CHAPTER 22

ORGANIC AND BIOLOGICAL MOLECULES

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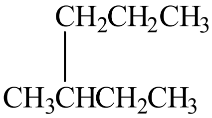
Questions

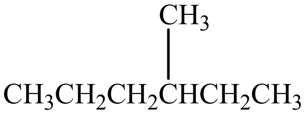
1. a. 1-sec-butylpropane



$CH_3\overset{\overset{CH_2CH_2CH_3}{|}}{C}HCH_2CH_3$

3-methylhexane is correct.

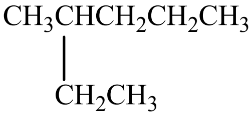
b. 4-methylhexane



$CH_3CH_2CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_3$

3-methylhexane is correct.

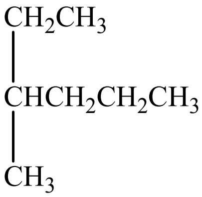
c. 2-ethylpentane



$CH_3\underset{\underset{CH_2CH_3}{|}}{C}HCH_2CH_2CH_3$

3-methylhexane is correct.

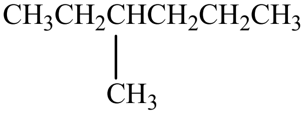
d. 1-ethyl-1-methylbutane



$\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2CH_3}{|}}{C}}HCH_2CH_2CH_3$

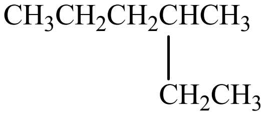
3-methylhexane is correct.

e. 3-methylhexane



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

f. 4-ethylpentane

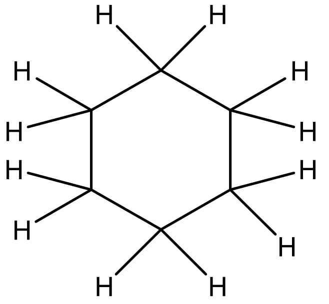


$CH_3CH_2CH_2\underset{\underset{CH_2CH_3}{|}}{C}HCH_3$

3-methylhexane is correct.

All six of these compounds are the same. They only differ from each other by rotations about one or more carbon-carbon single bonds. Only one isomer of C_7H_{16} is present in all of these names, 3-methylhexane.

2. a. C_6H_{12} can exhibit structural, geometric, and optical isomerism. Two structural isomers (of many) are:

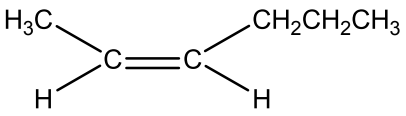


cyclohexane

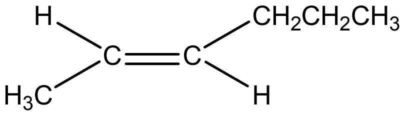
$CH_2{=}CHCH_2CH_2CH_2CH_3$

1-hexene

The structural isomer 2-hexene (plus others) exhibits geometric isomerism.

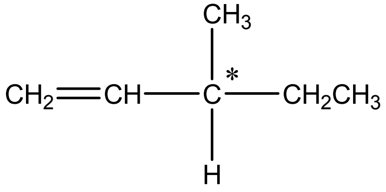


cis



trans

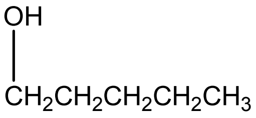
The structural isomer 3-methyl-1-pentene exhibits optical isomerism (the asterisk marks the chiral carbon).



$$CH_2{=}CH{-}\overset{CH_3}{\underset{H}{C^*}}{-}CH_2CH_3$$

Optical isomerism is also possible with some of the cyclobutane and cyclopropane structural isomers.

b. $C_5H_{12}O$ can exhibit structural and optical isomerism. Two structural isomers (of many) are:



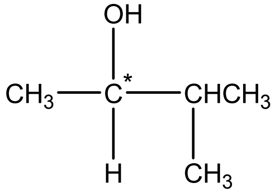
$$\overset{OH}{CH_2}CH_2CH_2CH_2CH_3$$

1-pentanol

$CH_3{-}O{-}CH_2CH_2CH_2CH_3$

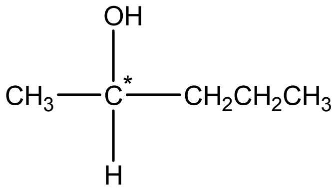
butyl methyl ether

Two of the optically active isomers having a $C_5H_{12}O$ formula are:



$$CH_3{-}\overset{OH}{\underset{H}{C^*}}{-}\underset{CH_3}{CH}CH_3$$

3-methyl-2-butanol

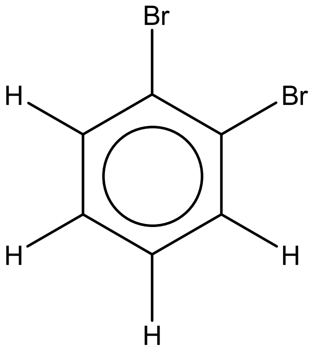


$$CH_3{-}\overset{OH}{\underset{H}{C^*}}{-}CH_2CH_2CH_3$$

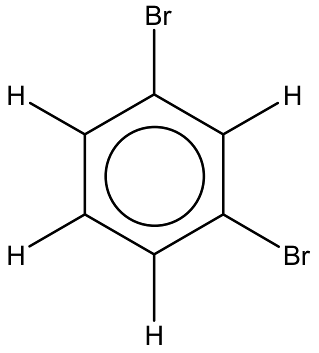
2-pentanol

No isomers of $C_5H_{12}O$ exhibit geometric isomerism because no double bonds or ring structures are possible with 12 hydrogens present.

c. We will assume the structure having the $C_6H_4Br_2$ formula is a benzene ring derivative. $C_6H_4Br_2$ exhibits structural isomerism only. Two structural isomers of $C_6H_4Br_2$ are:



o-dibromobenzene
or 1,2-dibromobenzene

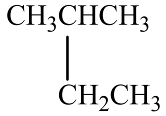


m-dibromobenzene
or 1,3-dibromobenzene

The benzene ring is planar and does not exhibit geometric isomerism. It also does not exhibit optical activity. All carbons only have three atoms bonded to them; it is impossible for benzene to be optically active.

Note: There are possible noncyclic structural isomers having the formula $C_6H_4Br_2$. These noncyclic isomers can, in theory, exhibit geometrical and optical isomerism. But they are beyond the introduction to organic chemistry given in this text.

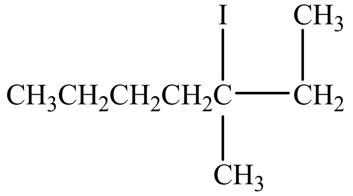
3. a.



$$\begin{array}{l} CH_3CHCH_3 \\ \quad\;\; | \\ \quad\;\; CH_2CH_3 \end{array}$$

The longest chain is 4 carbons long. The correct name is 2-methylbutane.

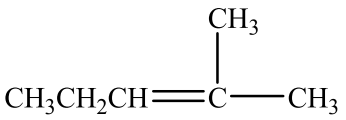
b.



$$\begin{array}{rcl} & I & CH_3 \\ & | & | \\ CH_3CH_2CH_2CH_2 & C & \!\!-\!\!-\!\!-\, CH_2 \\ & | & \\ & CH_3 & \end{array}$$

The longest chain is 7 carbons long, and we would start the numbering system at the other end for lowest possible numbers. The correct name is 3-iodo-3-methylheptane.

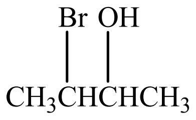
c.



$$CH_3CH_2CH=\overset{\overset{CH_3}{|}}{C}-CH_3$$

This compound cannot exhibit cis–trans isomerism since one of the double bonded carbons has the same two groups (CH_3) attached. The numbering system should also start at the other end to give the double bond the lowest possible number. 2-methyl-2-pentene is correct.

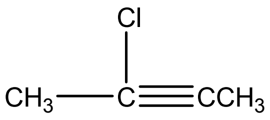
d.



$$CH_3\overset{\overset{Br}{|}}{C}H\overset{\overset{OH}{|}}{C}HCH_3$$

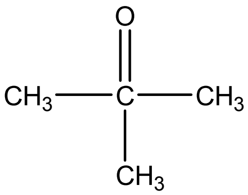
The OH functional group gets the lowest number. 3-bromo-2-butanol is correct.

4. a. 2-Chloro-2-butyne would have 5 bonds to the second carbon. Carbon never expands its octet.



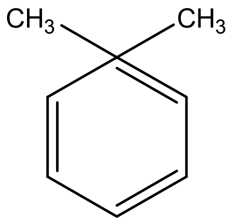
$$CH_3-\overset{\overset{Cl}{|}}{C}\equiv CCH_3$$

b. 2-Methyl-2-propanone would have 5 bonds to the second carbon.

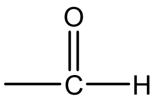


$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{O}{\|}}{C}}-CH_3$$

c. Carbon-1 in 1,1-dimethylbenzene would have 5 bonds.



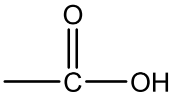
d. You cannot have an aldehyde functional group off a middle carbon in a chain. Aldehyde groups:



$$-\overset{\overset{O}{\|}}{C}-H$$

can only be at the beginning and/or the end of a chain of carbon atoms.

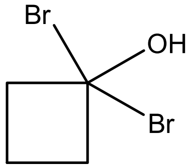
e. You cannot have a carboxylic acid group off a middle carbon in a chain. Carboxylic groups:



$$-\overset{O}{\overset{\|}{C}}-OH$$

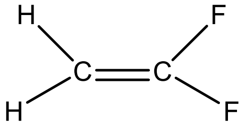
must be at the beginning and/or the end of a chain of carbon atoms.

f. In cyclobutanol, the 1 and 5 positions refer to the same carbon atom. 5,5-Dibromo-1-cyclobutanol would have five bonds to carbon-1. This is impossible; carbon never expands its octet.



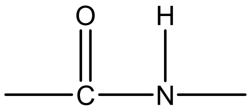
5. Hydrocarbons are nonpolar substances exhibiting only London dispersion forces. Size and shape are the two most important structural features relating to the strength of London dispersion forces. For size, the bigger the molecule (the larger the molar mass), the stronger are the London dispersion forces, and the higher is the boiling point. For shape, the more branching present in a compound, the weaker are the London dispersion forces, and the lower is the boiling point.

6. In order to hydrogen-bond, the compound must have at least one N–H, O–H or H–F covalent bond in the compound. In Table 22.4, alcohols and carboxylic acids have an O-H covalent bond, so they can hydrogen-bond. In addition, primary and secondary amines have at least one N-H covalent bond, so they can hydrogen-bond.



CH_2CF_2 cannot form hydrogen bonds because it has no hydrogens covalently bonded to the fluorine atoms.

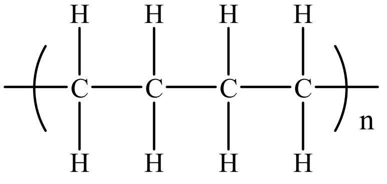
7. The amide functional group is:



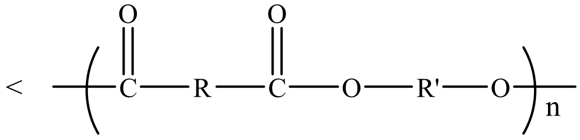
$$-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-$$

When the amine end of one amino acid reacts with the carboxylic acid end of another amino acid, the two amino acids link together by forming an amide functional group. A polypeptide has many amino acids linked together, with each linkage made by the formation of an amide functional group. Because all linkages result in the presence of the amide functional group, the resulting polymer is called a polyamide. For nylon, the monomers also link together by forming the amide functional group (the amine end of one monomer reacts with the carboxylic acid end of another monomer to give the amide functional group linkage). Hence nylon is also a polyamide.

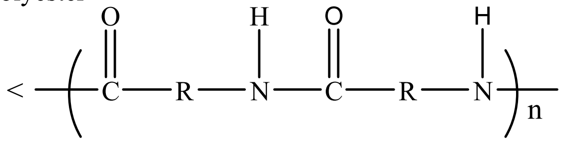
The correct order of strength is:



polyhydrocarbon
weakest fibers



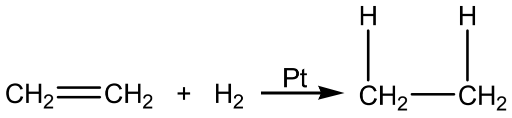
polyester



polyamide
strongest fibers

The difference in strength is related to the types of intermolecular forces present. All these types of polymers have London dispersion forces. However, the polar ester group in polyesters and the polar amide group in polyamides give rise to additional dipole forces. The polyamide has the ability to form relatively strong hydrogen-bonding interactions, hence why it would form the strongest fibers.

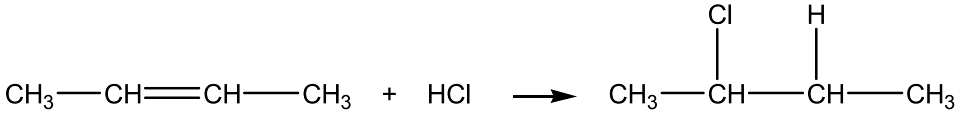
8. a.



$CH_2{=}CH_2 + H_2 \xrightarrow{Pt} CH_2H{-}CH_2H$

ethene ethane

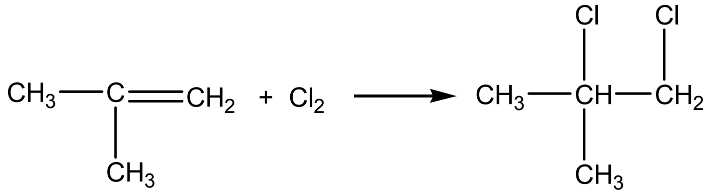
b.



$CH_3{-}CH{=}CH{-}CH_3 + HCl \longrightarrow CH_3{-}CHCl{-}CH_2{-}CH_3$

2-butene (cis or trans) 2-chlorobutane

c.

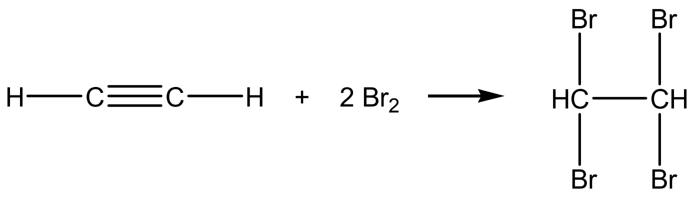


$CH_3{-}C(CH_3){=}CH_2 + Cl_2 \longrightarrow CH_3{-}CCl(CH_3){-}CH_2Cl$

2-methyl-1-propene
(or 2-methylpropene)

1,2-dichloro-2-methylpropane

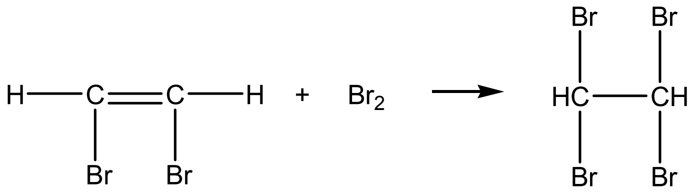
d.



$H{-}C{\equiv}C{-}H + 2\ Br_2 \longrightarrow HCBr_2{-}CHBr_2$

ethyne 1,1,2,2-tetrabromoethane

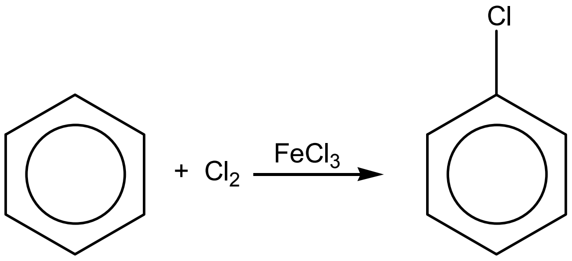
Another possibility would be:



$$HBrC{=}CBrH + Br_2 \longrightarrow Br_2HC{-}CHBr_2$$

1,2-dibromoethene 1,1,2,2-tetrabromoethane

e.

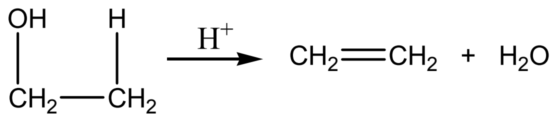


benzene chlorobenzene

f. $CH_3CH_3 \xrightarrow[500^\circ C]{Cr_2O_3} CH_2{=}CH_2 + H_2$

ethane ethene

or



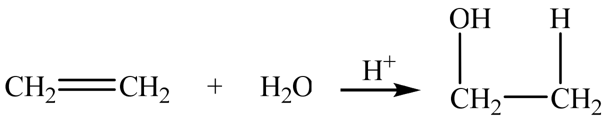
$$CH_2(OH){-}CH_2(H) \xrightarrow{H^+} CH_2{=}CH_2 + H_2O$$

ethanol ethene

This reaction is not explicitly discussed in the text. This is the reverse of the reaction used to produce alcohols. This reaction is reversible. Which organic substance dominates is determined by LeChatelier's principle. For example, if the alcohol is wanted, then water is removed as reactants are converted to products, driving the reaction to produce more water (and more alcohol).

9.

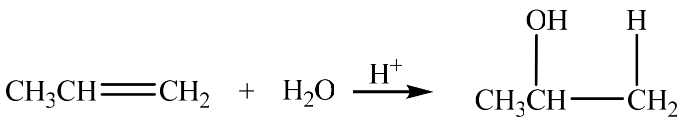
a.



$$CH_2{=}CH_2 + H_2O \xrightarrow{H^+} CH_2(OH){-}CH_2(H)$$

1° alcohol

b.

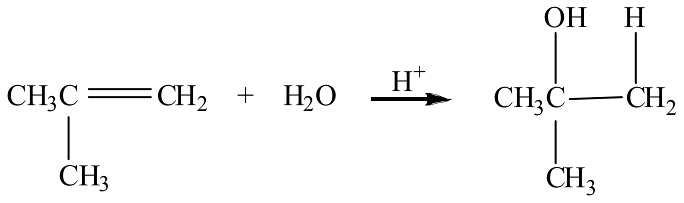


$$CH_3CH{=}CH_2 + H_2O \xrightarrow{H^+} CH_3CH(OH){-}CH_2(H)$$

major product

2° alcohol

c.

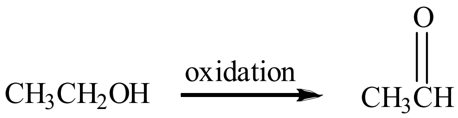


$CH_3\underset{CH_3}{C}{=}CH_2 + H_2O \xrightarrow{H^+} CH_3\underset{CH_3}{\overset{OH}{C}}-\overset{H}{C}H_2$

3° alcohol

major product

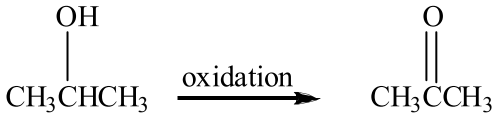
d.



$CH_3CH_2OH \xrightarrow{\text{oxidation}} CH_3\overset{O}{\overset{\|}{C}}H$

aldehyde

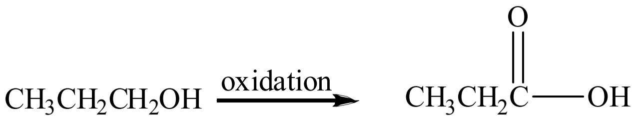
e.



$CH_3\overset{OH}{C}HCH_3 \xrightarrow{\text{oxidation}} CH_3\overset{O}{\overset{\|}{C}}CH_3$

ketone

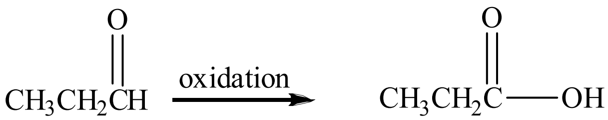
f.



$CH_3CH_2CH_2OH \xrightarrow{\text{oxidation}} CH_3CH_2\overset{O}{\overset{\|}{C}}-OH$

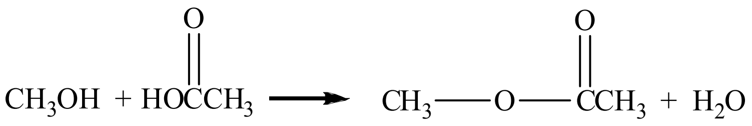
carboxylic acid

or



$CH_3CH_2\overset{O}{\overset{\|}{C}}H \xrightarrow{\text{oxidation}} CH_3CH_2\overset{O}{\overset{\|}{C}}-OH$

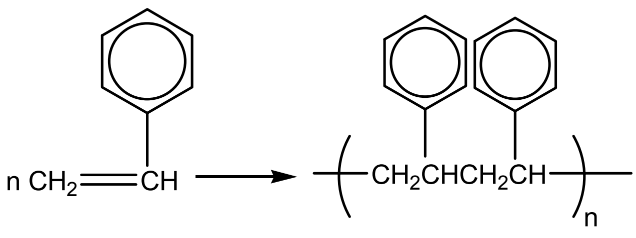
g.



$CH_3OH + HO\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow CH_3-O-\overset{O}{\overset{\|}{C}}CH_3 + H_2O$

ester

10. Polystyrene is an addition polymer formed from the monomer styrene.



a. Syndiotactic polystyrene has all of the benzene ring side groups aligned on alternate sides of the chain. This ordered alignment of the side groups allows individual polymer chains of polystyrene to pack together efficiently, maximizing the London dispersion forces. Stronger London dispersion forces translate into stronger polymers.

b. By copolymerizing with butadiene, double bonds exist in the carbon backbone of the polymer. These double bonds can react with sulfur to form crosslinks (bonds) between individual polymer chains. The crosslinked polymer is stronger.

c. The longer the chain of polystyrene, the stronger are the London dispersion forces between polymer chains.

d. In linear (versus branched) polystyrene, chains pack together more efficiently, resulting in stronger London dispersion forces.

11. a. A polyester forms when an alcohol functional group reacts with a carboxylic acid functional group. The monomer for a homopolymer polyester must have an alcohol functional group and a carboxylic acid functional group present in the structure.

b. A polyamide forms when an amine functional group reacts with a carboxylic acid functional group. For a copolymer polyamide, one monomer would have at least two amine functional groups present, and the other monomer would have at least two carboxylic acid functional groups present. For polymerization to occur, each monomer must have two reactive functional groups present.

c. To form an addition polymer, a carbon-carbon double bond must be present. To form a polyester, the monomer would need the alcohol and carboxylic acid functional groups present. To form a polyamide, the monomer would need the amine and carboxylic acid functional groups present. The two possibilities are for the monomer to have a carbon-carbon double bond, an alcohol functional group, and a carboxylic acid functional group present or to have a carbon-carbon double bond, an amine functional group, and a carboxylic acid functional group present.

12. Proteins are polymers made up of monomer units called amino acids. One of the functions of proteins is to provide structural integrity and strength for many types of tissues. In addition, proteins transport and store oxygen and nutrients, catalyze many reactions in the body, fight invasion by foreign objects, participate in the body’s many regulatory systems, and transport electrons in the process of metabolizing nutrients.

Carbohydrate polymers, such as starch and cellulose, are composed of the monomer units called monosaccharides or simple sugars. Carbohydrates serve as a food source for most organisms.

Nucleic acids are polymers made up of monomer units called nucleotides. Nucleic acids store and transmit genetic information and are also responsible for the synthesis of various proteins needed by a cell to carry out its life functions.

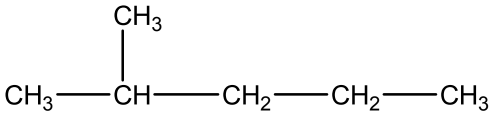
Exercises

Hydrocarbons

13. i.

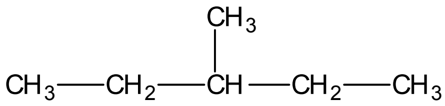
$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$$

ii.



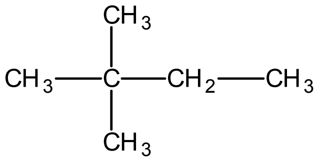
$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_2-CH_3$$

iii.



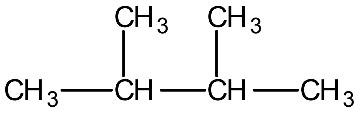
$$CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_3$$

iv.



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3$$

v.



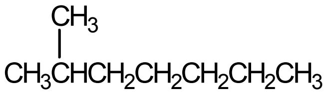
$$CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

All other possibilities are identical to one of these five compounds.

14. See Exercise 13 for the structures. The names of structures i-v respectively, are hexane (or n-hexane), 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane.

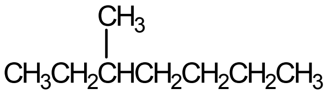
15. A difficult task in this problem is recognizing different compounds from compounds that differ by rotations about one or more C–C bonds (called conformations). The best way to distinguish different compounds from conformations is to name them. Different name = different compound; same name = same compound, so it is not an isomer but instead is a conformation.

a.



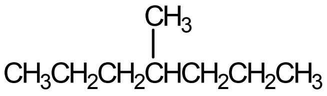
$$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_2CH_2CH_3$$

2-methylheptane



$$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_2CH_3$$

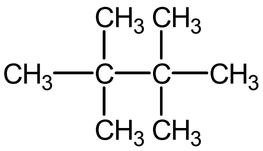
3-methylheptane



$$CH_3CH_2CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_3$$

4-methylheptane

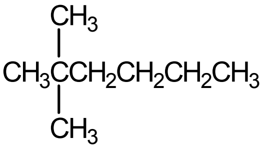
b.



$$\mathrm{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3}$$

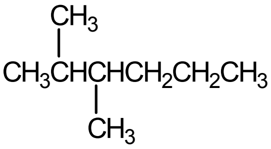
2,2,3,3-tetramethylbutane

16. a.



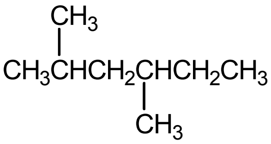
$$\mathrm{CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2CH_2CH_3}$$

2,2-dimethylhexane



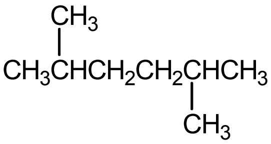
$$\mathrm{CH_3\overset{CH_3}{C}H\underset{CH_3}{C}HCH_2CH_2CH_3}$$

2,3-dimethylhexane



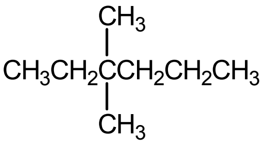
$$\mathrm{CH_3\overset{CH_3}{C}HCH_2\underset{CH_3}{C}HCH_2CH_3}$$

2,4-dimethylhexane



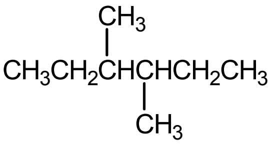
$$\mathrm{CH_3\overset{CH_3}{C}HCH_2CH_2\underset{CH_3}{C}HCH_3}$$

2,5-dimethylhexane



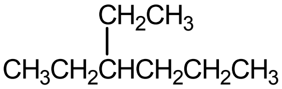
$$\mathrm{CH_3CH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2CH_3}$$

3,3-dimethylhexane



$$\mathrm{CH_3CH_2\overset{CH_3}{C}H\underset{CH_3}{C}HCH_2CH_3}$$

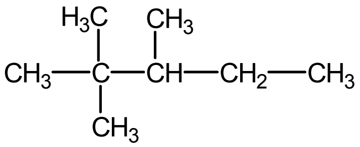
3,4-dimethylhexane



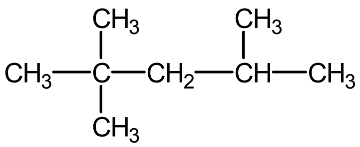
$$\mathrm{CH_3CH_2\overset{CH_2CH_3}{C}HCH_2CH_2CH_3}$$

3-ethylhexane

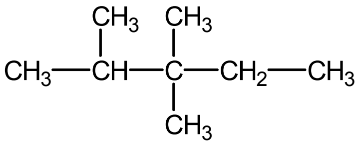
b.


$CH_3-\underset{CH_3}{\overset{H_3C}{C}}-\overset{CH_3}{CH}-CH_2-CH_3$

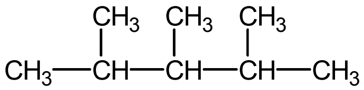
2,2,3-trimethylpentane


$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{CH}-CH_3$

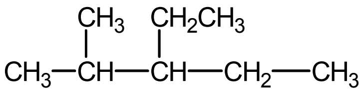
2,2,4-trimethylpentane


$CH_3-\overset{CH_3}{CH}-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_3$

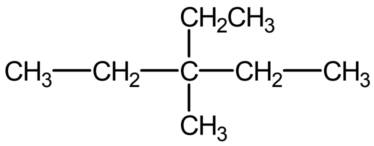
2,3,3-trimethylpentane


$CH_3-\overset{CH_3}{CH}-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_3$

2,3,4-trimethylpentane

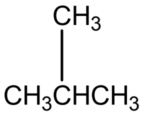

$CH_3-\overset{CH_3}{CH}-\overset{CH_2CH_3}{CH}-CH_2-CH_3$

3-ethyl-2-methylpentane

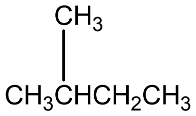

$CH_3-CH_2-\underset{CH_3}{\overset{CH_2CH_3}{C}}-CH_2-CH_3$

3-ethyl-3-methylpentane

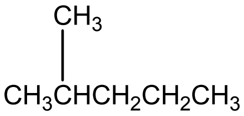
17. a.


$CH_3\overset{CH_3}{C}HCH_3$

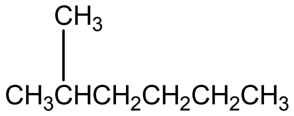
b.


$CH_3\overset{CH_3}{C}HCH_2CH_3$

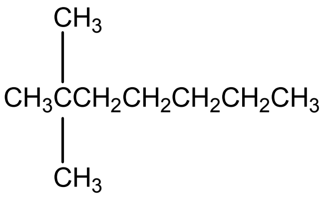
c.


$CH_3\overset{CH_3}{C}HCH_2CH_2CH_3$

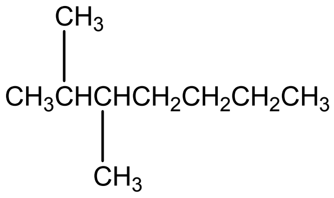
d.


$CH_3\overset{CH_3}{C}HCH_2CH_2CH_2CH_3$

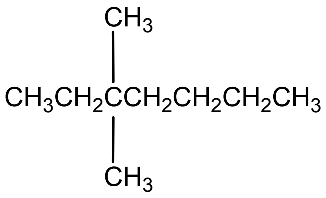
18. a.


$CH_3\underset{CH_3}{\overset{CH_3}{C}}CH_2CH_2CH_2CH_2CH_3$

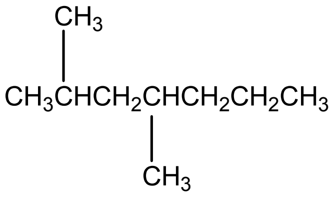
b.


$CH_3\overset{CH_3}{C}H\underset{CH_3}{C}HCH_2CH_2CH_2CH_3$

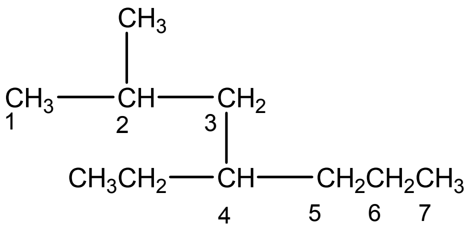
c.


$CH_3CH_2\underset{CH_3}{\overset{CH_3}{C}}CH_2CH_2CH_2CH_3$

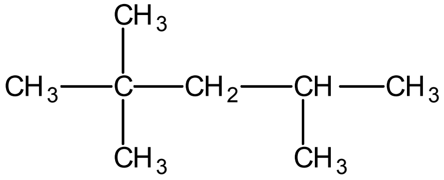
d.


$CH_3\overset{CH_3}{C}HCH_2\underset{CH_3}{C}HCH_2CH_2CH_3$

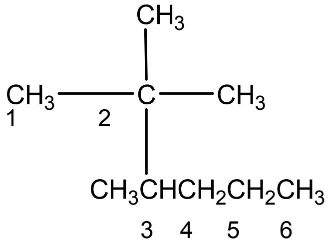
19. a.



b.

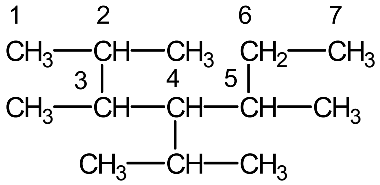


c.



d. For 3-isobutylhexane, the longest chain is 7 carbons long. The correct name is 4-ethyl-2-methylheptane. For 2-tert-butylpentane, the longest chain is 6 carbons long. The correct name is 2,2,3-trimethylhexane.

20.



4-isopropyl-2,3,5-trimethylheptane

21. a. 2,2,4-trimethylhexane b. 5-methylnonane c. 2,2,4,4-tetramethylpentane

d. 3-ethyl-3-methyloctane

Note: For alkanes, always identify the longest carbon chain for the base name first, then number the carbons to give the lowest overall numbers for the substituent groups.

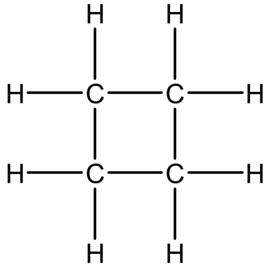
22. The hydrogen atoms in ring compounds are commonly omitted. In organic compounds, carbon atoms satisfy the octet rule of electrons by forming four bonds to other atoms. Therefore, add C-H bonds to the carbon atoms in the ring in order to give each C atom four bonds. You can also determine the formula of these cycloalkanes by using the general formula C_nH_{2n}.

a. isopropylcyclobutane; C_7H_{14} b. 1-tert-butyl-3-methylcyclopentane; $C_{10}H_{20}$

c. 1,3-dimethyl-2-propylcyclohexane; $C_{11}H_{22}$

23.

$CH_3—CH_2—CH_2—CH_3$



Each carbon is bonded to four other carbon and/or hydrogen atoms in a saturated hydrocarbon (only single bonds are present).

24.

$CH_2{=}CH_2$ $HC{\equiv}C—CH{=}CH_2$

An unsaturated hydrocarbon has at least one carbon-carbon double and/or triple bond in the structure.

25. a. 1-butene b. 4-methyl-2-hexene c. 2,5-dimethyl-3-heptene

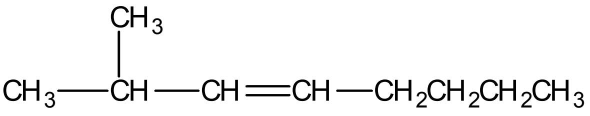
Note: The multiple bond is assigned the lowest number possible.

26. a. 2,3-dimethyl-2-butene b. 4-methyl-2-hexyne

c. 2,3-dimethyl-1-pentene

27. a. $CH_3–CH_2–CH{=}CH–CH_2–CH_3$ b. $CH_3–CH{=}CH–CH{=}CH–CH_2CH_3$

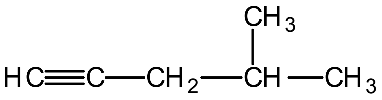
c.



$CH_3—\overset{CH_3}{CH}—CH{=}CH—CH_2CH_2CH_2CH_3$

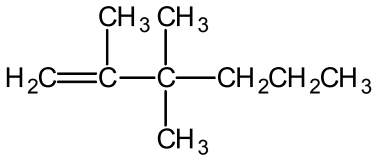
28.

a.



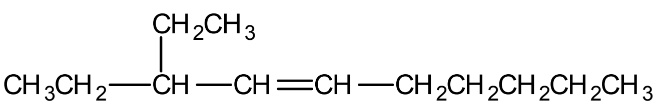
$HC{\equiv}C—CH_2—\overset{CH_3}{CH}—CH_3$

b.



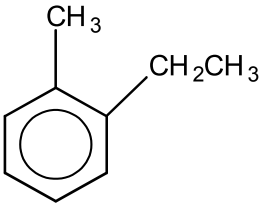
$H_2C{=}\overset{CH_3}{C}—\underset{CH_3}{\overset{CH_3}{C}}—CH_2CH_2CH_3$

c.

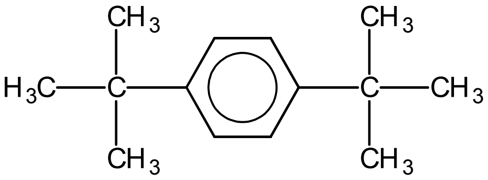


$CH_3CH_2—\overset{CH_2CH_3}{CH}—CH{=}CH—CH_2CH_2CH_2CH_2CH_3$

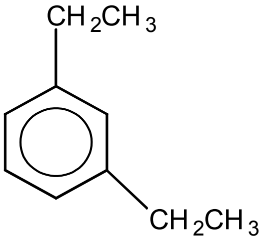
29. a.



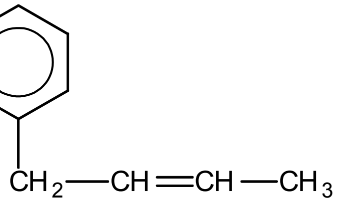
b.



c.



d.



30. isopropylbenzene or 2-phenylpropane

31. a. 1,3-dichlorobutane b. 1,1,1-trichlorobutane

c. 2,3-dichloro-2,4-dimethylhexane d. 1,2-difluoroethane

32. a. 3-chloro-l-butene b. 1-ethyl-3-methycyclopentene

c. 3-chloro-4-propylcyclopentene d. 1,2,4-trimethylcyclohexane

e. 2-bromotoluene (or 1-bromo-2-methylbenzene) f. 1-bromo-2-methylcyclohexane

g. 4-bromo-3-methylcyclohexene

Note: If the location of the double bond is not given in the name, it is assumed to be located between C_1 and C_2. Also, when the base name can be numbered in equivalent ways, give the first substituent group the lowest number; e.g., for part f, 1-bromo-2-methylcyclohexane is preferred to 2-bromo-1-methycyclohexane.

Isomerism

33. $CH_2Cl–CH_2Cl$, 1,2-dichloroethane: There is free rotation about the C–C single bond that doesn't lead to different compounds. CHCl=CHCl, 1,2-dichloroethene: There is no rotation about the C=C double bond. This creates the cis and trans isomers, which are different compounds.

34. a. All of 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

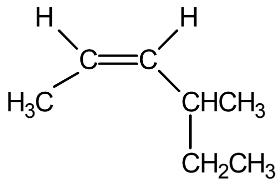
Compounds ii and iii are identical compounds, so they would have the same physical properties.

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.

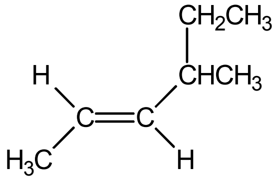
c. Compound iv does not have carbon atoms in a double bond that each have two different groups attached. Compound iv does not exhibit cis-trans isomerism.

35. To exhibit cis-trans isomerism, each carbon in the double bond must have two structurally different groups bonded to it. In Exercise 25, this occurs for compounds b and c. The cis isomer has the bulkiest groups on the same side of the double bond while the trans isomer has the bulkiest groups on opposite sides of the double bond. The cis and trans isomers for 25b and 25c are:

25 b.

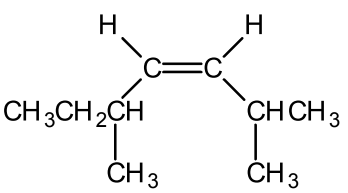


cis

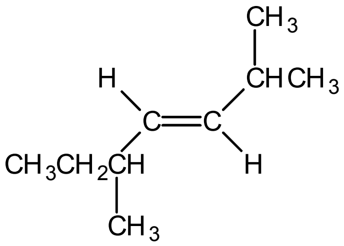


trans

25 c.



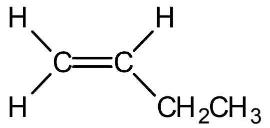
cis

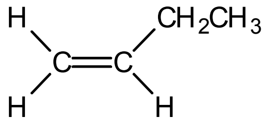


trans

Similarly, all the compounds in Exercise 27 exhibit *cis-trans* isomerism.

In compound a of Exercise 25, the first carbon in the double bond does not contain two different groups. The first carbon in the double bond contains two H atoms. To illustrate that this compound does not exhibit *cis-trans* isomerism, let's look at the potential c*is-trans* isomers.





These are the same compounds; they only differ by a simple rotation of the molecule. Therefore, they are not isomers of each other but instead are the same compound.

36. In Exercise 26, none of the compounds can exhibit *cis-trans* isomerism since none of the carbons with the multiple bond have two different groups bonded to each. In Exercise 28, only 3-ethyl-4-decene can exhibit *cis-trans* isomerism since the fourth and fifth carbons each have two different groups bonded to the carbon atoms with the double bond.

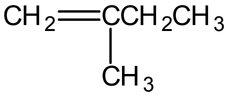
37. C_5H_{10} has the general formula for alkenes, C_nH_{2n}. To distinguish the different isomers from each other, we will name them. Each isomer must have a different name.

$CH_2{=}CHCH_2CH_2CH_3$

1-pentene

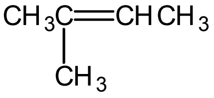
$CH_3CH{=}CHCH_2CH_3$

2-pentene



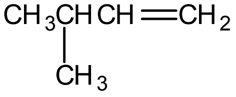
$CH_2{=}\underset{CH_3}{C}CH_2CH_3$

2-methyl-1-butene



$CH_3\underset{CH_3}{C}{=}CHCH_3$

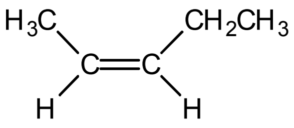
2-methyl-2-butene



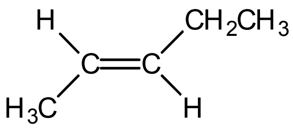
$CH_3\underset{CH_3}{CH}CH{=}CH_2$

3-methyl-1-butene

38. Only 2-pentene exhibits cis-trans isomerism. The isomers are:



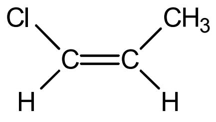
cis



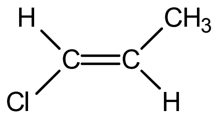
trans

The other isomers of C_5H_{10} do not contain carbons in the double bonds that each have two different groups attached.

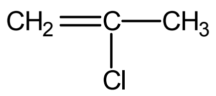
39. To help distinguish the different isomers, we will name them.



cis-1-chloro-1-propene

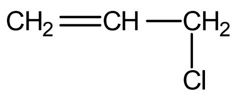


trans-1-chloro-1-propene



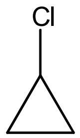
$\mathrm{CH_2{=}\underset{\underset{\displaystyle Cl}{|}}{C}{-}CH_3}$

2-chloro-1-propene



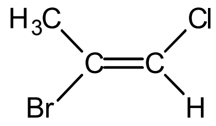
$\mathrm{CH_2{=}CH{-}\underset{\underset{\displaystyle Cl}{|}}{CH_2}}$

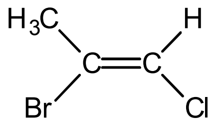
3-chloro-1-propene

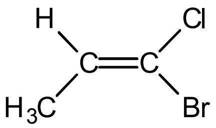


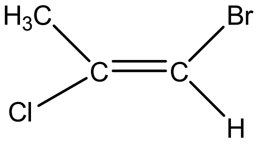
chlorocyclopropane

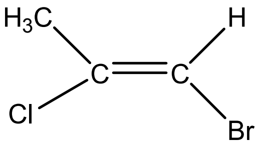
40. HCBrCl–CH=CH_2

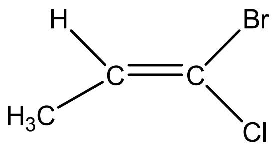


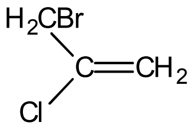


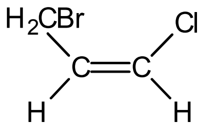


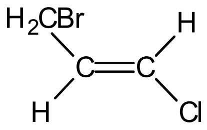


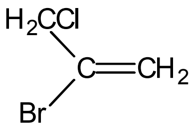


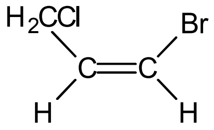


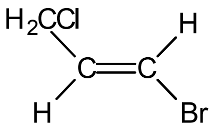




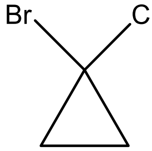


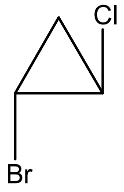




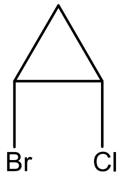


The cyclic isomers of bromochloropropene (C_3H_4BrCl) are:



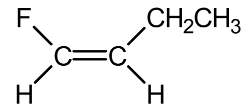


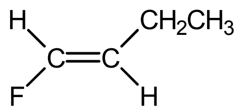
trans

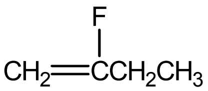


cis

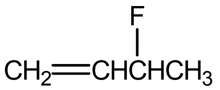
41.



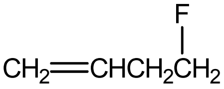




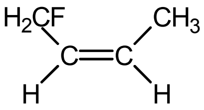
$CH_2=\overset{F}{C}CH_2CH_3$

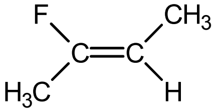


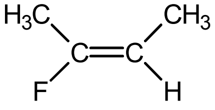
$CH_2=CH\overset{F}{C}HCH_3$

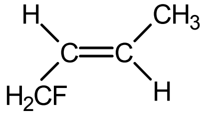


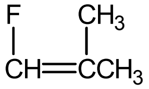
$CH_2=CHCH_2\overset{F}{C}H_2$



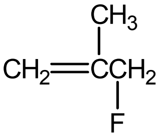






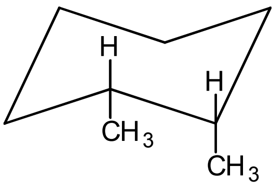


$\overset{F}{C}H=\overset{CH_3}{C}CH_3$

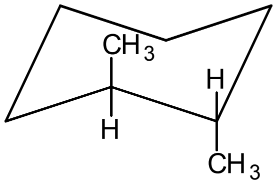


$CH_2=\overset{CH_3}{C}\underset{F}{C}H_2$

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.

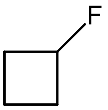


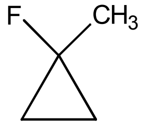
cis

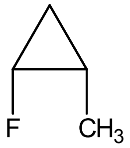


trans

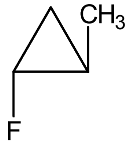
The cyclic structural and geometric isomers of C_4H_7F are:



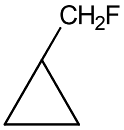




cis

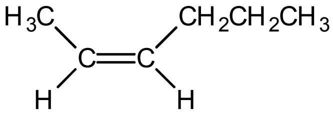


trans

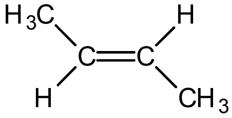


43.

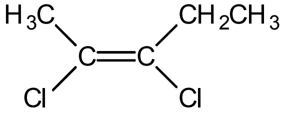
a.



b.



c.



44. a. cis-1-bromo-1-propene b. cis-4-ethyl-3-methyl-3-heptene

c. trans-1,4-diiodo-2-propyl-1-pentene

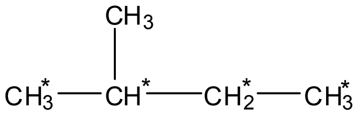
Note: In general, cis-trans designations refer to the relative positions of the largest groups. In compound b, the largest group off the first carbon in the double bond is CH_2CH_3, and the largest group off the second carbon in the double bond is $CH_2CH_2CH_3$. Because their relative placement is on the same side of the double bond, this is the cis isomer.

45. a.

$\mathrm{CH_3^{*}{-}CH_2^{*}{-}CH_2^{*}{-}CH_2{-}CH_3}$

There are three different types of hydrogens in n-pentane (see asterisks). Thus there are three monochloro isomers of n-pentane (1-chloropentane, 2-chloropentane, and 3-chloropentane).

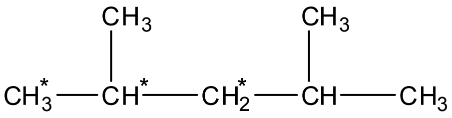
b.



$\mathrm{CH_3^{*}{-}\overset{\overset{CH_3}{|}}{CH^{*}}{-}CH_2^{*}{-}CH_3^{*}}$

There are four different types of hydrogens in 2-methylbutane, so four monochloro isomers of 2-methylbutane are possible.

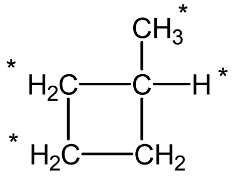
c.



$\mathrm{CH_3^{*}{-}\overset{\overset{CH_3}{|}}{CH^{*}}{-}CH_2^{*}{-}\overset{\overset{CH_3}{|}}{CH}{-}CH_3}$

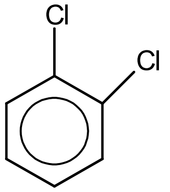
There are three different types of hydrogens, so three monochloro isomers are possible.

d.

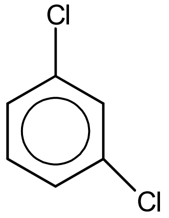


There are four different types of hydrogens, so four monochloro isomers are possible.

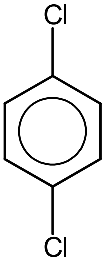
46. a.



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.

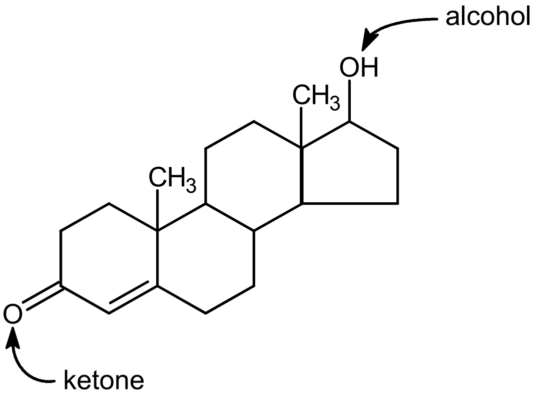
d. 1,3,5-Trichlorobenzene will be the most difficult to synthesize since all Cl groups are meta to each other in this compound.

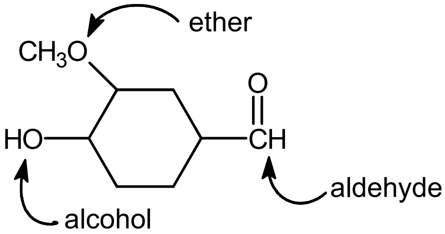
Functional Groups

47. Reference Table 22.5 for the common functional groups.

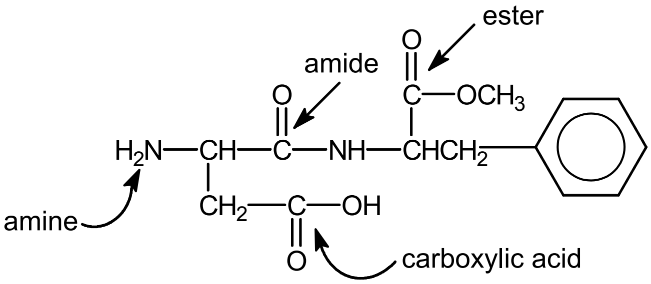
a. ketone b. aldehyde c. carboxylic acid d. amine

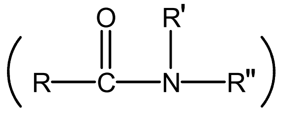
48. a. b.



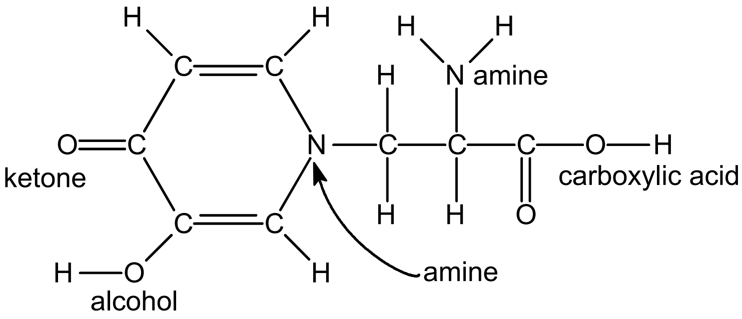


c.



Note: The amide functional group  $\left(R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle R'}{|}}{N}-R''\right)$ is not covered in Section 22.4 of the text. We point it out for your information.

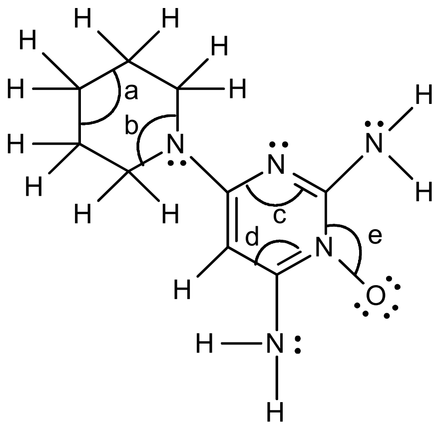
49. a.



b. 5 carbons in the ring and the carbon in –CO_2H: sp^2; the other two carbons: sp^3

c. 24 sigma bonds; 4 pi bonds

50. Hydrogen atoms are usually omitted from ring structures. In organic compounds, the carbon atoms form four bonds. With this in mind, the following structure has the missing hydrogen atoms included in order to give each carbon atom the four bond requirement.



a. Minoxidil would be more soluble in acidic solution. The nitrogens with lone pairs can be protonated, forming a water soluble cation.

b. The two nitrogens in the ring with double bonds are sp^2 hybridized. The other three N's are sp^3 hybridized.

c. The five carbon atoms in the ring with one nitrogen are all sp^3 hybridized. The four carbon atoms in the other ring with double bonds are all sp^2 hybridized.

d. Angles a and b ≈ 109.5°; angles c, d, and e ≈ 120°

e. 31 sigma bonds

f. 3 pi bonds

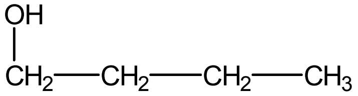
51. a. 3-chloro-1-butanol; because the carbon containing the OH group is bonded to just 1 other carbon (1 R group), this is a primary alcohol.

b. 3-methyl-3-hexanol; because the carbon containing the OH group is bonded to three other carbons (3 R groups), this is a tertiary alcohol.

c. 2-methylcyclopentanol; secondary alcohol (2 R groups bonded to carbon containing the OH group). *Note*: In ring compounds, the alcohol group is assumed to be bonded to C_1, so the number designation is commonly omitted for the alcohol group.

52.

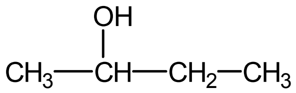
a.



$\overset{\mathrm{OH}}{\overset{|}{\mathrm{CH_2}}}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_3}$

primary alcohol

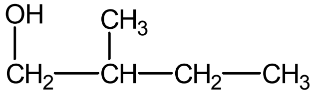
b.



$\mathrm{CH_3}-\overset{\mathrm{OH}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\mathrm{CH_3}$

secondary alcohol

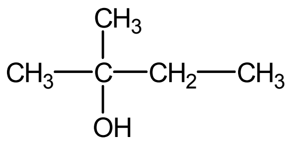
c.



$\overset{OH}{CH_2}—\overset{CH_3}{CH}—CH_2—CH_3$

primary alcohol

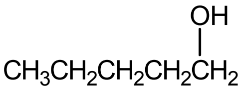
d.



$CH_3—\underset{OH}{\overset{CH_3}{C}}—CH_2—CH_3$

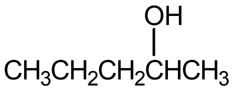
tertiary alcohol

53.



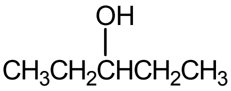
$CH_3CH_2CH_2CH_2\overset{OH}{CH_2}$

1-pentanol



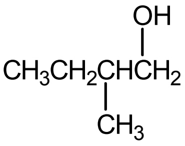
$CH_3CH_2CH_2\overset{OH}{C}HCH_3$

2-pentanol



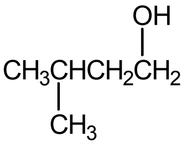
$CH_3CH_2\overset{OH}{C}HCH_2CH_3$

3-pentanol



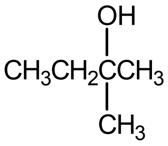
$CH_3CH_2\underset{CH_3}{C}H\overset{OH}{CH_2}$

2-methyl-1-butanol



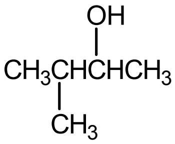
$CH_3\underset{CH_3}{C}HCH_2\overset{OH}{CH_2}$

3-methyl-1-butanol



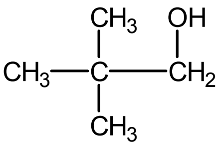
$CH_3CH_2\underset{CH_3}{\overset{OH}{C}}CH_3$

2-methyl-2-butanol



$CH_3\underset{CH_3}{C}H\overset{OH}{C}HCH_3$

3-methyl-2-butanol

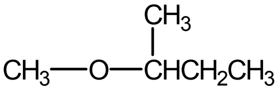


$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—\overset{OH}{CH_2}$

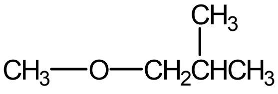
2,2-dimethyl-1-propanol

There are six isomeric ethers with formula $C_5H_{12}O$. The structures follow:

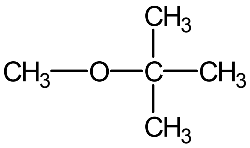
$CH_3—O—CH_2CH_2CH_2CH_3$



$CH_3—O—\overset{CH_3}{C}HCH_2CH_3$

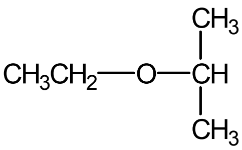


$CH_3—O—CH_2\overset{CH_3}{C}HCH_3$



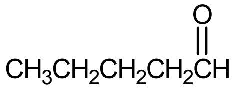
$CH_3—O—\underset{CH_3}{\overset{CH_3}{C}}—CH_3$

$CH_3CH_2—O—CH_2CH_2CH_3$

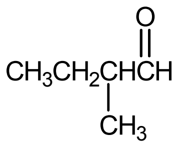


$CH_3CH_2—O—\underset{CH_3}{\overset{CH_3}{CH}}$

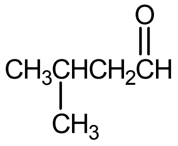
54. There are four aldehydes and three ketones with formula $C_5H_{10}O$. The structures follow:


$CH_3CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}H$

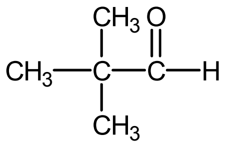
pentanal


$CH_3CH_2\underset{\underset{CH_3}{|}}{C}H\overset{\overset{O}{\|}}{C}H$

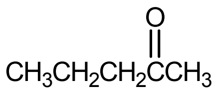
2-methylbutanal


$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2\overset{\overset{O}{\|}}{C}H$

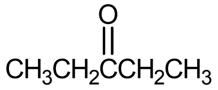
3-methylbutanal


$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{O}{\|}}{C}-H$

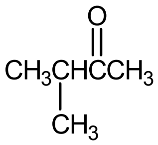
2,2-dimethylpropanal


$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$

2-pentanone


$CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3$

3-pentanone

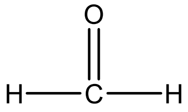

$CH_3\underset{\underset{CH_3}{|}}{C}H\overset{\overset{O}{\|}}{C}CH_3$

3-methyl-2-butanone

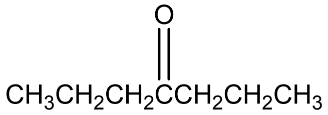
55. a. 4,5-dichloro-3-hexanone b. 2,3-dimethylpentanal

c. 3-methylbenzaldehyde or m-methylbenzaldehyde

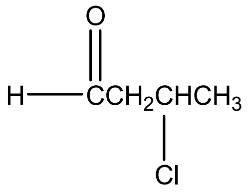
56. a.


$H-\overset{\overset{O}{\|}}{C}-H$

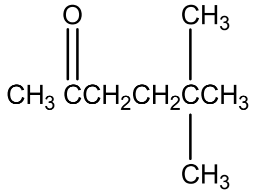
b.


$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_2CH_2CH_3$

c.


$H-\overset{\overset{O}{\|}}{C}CH_2\underset{\underset{Cl}{|}}{C}HCH_3$

d.

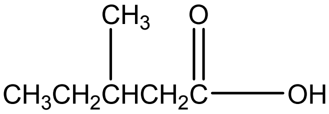

$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_3$

57. a. 4-chlorobenzoic acid or p-chlorobenzoic acid

b. 3-ethyl-2-methylhexanoic acid

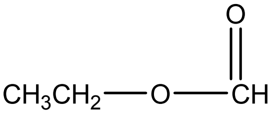
c. methanoic acid (common name = formic acid)

58. a.



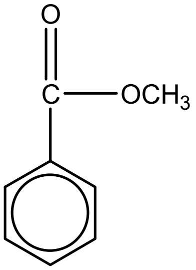
$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2\overset{O}{\overset{\|}{C}}-OH$

b.

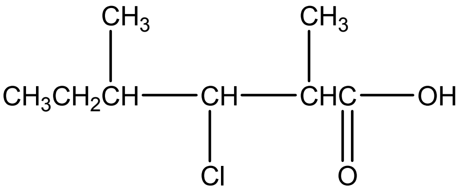


$CH_3CH_2-O-\overset{O}{\overset{\|}{C}}H$

c.



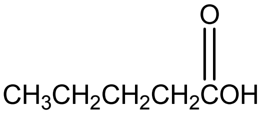
d.



$CH_3CH_2\overset{CH_3}{\overset{|}{C}}H-\underset{Cl}{\underset{|}{C}}H-\overset{CH_3}{\overset{|}{C}}H\underset{O}{\underset{\|}{C}}-OH$

59. Only statement d is false. The other statements refer to compounds having the same formula but different attachment of atoms; they are structural isomers.

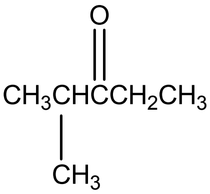
a.



$CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}OH$

Both have a formula of $C_5H_{10}O_2$.

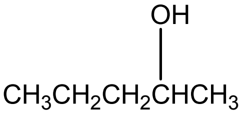
b.



$CH_3\underset{CH_3}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}CH_2CH_3$

Both have a formula of $C_6H_{12}O$.

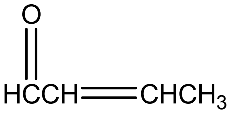
c.



$CH_3CH_2CH_2\overset{OH}{\overset{|}{C}}HCH_3$

Both have a formula of $C_5H_{12}O$.

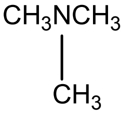
d.



$H\overset{O}{\overset{\|}{C}}CH=CHCH_3$

2-Butenal has a formula of C_4H_6O while the alcohol has a formula of C_4H_8O.

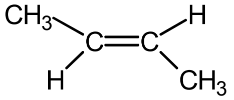
e.

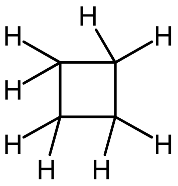


$CH_3\underset{CH_3}{\underset{|}{N}}CH_3$

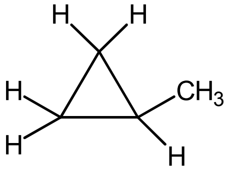
Both have a formula of C_3H_9N.

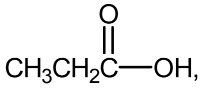
60.

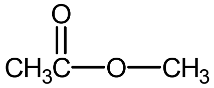
a. trans-2-butene:  , formula = C_4H_8



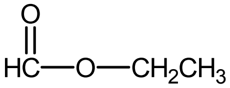
or

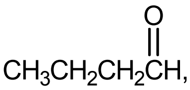


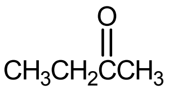
b. propanoic acid:  $CH_3CH_2\overset{O}{\overset{\|}{C}}—OH$, formula = $C_3H_6O_2$

 $CH_3\overset{O}{\overset{\|}{C}}—O—CH_3$

or

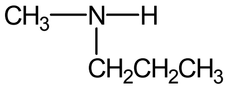
 $H\overset{O}{\overset{\|}{C}}—O—CH_2CH_3$

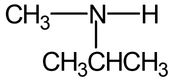
c. butanal:  $CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H$, formula = C_4H_8O

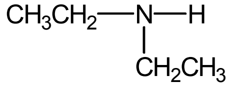
 $CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3$

d. butylamine: $CH_3CH_2CH_2CH_2NH_2$, formula = $C_4H_{11}N$:

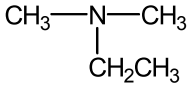
A secondary amine has two R groups bonded to N.

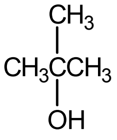
 $CH_3—\underset{CH_2CH_2CH_3}{\underset{|}{N}}—H$

 $CH_3—\underset{CH_3CHCH_3}{\underset{|}{N}}—H$

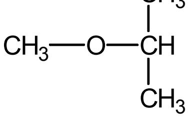
 $CH_3CH_2—\underset{CH_2CH_3}{\underset{|}{N}}—H$

e. A tertiary amine has three R groups bonded to N. (See answer d for structure of butylamine.)

 $CH_3—\underset{CH_2CH_3}{\underset{|}{N}}—CH_3$

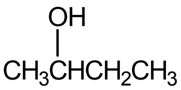
f. 2-methyl-2-propanol:  $CH_3\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}CH_3$, formula = $C_4H_{10}O$

$CH_3—O—CH_2CH_2CH_3$

 $CH_3—O—\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{CH}}}}$

$CH_3CH_2—O—CH_2CH_3$

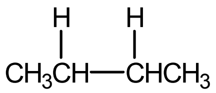
g. A secondary alcohol has two R groups attached to the carbon bonded to the OH group. (See answer f for the structure of 2-methyl-2-propanol.)



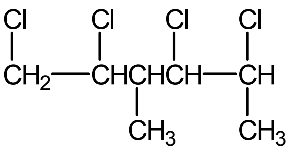
$CH_3\overset{\overset{\text{OH}}{|}}{C}HCH_2CH_3$

Reactions of Organic Compounds

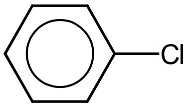
61.

a. 

$CH_3\overset{\overset{\text{H}}{|}}{C}H—\overset{\overset{\text{H}}{|}}{C}HCH_3$

b. 

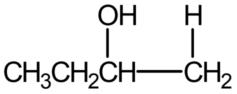
$\overset{\overset{\text{Cl}}{|}}{C}H_2—\underset{\underset{CH_3}{|}}{\overset{\overset{\text{Cl}}{|}}{C}}H\overset{\overset{\text{Cl}}{|}}{C}H—\underset{\underset{CH_3}{|}}{\overset{\overset{\text{Cl}}{|}}{C}}H$

c. 

$+ HCl$

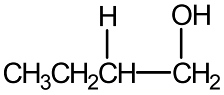
d. $C_4H_8(g) + 6\ O_2(g) \rightarrow 4\ CO_2(g) + 4\ H_2O(g)$

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



$CH_3CH_2\overset{\overset{\text{OH}}{|}}{C}H—\overset{\overset{\text{H}}{|}}{C}H_2$

major product

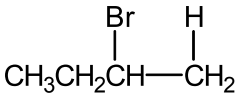


$CH_3CH_2\overset{\overset{\text{H}}{|}}{C}H—\overset{\overset{\text{OH}}{|}}{C}H_2$

minor product

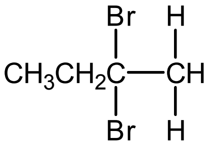
We would get both products in this reaction. Using the rule given in the problem, the first compound listed is the major product. In the reactant, the terminal carbon has more hydrogens bonded to it (2 versus 1), so H forms a bond to this carbon, and OH forms a bond to the other carbon in the double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

b.



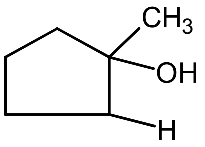
$CH_3CH_2\overset{\overset{\text{Br}}{|}}{C}H—\overset{\overset{\text{H}}{|}}{C}H_2$

c.

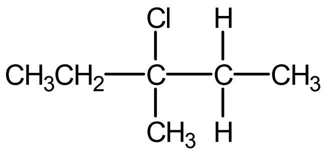


$CH_3CH_2\underset{\underset{\text{Br}}{|}}{\overset{\overset{\text{Br}}{|}}{C}}—\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{H}}{|}}{C}}H$

d.

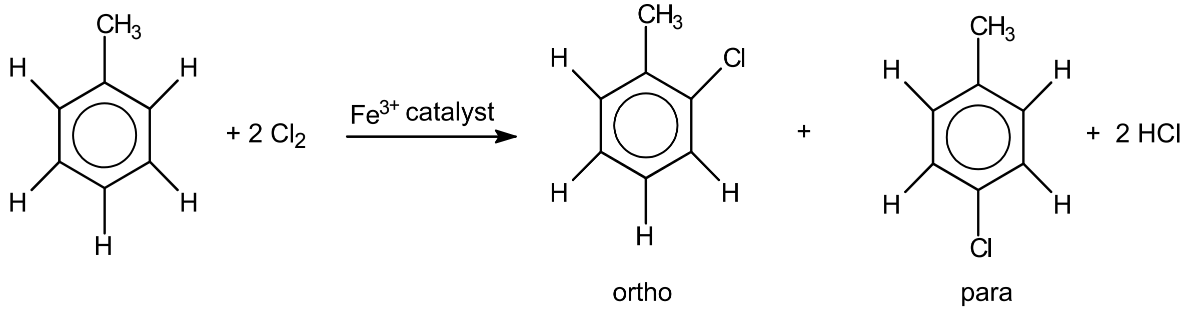


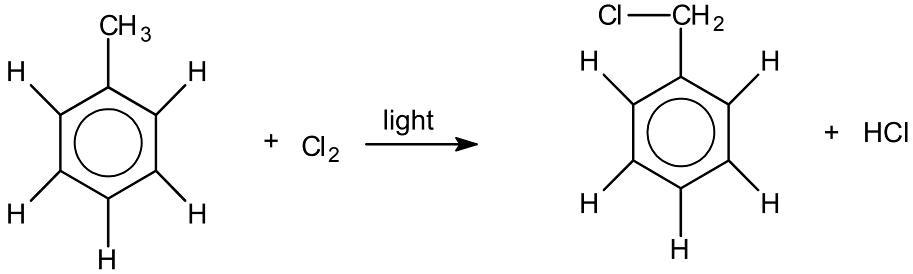
e.



$$\begin{array}{ccccc} & & \text{Cl} & & \text{H} \\ & & | & & | \\ \text{CH}_3\text{CH}_2 & - & \text{C} & - & \text{C}-\text{CH}_3 \\ & & | & & | \\ & & \text{CH}_3 & & \text{H} \end{array}$$

63.



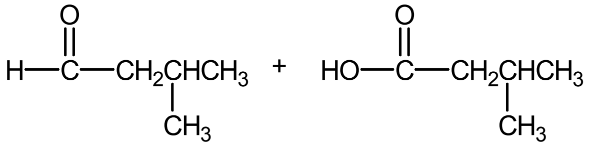


To substitute for the benzene ring hydrogens, an iron(III) catalyst must be present. Without this special iron catalyst, the benzene ring hydrogens are unreactive. To substitute for an alkane hydrogen, light must be present. For toluene, the light-catalyzed reaction substitutes a chlorine for a hydrogen in the methyl group attached to the benzene ring.

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.

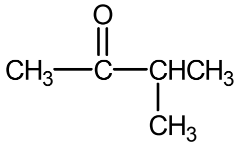
65. Primary alcohols (a, d, and f) are oxidized to aldehydes, which can be oxidized further to carboxylic acids. Secondary alcohols (b, e, and f) are oxidized to ketones, and tertiary alcohols (c and f) do not undergo this type of oxidation reaction. Note that compound f contains a primary, secondary, and tertiary alcohol. For the primary alcohols (a, d, and f), we listed both the aldehyde and the carboxylic acid as possible products.

a.



$$\mathrm{H{-}\overset{O}{\overset{\|}{C}}{-}CH_2\underset{\underset{CH_3}{|}}{C}HCH_3 \;+\; HO{-}\overset{O}{\overset{\|}{C}}{-}CH_2\underset{\underset{CH_3}{|}}{C}HCH_3}$$

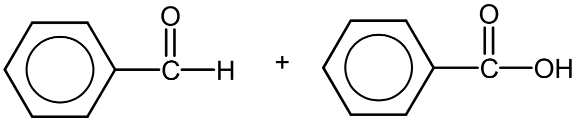
b.



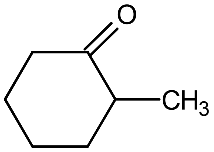
$$\mathrm{CH_3{-}\overset{O}{\overset{\|}{C}}{-}\underset{\underset{CH_3}{|}}{C}HCH_3}$$

c. No reaction

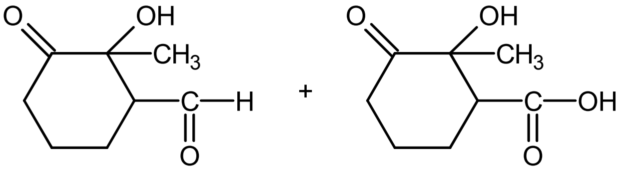
d.



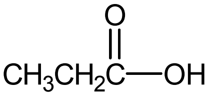
e.



f.

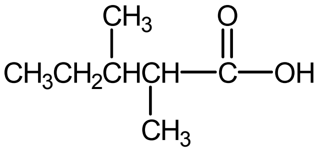


66. a.



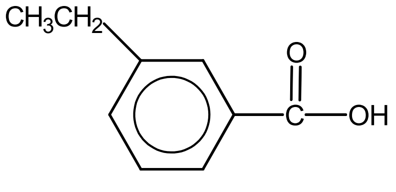
$$\mathrm{CH_3CH_2\overset{O}{\overset{\|}{C}}{-}OH}$$

b.



$$\mathrm{CH_3CH_2\overset{\overset{CH_3}{|}}{C}H\underset{\underset{CH_3}{|}}{C}H{-}\overset{O}{\overset{\|}{C}}{-}OH}$$

c.



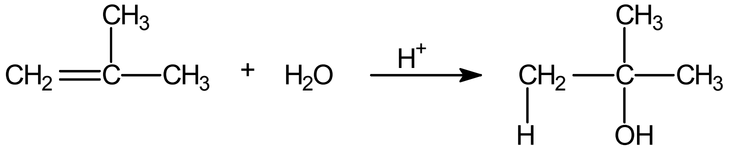
67. a. $CH_3CH{=}CH_2 + Br_2 \rightarrow CH_3CHBrCH_2Br$ (addition reaction of Br_2 with propene)

b.

$$CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3 \xrightarrow{\text{oxidation}} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

Oxidation of 2-propanol yields acetone (2-propanone).

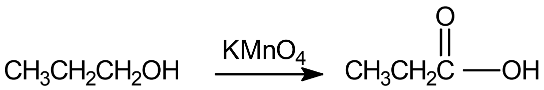
c.



$$CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_3 + H_2O \xrightarrow{H^+} \underset{\underset{\displaystyle H}{|}}{CH_2}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_3$$

Addition of H_2O to 2-methylpropene would yield tert-butyl alcohol (2-methyl-2-propanol) as the major product.

d.

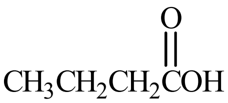


$$CH_3CH_2CH_2OH \xrightarrow{KMnO_4} CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Oxidation of 1-propanol would eventually yield propanoic acid. Propanal is produced first in this reaction and is then oxidized to propanoic acid.

68. a. $CH_2{=}CHCH_2CH_3$ will react with Cl_2 without any catalyst present. $CH_3CH_2CH_2CH_3$ reacts with Cl_2 only when ultraviolet light is present.

b.

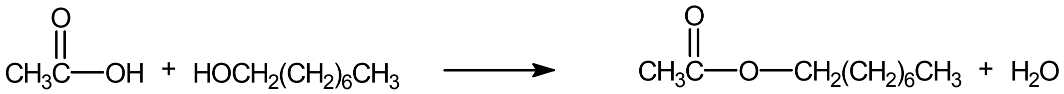


$CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}OH$ is an acid, so this compound should react positively with a base like $NaHCO_3$. The other compound is a ketone, which will not react with a base.

c. $CH_3CH_2CH_2OH$ can be oxidized with $KMnO_4$ to propanoic acid. 2-Propanone (a ketone) will not react with $KMnO_4$.

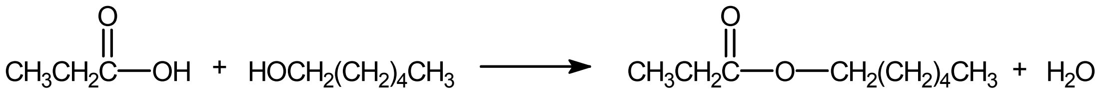
d. $CH_3CH_2NH_2$ is an amine, so it behaves as a base in water. Dissolution of some of this base in water will produce a solution with a basic pH. The ether, CH_3OCH_3, will not produce a basic pH when dissolved in water.

69. Reaction of a carboxylic acid with an alcohol can produce these esters.



$$\mathrm{CH_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—OH} + \mathrm{HOCH_2(CH_2)_6CH_3} \longrightarrow \mathrm{CH_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—O—}\mathrm{CH_2(CH_2)_6CH_3} + \mathrm{H_2O}$$

ethanoic acid (acetic acid) octanol n-octylacetate

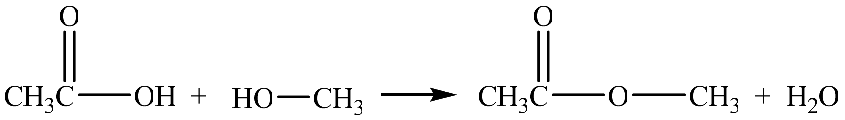


$$\mathrm{CH_3CH_2}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—OH} + \mathrm{HOCH_2(CH_2)_4CH_3} \longrightarrow \mathrm{CH_3CH_2}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—O—}\mathrm{CH_2(CH_2)_4CH_3} + \mathrm{H_2O}$$

propanoic acid hexanol

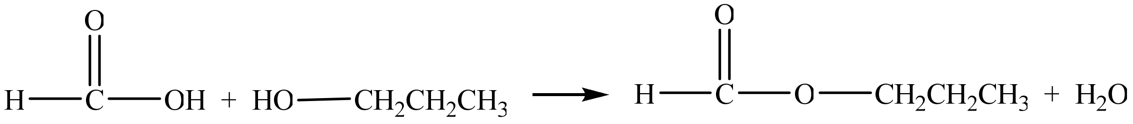
70. When an alcohol is reacted with a carboxylic acid, an ester is produced.

a.



$$\mathrm{CH_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—OH} + \text{HO—}\mathrm{CH_3} \longrightarrow \mathrm{CH_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—O—}\mathrm{CH_3} + \mathrm{H_2O}$$

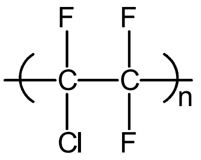
b.



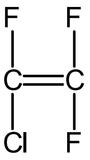
$$\text{H—}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—OH} + \text{HO—}\mathrm{CH_2CH_2CH_3} \longrightarrow \text{H—}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—O—}\mathrm{CH_2CH_2CH_3} + \mathrm{H_2O}$$

Polymers

71. The backbone of the polymer contains only carbon atoms, which indicates that Kel-F is an addition polymer. The smallest repeating unit of the polymer and the monomer used to produce this polymer are:



$$\left(\underset{\mathrm{Cl}}{\overset{\mathrm{F}}{\mathrm{C}}}\text{—}\underset{\mathrm{F}}{\overset{\mathrm{F}}{\mathrm{C}}}\right)_n$$

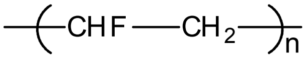


$$\underset{\mathrm{Cl}}{\overset{\mathrm{F}}{\mathrm{C}}}=\underset{\mathrm{F}}{\overset{\mathrm{F}}{\mathrm{C}}}$$

Note: Condensation polymers generally have O or N atoms in the backbone of the polymer.

72. a.

repeating unit:

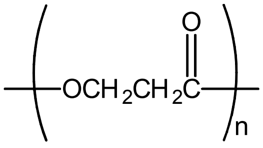


$$\text{—}\left(\mathrm{CHF}\text{—}\mathrm{CH_2}\text{—}\right)_n$$

monomer: $\mathrm{CHF{=}CH_2}$

b.

repeating unit:

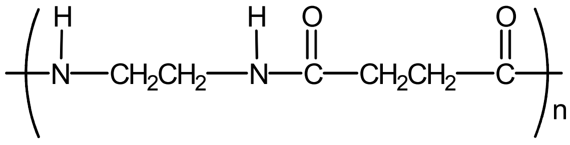


$$-\left(-OCH_2CH_2\overset{O}{\overset{\|}{C}}-\right)_n-$$

monomer: HO–CH_2CH_2–CO_2H

c.

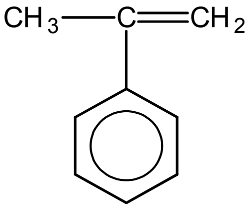
repeating unit:



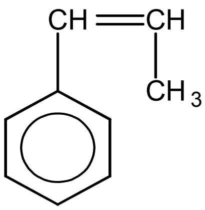
$$-\left(-\overset{H}{\overset{|}{N}}-CH_2CH_2-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-CH_2CH_2-\overset{O}{\overset{\|}{C}}-\right)_n-$$

copolymer of: $H_2NCH_2CH_2NH_2$ and $HO_2CCH_2CH_2CO_2H$

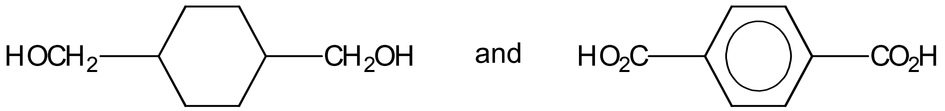
d. monomer:



e. monomer:

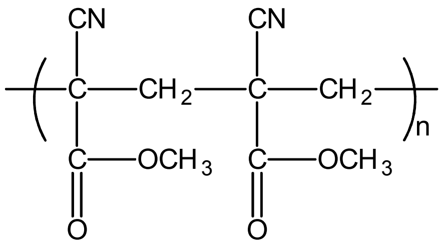


f. copolymer of:



Addition polymers: a, d, and e; condensation polymers: b, c, and f; copolymer: c and f

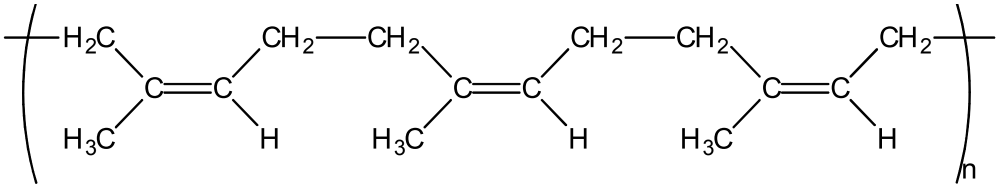
73.



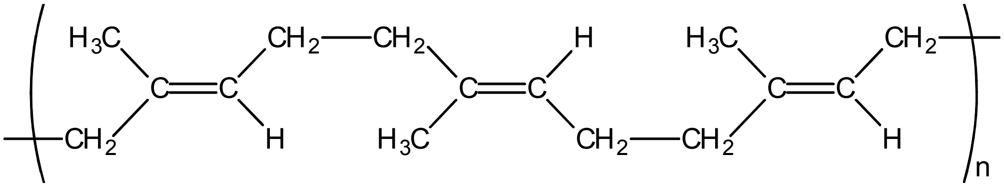
Super glue is an addition polymer formed by reaction of the C=C bond in methyl cyanoacrylate.

74. a. 2-methyl-1,3-butadiene

b.

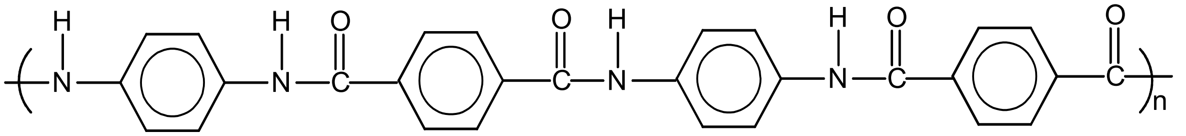


cis-polyisoprene (natural rubber)

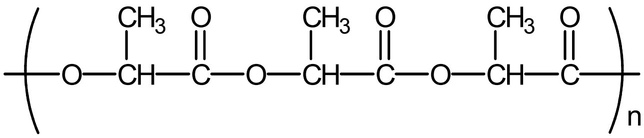


trans-polyisoprene (gutta percha)

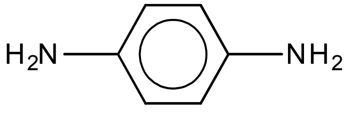
75. H_2O is eliminated when Kevlar forms. Two repeating units of Kevlar are:



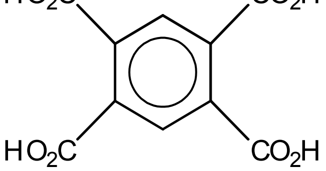
76. This condensation polymer forms by elimination of water. The ester functional group repeats, hence the term polyester.



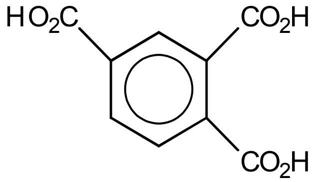
77. This is a condensation polymer, where two molecules of H_2O form when the monomers link together.



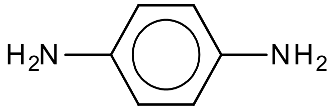
and



78.

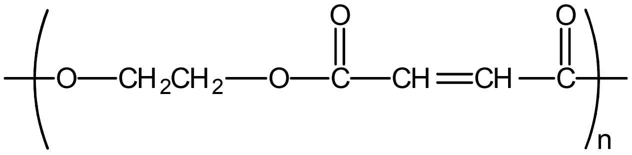


and



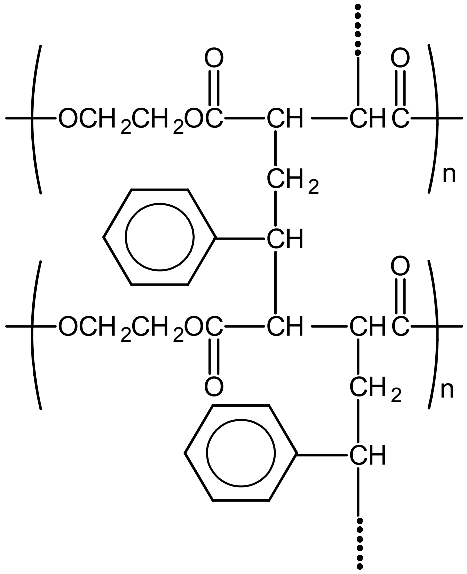
79. Divinylbenzene has two reactive double bonds that are used during formation of the polymer. The key is for the double bonds to insert themselves into two different polymer chains during the polymerization process. When this occurs, the two chains are bonded together (are cross-linked). The chains cannot move past each other because of the crosslinks, making the polymer more rigid.

80. a.



$$\left(-O-CH_2CH_2-O-\overset{O}{\overset{\|}{C}}-CH=CH-\overset{O}{\overset{\|}{C}}- \right)_n$$

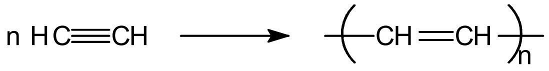
b.



81. a. The polymer formed using 1,2-diaminoethane will exhibit relatively strong hydrogen-bonding interactions between adjacent polymer chains. Hydrogen bonding is not present in the ethylene glycol polymer (a polyester polymer forms), so the 1,2-diaminoethane polymer will be stronger.

b. The presence of rigid groups (benzene rings or multiple bonds) makes the polymer stiffer. Hence the monomer with the benzene ring will produce the more rigid polymer.

c. Polyacetylene will have a double bond in the carbon backbone of the polymer.



$$n\ HC{\equiv}CH \longrightarrow \left(CH{=}CH \right)_n$$

The presence of the double bond in polyacetylene will make polyacetylene a more rigid polymer than polyethylene. Polyethylene doesn't have C=C bonds in the backbone of the polymer (the double bonds in the monomers react to form the polymer).

82. At low temperatures, the polymer is coiled into balls. The forces between poly(lauryl methacrylate) and oil molecules will be minimal, and the effect on viscosity will be minimal. At higher temperatures, the chains of the polymer will unwind and become tangled with the oil molecules, increasing the viscosity of the oil. Thus the presence of the polymer counteracts the temperature effect, and the viscosity of the oil remains relatively constant.

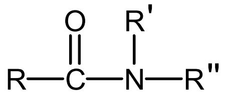
Natural Polymers

83. a. Serine, tyrosine, and threonine contain the -OH functional group in the R group.

b. Aspartic acid and glutamic acid contain the -COOH functional group in the R group.

c. An amine group has a nitrogen bonded to other carbon and/or hydrogen atoms. Histidine, lysine, arginine, and tryptophan contain the amine functional group in the R group.

d. The amide functional group is:

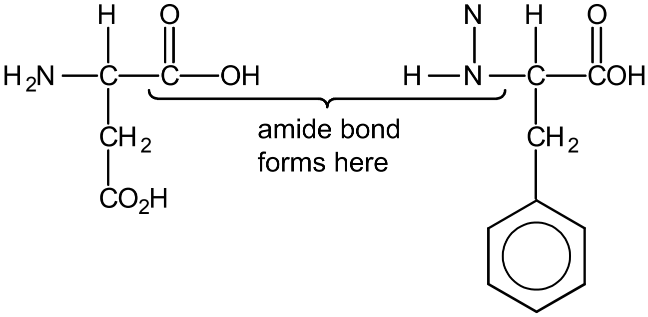


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle R'}{|}}{N}-R''$$

This functional group is formed when individual amino acids bond together to form the peptide linkage. Glutamine and asparagine have the amide functional group in the R group.

84. Crystalline amino acids exist as zwitterions, $^{+}H_3NCRHCOO^{-}$, held together by ionic forces. The ionic interparticle forces are strong. Before the temperature gets high enough to melt the solid, the amino acid decomposes.

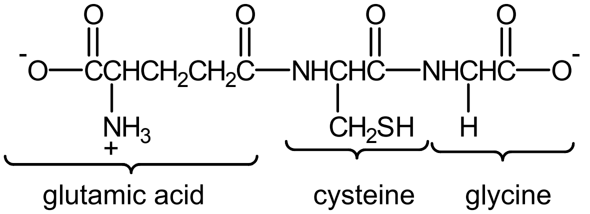
85. a. Aspartic acid and phenylalanine make up aspartame.



b. Aspartame contains the methyl ester of phenylalanine. This ester can hydrolyze to form methanol:

$RCO_2CH_3 + H_2O \rightleftharpoons RCO_2H + HOCH_3$

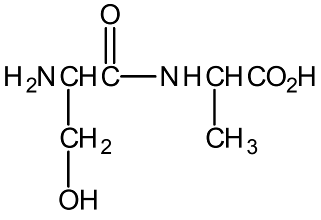
86.



$$^{-}O-\overset{O}{\overset{\|}{C}}\underset{\underset{+}{NH_3}}{C}HCH_2CH_2\overset{O}{\overset{\|}{C}}-NH\underset{CH_2SH}{C}H\overset{O}{\overset{\|}{C}}-NH\underset{H}{C}H\overset{O}{\overset{\|}{C}}-O^{-}$$

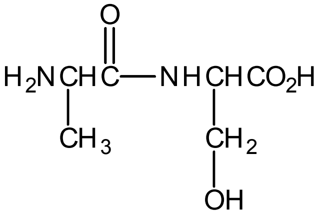
Glutamic acid, cysteine, and glycine are the three amino acids in glutathione. Glutamic acid uses the -COOH functional group in the R group to bond to cysteine instead of the carboxylic acid group bonded to the α-carbon. The cysteine-glycine bond is the typical peptide linkage.

87.



$$H_2N\underset{\underset{OH}{CH_2}}{CH}\overset{O}{\overset{\|}{C}}-NH\underset{CH_3}{CH}CO_2H$$

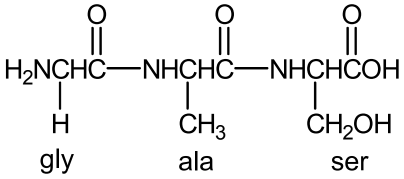
ser - ala



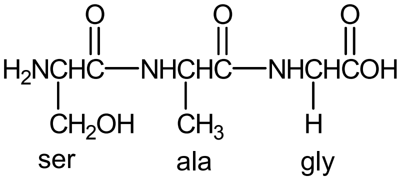
$$H_2N\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}-NH\underset{\underset{OH}{CH_2}}{CH}CO_2H$$

ala - ser

88.



$$H_2N\underset{H}{CH}\overset{O}{\overset{\|}{C}}-NH\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}-NH\underset{CH_2OH}{CH}\overset{O}{\overset{\|}{C}}OH$$



$$H_2N\underset{CH_2OH}{CH}\overset{O}{\overset{\|}{C}}-NH\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}-NH\underset{H}{CH}\overset{O}{\overset{\|}{C}}OH$$

There are six possible tripeptides with gly, ala, and ser. The other four tripeptides are gly-ser-ala, ser-gly-ala, ala-gly-ser, and ala-ser-gly.

89. a. Six tetrapeptides are possible. From NH_2 to CO_2H end:

phe-phe-gly-gly, gly-gly-phe-phe, gly-phe-phe-gly,

phe-gly-gly-phe, phe-gly-phe-gly, gly-phe-gly-phe

b. Twelve tetrapeptides are possible. From NH_2 to CO_2H end:

phe-phe-gly-ala, phe-phe-ala-gly, phe-gly-phe-ala,

phe-gly-ala-phe, phe-ala-phe-gly, phe-ala-gly-phe,

gly-phe-phe-ala, gly-phe-ala-phe, gly-ala-phe-phe

ala-phe-phe-gly, ala-phe-gly-phe, ala-gly-phe-phe

90. There are 5 possibilities for the first amino acid, 4 possibilities for the second amino acid, 3 possibilities for the third amino acid, 2 possibilities for the fourth amino acid, and 1 possibility for the last amino acid. The number of possible sequences is:

$5 \times 4 \times 3 \times 2 \times 1 = 5! = 120$ different pentapeptides

91. a. Ionic: Need NH_2 on side chain of one amino acid with CO_2H on side chain of the other amino acid. The possibilities are:

NH_2 on side chain = His, Lys, or Arg; CO_2H on side chain = Asp or Glu

b. Hydrogen bonding: Need N–H or O–H bond present in side chain. The hydrogen bonding interaction occurs between the X– H bond and a carbonyl group from any amino acid.

X–H · · · · · · · O = C (carbonyl group)

Ser Asn   Any amino acid
Glu Thr
Tyr Asp
His Gln
Arg Lys

c. Covalent: Cys–Cys (forms a disulfide linkage)

d. London dispersion: All amino acids with nonpolar R groups. They are:

Gly, Ala, Pro, Phe, Ile, Trp, Met, Leu, and Val

e. Dipole-dipole: Need side chain with OH group. Tyr, Thr and Ser all could form this specific dipole-dipole force with each other since all contain an OH group in the side chain.

92. Reference Exercise 91 for a more detailed discussion of these various interactions.

a. Covalent

b. Hydrogen bonding

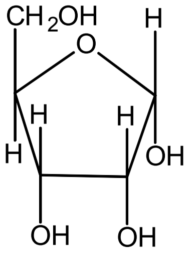
c. Ionic

d. London dispersion

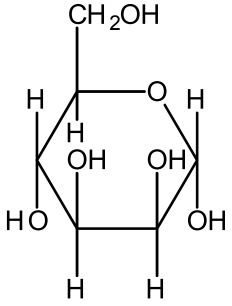
93. Glutamic acid: R = $-CH_2CH_2CO_2H$; valine: R = $-CH(CH_3)_2$; a polar side chain is replaced by a nonpolar side chain. This could affect the tertiary structure of hemoglobin and the ability of hemoglobin to bind oxygen.

94. Glutamic acid: R = $-CH_2CH_2COOH$; glutamine: R = $-CH_2CH_2CONH_2$; the R groups only differ by OH versus NH_2. Both of these groups are capable of forming hydrogen-bonding interactions, so the change in intermolecular forces is minimal. Thus this change is not critical because the secondary and tertiary structures of hemoglobin should not be greatly affected.

95. See Figures 22.29 and 22.30 of the text for examples of the cyclization process.

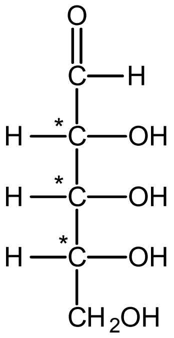


D-Ribose

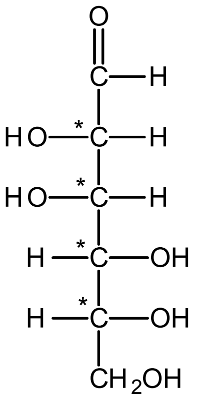


D-Mannose

96. The chiral carbon atoms are marked with asterisks. A chiral carbon atom has four different substituent groups attached.



D-Ribose



D-Mannose

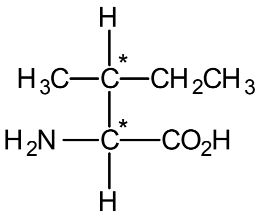
97. The aldohexoses contain 6 carbons and the aldehyde functional group. Glucose, mannose, and galactose are aldohexoses. Ribose and arabinose are aldopentoses since they contain 5 carbons with the aldehyde functional group. The ketohexose (6 carbons + ketone functional group) is fructose, and the ketopentose (5 carbons + ketone functional group) is ribulose.

98. This is an example of Le Chatelier's principle at work. For the equilibrium reactions among the various forms of glucose, reference Figure 22.30 of the text. The chemical tests involve reaction of the aldehyde group found only in the open-chain structure. As the aldehyde group is reacted, the equilibrium between the cyclic forms of glucose, and the open-chain structure will shift to produce more of the open-chain structure. This process continues until either the glucose or the chemicals used in the tests run out.

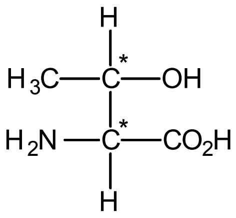
99. The α and β forms of glucose differ in the orientation of a hydroxy group on one specific carbon in the cyclic forms (see Figure 22.30 of the text). Starch is a polymer composed of only α-D-glucose, and cellulose is a polymer composed of only β-D-glucose.

100. Humans do not possess the necessary enzymes to break the β-glycosidic linkages found in cellulose. Cows, however, do possess the necessary enzymes to break down cellulose into the β-D-glucose monomers and therefore can derive nutrition from cellulose.

101. A chiral carbon has four different groups attached to it. A compound with a chiral carbon is optically active. Isoleucine and threonine contain more than the one chiral carbon atom (see asterisks).



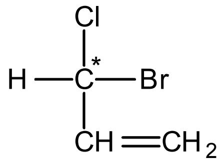
isoleucine



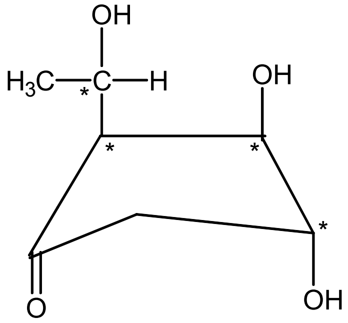
threonine

102. There is no chiral carbon atom in glycine since it contains no carbon atoms with four different groups bonded to it.

103. Only one of the isomers is optically active. The chiral carbon in this optically active isomer is marked with an asterisk.



104.

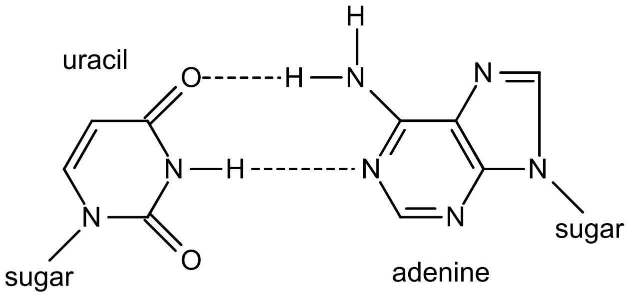


The compound has four chiral carbon atoms. The fourth group bonded to the three chiral carbon atoms in the ring is a hydrogen atom.

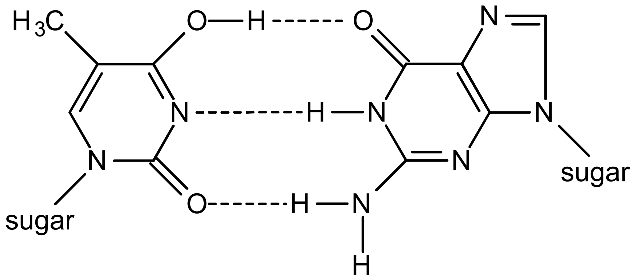
105. The complementary base pairs in DNA are cytosine (C) and guanine (G) and thymine (T) and adenine (A). The complementary sequence is C–C–A–G–A–T–A–T–G

106. For each letter, there are 4 choices; A, T, G, or C. Hence the total number of codons is 4 × 4 × 4 = 64.

107. Uracil will hydrogen bond to adenine. The dashed lines represent the H-bonding interactions.



108. The tautomer could hydrogen bond to guanine, forming a G–T base pair instead of A–T.



109. Base pair:

RNA	DNA
A	T
G	C
C	G
U	A

a. Glu: CTT, CTC

Met: TAC

Phe: AAA, AAG

Val: CAA, CAG, CAT, CAC

Trp: ACC

Asp: CTA, CTG

b. DNA sequence for trp-glu-phe-met:

ACC –CTT –AAA –TAC
or or
CTC AAG

c. Due to glu and phe, there is a possibility of four different DNA sequences. They are:

ACC–CTT–AAA–TAC or ACC–CTC–AAA–TAC or

ACC–CTT–AAG–TAC or ACC–CTC–AAG –TAC

d.

$$\underbrace{\mathrm{T—A—C}}_{\text{met}}\mathrm{—}\underbrace{\mathrm{C—T—G}}_{\text{asp}}\mathrm{—}\underbrace{\mathrm{A—A—G}}_{\text{phe}}$$

e. TAC–CTA–AAG; TAC–CTA–AAA; TAC–CTG–AAA

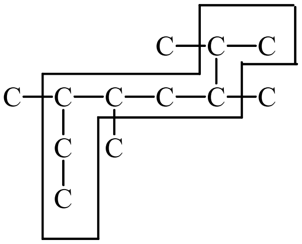
110. In sickle cell anemia, glutamic acid is replaced by valine. DNA codons: Glu: CTT, CTC; Val: CAA, CAG, CAT, CAC; replacing the middle T with an A in the code for Glu will code for Val.

CTT → CAT or CTC → CAC
Glu Val Glu Val

Additional Exercises

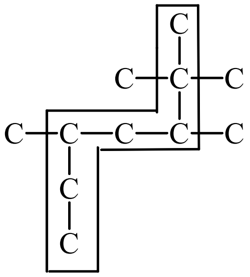
111. We omitted the hydrogens for clarity. The number of hydrogens bonded to each carbon is the number necessary to form four bonds.

a.



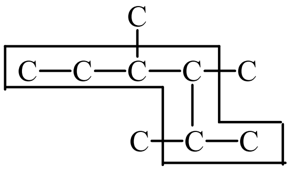
2,3,5,6-tetramethyloctane

b.



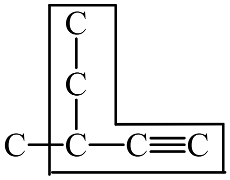
2,2,3,5-tetramethylheptane

c.



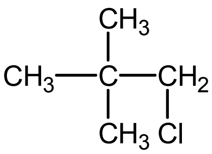
2,3,4-trimethylhexane

d.



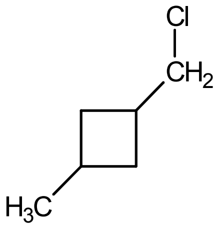
3-methyl-1-pentyne

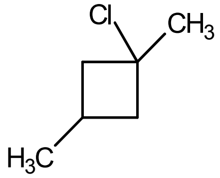
112. a. Only one monochlorination product can form (1-chloro-2,2-dimethylpropane). The other possibilities differ from this compound by a simple rotation, so they are not different compounds.

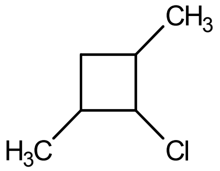


$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{Cl}{CH_2}$

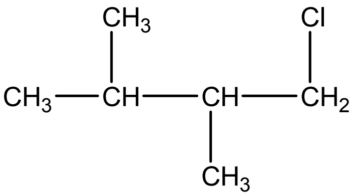
b. Three different monochlorination products are possible (ignoring cis-trans isomers).



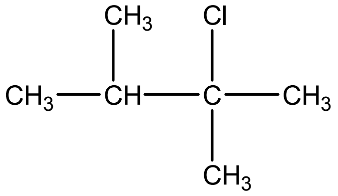




c. Two different monochlorination products are possible (the other possibilities differ by a simple rotation of one of these two compounds).

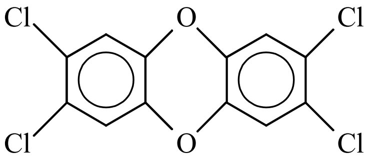


$$\mathrm{CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}\overset{\overset{\displaystyle Cl}{|}}{CH_2}}$$



$$\mathrm{CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle Cl}{|}}{C}}{-}CH_3}$$

113.



There are many possibilities for isomers. Any structure with four chlorines replacing four hydrogens in any four of the numbered positions would be an isomer; i.e., 1,2,3,4-tetrachloro-dibenzo-p-dioxin is a possible isomer.

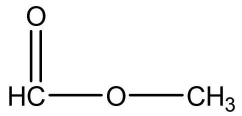
114. We would expect compounds b and d to boil at the higher temperatures because they exhibit additional dipole forces that the nonpolar compounds in a, c, and e do not exhibit. London dispersion (LD) forces are the intermolecular forces exhibited by compounds a, c, and e. Size and shape are the two main factors that affect the strength of LD forces. Compounds a and e have a formula of C_5H_{12}, and the bigger compound c has a formula of C_6H_{14}. The smaller compounds in a and e will boil at the two lowest boiling points. Between a and e, compound a has a more elongated structure which leads to stronger LD forces; compound a boils at 36°C, and compound e boils at 9.5°C.

115. The isomers are:

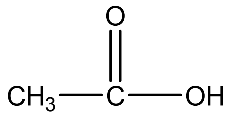
$CH_3{-}O{-}CH_3$	CH_3CH_2OH
dimethyl ether, −23°C	ethanol, 78.5°C

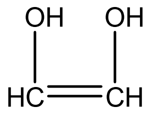
Ethanol, with its ability to form the relatively strong hydrogen-bonding interactions, boils at the higher temperature.

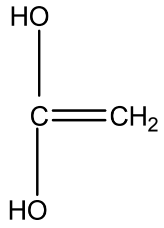
116. The isomers are:



boils at lowest temperature
(no H-bonding)





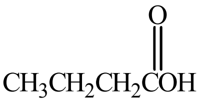


With the exception of the first isomer, the other isomers can form the relatively strong hydrogen bonding interactions. The isomers that can hydrogen bond will boil at higher temperatures.

117. Alcohols consist of two parts, the polar OH group and the nonpolar hydrocarbon chain attached to the OH group. As the length of the nonpolar hydrocarbon chain increases, the solubility of the alcohol decreases in water, a very polar solvent. In methyl alcohol (methanol), the polar OH group overrides the effect of the nonpolar CH_3 group, and methyl alcohol is soluble in water. In stearyl alcohol, the molecule consists mostly of the long nonpolar hydrocarbon chain, so it is insoluble in water.

118. $CH_3CH_2CH_2CH_2CH_2CH_2CH_2COOH + OH^- \rightarrow CH_3–(CH_2)_6–COO^- + H_2O$; octanoic acid is more soluble in 1 *M* NaOH. Added OH^- will remove the acidic proton from octanoic acid, creating a charged species. As is the case with any substance with an overall charge, solubility in water increases. When morphine is reacted with H^+, the amine group is protonated, creating a positive charge on morphine ($R_3N + H^+ \rightarrow R_3\overset{+}{N}H$). By treating morphine with HCl, an ionic compound results that is more soluble in water and in the bloodstream than the neutral covalent form of morphine.

119. The structures, the types of intermolecular forces exerted, and the boiling points for the compounds are:

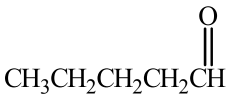


$CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}OH$

butanoic acid, 164°C
LD + dipole + H bonding

$CH_3CH_2CH_2CH_2CH_2OH$

1-pentanol, 137 °C
LD + H bonding



$CH_3CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}H$

pentanal, 103 °C
LD + dipole

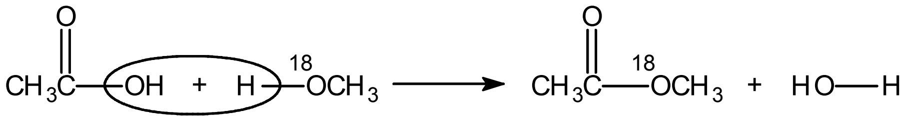
$CH_3CH_2CH_2CH_2CH_2CH_3$

n-hexane, 69 °C
LD only

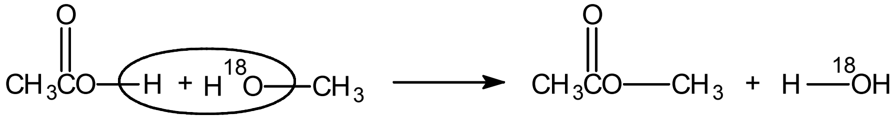
All these compounds have about the same molar mass. Therefore, the London dispersion (LD) forces in each are about the same. The other types of forces determine the boiling-point order. Since butanoic acid and 1-pentanol both exhibit hydrogen bonding interactions, these two compounds will have the two highest boiling points. Butanoic acid has the highest boiling point since it exhibits H bonding along with dipole-dipole forces due to the polar C=O bond.

120. Water is produced in this reaction by removing an OH group from one substance and H from the other substance. There are two ways to do this:

i.



ii.



Because the water produced is not radioactive, methyl acetate forms by the first reaction, where all the oxygen-18 ends up in methyl acetate.

121. $85.63 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 7.130 \text{ mol C}$; $14.37 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 14.26 \text{ mol H}$

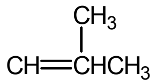
Because the mol H to mol C ratio is 2 : 1 (14.26/7.130 = 2.000), the empirical formula is CH_2. The empirical formula mass ≈ 12 + 2(1) = 14. Since 4 × 14 = 56 puts the molar mass between 50 and 60, the molecular formula is C_4H_8. The isomers of C_4H_8 are:

$CH_2{=}CHCH_2CH_3$

1-butene

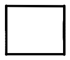
$CH_3CH{=}CHCH_3$

2-butene

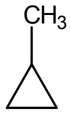


$CH{=}\overset{CH_3}{\overset{|}{C}}HCH_3$

2-methyl-1-propene



cyclobutane

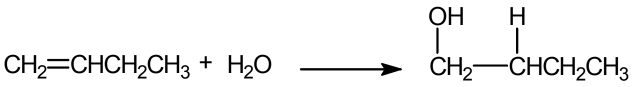


methylcyclopropane

Only the alkenes will react with H_2O to produce alcohols, and only 1-butene will produce a secondary alcohol for the major product and a primary alcohol for the minor product.

$$CH_2{=}CHCH_2CH_3 + H_2O \longrightarrow \overset{H}{\underset{}{\overset{|}{C}}}H_2 - \overset{OH}{\overset{|}{C}}HCH_2CH_3$$

2° alcohol, major product

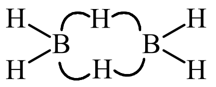


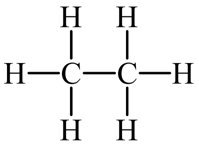
$$CH_2{=}CHCH_2CH_3 + H_2O \longrightarrow \overset{OH}{\overset{|}{C}}H_2 - \overset{H}{\overset{|}{C}}HCH_2CH_3$$

1° alcohol, minor product

2-Butene will produce only a secondary alcohol when reacted with H_2O, and 2-methyl-1-propene will produce a tertiary alcohol as the major product and a primary alcohol as the minor product.

122. B_2H_6, $2(3) + 6(1) = 12\ e^-$ C_2H_6, $2(4) + 6(1) = 14\ e^-$





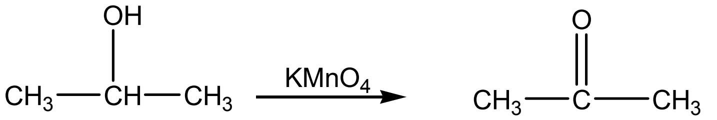
B_2H_6 has three-centered bonds. In these bonds, a single pair of electrons is used to bond all three atoms together. Because these three centered bonds are extremely electron-deficient, they are highly reactive. C_2H_6 has two more valence electrons than B_2H_6 and does not require three-centered bonds to attach the atoms together. C_2H_6 is much more stable.

123. $KMnO_4$ will oxidize primary alcohols to aldehydes and then to carboxylic acids. Secondary alcohols are oxidized to ketones by $KMnO_4$. Tertiary alcohols and ethers are not oxidized by $KMnO_4$.

The three isomers and their reactions with $KMnO_4$ are:

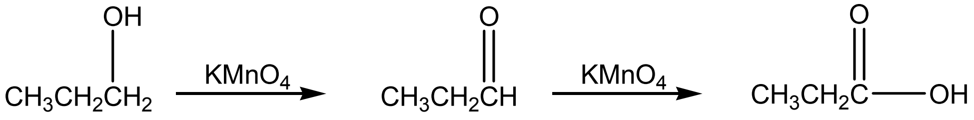
$$CH_3{-}O{-}CH_2CH_3 \xrightarrow{KMnO_4} \text{no reaction}$$

ether



$$CH_3{-}\overset{OH}{\overset{|}{C}}H{-}CH_3 \xrightarrow{KMnO_4} CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3$$

2° alcohol 2-propanone (acetone)

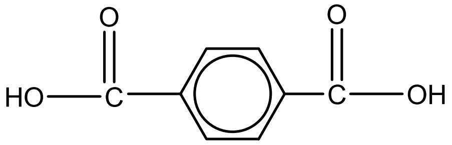


$$CH_3CH_2\overset{OH}{\overset{|}{C}}H_2 \xrightarrow{KMnO_4} CH_3CH_2\overset{O}{\overset{\|}{C}}H \xrightarrow{KMnO_4} CH_3CH_2\overset{O}{\overset{\|}{C}}{-}OH$$

1° alcohol propanal propanoic acid

The products of the reactions with excess $KMnO_4$ are 2-propanone and propanoic acid.

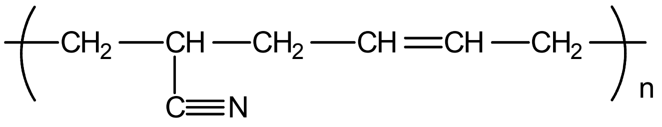
124. When addition polymerization of monomers with C=C bonds occurs, the backbone of the polymer chain consists of only carbon atoms. Because the backbone contains oxygen atoms, this is not an addition polymer; it is a condensation polymer. Because the ester functional group is present, we have a polyester condensation polymer. To form an ester functional group, we need the carboxylic acid and alcohol functional groups present in the monomers. From the structure of the polymer, we have a copolymer formed by the following monomers.



$HO—CH_2—CH_2—OH$

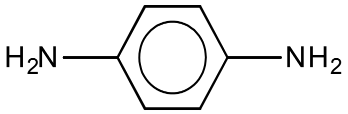
125. In nylon, hydrogen-bonding interactions occur due to the presence of N–H bonds in the polymer. For a given polymer chain length, there are more N–H groups in Nylon-46 as compared to Nylon-6. Hence Nylon-46 forms a stronger polymer compared to Nylon-6 due to the increased hydrogen-bonding interactions.

126. The monomers for nitrile are CH_2=CHCN (acrylonitrile) and CH_2=CHCH=CH_2 (butadiene). The structure of polymer nitrile is:

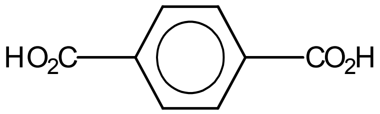


$$\left(CH_2—\underset{\displaystyle C\equiv N}{CH}—CH_2—CH=CH—CH_2\right)_n$$

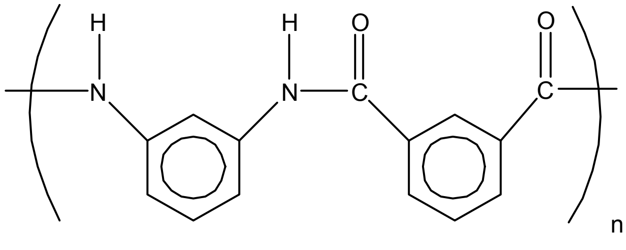
127. a.



and

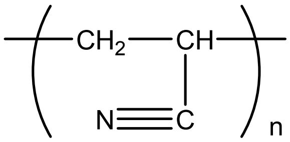


b. Repeating unit:



The two polymers differ in the substitution pattern on the benzene rings. The Kevlar chain is straighter, and there is more efficient hydrogen-bonding between Kevlar chains than between Nomex chains.

128. Polyacrylonitrile:



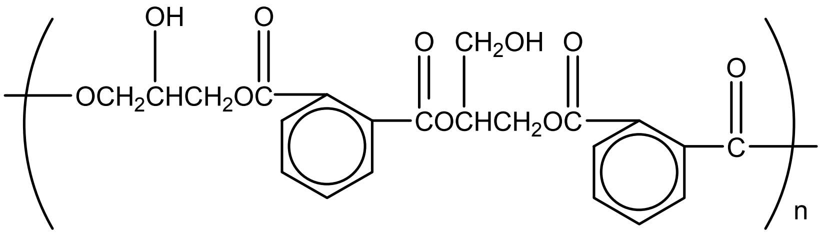
The CN triple bond is very strong and will not easily break in the combustion process. A likely combustion product is the toxic gas hydrogen cyanide, HCN(g).

129. a. The bond angles in the ring are about 60°. VSEPR predicts bond angles close to 109°. The bonding electrons are closer together than they prefer, resulting in strong electron-electron repulsions. Thus ethylene oxide is unstable (reactive).

b. The ring opens up during polymerization; the monomers link together through the formation of O–C bonds.

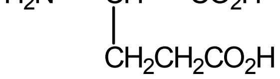
$$-\!\left(O-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2\right)_n-$$

130.



Two linkages are possible with glycerol. A possible repeating unit with both types of linkages is shown above. With either linkage, there are unreacted OH groups on the polymer chains. These can react with the acid groups of phthalic acid to form crosslinks among various polymer chains.

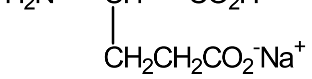
131. Glutamic acid:



$$H_2N-\underset{\displaystyle CH_2CH_2CO_2H}{\underset{|}{CH}}-CO_2H$$

One of the two acidic protons in the carboxylic acid groups is lost to form MSG. Which proton is lost is impossible for you to predict.

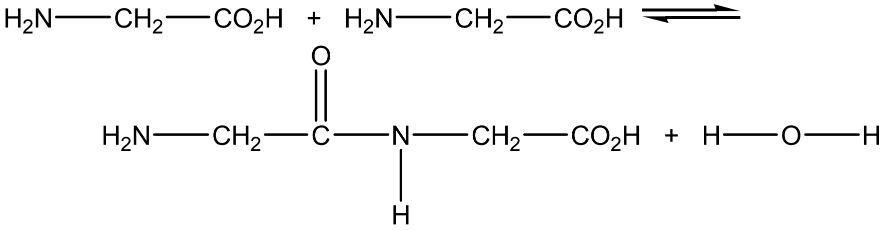
Monosodium glutamate:



$$H_2N-\underset{\displaystyle CH_2CH_2CO_2^-Na^+}{\underset{|}{CH}}-CO_2H$$

In MSG, the acidic proton from the carboxylic acid in the R group is lost, allowing formation of the ionic compound.

132. a.



$$H_2N{-}CH_2{-}CO_2H + H_2N{-}CH_2{-}CO_2H \rightleftharpoons H_2N{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle H}{|}}{N}{-}CH_2{-}CO_2H + H{-}O{-}H$$

Bonds broken:	Bonds formed:
1 C–O (358 kJ/mol)	1 C–N (305 kJ/mol)
1 H–N (391 kJ/mol)	1 H–O (467 kJ/mol)

$\Delta H = 358 + 391 - (305 + 467) = -23$ kJ

b. ΔS for this process is negative (unfavorable) because order increases (disorder decreases).

c. $\Delta G = \Delta H - T\Delta S$; ΔG is positive because of the unfavorable entropy change. The reaction is not spontaneous.

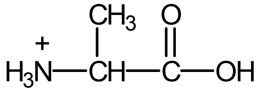
133. $\Delta G = \Delta H - T\Delta S$; for the reaction, we break a P–O and O–H bond and form a P–O and O–H bond, so $\Delta H \approx 0$. ΔS for this process is negative because positional probability decreases. Thus $\Delta G > 0$, and the reaction is not spontaneous.

134. Both proteins and nucleic acids must form for life to exist. From the simple analysis, it looks as if life can't exist, an obviously incorrect assumption. A cell is not an isolated system. There is an external source of energy to drive the reactions. A photosynthetic plant uses sunlight, and animals use the carbohydrates produced by plants as sources of energy. When all processes are combined, ΔS_{univ} must be greater than zero, as is dictated by the second law of thermodynamics.

135. Alanine can be thought of as a diprotic acid. The first proton to leave comes from the carboxylic acid end with $K_a = 4.5 \times 10^{-3}$. The second proton to leave comes from the protonated amine end (K_a for $R{-}NH_3^+ = K_w/K_b = 1.0 \times 10^{-14}/7.4 \times 10^{-5} = 1.4 \times 10^{-10}$).

In 1.0 *M* H^+, both the carboxylic acid and the amine end will be protonated since H^+ is in excess. The protonated form of alanine is below. In 1.0 *M* OH^-, the dibasic form of alanine will be present because the excess OH^- will remove all acidic protons from alanine. The dibasic form of alanine follows.

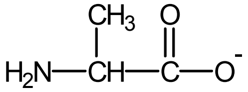
1.0 *M* H^+ :



$$\overset{+}{H_3N}{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$$

protonated form

1.0 *M* OH^- :



$$H_2N{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^-$$

dibasic form

136. The number of approximate base pairs in a DNA molecule is:

$$\frac{4.5 \times 10^9 \text{ g/mol}}{600 \text{ g/mol}} = 8 \times 10^6 \text{ base pairs}$$

The approximate number of complete turns in a DNA molecule is:

$$8 \times 10^6 \text{ base pairs} \times \frac{0.34 \text{ nm}}{\text{base pair}} \times \frac{1 \text{ turn}}{3.4 \text{ nm}} = 8 \times 10^5 \text{ turns}$$

137. For denaturation, heat is added so it is an endothermic process. Because the highly ordered secondary structure is disrupted, positional probability increases, so entropy will increase. Thus ΔH and ΔS are both positive for protein denaturation.

138. a. $^+H_3NCH_2COO^- + H_2O \rightleftharpoons H_2NCH_2CO_2^- + H_3O^+$

$$K_{eq} = K_a(-NH_3^+) = \frac{K_w}{K_b(-NH_2)} = \frac{1.0 \times 10^{-14}}{6.0 \times 10^{-5}} = 1.7 \times 10^{-10}$$

b. $H_2NCH_2CO_2^- + H_2O \rightleftharpoons H_2NCH_2CO_2H + OH^-$

$$K_{eq} = K_b(-CO_2^-) = \frac{K_w}{K_a(-CO_2H)} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-3}} = 2.3 \times 10^{-12}$$

c. $^+H_3NCH_2CO_2H \rightleftharpoons 2\ H^+ + H_2NCH_2CO_2^-$

$$K_{eq} = K_a(-CO_2H) \times K_a(-NH_3^+) = (4.3 \times 10^{-3})(1.7 \times 10^{-10}) = 7.3 \times 10^{-13}$$

Challenge Problems

139. For the reaction:

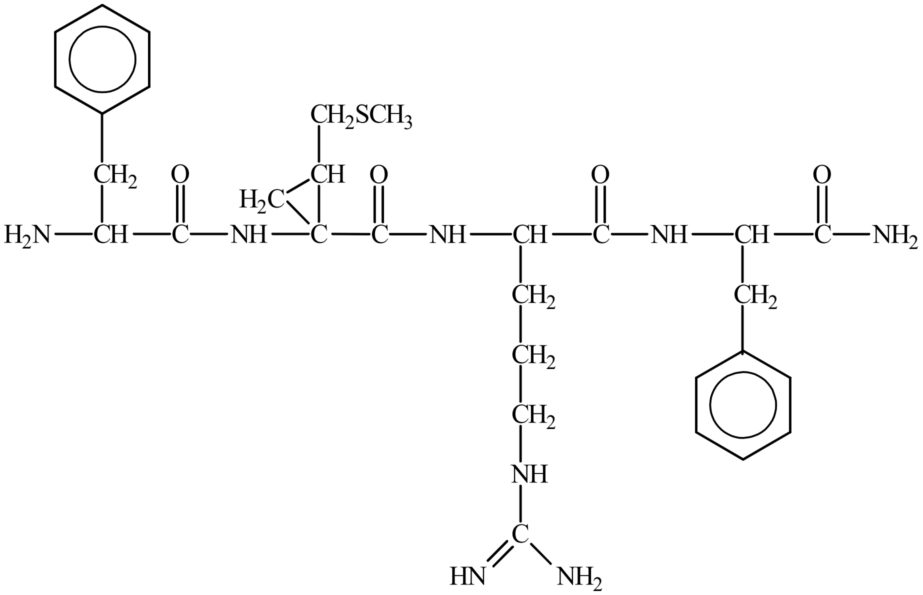
$^+H_3NCH_2CO_2H \rightleftharpoons 2\ H^+ + H_2NCH_2CO_2^-$ $K_{eq} = 7.3 \times 10^{-13} = K_a(\text{-}CO_2H) \times K_a(\text{-}NH_3^+)$

$$7.3 \times 10^{-13} = \frac{[H^+]^2[H_2NCH_2CO_2^-]}{[^+H_3NCH_2CO_2H]} = [H^+]^2,\ [H^+] = (7.3 \times 10^{-13})^{1/2}$$

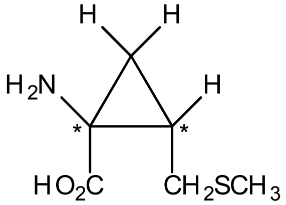
$[H^+] = 8.5 \times 10^{-7}\ M$; pH = $-\log[H^+]$ = 6.07 = isoelectric point

140. a. The new amino acid is most similar to methionine due to its $-CH_2CH_2SCH_3$ R group.

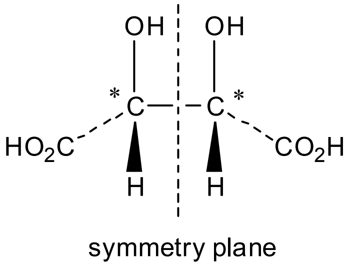
b. The new amino acid replaces methionine. The structure of the tetrapeptide is:



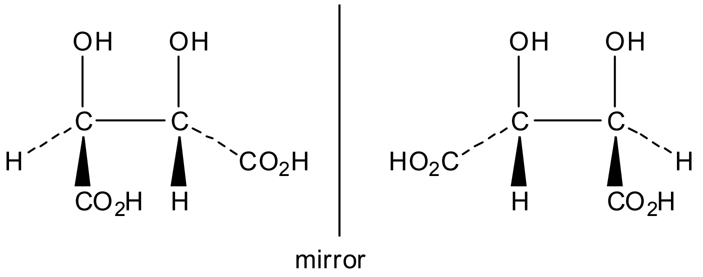
c. The chiral carbons are indicated with an asterisk.



141. a. Even though this form of tartaric acid contains 2 chiral carbon atoms (see asterisks in the following structure), the mirror image of this form of tartaric acid is superimpossible. Therefore, it is not optically active. An easier way to identify optical activity in molecules with two or more chiral carbon atoms is to look for a plane of symmetry in the molecule. If a molecule has a plane of symmetry, then it is never optically active. A plane of symmetry is a plane that bisects the molecule where one side exactly reflects on the other side.

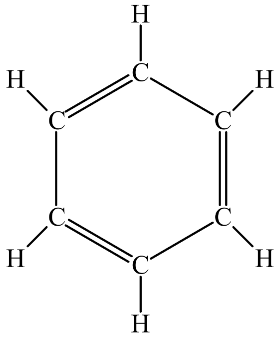


b. The optically active forms of tartaric acid have no plane of symmetry. The structures of the optically active forms of tartaric acid are:



These two forms of tartaric acid are nonsuperimposable.

142. One of the resonance structures for benzene is:



To break $C_6H_6(g)$ into C(g) and H(g) requires breaking 6 C–H bonds, 3 C=C bonds, and 3 C–C bonds:

$$C_6H_6(g) \rightarrow 6\ C(g) + 6\ H(g) \qquad \Delta H = 6\ D_{C-H} + 3\ D_{C=C} + 3\ D_{C-C}$$

$$\Delta H = 6(413\text{ kJ}) + 3(614\text{ kJ}) + 3(347\text{ kJ}) = 5361\text{ kJ}$$

The question asks for ΔH_f° for $C_6H_6(g)$, which is ΔH for the reaction:

$$6\ C(s) + 3\ H_2(g) \rightarrow C_6H_6(g) \qquad \Delta H = \Delta H^\circ_{f,\,C_6H_6(g)}$$

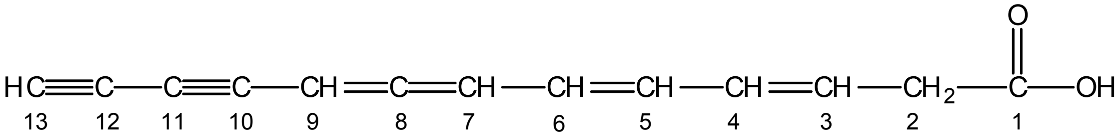
To calculate ΔH for this reaction, we will use Hess's law along with the ΔH_f° value for C(g) and the bond energy value for H_2 ($D_{H_2} = 432$ kJ/mol).

$$\begin{aligned}
6\ C(g) + 6\ H(g) &\rightarrow C_6H_6(g) &\qquad \Delta H_1 &= -5361\text{ kJ} \\
6\ C(s) &\rightarrow 6\ C(g) &\qquad \Delta H_2 &= 6(717\text{ kJ}) \\
3\ H_2(g) &\rightarrow 6\ H(g) &\qquad \Delta H_3 &= 3(432\text{ kJ}) \\
\hline
6\ C(s) + 3\ H_2(g) &\rightarrow C_6H_6(g) &\qquad \Delta H &= \Delta H_1 + \Delta H_2 + \Delta H_3 = 237\text{ kJ}
\end{aligned}$$

$$\Delta H^\circ_{f,\,C_6H_6(g)} = 237\text{ kJ/mol}$$

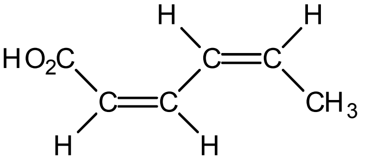
The experimental ΔH_f° for $C_6H_6(g)$ is more stable (lower in energy) by 154 kJ than the ΔH_f° calculated from bond energies (83 - 237 = -154 kJ). This extra stability is related to benzene's ability to exhibit resonance. Two equivalent Lewis structures can be drawn for benzene. The π bonding system implied by each Lewis structure consists of three localized π bonds. This is not correct because all C–C bonds in benzene are equivalent. We say the π electrons in benzene are delocalized over the entire surface of C_6H_6 (see Section 9.5 of the text). The large discrepancy between ΔH_f° values is due to the delocalized π electrons, whose effect was not accounted for in the calculated ΔH_f° value. The extra stability associated with benzene can be called resonance stabilization. In general, molecules that exhibit resonance are usually more stable than predicted using bond energies.

143.

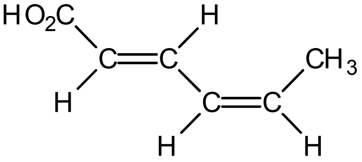


$$HC\equiv C-C\equiv C-CH=C=CH-CH=CH-CH=CH-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

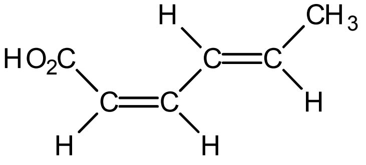
144.



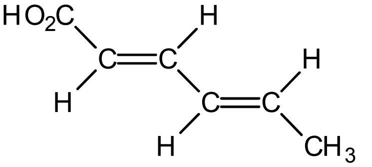
cis-2-cis-4-hexadienoic acid



trans-2-cis-4-hexadienoic acid



cis-2-trans-4-hexadienoic acid

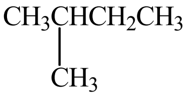


trans-2-trans-4-hexadienoic acid

145. a. The three structural isomers of C_5H_{12} are:

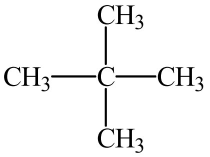
$CH_3CH_2CH_2CH_2CH_3$

n-pentane



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

2-methylbutane



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

2,2-dimethylpropane

n-Pentane will form three different monochlorination products: 1-chloropentane, 2-chloropentane, and 3-chloropentane (the other possible monochlorination products differ by a simple rotation of the molecule; they are not different products from the ones listed). 2,2-Dimethylpropane will only form one monochlorination product: 1-chloro-2,2-dimethylpropane. 2-Methylbutane is the isomer of C_5H_{12} that forms four different monochlorination products: 1-chloro-2-methylbutane, 2-chloro-2-methyl-butane, 3-chloro-2-methylbutane (or we could name this compound 2-chloro-3-methylbutane), and 1-chloro-3-methylbutane.

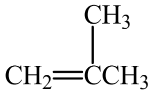
b. The isomers of C_4H_8 are:

$CH_2{=}CHCH_2CH_3$

1-butene

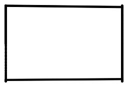
$CH_3CH{=}CHCH_3$

2-butene

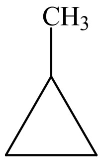


$CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}CH_3$

2-methyl-1-propene or
2-methylpropene

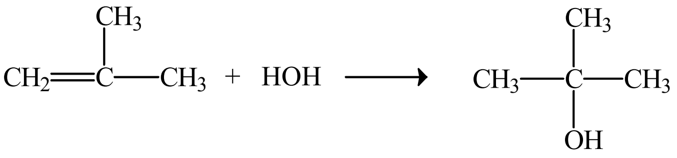


cyclobutane



methylcyclopropane

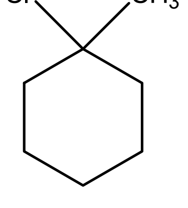
The cyclic structures will not react with H_2O; only the alkenes will add H_2O to the double bond. From Exercise 62, the major product of the reaction of 1-butene and H_2O is 2-butanol (a 2° alcohol). 2-Butanol is also the major (and only) product when 2-butene and H_2O react. 2-Methylpropene forms 2-methyl-2-propanol as the major product when reacted with H_2O; this product is a tertiary alcohol. Therefore, the C_4H_8 isomer is 2-methylpropene.



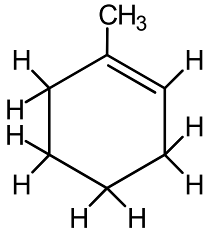
$$CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH_3 + HOH \longrightarrow CH_3{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}CH_3$$

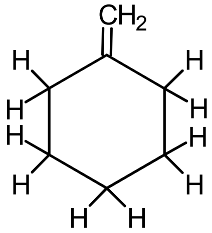
2-methyl-2-propanol
(a 3° alcohol, 3 R
groups)

c. The structure of 1-chloro-1-methylcyclohexane is:

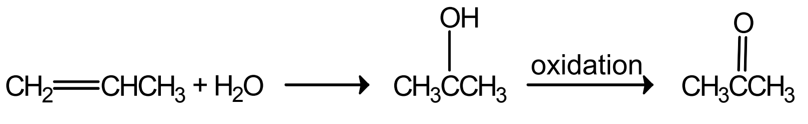


The addition reaction of HCl with an alkene is a likely choice for this reaction (see Exercise 62). The two isomers of C_7H_{12} that produce 1-chloro-1-methylcyclohexane as the major product are:





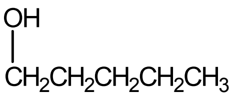
d. Working backwards, 2° alcohols produce ketones when they are oxidized (1° alcohols produce aldehydes, then carboxylic acids). The easiest way to produce the 2° alcohol from a hydrocarbon is to add H_2O to an alkene. The alkene reacted is 1-propene (or propene).



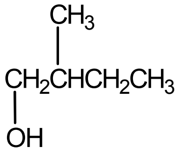
$$CH_2{=}CHCH_3 + H_2O \longrightarrow CH_3\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow{\text{oxidation}} CH_3\overset{O}{\overset{\|}{C}}CH_3$$

propene acetone

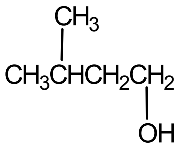
e. The $C_5H_{12}O$ formula has too many hydrogens to be anything other than an alcohol (or an unreactive ether). 1° Alcohols are first oxidized to aldehydes, then to carboxylic acids. Therefore, we want a 1° alcohol. The 1° alcohols with formula $C_5H_{12}O$ are:



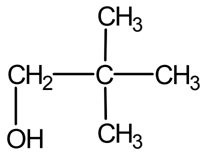
1-pentanol



2-methyl-1-butanol



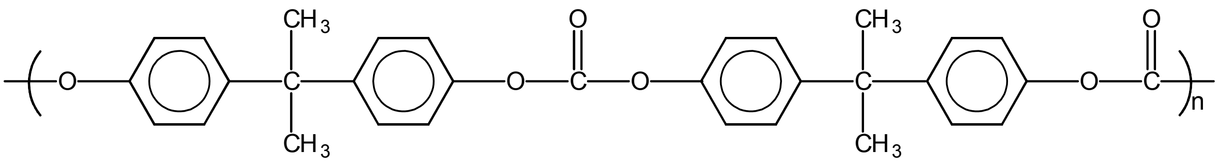
3-methyl-1-butanol



2,2-dimethyl-1-propanol

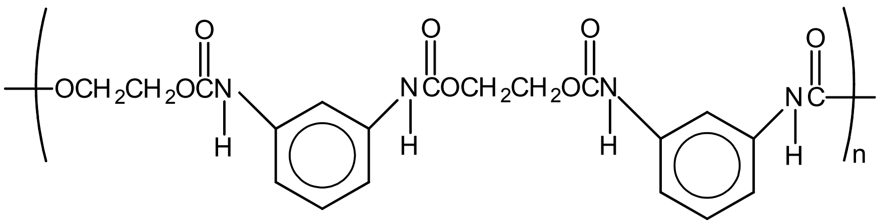
There are other alcohols with formula $C_5H_{12}O$, but they are all 2° or 3° alcohols, which do not produce carboxylic acids when oxidized.

146. a.

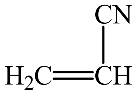


b. Condensation; HCl is eliminated when the polymer bonds form.

147.



148. a.

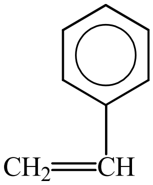


$H_2C{=}CH(CN)$

acrylonitrile

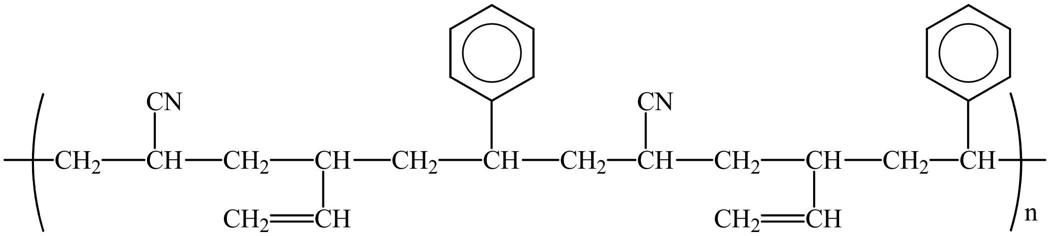
$CH_2{=}CH{-}CH{=}CH_2$

butadiene



styrene

The structure of ABS plastic assuming a 1 : 1 : 1 mole ratio is:



Note: Butadiene does not polymerize in a linear fashion in ABS plastic (unlike other butadiene polymers). There is no way for you to be able to predict this.

b. Only acrylonitrile contains nitrogen. If we have 100.00 g of polymer:

$$8.80 \text{ g N} \times \frac{1 \text{ mol } C_3H_3N}{14.01 \text{ g N}} = \frac{53.06 \text{ g } C_3H_3N}{1 \text{ mol } C_3H_3 \text{ N}} = 33.3 \text{ g } C_3H_3N$$

$$\text{Mass \% } C_3H_3N = \frac{33.3 \text{ g } C_3H_3N}{100.00 \text{ g polymer}} = 33.3\% \ C_3H_3N$$

Br_2 adds to double bonds of alkenes (benzene's delocalized π bonds in the styrene monomer will not react with Br_2 unless a special catalyst is present). Only butadiene in the polymer has a reactive double bond. From the polymer structure in part a, butadiene will react in a 1 : 1 mol ratio with Br_2.

$$0.605\text{ g Br}_2 \times \frac{1\text{ mol Br}_2}{159.8\text{ g Br}_2} \times \frac{1\text{ mol C}_4\text{H}_6}{\text{mol Br}_2} \times \frac{54.09\text{ g C}_4\text{H}_6}{\text{mol C}_4\text{H}_6} = 0.205\text{ g C}_4\text{H}_6$$

$$\text{Mass \% C}_4\text{H}_6 = \frac{0.205\text{ g}}{1.20\text{ g}} \times 100 = 17.1\%\text{ C}_4\text{H}_6$$

Mass % styrene (C_8H_8) = 100.0 − 33.3 − 17.1 = 49.6% C_8H_8.

c. If we have 100.0 g of polymer:

$$33.3\text{ g C}_3\text{H}_3\text{N} \times \frac{1\text{ mol C}_3\text{H}_3\text{N}}{53.06\text{ g}} = 0.628\text{ mol C}_3\text{H}_3\text{N}$$

$$17.1\text{ g C}_4\text{H}_6 \times \frac{1\text{ mol C}_4\text{H}_6}{54.09\text{ g C}_4\text{H}_6} = 0.316\text{ mol C}_4\text{H}_6$$

$$49.6\text{ g C}_8\text{H}_8 \times \frac{1\text{ mol C}_8\text{H}_8}{104.14\text{ g C}_8\text{H}_8} = 0.476\text{ mol C}_8\text{H}_8$$

$$\text{Dividing by 0.316:}\quad \frac{0.628}{0.316} = 1.99;\quad \frac{0.316}{0.316} = 1.00;\quad \frac{0.476}{0.316} = 1.51$$

This is close to a mole ratio of 4 : 2 : 3. Thus there are 4 acrylonitrile to 2 butadiene to 3 styrene molecules in this polymer sample, or $(A_4B_2S_3)_n$.

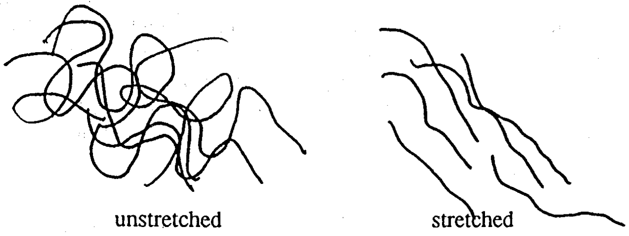
149. a. The temperature of the rubber band increases when it is stretched.

b. Exothermic because heat is released.

c. As the polymer chains that make up the rubber band are stretched, they line up more closely together, resulting in stronger London dispersion forces between the chains. Heat is released as the strength of the intermolecular forces increases.

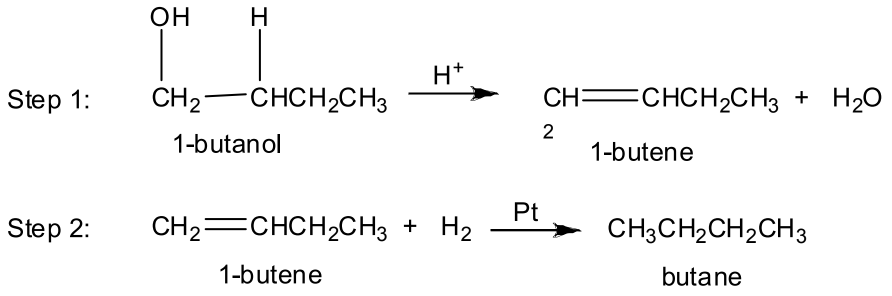
d. Stretching is not spontaneous, so ΔG is positive. $\Delta G = \Delta H - T\Delta S$; since ΔH is negative, ΔS must be negative in order to give a positive ΔG.

e.



The structure of the stretched polymer chains is more ordered (has a smaller positional probability). Therefore, entropy decreases as the rubber band is stretched.

150. a.



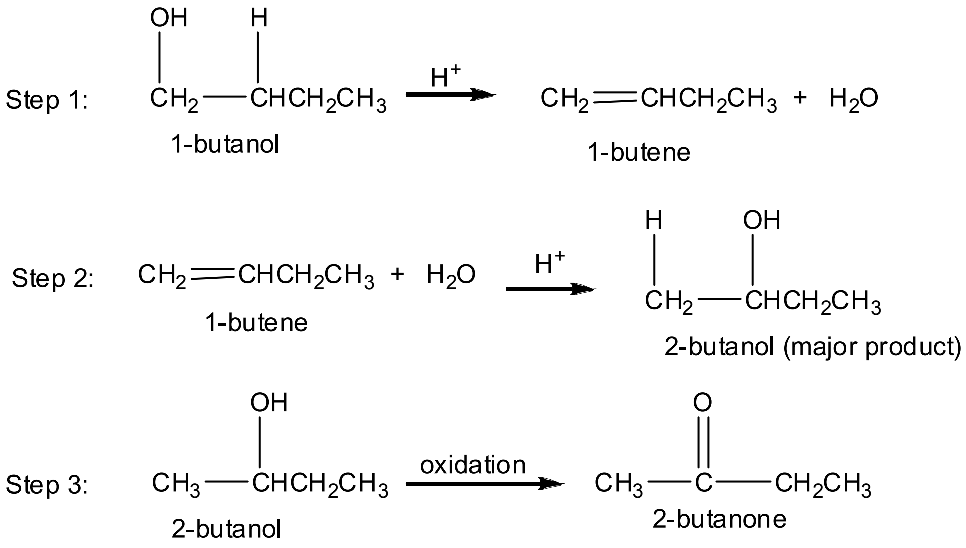
Step 1: $CH_2(OH)\text{—}CH(H)CH_2CH_3 \xrightarrow{H^+} CH_2{=}CHCH_2CH_3 + H_2O$

1-butanol → 1-butene

Step 2: $CH_2{=}CHCH_2CH_3 + H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_3$

1-butene → butane

b.



Step 1: $CH_2(OH)\text{—}CH(H)CH_2CH_3 \xrightarrow{H^+} CH_2{=}CHCH_2CH_3 + H_2O$

1-butanol → 1-butene

Step 2: $CH_2{=}CHCH_2CH_3 + H_2O \xrightarrow{H^+} CH_2(H)\text{—}CH(OH)CH_2CH_3$

1-butene → 2-butanol (major product)

Step 3: $CH_3\text{—}CH(OH)CH_2CH_3 \xrightarrow{\text{oxidation}} CH_3\text{—}C(=O)\text{—}CH_2CH_3$

2-butanol → 2-butanone

151. $$4.2 \times 10^{-3}\ \text{g } K_2CrO_7 \times \frac{1\ \text{mol } K_2Cr_2O_7}{294.20\ \text{g}} \times \frac{1\ \text{mol } Cr_2O_7^{2-}}{\text{mol } K_2Cr_2O_7} \times \frac{3\ \text{mol } C_2H_5OH}{2\ \text{mol } Cr_2O_7^{2-}}$$

$$= 2.1 \times 10^{-5}\ \text{mol } C_2H_5OH$$

$$n_{\text{breath}} = \frac{PV}{RT} = \frac{\left(750.\ \text{mm Hg} \times \frac{1\ \text{atm}}{760\ \text{mm Hg}}\right) \times 0.500\ \text{L}}{\frac{0.08206\ \text{L atm}}{\text{K mol}} \times 303\ \text{K}} = 0.0198\ \text{mol breath}$$

$$\text{Mol \% } C_2H_5OH = \frac{2.1 \times 10^{-5}\ \text{mol } C_2H_5OH}{0.0198\ \text{mol total}} \times 100 = 0.11\%\ \text{alcohol}$$

152. Assuming 1.000 L of the hydrocarbon (C_xH_y), then the volume of products will be 4.000 L, and the mass of products ($H_2O + CO_2$) will be:

1.391 g/L × 4.000 L = 5.564 g products

$$\text{Moles } C_xH_y = n_{C_xH_y} = \frac{PV}{RT} = \frac{0.959 \text{ atm} \times 1.000 \text{ L}}{\frac{0.08206 \text{ L atm}}{\text{K mol}} \times 298 \text{ K}} = 0.0392 \text{ mol}$$

$$\text{Moles products} = n_p = \frac{PV}{RT} = \frac{1.51 \text{ atm} \times 4.000 \text{ L}}{\frac{0.08206 \text{ L atm}}{\text{K mol}} \times 375 \text{ K}} = 0.196 \text{ mol}$$

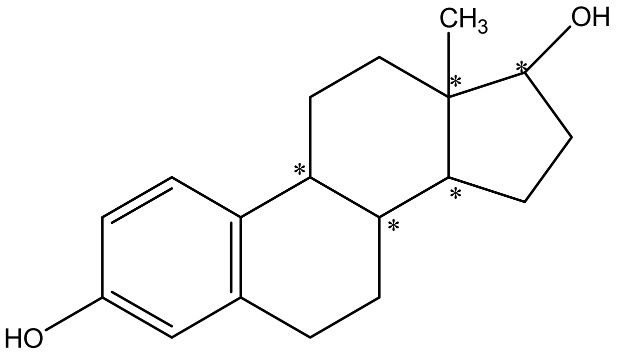
C_xH_y + oxygen $\rightarrow x\, CO_2 + y/2\, H_2O$; setting up two equations:

$0.0392x + 0.0392(y/2) = 0.196$ (moles of products)

$0.0392x(44.01 \text{ g/mol}) + 0.0392(y/2)(18.02 \text{ g/mol}) = 5.564 \text{ g}$ (mass of products)

Solving: $x = 2$ and $y = 6$, so the formula of the hydrocarbon is C_2H_6.

153. 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.

Integrative Problems

154. a. $0.5063 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g}} \times \frac{1 \text{ mol C}}{\text{mol } CO_2} \times \frac{12.01 \text{ g C}}{\text{mol C}} = 0.1382 \text{ g C}$

$$\text{Mass \%C} = \frac{0.1382 \text{ g C}}{0.1450 \text{ g compound}} \times 100 = 95.31\%$$

Mass %H = 100.00 – 95.31 = 4.69%H

Assuming 100.00 g compound:

$$95.31 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 7.936 \text{ mol C}/4.653 = 1.706 \text{ mol C}$$

$$4.69 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 4.653 \text{ mol H}/4.653 = 1 \text{ mol H}$$

Multiplying by 10 gives the empirical formula $C_{17}H_{10}$.

b. $$\text{Mol helicene} = 0.0125 \text{ kg} \times \frac{0.0175 \text{ mol helicene}}{\text{kg solvent}} = 2.19 \times 10^{-4} \text{ mol helicene}$$

$$\text{Molar mass} = \frac{0.0938 \text{ g}}{2.19 \times 10^{-4} \text{ mol}} = 428 \text{ g/mol}$$

Empirical formula mass ≈ 17(12) + 10(1) = 214 g/mol

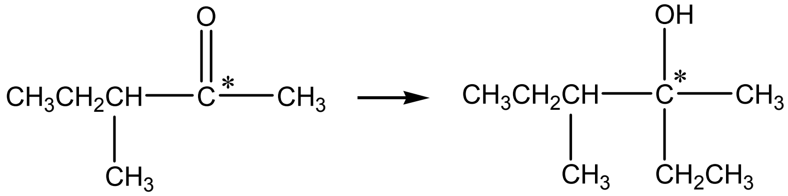
Because $\frac{428}{214} = 2.00$, the molecular formula is $(C_{17}H_{10}) \times 2 = C_{34}H_{20}$

c. $C_{34}H_{20}(s) + 39\ O_2(g) \rightarrow 34\ CO_2(g) + 10\ H_2O(l)$

155. a. Zn^{2+} has the $[Ar]3d^{10}$ electron configuration, and zinc does form +2 charged ions.

$$\text{Mass \% Zn} = \frac{\text{mass of 1 mol Zn}}{\text{mass of 1 mol } CH_3CH_2ZnBr} \times 100 = \frac{65.38 \text{ g}}{174.34 \text{ g}} \times 100 = 37.50\% \text{ Zn}$$

b. The reaction is:



The hybridization changes from sp^2 to sp^3.

c. 3,4-dimethyl-3-hexanol

Marathon Problems

156. a. urea, ammonium cyanate
b. saturated
c. tetrahedral
d. straight-chain or normal
e. bonds
f. –ane
g. longest
h. number
i. combustion
j. substitution
k. addition
l. hydrogenation
m. aromatic
n. functional
o. primary
p. carbon monoxide
q. fermentation
r. carbonyl
s. oxidation
t. carboxyl
u. esters, alcohol

157. a. statement (17)
b. statement (13)
c. statement (15)
d. statement (12)
e. statement (8)
f. statement (9)
g. statement (16)
h. statement (2)
i. statement (4)
j. statement (10)
k. statement (11)
l. statement (7)
m. statement (14)
n. statement (3)
o. statement (6)
p. statement (1)
q. statement (5)

158. a. deoxyribonucleic acid
b. nucleotides
c. ribose
d. ester
e. complementary
f. thymine, guanine
g. gene
h. transfer, messenger
i. DNA