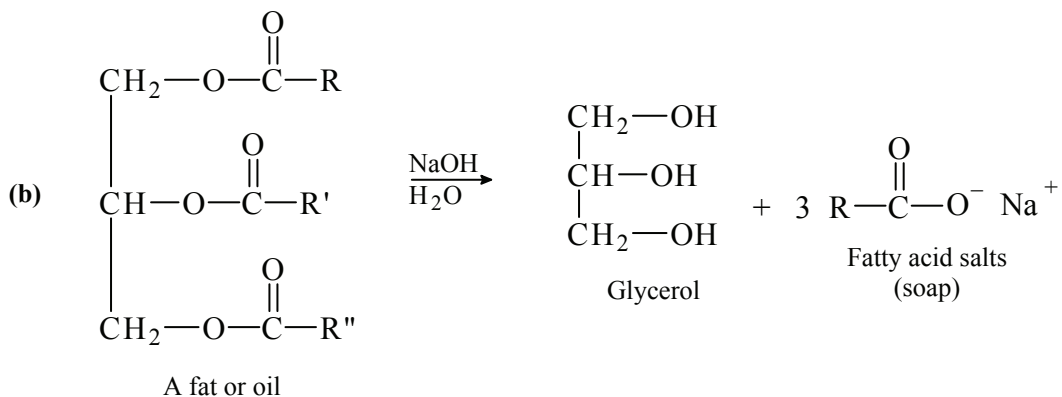
With a molar mass of 60.2 g/mol for the alcohol, there can only be 1 oxygen atom and 3 carbon atoms in the molecule, so the formula must be  $\text{C}_3\text{H}_8\text{O}$ . The alcohol has one of the following two molecular formulas.



**24.73** There are 18 structural isomers and 10 of them are chiral. The asymmetric carbon atoms are marked with an asterisk.



- 24.74 (a) Reaction between glycerol and carboxylic acid (formation of an ester).



- (c) Molecules having more C=C bonds are harder to pack tightly together. Consequently, the compound has a lower melting point.
- (d) H<sub>2</sub> gas with either a heterogeneous or homogeneous catalyst would be used. See Section 13.6 of the text.
- (e) Number of moles of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> reacted is:

$$20.6 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.142 \text{ mol Na}_2\text{S}_2\text{O}_3}{1 \text{ L}} = 2.93 \times 10^{-3} \text{ mol Na}_2\text{S}_2\text{O}_3$$

The mole ratio between I<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is 1:2. The number of grams of I<sub>2</sub> left over is:

$$(2.93 \times 10^{-3} \text{ mol Na}_2\text{S}_2\text{O}_3) \times \frac{1 \text{ mol I}_2}{2 \text{ mol Na}_2\text{S}_2\text{O}_3} \times \frac{253.8 \text{ g I}_2}{1 \text{ mol I}_2} = 0.372 \text{ g I}_2$$

$$\text{Number of grams of I}_2 \text{ reacted is: } (43.8 - 0.372) \text{ g} = 43.4 \text{ g I}_2$$

The *iodine number* is the number of grams of iodine that react with 100 g of corn oil.

$$\text{iodine number} = \frac{43.4 \text{ g I}_2}{35.3 \text{ g corn oil}} \times 100 \text{ g corn oil} = \mathbf{123}$$