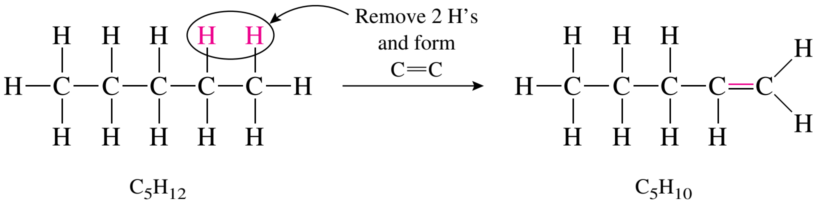
2.4 Degree of Unsaturation

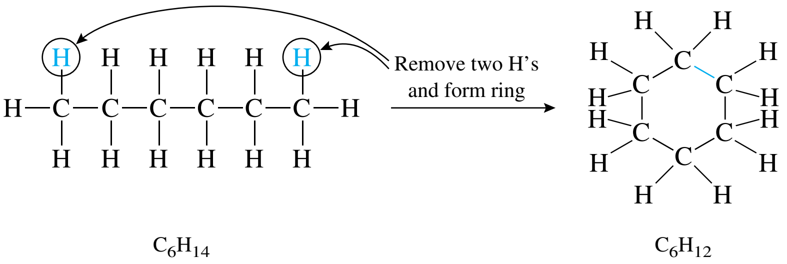
The task of drawing isomers for a particular formula can be made easier by comparing the number of hydrogens with the number of carbons in the formula. Such a comparison allows the calculation of the **degree of unsaturation,** which furnishes useful information about possible structures that will fit the formula (such as whether double bonds can be present) and provides a starting point for drawing isomers.

The isomers shown in Figure 2.4 have the maximum number of hydrogens possible for a compound with six carbons. The maximum number of H's can easily be calculated from the number of C's present. To see how the formula arises, consider a straight, or linear, chain of some number of C's. Each C has two H's bonded to it, with the exception that the two end C's have one additional H, because they are bonded to only one C. Therefore, for *n* carbons, the maximum number of hydrogens is $2n + 2$. The general formula for a hydrocarbon with the maximum number of hydrogens is C_nH_{2n+2}. As an example, C_5H_{12} has the maximum number of H's for 5 C's [$2(5) + 2 = 12$].

Now let's see what happens to the number of hydrogens in a compound if a double bond is present. To form a double bond, a hydrogen must be removed from each of two adjacent carbons. Therefore, a compound with one double bond has two fewer H's than the maximum.



Similarly, to form a ring from a chain of carbons, one H must be removed from both end C's so that they can be bonded together. A compound with a ring also has two fewer H's than the maximum number.



Any compound whose formula has *two* hydrogens less than the maximum number possible ($2n + 2$) must contain *one* double bond or *one* ring. The total number of multiple bonds plus rings is called the **degree of unsaturation (DU)** and is equal to 1 for this case. The DU of a compound can be calculated by using the following formula:

$$DU = \frac{\text{(Maximum possible H's)} - \text{(Actual H's)}}{2}$$

For a hydrocarbon with the formula C_nH_x the degree of unsaturation is

$$DU = \frac{(2n + 2) - x}{2}$$

where

n = actual C's present

x = actual H's present

The DU is very useful when drawing isomers. Let's look at a simple example. Suppose we are asked to draw the constitutional isomers with the formula C_5H_{10}. The DU for C_5H_{10} is $[(2(5) + 2) - 10]/2 = 1$. Therefore, this compound must have one double bond or one ring. Any compound that has five C's and one double bond or one ring will fit the formula. Although C_5H_{12} has only three isomers, having two fewer H's actually increases the number of isomers, because there is now a double bond or a ring to vary.

As structures become more complex, drawing them as a **line** or **Kekulé structure,** in which each bond is shown as a line, becomes more time consuming. The method of grouping together atoms that are bonded to the same atom to give a **condensed structure,** which was presented in Chapter 1, can be used, but even this becomes tedious. *An even faster method, called a* ***skeletal structure,*** *shows the C—C bonds as lines.* Each line is assumed to have a C at each end unless another atom is shown. Hydrogens on the C's are not shown. (However, if a carbon is shown with a C, the hydrogens on it must also be shown as H's.) All other atoms (N, O, Cl, and so on) must be shown, along with any hydrogens bonded to them. Unshared pairs of electrons may or may not be shown. Sometimes the various methods are mixed to emphasize a particular feature. Figure 2.5 shows four of the possible isomers of $C_5H_{10}O$ using these various methods.

Important Convention

PROBLEM 2.5

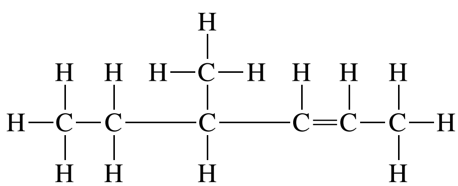
Calculate the DU for these formulas and draw two constitutional isomers for each:

a) $C_{10}H_{22}$ **b)** C_9H_{16} **c)** C_6H_6

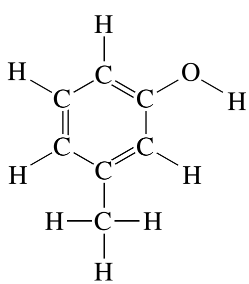
PROBLEM 2.6

Convert these structures to skeletal structures:

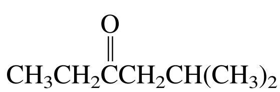
a)



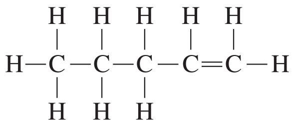
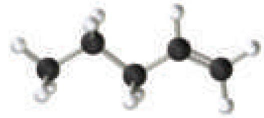
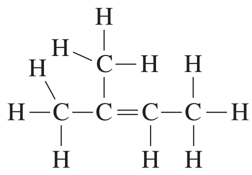
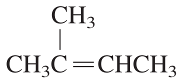
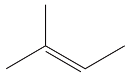
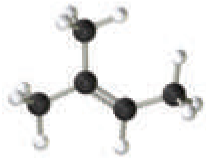
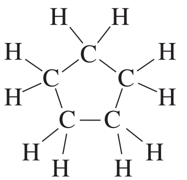
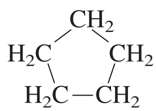
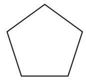
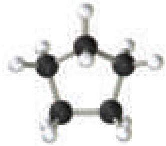
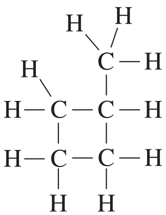
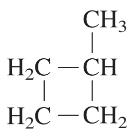
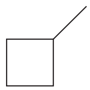
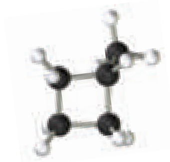
b)



c)



d)

Line structure or Kekulé structure	Condensed structure	Skeletal structure	Molecular model
	$CH_3CH_2CH_2CH{=}CH_2$		
	 or $(CH_3)_2C{=}CHCH_3$		
			
			

ⓐ This represents a C bonded to one other C (at the other end of the line). It must be bonded to three H's to complete its valence.

ⓑ This represents a C bonded to two other C's. It is also bonded to two H's that are not shown.

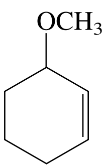
ⓒ This represents a C double bonded to another C. It is also bonded to two H's that are not shown.

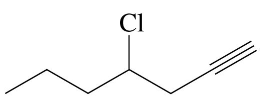
Figure 2.5

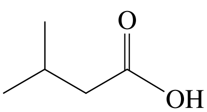
LINE, CONDENSED, AND SKELETAL STRUCTURES AND MOLECULAR MODELS FOR SOME ISOMERS OF C_5H_{10}.

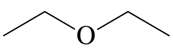
PROBLEM 2.7

Convert these skeletal structures to line structures:

a) 

b) 

c) 

d) 

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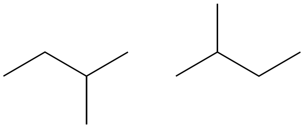
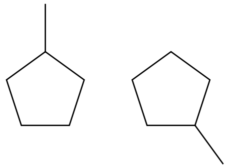
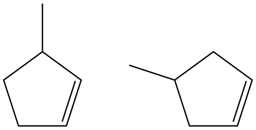
Click *Coached Tutorial Problems* to practice **Drawing Skeletal Structures** and **Recognizing Isomerism.**

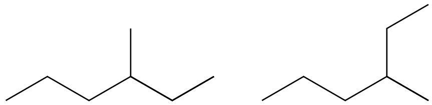
PROBLEM 2.8

Determine whether these structures represent the same compound or isomers:

a) 

b) 

c) 

d) 

e) $CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_3$ $\quad$ $CH_3CH_2CH_2\overset{\overset{CH_3}{|}}{C}HCH_3$

f) $CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_3$ $\quad$ $CH_3CH_2CH_2CH_2\overset{\overset{CH_3}{|}}{C}HCH_3$

The DU can also be calculated for formulas that have atoms other than C and H. Because halogens are monovalent, they are counted as hydrogens in the DU calculation. For example, $C_5H_{11}Cl$ is counted as C_5H_{12} and has DU = 0—it is saturated.

Oxygen is divalent. If an O is added to a structure, it can, for example, be inserted between a C and H or between two C's without changing the number of hydrogens. Therefore, we can ignore oxygens when performing a DU calculation. The DU for $C_6H_{10}O$ is 2, the same as that for C_6H_{10}. This compound must have two double bonds, one triple bond (a triple bond contributes 2 to the DU), one double bond and one ring, or two rings. Although the presence of oxygen is ignored in calculating the DU, oxygen can, of course, be involved in the features, double bonds or rings, that contribute to the DU. Figure 2.6 shows several isomers for $C_6H_{10}O$.

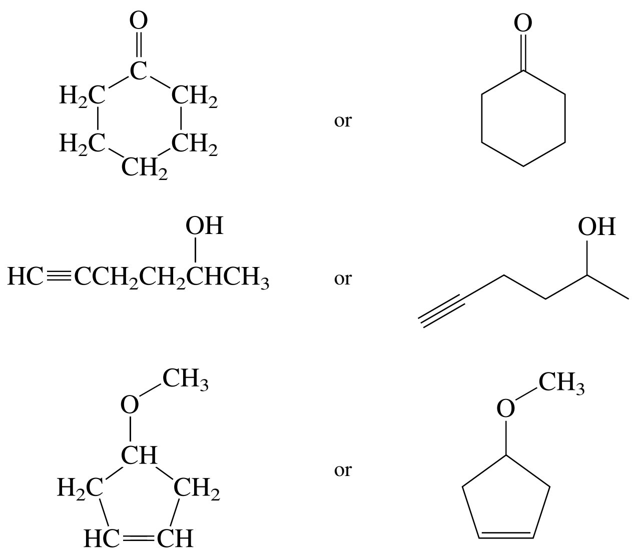


Figure 2.6

THREE (OF MANY) CONSTITUTIONAL ISOMERS OF $C_6H_{10}O$.

Finally, let's consider the effect of nitrogen on a DU calculation. Nitrogen is trivalent. If an N is added to a structure by inserting it between two atoms, one H must also be added to satisfy the third valence of the N. Therefore, each nitrogen that is present in a compound increases the maximum number of H's by one. For example, the maximum number of H's for $C_{10}H_{15}N$ is $2(10) + 2 + 1 = 23$. The DU is $(23 - 15)/2 = 4$.

You must be very careful when using a shorthand method to show structures. Beginning organic chemistry students commonly forget about hydrogens or do not recognize other features of such structures. *It is often a good idea to redraw the structures more completely, showing each carbon and all the hydrogens, until you are very comfortable with them and can automatically picture all the features of the molecule.*

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PRACTICE PROBLEM 2.2

Calculate the DU for $C_8H_{13}BrO$.

Solution

Br counts as an H and O can be ignored, so calculate as though the formula were C_8H_{14}. $DU = \frac{1}{2}[(2)(8) + 2 - 14] = 2$.

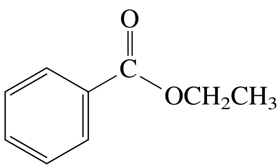
PROBLEM 2.9

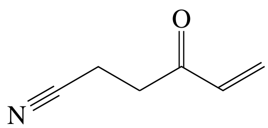
Calculate the DU for these formulas and draw two constitutional isomers for each:

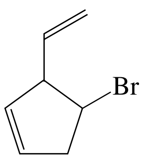
a) $C_{10}H_{20}O$ **b)** C_6H_9N **c)** $C_7H_{14}F_2$
d) C_6H_8ClN **e)** $C_9H_{15}NO$

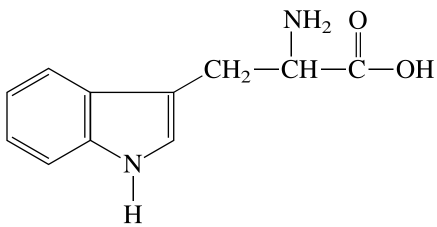
PROBLEM 2.10

Determine the DU for each of these structures:

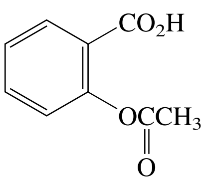
a)


b)


c)


d)


Tryptophan (an amino acid)

e)


Acetylsalicylic acid (aspirin)

BioLink