Chapter 21 Review Questions and Text Homework Solutions

Review Questions

1. A hydrocarbon is a compound composed of only carbon and hydrogen. A saturated hydro-carbon has only carbon-carbon single bonds in the molecule. An unsaturated hydrocarbon has one or more carbon-carbon multiple bonds but may also contain carbon-carbon single bonds. A normal hydrocarbon has one chain of consecutively bonded carbon atoms, with each carbon atom in the chain bonded to one or two other carbon atoms. A branched hydrocarbon has at least one carbon atom in the structure that forms bonds to three or four other carbon atoms; the structure is not one continuous chain of carbon atoms.

An alkane is a saturated hydrocarbon composed of only C−C and C−H single bonds. Each carbon in an alkane is bonded to four other atoms (either C or H atoms). If the compound contains a ring in the structure and is composed of only C−C and C−H single bonds, then it is called a cyclic alkane.

Alkanes: general formula = C_nH_{2n+2}; all carbons are sp^3 hybridized; bond angles = 109.5˚

Cyclic alkanes: general formula C_nH_{2n} (if only one ring is present in the compound); all carbons are sp^3 hybridized; prefers 109.5˚ bond angles, but rings with three carbons or four carbons or five carbons are forced into bond angles less than 109.5˚.

In cyclopropane, a ring compound made up of three carbon atoms, the bond angles are forced into 60˚ in order to form the three-carbon ring. With four bonds to each carbon, the carbons prefer 109.5˚ bond angles. This just can't happen for cyclopropane. Because cyclopropane is forced to form bond angles smaller than it prefers, it is very reactive.

The same is true for cyclobutane. Cyclobutane is composed of a four-carbon ring. In order to form a ring compound with four carbons, the carbons in the ring are forced to form 90˚ bond angles; this is much smaller than the preferred 109.5˚ bond angles.

Cyclopentane (five-carbon rings) also has bond angles slightly smaller than 109.5˚, but they are very close (108˚), so cyclopentane is much more stable than cyclopropane or cyclobutane. For rings having six or more carbons, the observed bonds are all 109.5˚.

Straight chain hydrocarbons just indicates that there is one chain of consecutively bonded C-atoms in the molecule. They are not in a straight line which infers 180˚ bond angles. The bond angles are the predicted 109.5˚.

To determine the number of hydrogens bonded to the carbons in cyclic alkanes (or any alkane where they may have been omitted), just remember that each carbon has four bonds. In cycloalkanes, only the C−C bonds are shown. It is assumed you know that the remaining bonds on each carbon are C−H bonds. The number of C−H bonds is that number required to give the carbon four total bonds.

2.   Alkenes are unsaturated hydrocarbons that contain a carbon-carbon double bond. Carbon-carbon single bonds may also be present. Alkynes are unsaturated hydrocarbons that contain a carbon-carbon triple bond.

Alkenes: C_nH_{2n} is the general formula. The carbon atoms in the C=C bond exhibit 120° bond angles. The double-bonded carbon atoms are sp^2 hybridized. The three sp^2 hybrid orbitals form three sigma bonds to the attached atoms. The unhybridized p atomic orbital on each sp^2 hybridized carbon overlap side to side to form the π bond in the double bond. Because the p orbitals must overlap parallel to each other, there is no rotation in the double bond (this is true whenever π bonds are present). See Figure 21.7 for the bonding in the simplest alkene, C_2H_4.

Alkynes: C_nH_{2n-2} is the general formula. The carbon atoms in the C−C bond exhibit 180° bond angles. The triple bonded carbons are sp hybridized. The two sp hybrid orbitals form two sigma bonds to the bonded atoms. The two unhybridized p atomic orbitals overlap with two unhybridized p atomic orbitals on the other carbon in the triple bond, forming two π bonds. If the z-axis is the internuclear axis, then one π bond would form by parallel overlap of p_y orbitals on each carbon and the other π bond would form by parallel overlap of p_x orbitals. As is the case with alkenes, alkynes have restricted rotation due to the π bonds. See Figure 21.10 for the bonding in the simplest alkyne, C_2H_2.

Any time a multiple bond or a ring structure is added to a hydrocarbon, two hydrogens are lost from the general formula. The general formula for a hydrocarbon having one double bond and one ring structure would lose four hydrogens from the alkane general formula. The general formula would be C_nH_{2n-2}.

3.   Aromatic hydrocarbons are a special class of unsaturated hydrocarbons based on the benzene ring. Benzene has the formula C_6H_6. It is a planar molecule (all atoms are in the same plane). The bonding in benzene is discussed in detail in Section 4.7 of the text. Figures 4.57-4.59 detail the bonding in benzene.

C_6H_6, has $6(4) + 6(1) = 30$ valence electrons. The two resonance Lewis structures for benzene are:
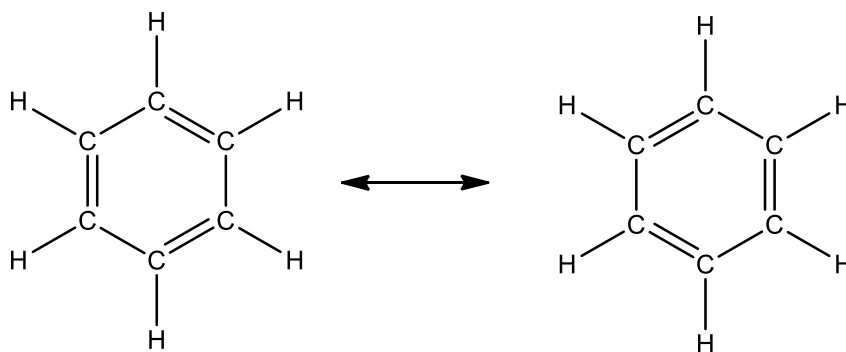

These are abbreviated as:
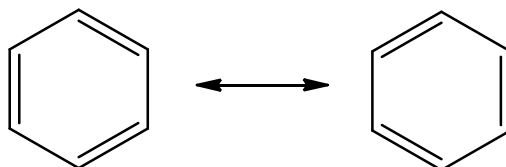
Each carbon in benzene is attached to three other atoms; it exhibits trigonal planar geometry with 120° bond angles. Each carbon is sp^2 hybridized. The sp^2 hybrid orbitals form three sigma bonds to each carbon. The unhybridized p atomic orbital on each carbon overlap side to side with unhybridized p orbitals on adjacent carbons to form the π bonds. All six of the carbons in the six-membered ring have one unhybridized p atomic orbital. All six of the unhybridized p orbitals overlap side to side to give a ring of electron density above and below the six-membered ring of benzene.

The six π electrons in the π bonds in benzene can roam about above and below the entire ring surface; these π electrons are delocalized. This is important because all six carbon-carbon bonds in benzene are equivalent in length and strength. The Lewis structures say something different (three of the bonds are single and three of the bonds are double). This is not correct. To explain the equivalent bonds, the π bonds can't be situated between two carbon atoms as is the case in alkenes and alkynes; that is, the π bonds can't be localized. Instead, the six π electrons can roam about over a much larger area; they are delocalized over the entire surface of the molecule. All this is implied in the following shorthand notation for benzene.
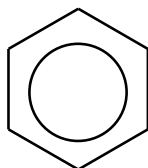
4.   A short summary of the nomenclature rules for alkanes, alkenes, and alkynes follow. See the text for details.

a. Memorize the base names of C_1–C_{10} carbon chains (see Table 21.1). When the C_1–C_{10} carbon chains are named as a substituent, change the –ane suffix to–yl.

b. Memorize the additional substituent groups in Table 21.2.

c. Names are based on the longest continuous carbon chain in the molecule. Alkanes use the suffix –ane, alkenes end in –ene, and alkynes end in –yne.

d. To indicate the position of a branch or substituent, number the longest chain of carbons consecutively in order to give the lowest numbers to the substituents or branches. Identify the number of the carbon that the substituent is bonded to by writing the number in front of the name of the substituent.

e. Name substituents in alphabetical order.

f. Use a prefix (di–, tri–, tetra–, etc.) to indicate the number of a substituent if more than one is present. Note that if, for example, three methyl substituent groups are bonded to carbons on the longest chain, use the tri-prefix but also include three numbers indicating the positions of the methyl groups on the longest chain. Also note that prefixes like di–, tri–, tetra–, etc. are not considered when determining the alphabetical order of the substituent groups.

g. A cyclic hydrocarbon is designated by the prefix cyclo–.

h.   For alkenes and alkynes, the position of the double or triple bond is indicated with a number placed directly in front of the base name of the longest chain. If more than one multiple bond is present, the number of multiple bonds is indicted in the base name using the prefix di–, tri–, tetra–, etc., but also a number for the position of each multiple bond is indicated in front of the base name. When numbering the longest chain, if double or triple bonds are present, give the multiple bonds the lowest number possible (not the substituent groups).

This is a start. As you will find out, there are many interesting situations that can come up which aren't covered by these rules. We will discuss them as they come up.

For aromatic nomenclature rules, reference Section 21.3 of the text.

The errors in the names are discussed below.

a.   The longest chain gives the base name.

b.   The suffix –ane indicates only alkanes. Alkenes and alkynes have different suffixes as do other "types" of organic compounds.

c.   Smallest numbers are used to indicate the position of substituents.

d.   Numbers are required to indicate the positions of double or triple bonds.

e.   Multiple bonds (double or triple) get the lowest number.

f.   The term *ortho–* in benzene nomenclature indicates substituents in the benzene ring bonded to C–1 and C–2. The term *meta–* describes C–1 and C–3 substituent groups, while *par*a– is used for C–1 and C–4 substituent groups.

6.   Resonance: All atoms are in the same position. Only the positions of π electrons are different.

Isomerism: Atoms are in different locations in space.

Isomers are distinctly different substances. Resonance is the use of more than one Lewis structure to describe the bonding in a single compound. Resonance structures are **not** isomers.

Structural isomers: Same formula but different bonding, either in the kinds of bonds present or the way in which the bonds connect atoms to each other.

Geometrical isomers: Same formula and same bonds, but differ in the arrangement of atoms in space about a rigid bond or ring.

To distinguish isomers from molecules that differ by rotations about some bonds, name them. If two structures have different names, they are different isomers (different compounds). If the two structures have the same name, then they are the same compound. The two compounds may look different, but if they have the same names, they are the same compounds that only differ by some rotations about single bonds in the molecule.

An alkene and a cyclic alkane having the C_4H_8 formula are:

$$H_2C =\!\!= CHCH_2CH_3$$
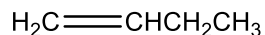
1-butene

cyclobutane (2 hydrogens
are bonded to each carbon)

For *cis*-trans isomerism (geometric isomerism), you must have at least two carbons with restricted rotation (double bond or ring) that each have two different groups bonded to it. The *cis* isomer will generally have the largest groups bonded to the two carbons with restricted rotation on the same side of the double bond or ring. The *trans* isomer generally has the largest groups bonded to the two carbons with restricted rotation on opposite sides of the double bond or ring.

For alcohols and ethers, consider the formula C_3H_8O. An alcohol and an ether that have this formula are:

$$\overset{\displaystyle OH}{\underset{\displaystyle}{CH_3CH_2CH_2}}$$

alcohol

$$CH_3 - O - CH_2CH_3$$
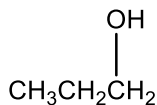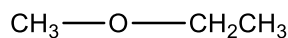
ether

For aldehydes and ketones, consider the formula C_4H_8O. An aldehyde and a ketone that have this formula are:

$$\overset{\displaystyle O}{\overset{\displaystyle \|}{CH_3CH_2CH_2CH}}$$

aldehyde

$$\overset{\displaystyle O}{\overset{\displaystyle \|}{CH_3CH_2CCH_3}}$$
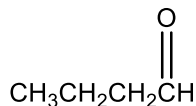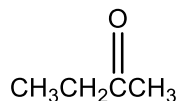
ketone

Esters are structural isomers of carboxylic acids. An ester and a carboxylic acid having the formula $C_2H_4O_2$ are:

$$\overset{\displaystyle O}{\overset{\displaystyle \|}{CH_3COH}}$$

carboxylic acid

$$CH_3 - O - \overset{\displaystyle O}{\overset{\displaystyle \|}{CH}}$$
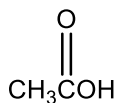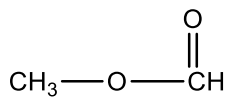
ester

Optical isomers: The same formula and the same bonds, but the compounds are nonsuper-imposable mirror images of each other.   The key to identifying optical isomerism in organic compounds is to look for a tetrahedral carbon atom with four different substituents attached. When four different groups are bonded to a carbon atom, then a nonsuperimposable mirror image does exist.

1−bromo−1−chloroethane

$$CH_3—\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\overset{*}{}—CH_3$$

Br—C*—CH₃
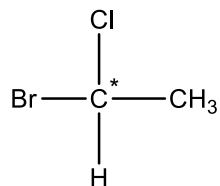
The carbon with the asterisk has 4 different groups bonded to it (1−Br; 2−Cl; 3−CH₃; 4−H). This compound has a nonsuperimposable mirror image.
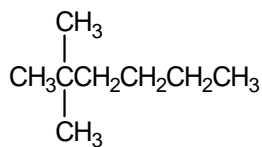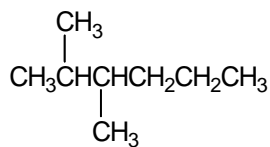
1−bromo−2−chloroethane

Br—C—C—H
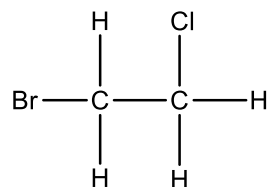
Neither of the two carbons have four different groups bonded to it. The mirror image of this molecule will be superimposable (it does not exhibit optical isomerism).

Text Homework

16.   a.
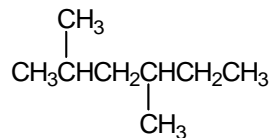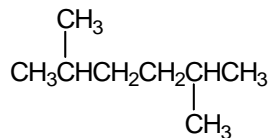
$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_2CH_2CH_2CH_3$$

2,2-dimethylhexane

$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}H\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CH_2CH_3$$

2,3-dimethylhexane

$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CH_3$$

2,4-dimethylhexane

$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3$$

2,5-dimethylhexane

$$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_2CH_2CH_3$$

3,3-dimethylhexane

$$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}H\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CH_3$$

3,4-dimethylhexane

$$CH_3CH_2\overset{\overset{\displaystyle CH_2CH_3}{|}}{C}HCH_2CH_2CH_3$$

3-ethylhexane

b.

H₃C   CH₃

CH₃—C—CH—CH₂—CH₃
      |
      CH₃

2,2,3-trimethylpentane

CH₃   CH₃

CH₃—C—CH₂—CH—CH₃
      |
      CH₃

2,2,4-trimethylpentane

CH₃ CH₃

CH₃—CH—C—CH₂—CH₃
          |
          CH₃

2,3,3-trimethylpentane

CH₃ CH₃ CH₃

CH₃—CH—CH—CH—CH₃

2,3,4-trimethylpentane

CH₃ CH₂CH₃

CH₃—CH—CH—CH₂—CH₃

3-ethyl-2-methylpentane

CH₂CH₃

CH₃—CH₂—C—CH₂—CH₃
          |
          CH₃
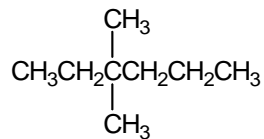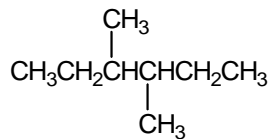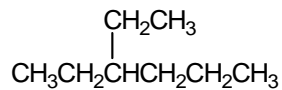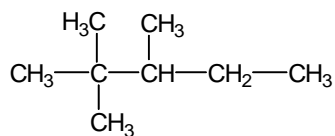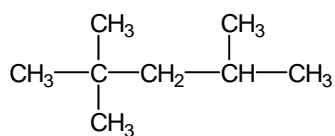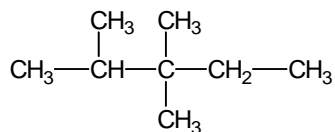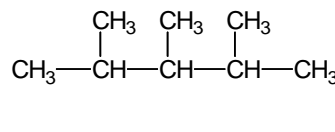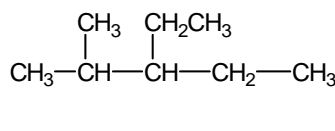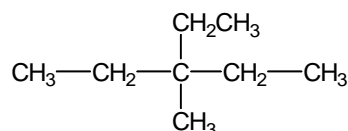
3-ethyl-3-methylpentane

34.   a.   All these structures have the formula C_5H_8. The compounds with the same physical
           properties will be the compounds that are identical to each other, i.e., compounds that only
           differ by rotations of C–C single bonds. To recognize identical compounds, name them. The
           names of the compounds are:

           i.   trans-1,3-pentadiene   ii.   cis-1,3-pentadiene

           iii.   cis-1,3-pentadiene   iv.   2-methyl-1,3-butadiene

   Compounds ii and iii are identical compounds, so they would have the same physical
      properties.

      b.   Compound i is a trans isomer because the bulkiest groups off the $C_3=C_4$ double bond are on
           opposite sides of the double bond.

      c.   Compound iv does not have carbon atoms in a double bond that each have two different groups
           attached. Compound iv does not exhibit cis-trans isomerism.

42.   The *cis* isomer has the CH_3 groups on the same side of the ring. The *trans* isomer has the CH_3
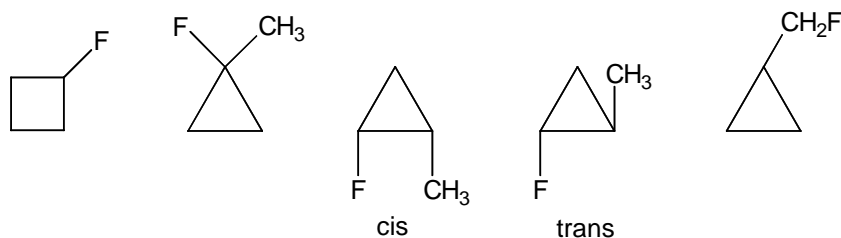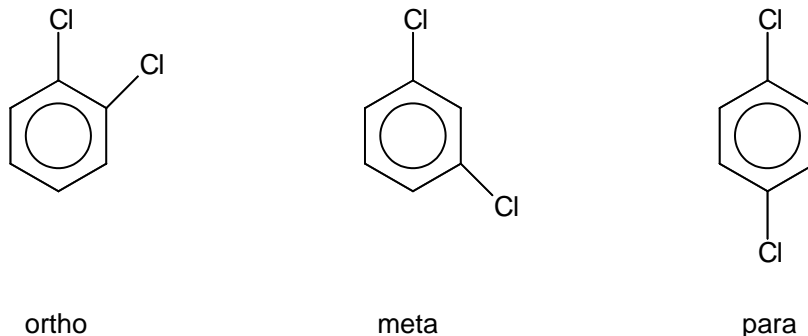   groups on opposite sides of the ring.
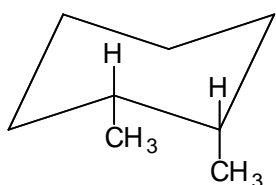
cis
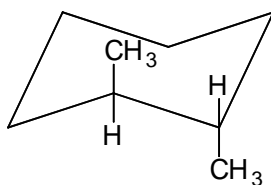
trans

The cyclic structural and geometric isomers of C_4H_7F are:

46.   a.

ortho   meta   para

b. There are three trichlorobenzenes (1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, and 1,3,5-trichlorobenzene).

c. The meta isomer will be very difficult to synthesize.

d. 1,3,5-Trichlorobenzene will be the most difficult to synthesize since all Cl groups are meta to each other in this compound.

62.   a.   The two possible products for the addition of HOH to this alkene are:

major product   minor product
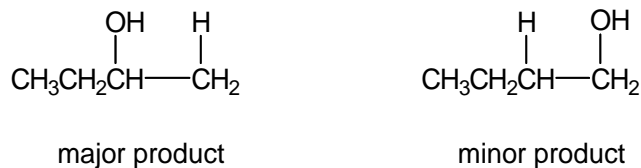
We would get both products in this reaction. Using the rule given in the problem, the first compound listed is the major product. In the reactant, the terminal carbon has more hydrogens bonded to it (2 versus 1), so H forms a bond to this carbon, and OH forms a bond to the other carbon in the double bond for the major product. We will list only the major product for the remaining parts to this problem.
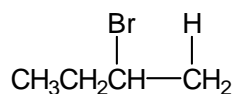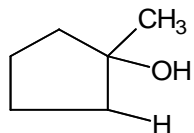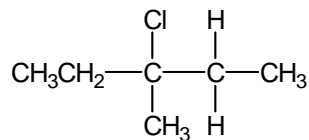
b.   c.
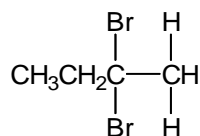
d.

e.

64.   When $CH_2{=}CH_2$ reacts with HCl, there is only one possible product, chloroethane. When Cl_2 is reacted with CH_3CH_3 (in the presence of light), there are six possible products because any number of the six hydrogens in ethane can be substituted for by Cl. The light-catalyzed substitution reaction is very difficult to control; hence it is not a very efficient method of producing monochlorinated alkanes.

104.
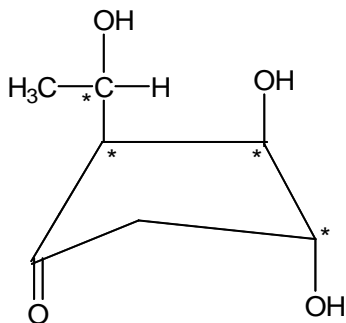
The compound has four chiral carbon atoms (marked with *). The fourth group bonded to the three chiral carbon atoms in the ring is a hydrogen atom.

154.   The five chiral carbons are marked with an asterisk.
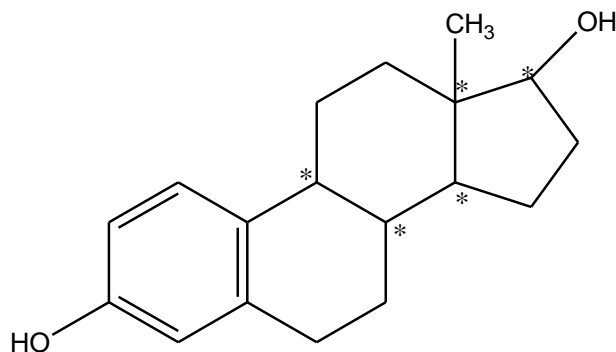
Each of these five carbons has four different groups bonded to it. The fourth bond that is not shown for any of the five chiral carbons is a C–H bond.