CHAPTER 21

ORGANIC CHEMISTRY

Hydrocarbons

1. A hydrocarbon is a compound composed of only carbon and hydrogen. A saturated hydrocarbon has only carbon-carbon single bonds in the molecule. An unsaturated hydrocarbon has one or more carbon-carbon multiple bonds but may also contain carbon-carbon single bonds. A normal hydrocarbon has one chain of consecutively bonded carbon atoms. A branched hydrocarbon has at least one carbon atom not bonded to the end carbon of a chain of consecutively bonded carbon atoms. Instead, at least one carbon atom forms a bond to an inner carbon atom in the chain of consecutively bonded carbon atoms.

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

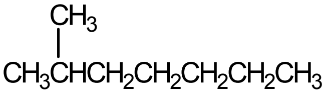
3. In order to form, cyclopropane and cyclobutane are forced to form bond angles much smaller than the preferred 109.5° bond angles. Cyclopropane and cyclobutane easily react in order to obtain the preferred 109.5° bond angles.

4. Aromatic hydrocarbons are a special class of unsaturated hydrocarbons based on the benzene ring. Benzene has the formula C_6H_6. It is a planar molecule (all atoms are in the same plane). Each carbon in benzene is attached to three other atoms; it exhibits trigonal planar geometry with 120° bond angles. Each carbon is sp^2 hybridized. The sp^2 hybrid orbitals go to form the three sigma bonds to each carbon. The unhybridized p atomic orbitals on each carbon overlap side to side with unhybridized p orbitals on adjacent carbons to form the π bonds. All six of the carbons in the six-membered ring have one unhybridized p atomic orbital. All six of the unhybridized p orbitals ovlerlap side to side to give a ring of electron density above and below the planar six-membered ring of benzene.

   The six π electrons in the π bonds in benzene can roam about above and below the entire ring surface; these π electrons are delocalized. This is important because all six carbon-carbon bonds in benzene are equivalent in length and strength. The Lewis structures say something different (three of the bonds are single, and three of the bonds are double). This is not correct. To explain the equivalent bonds, the π bonds can't be situated between two carbon atoms, as is the case in simple alkenes and alkynes; that is, the π bonds can't be localized. Instead, the six π electrons can roam about over a much larger area; they are delocalized over the entire surface of the molecule.

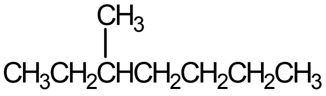
5. A difficult task in this problem is recognizing different compounds from compounds that differ by rotations about one or more C–C bonds (called conformations). The best way to distinguish different compounds from conformations is to name them. Different name = different compound; same name = same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

a.



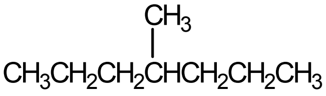
$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_2CH_2CH_3$

2-methylheptane



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

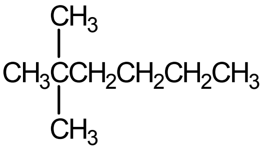
3-methylheptane



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

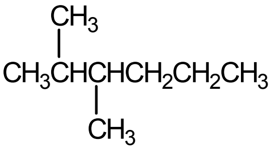
4-methylheptane

b.



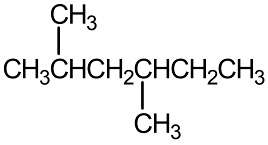
$CH_3\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_2CH_2CH_2CH_3$

2,2-dimethylhexane



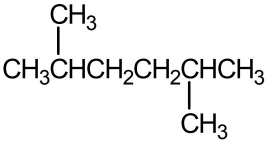
$CH_3\overset{CH_3}{\overset{|}{C}}H\underset{CH_3}{\underset{|}{C}}HCH_2CH_2CH_3$

2,3-dimethylhexane



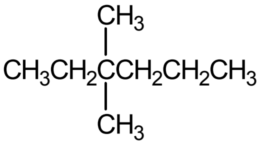
$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2\underset{CH_3}{\underset{|}{C}}HCH_2CH_3$

2,4-dimethylhexane



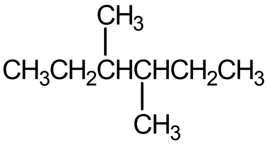
$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2\underset{CH_3}{\underset{|}{C}}HCH_3$

2,5-dimethylhexane



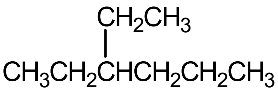
$CH_3CH_2\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_2CH_2CH_3$

3,3-dimethylhexane



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

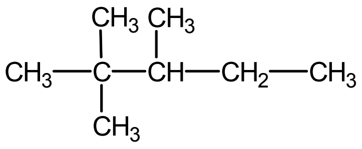
3,4-dimethylhexane



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

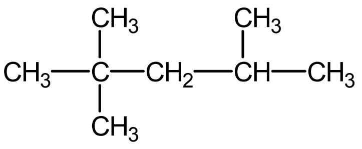
3-ethylhexane

c.



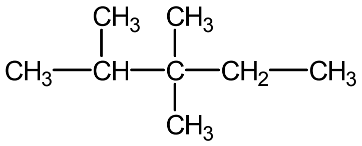
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_3$$

2,2,3-trimethylpentane



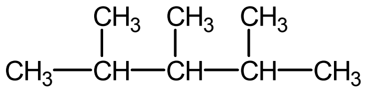
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

2,2,4-trimethylpentane



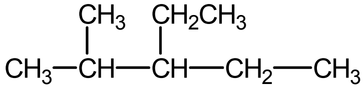
$$CH_3-\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3$$

2,3,3-trimethylpentane



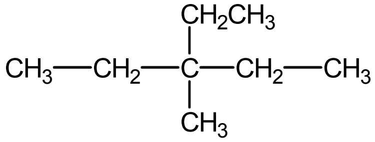
$$CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

2,3,4-trimethylpentane



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

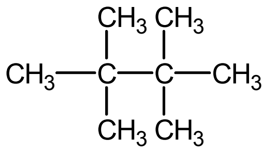
3-ethyl-2-methylpentane



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

3-ethyl-3-methylpentane

d.



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

2,2,3,3-tetramethylbutane

6. There is only one consecutive chain of C atoms in the molecule. They are not all in a true straight line since the bond angles at each carbon atom are the tetrahedral angles of 109.5°.

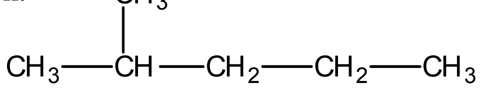
7. London dispersion (LD) forces are the primary intermolecular forces exhibited by hydrocarbons. The strength of the LD forces depends on the surface-area contact among neighboring molecules. As branching increases, there is less surface-area contact among neighboring molecules, leading to weaker LD forces and lower boiling points.

8. i.

$CH_3–CH_2–CH_2–CH_2–CH_2–CH_3$

hexane

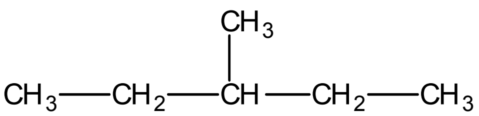
ii.



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

2-methylpentane

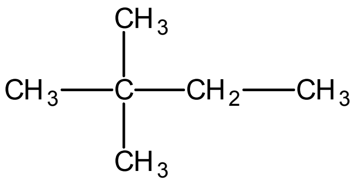
iii.



$CH_3CH_2CH(CH_3)CH_2CH_3$

3-methylpentane

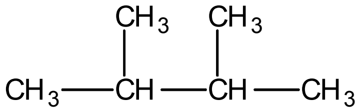
iv.



$CH_3C(CH_3)_2CH_2CH_3$

2,2-dimethylbutane

v.

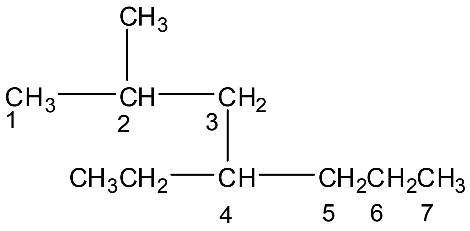


$CH_3CH(CH_3)CH(CH_3)CH_3$

2,3-dimethylbutane

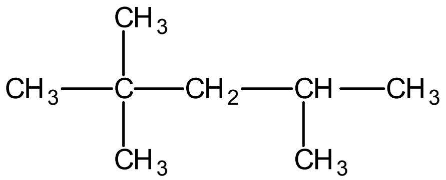
All other possibilities are identical to one of these five compounds.

9. a.



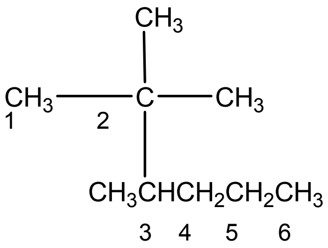
$CH_3CH(CH_3)CH_2CH(CH_2CH_3)CH_2CH_2CH_3$

b.



$CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$

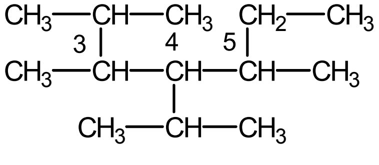
c.



$CH_3C(CH_3)_2CH(CH_3)CH_2CH_2CH_3$

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

10.



$CH_3CH(CH_3)CH(CH_3)CH(CH(CH_3)_2)CH(CH_3)CH_2CH_3$

4-isopropyl-2,3,5-trimethylheptane

11. 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.

12. 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; $C_{11}H_{22}$

13. a. 1-butene b. 2-methyl-2-butene

c. 2,5-dimethyl-3-heptene d. 2,3-dimethyl-1-pentene

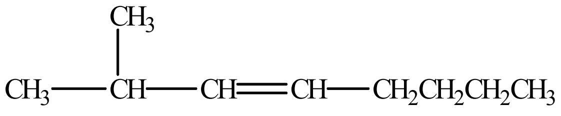
e. 1-ethyl-3-methylcyclopentene (double bond assumed between C_1 and C_2)

f. 4-ethyl-3-methylcyclopentene g. 4-methyl-2-pentyne

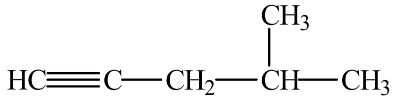
Note: Multiple bonds are assigned the lowest number possible.

14. a. $CH_3-CH_2-CH=CH-CH_2-CH_3$ b. $CH_3-CH=CH-CH=CH-CH_2CH_3$

c. d.



$$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH=CH-CH_2CH_2CH_2CH_3$$



$$HC\equiv C-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_3$$

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

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

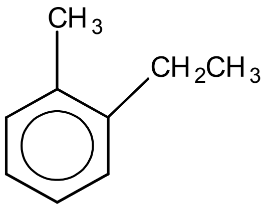
e. 3-iodo-1-butene

f. 2-bromotoluene (or o-bromotoluene or 1-bromo-2-methylbenzene)

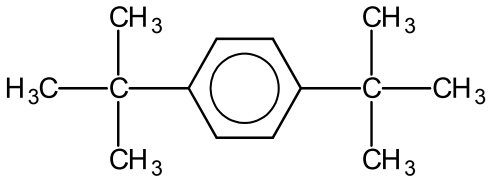
g. 1-bromo-2-methylcyclohexane

h. 4-bromo-3-methylcyclohexene (double bond assumed between C_1 and C_2)

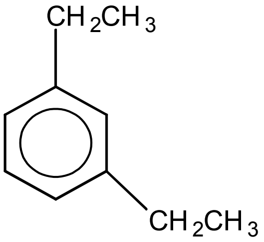
16. a.



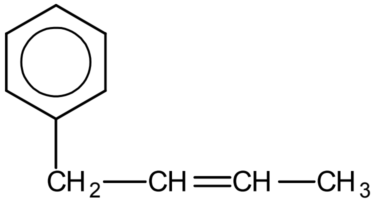
b.



c.



d.



17. isopropylbenzene or 2-phenylpropane

Isomerism

18. Resonance: All atoms are in the same position; only the positions of π electrons are different.

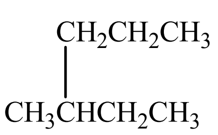
Isomerism: Atoms are in different locations in space.

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

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

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

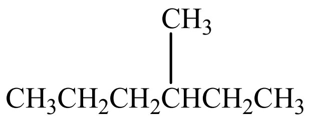
19. a. 1-sec-butylpropane



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

3-Methylhexane is correct.

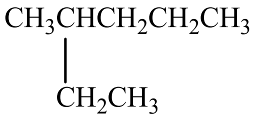
b. 4-methylhexane



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

3-Methylhexane is correct.

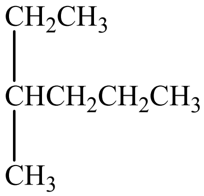
c. 2-ethylpentane



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

3-Methylhexane is correct.

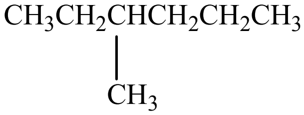
d. 1-ethyl-1-methylbutane



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

3-Methylhexane is correct.

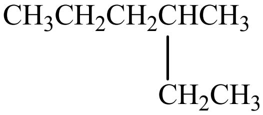
e. 3-methylhexane



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

This is a correct name.

f. 4-ethylpentane



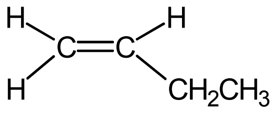
$CH_3CH_2CH_2\underset{\underset{CH_2CH_3}{|}}{C}HCH_3$

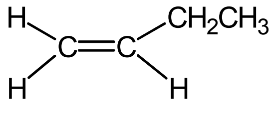
3-Methylhexane is correct.

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.

20. $CH_2Cl{-}CH_2Cl$, 1-2-dichloroethane; There is free rotation about the C–C single bond which 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.

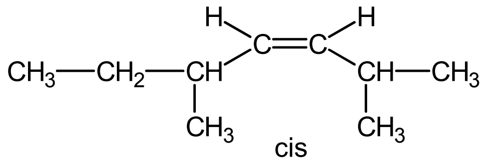
21. To exhibit cis-trans isomerism, a compound must first have restricted rotation about a carbon-carbon bond. This occurs in compounds with double bonds and ring compounds. Second, the compound must have two carbons in the restricted rotation environment that each have two different groups bonded. For example, the compound in Exercise 21.13a has a double bond, but the first carbon in the double bond has two H atoms attached. This compound does not exhibit cis-trans isomerism. To see this, let's draw the potential cis-trans isomers:

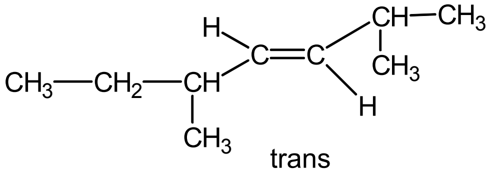




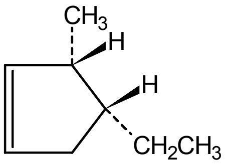
These are the same compounds; they only differ by a simply rotation of the molecule. Therefore, they are not isomers of each other, but instead, they are the same compound. The only compounds that fulfill the restricted rotation requirement *and* have two different groups attached to carbons in the restricted rotation are compounds c and f. The cis-trans isomerism for these follows.

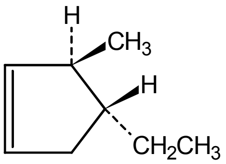
c.


cis


trans

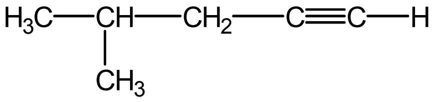
f.


cis


trans

▬ = out of plane of paper; ----- = into plane of paper

22. In Exercise 21.14, 3-hexene, 2,4-heptadiene, and 2-methyl-3-octene meet the requirements for cis-trans isomerism as outlined in Exercise 21.21. Only 4-methyl-1-pentyne does not exhibit cis-trans isomerism. Because of the triple bond in alkynes, the carbons with the restricted rotation only have one group bonded to them (not two groups, as is a necessity for geometric isomerism). See the structure below.



$$H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-C\equiv C-H$$

4-methyl-1-pentyne

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

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

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

b. Compound i is a trans isomer because the bulkiest groups bonded to the carbon atoms in the $C_3{=}C_4$ double bond are as far apart as possible.

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.

24. Two example isomers of C_4H_8 are:

$H_2C{=}CHCH_2CH_3$

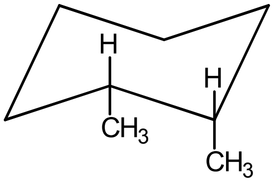
1-butene

cyclobutane (Two hydrogens are bonded to each carbon.)

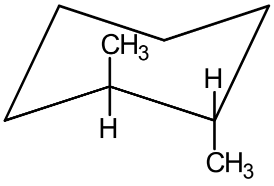
Other alkenes having the C_4H_8 are 2-butene and methylpropene. Methylcyclopropene is another cyclic isomer having the C_4H_8 formula.

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

25. 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.

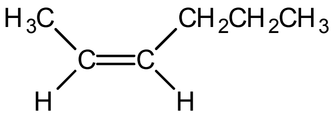


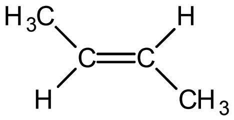
cis

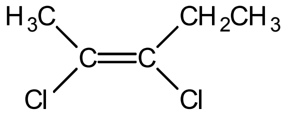


trans

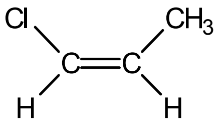
26.

a. 

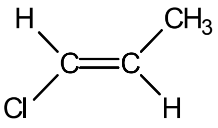
b. 

c. 

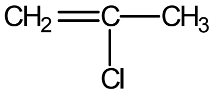
27. To help distinguish the different isomers, we will name them.



cis-1-chloro-1-propene

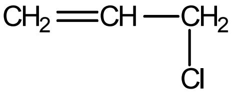


trans-1-chloro-1-propene



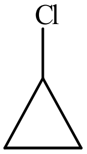
$CH_2{=}C(Cl){-}CH_3$

2-chloro-1-propene



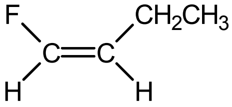
$CH_2{=}CH{-}CH_2Cl$

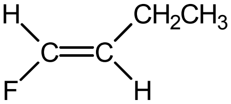
3-chloro-1-propene

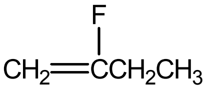


chlorocyclopropane

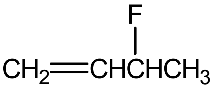
28.



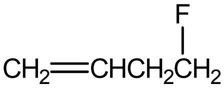




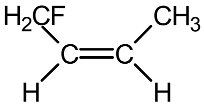
$CH_2{=}\overset{F}{C}CH_2CH_3$

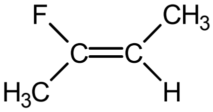


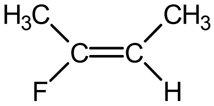
$CH_2{=}CH\overset{F}{C}HCH_3$

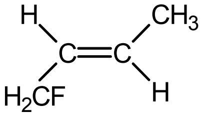


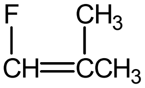
$CH_2{=}CHCH_2\overset{F}{C}H_2$



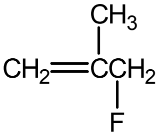




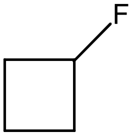


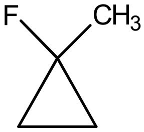


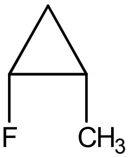
$\overset{F}{C}H{=}\overset{CH_3}{C}CH_3$



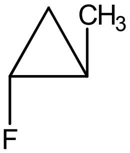
$CH_2{=}\overset{CH_3}{C}\underset{F}{C}H_2$







cis



trans

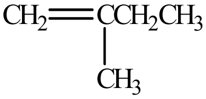
29. C_5H_{10} has the general formula for alkenes, C_nH_{2n}. To distinguish the different isomers from each other, we will name them. Each isomer must have a different name.

$CH_2{=}CHCH_2CH_2CH_3$

1-pentene

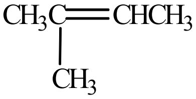
$CH_3CH{=}CHCH_2CH_3$

2-pentene



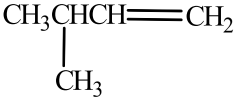
$CH_2{=}\underset{CH_3}{C}CH_2CH_3$

2-methyl-1-butene



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

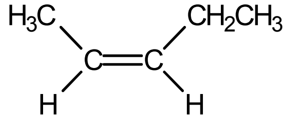
2-methyl-2-butene



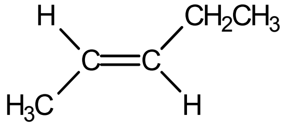
$CH_3\underset{CH_3}{C}HCH{=}CH_2$

3-methyl-1-butene

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



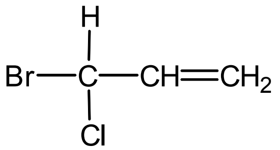
cis



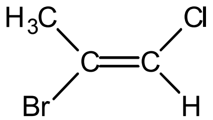
trans

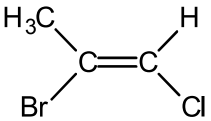
The other isomers of C_5H_{10} do not contain carbons in the double bond to which two different groups are attached.

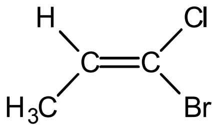
30.

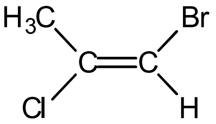


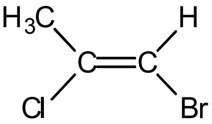
$\mathrm{Br{-}CHCl{-}CH{=}CH_2}$

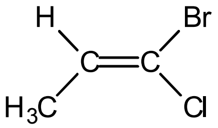


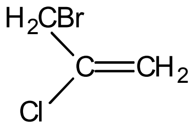


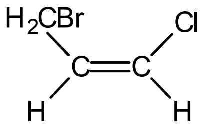


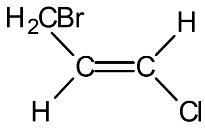


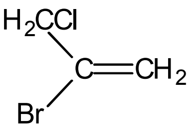


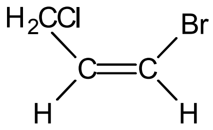


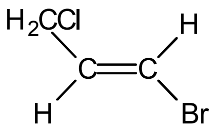












Note: 1-Bromo-1-chlorocyclopropane, cis-1-bromo-2-chlorocyclopropane, and trans-1-bromo-2-chlorocyclopropane are the ring structures that are isomers of bromochloropropene. We did not include the ring structures in the answer since their base name is not bromochloropropene.

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

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

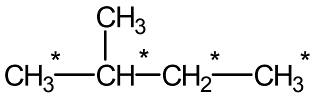
Note: In general, cis-trans designations refer to the relative positions of the largest groups. In compound b, the largest group off the first carbon in the double bond is CH_2CH_3, and the largest group off the second carbon in the double bond is $CH_2CH_2CH_3$. Since their relative placement is on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

32. a.

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

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).

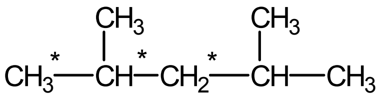
b.



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

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

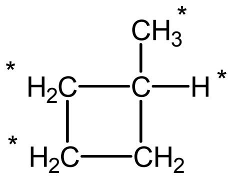
c.



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

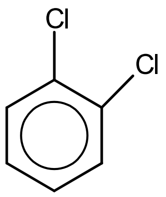
There are three different types of hydrogens, so three monochloro isomers are possible.

d.

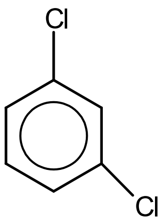


There are four different types of hydrogens, so four monochloro isomers are possible.

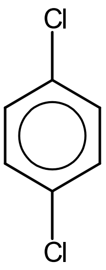
33. a.



ortho



meta



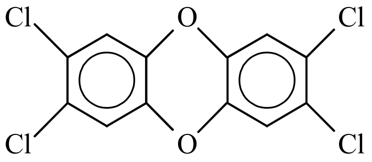
para

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.

34.

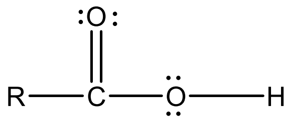


There are many possibilities for isomers. Any structure with four chlorines in any four of the numbered positions would be an isomer; i.e., 1,2,3,4-tetrachloro-dibenzo-p-dioxin is a possible isomer.

Functional Groups

35.

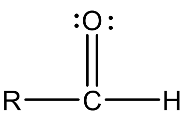
Carboxylic acid



$R-\overset{\overset{\displaystyle :O:}{\|}}{C}-\underset{\cdot\cdot}{\ddot{O}}-H$

RCOOH

Aldehyde

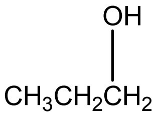


$R-\overset{\overset{\displaystyle :O:}{\|}}{C}-H$

RCHO

The R designation refers to the rest of the organic molecule beyond the specific functional group indicated in the formula. The R group may be a hydrogen but is usually a hydrocarbon fragment. The major point in the R group designation is that if the R group is an organic fragment, then the first atom in the R group is a carbon atom. What the R group has after the first carbon is not important to the functional group designation.

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



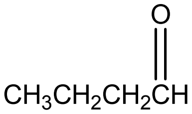
$CH_3CH_2\overset{\overset{\displaystyle OH}{|}}{CH_2}$

alcohol

$CH_3—O—CH_2CH_3$

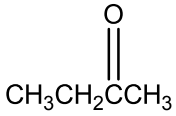
ether

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



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

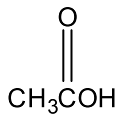
aldehyde



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

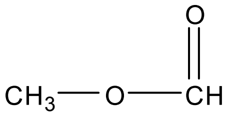
ketone

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



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

carboxylic acid



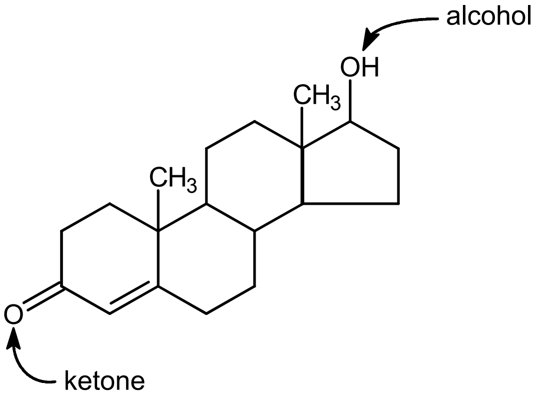
$CH_3-O-\overset{O}{\overset{\|}{C}}H$

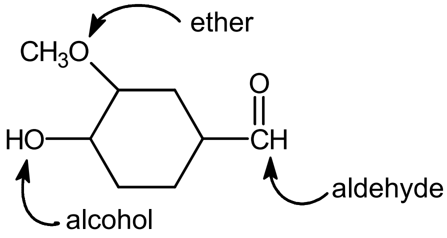
ester

37. Reference Table 21.4 for the common functional groups.

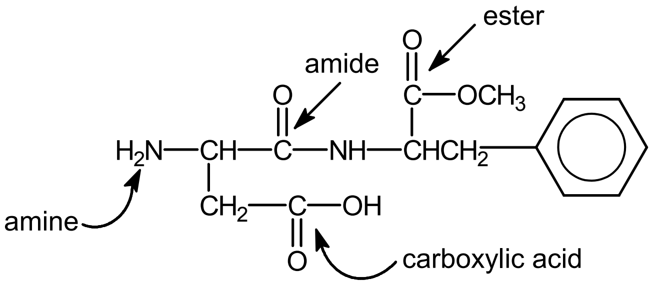
a. ketone b. aldehyde c. carboxylic acid d. amine

38. a. b.

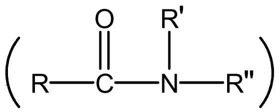




c.



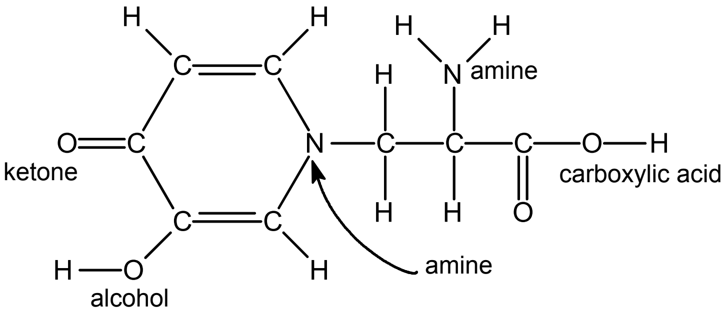
Note: The amide functional group:



$\left(R-\overset{O}{\overset{\|}{C}}-\overset{R'}{\overset{|}{N}}-R''\right)$

is mentioned in Section 21.6 of the text. We point it out for your information.

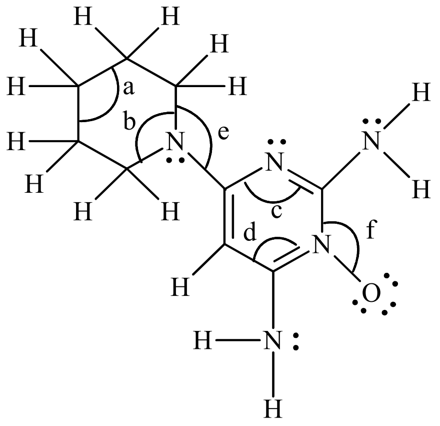
39. a.



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

c. 24 sigma bonds; 4 pi bonds

40. Hydrogen atoms are usually omitted from ring structures. In organic compounds, the carbon atoms generally 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 nitrogen atoms in the ring with the double bonds are sp^2 hybridized. The other three N atoms 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 the double bonds are all sp^2 hybridized.

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

e. 31 sigma bonds

f. 3 pi bonds

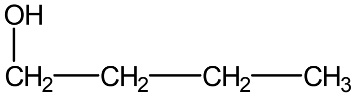
41. a. 3-chloro-1-butanol; since the carbon containing the OH group is bonded to just one other carbon (one R group), this is a primary alcohol.

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

c. 2-methylcyclopentanol; secondary alcohol (two 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.

42.

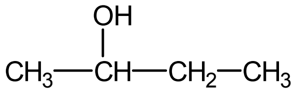
a.



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

primary alcohol

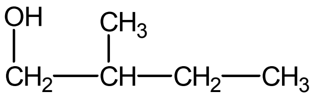
b.



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

secondary alcohol

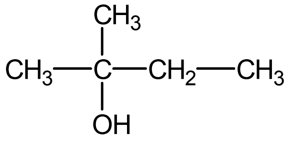
c.



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

primary alcohol

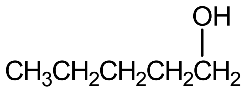
d.



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

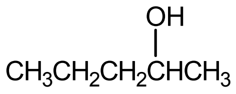
tertiary alcohol

43.



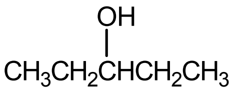
$\mathrm{CH_3CH_2CH_2CH_2\overset{\overset{OH}{|}}{CH_2}}$

1-pentanol



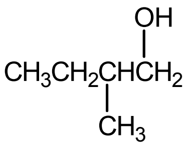
$\mathrm{CH_3CH_2CH_2\overset{\overset{OH}{|}}{C}HCH_3}$

2-pentanol



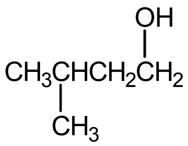
$\mathrm{CH_3CH_2\overset{\overset{OH}{|}}{C}HCH_2CH_3}$

3-pentanol



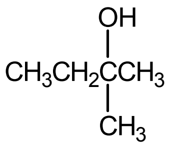
$\mathrm{CH_3CH_2\underset{\underset{CH_3}{|}}{C}H\overset{\overset{OH}{|}}{CH_2}}$

2-methyl-1-butanol



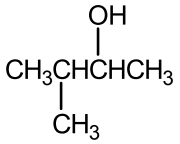
$\mathrm{CH_3\underset{\underset{CH_3}{|}}{C}HCH_2\overset{\overset{OH}{|}}{CH_2}}$

3-methyl-1-butanol



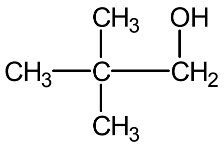
$\mathrm{CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}CH_3}$

2-methyl-2-butanol



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

3-methyl-2-butanol

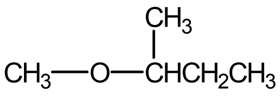


$\mathrm{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{OH}{|}}{CH_2}}$

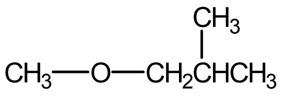
2,2-dimethyl-1-propanol

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

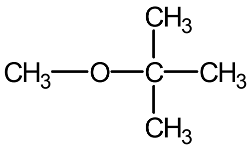
$CH_3{-}O{-}CH_2CH_2CH_2CH_3$



$CH_3{-}O{-}\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$

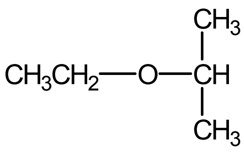


$CH_3{-}O{-}CH_2\overset{CH_3}{\overset{|}{C}}HCH_3$



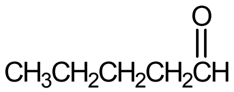
$CH_3{-}O{-}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-}CH_3$

$CH_3CH_2{-}O{-}CH_2CH_2CH_3$



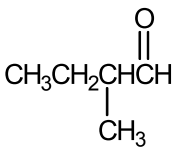
$CH_3CH_2{-}O{-}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}H$

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



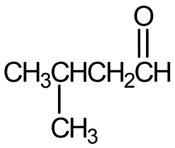
$CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}H$

pentanal



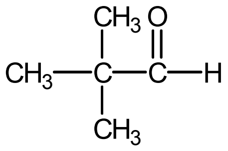
$CH_3CH_2\underset{CH_3}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}H$

2-methylbutanal



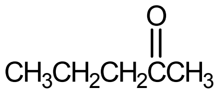
$CH_3\underset{CH_3}{\underset{|}{C}}HCH_2\overset{O}{\overset{\|}{C}}H$

3-methylbutanal



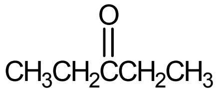
$CH_3{-}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-}\overset{O}{\overset{\|}{C}}{-}H$

2,2-dimethylpropanal



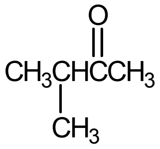
$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$

2-pentanone



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

3-pentanone



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

3-methyl-2-butanone

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

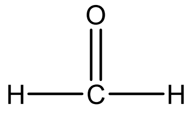
c. 3-methylbenzaldehyde or m-methylbenzaldehyde

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

b. 3-ethyl-2-methylhexanoic acid

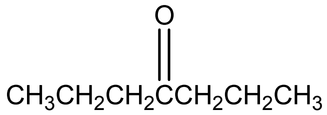
c. methanoic acid (common name = formic acid)

47. a.



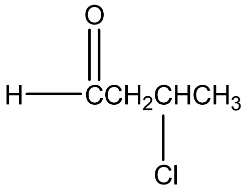
$H-\overset{O}{\overset{\|}{C}}-H$

b.



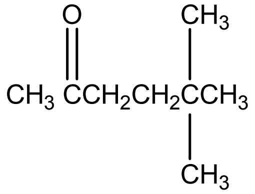
$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3$

c.



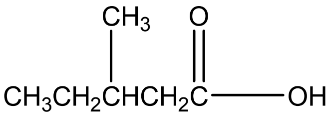
$H-\overset{O}{\overset{\|}{C}}CH_2\underset{Cl}{\underset{|}{C}}HCH_3$

d.



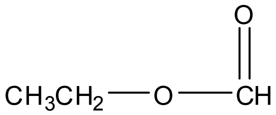
$CH_3\,\overset{O}{\overset{\|}{C}}CH_2CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_3$

48. a.



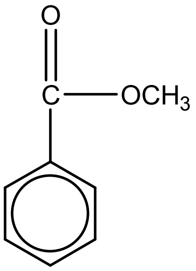
$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2\overset{O}{\overset{\|}{C}}-OH$

b.

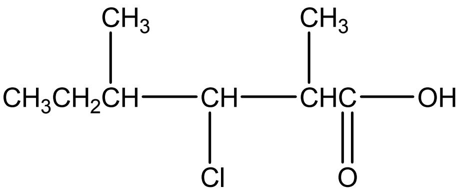


$CH_3CH_2-O-\overset{O}{\overset{\|}{C}}H$

c.

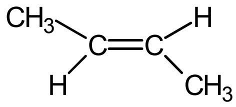


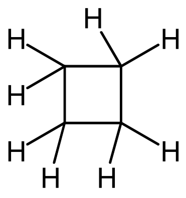
d.



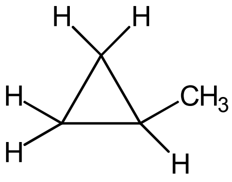
$CH_3CH_2\overset{\overset{CH_3}{|}}{C}H-\underset{\underset{Cl}{|}}{C}H-\overset{\overset{CH_3}{|}}{C}H\underset{\underset{O}{\|}}{C}-OH$

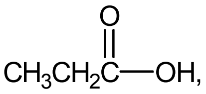
49.

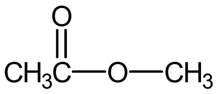
a. trans-2-butene:  , formula = C_4H_8



or

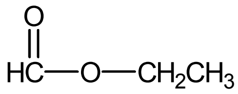


b. propanoic acid:  $CH_3CH_2\overset{O}{\overset{\|}{C}}-OH$, formula = $C_3H_6O_2$

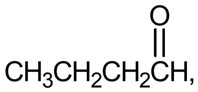


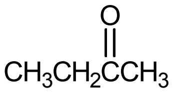
$CH_3\overset{O}{\overset{\|}{C}}-O-CH_3$

or



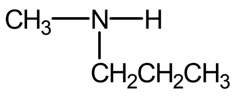
$H\overset{O}{\overset{\|}{C}}-O-CH_2CH_3$

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

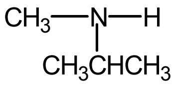

$CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_3$

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

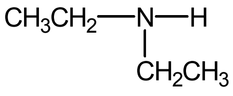
A secondary amine has two R groups bonded to N.


$CH_3{-}\underset{\underset{\displaystyle CH_2CH_2CH_3}{|}}{N}{-}H$

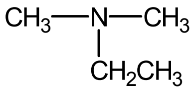
or

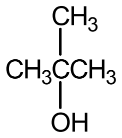

$CH_3{-}\underset{\underset{\displaystyle CH_3CHCH_3}{|}}{N}{-}H$

or

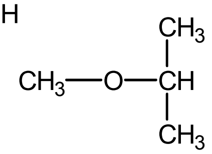

$CH_3CH_2{-}\underset{\underset{\displaystyle CH_2CH_3}{|}}{N}{-}H$

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


$CH_3{-}\underset{\underset{\displaystyle CH_2CH_3}{|}}{N}{-}CH_3$

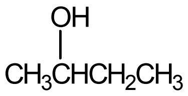
f. 2-methyl-2-propanol:  $CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}CH_3$, formula = $C_4H_{10}O$

$CH_3{-}O{-}CH_2CH_2CH_3$ or


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

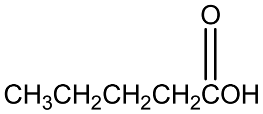
or $CH_3CH_2{-}O{-}CH_2CH_3$

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.)


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

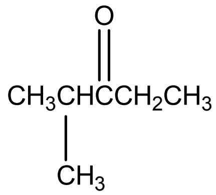
50. Only statement d is false. The other statements refer to compounds having the same formula but different attachment of atoms; they are structural isomers.

a.


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

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

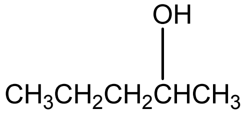
b.



$CH_3\underset{\vert}{\underset{CH_3}{CH}}\overset{O}{\overset{\Vert}{C}}CH_2CH_3$

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

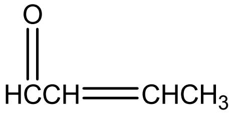
c.



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

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

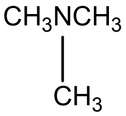
d.



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

2-butenal has a formula of C_4H_6O, whereas the alcohol has a formula of C_4H_8O.

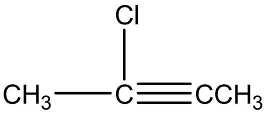
e.



$CH_3\underset{\vert}{\underset{CH_3}{N}}CH_3$

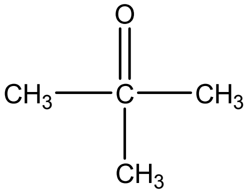
Both have a formula of C_3H_9N.

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



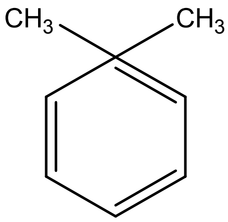
$CH_3{-}\overset{Cl}{\overset{\vert}{C}}{\equiv}CCH_3$

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

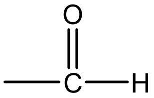


$CH_3{-}\underset{CH_3}{\underset{\vert}{\overset{O}{\overset{\Vert}{C}}}}{-}CH_3$

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



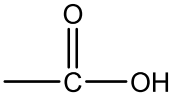
d. You cannot have an aldehyde functional group bonded to a middle carbon in a chain. Aldehyde groups, i.e.,



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

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

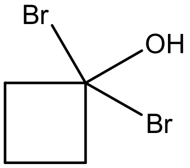
e. You cannot have a carboxylic acid group bonded to a middle carbon in a chain. Carboxylic groups, i.e.,



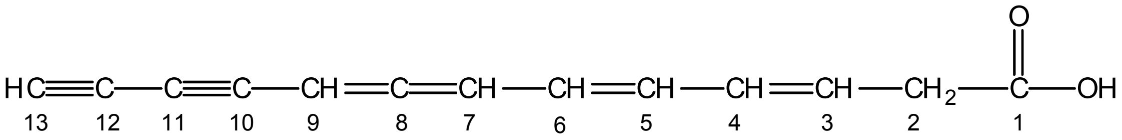
$$-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

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.



52.



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

Reactions of Organic Compounds

53. Substitution: An atom or group is replaced by another atom or group.

For example: H in benzene is replaced by Cl.

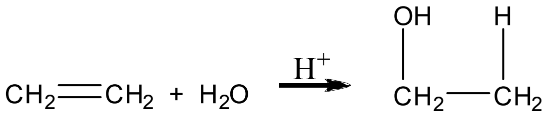
$$C_6H_6 + Cl_2 \xrightarrow{\text{catalyst}} C_6H_5Cl + HCl$$

Addition: Atoms or groups are added to a molecule.

For example: Cl_2 adds to ethene. $CH_2 = CH_2 + Cl_2 \rightarrow CH_2Cl–CH_2Cl$

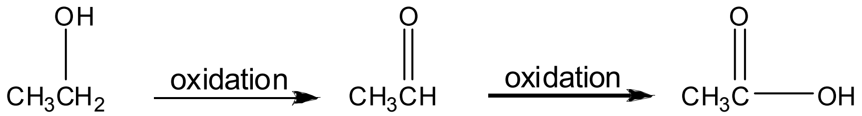
54. To react Cl_2 with an alkane, ultraviolet light must be present to catalyze the reaction. To react Cl_2 with benzene, a special iron catalyst is needed. Its formula is $FeCl_3$. For both of these hydrocarbons, if no catalyst is present, there is no reaction. This is not the case for reacting Cl_2 with alkenes or alkynes. In these two functional groups, the π electrons situated above and below the carbon-carbon multiple bond are easily attacked by substances that are attracted to the negative charge of the π electrons. . Hence the π bonds in alkenes and alkynes are why these are more reactive. Note that even though benzene has π electrons, it does not want to disrupt the delocalized π bonding. When Cl_2 reacts with benzene, it is the C–H bond that changes, not the π bonding.

55. a.



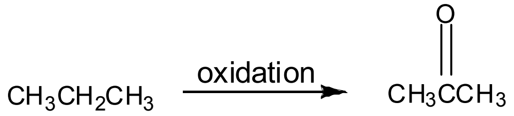
$$\mathrm{CH_2{=}CH_2 + H_2O \xrightarrow{H^+} \overset{\overset{OH}{|}}{CH_2}-\overset{\overset{H}{|}}{CH_2}}$$

b.



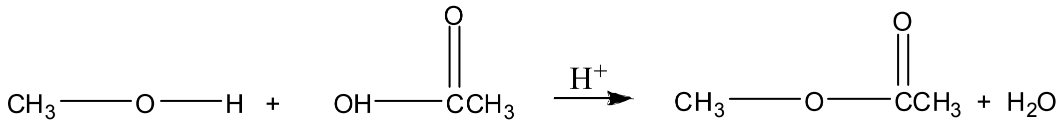
$$\mathrm{CH_3\overset{\overset{OH}{|}}{CH_2} \xrightarrow{oxidation} CH_3\overset{\overset{O}{\|}}{C}H \xrightarrow{oxidation} CH_3\overset{\overset{O}{\|}}{C}-OH}$$

c.



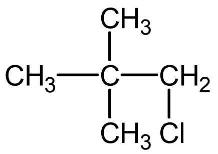
$$\mathrm{CH_3CH_2CH_3 \xrightarrow{oxidation} CH_3\overset{\overset{O}{\|}}{C}CH_3}$$

d.

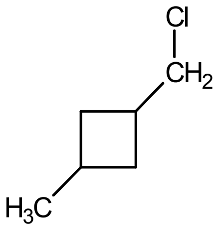


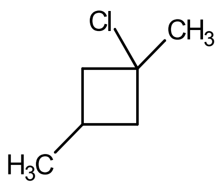
$$\mathrm{CH_3-O-H + OH-\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{H^+} CH_3-O-\overset{\overset{O}{\|}}{C}CH_3 + H_2O}$$

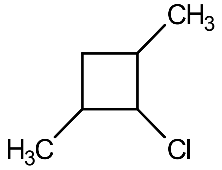
56. a. Only one monochlorination product can form (1-chloro-2,2-dimethylpropane); the other possibilities differ from this compound by a simple rotation, so they are not different compounds.



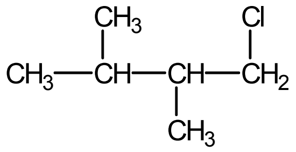
b. Three different monochlorination products are possible (ignoring cis-trans isomers).

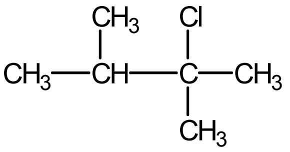






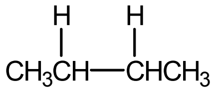
c. Two different monochlorination products are possible (the other possibilities differ by a simple rotation of one of these two compounds).


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

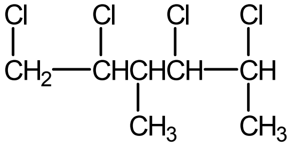

$\mathrm{CH_3{-}\overset{CH_3}{\overset{|}{CH}}{-}\underset{\underset{CH_3}{|}}{\overset{Cl}{\overset{|}{C}}}{-}CH_3}$

57.

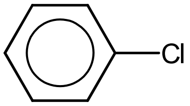
a.


$\mathrm{CH_3\overset{H}{\overset{|}{C}}H{-}\overset{H}{\overset{|}{C}}HCH_3}$

b.

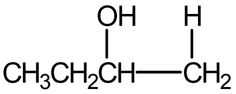

$\mathrm{\overset{Cl}{\overset{|}{CH_2}}{-}\overset{Cl}{\overset{|}{C}}H\underset{\underset{CH_3}{|}}{\overset{Cl}{\overset{|}{C}}}H\overset{Cl}{\overset{|}{C}}H{-}\underset{\underset{CH_3}{|}}{\overset{Cl}{\overset{|}{CH}}}}$

c.

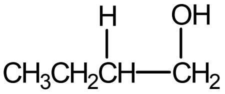

$+ \mathrm{HCl}$

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

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


$\mathrm{CH_3CH_2\overset{OH}{\overset{|}{C}}H{-}\overset{H}{\overset{|}{C}}H_2}$

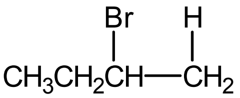
major product


$\mathrm{CH_3CH_2\overset{H}{\overset{|}{C}}H{-}\overset{OH}{\overset{|}{C}}H_2}$

minor product

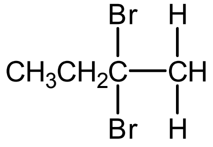
We would get both products in this reaction. Using the rule given in the problem, the first compound listed is the major product. In the reactant, the terminal carbon has more hydrogens bonded to it (2 versus 1) so H forms a bond to this carbon, and OH forms a bond to the other carbon in the double bond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

b.



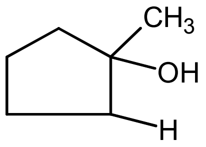
$\mathrm{CH_3CH_2\overset{Br}{C}H{-}\overset{H}{C}H_2}$

c.

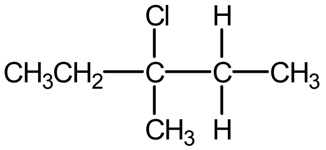


$\mathrm{CH_3CH_2\overset{Br}{\underset{Br}{C}}{-}\overset{H}{\underset{H}{C}}H}$

d.



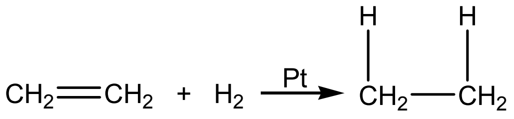
e.



$\mathrm{CH_3CH_2{-}\overset{Cl}{\underset{CH_3}{C}}{-}\overset{H}{\underset{H}{C}}{-}CH_3}$

59. 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.

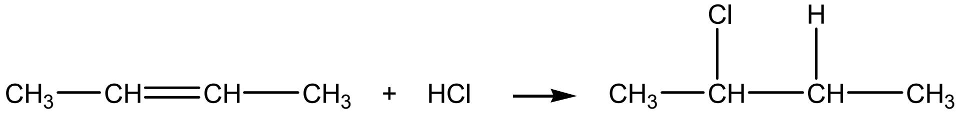
60. a.



$\mathrm{CH_2{=}CH_2 + H_2 \xrightarrow{Pt} \overset{H}{C}H_2{-}\overset{H}{C}H_2}$

ethene ethane

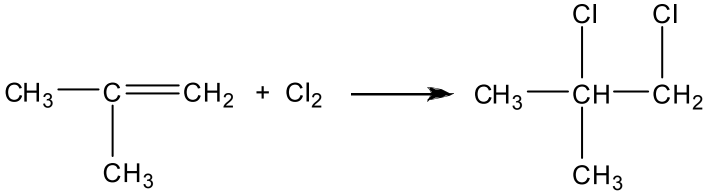
b.



$\mathrm{CH_3{-}CH{=}CH{-}CH_3 + HCl \longrightarrow CH_3{-}\overset{Cl}{C}H{-}\overset{H}{C}H{-}CH_3}$

2-butene (cis or trans) 2-chlorobutane

c.

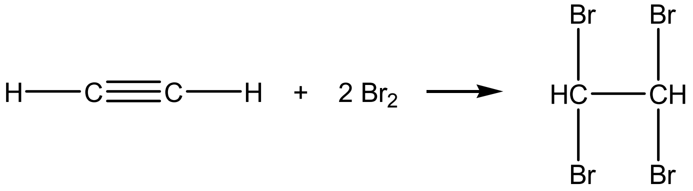


$\mathrm{CH_3{-}\underset{CH_3}{C}{=}CH_2 + Cl_2 \longrightarrow CH_3{-}\overset{Cl}{\underset{CH_3}{C}}H{-}\overset{Cl}{C}H_2}$

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

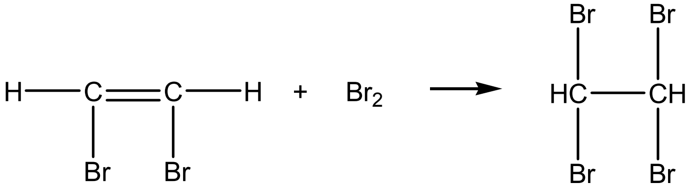
1,2-dichloro-2-methylpropane

d.



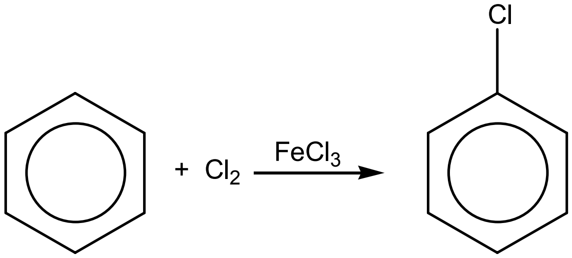
ethyne 1,1,2,2-tetrabromoethane

or



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

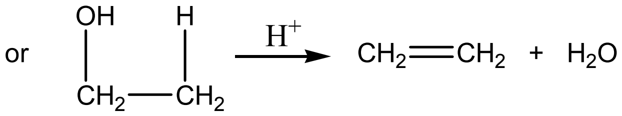
e.



benzene chlorobenzene

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

ethane ethene



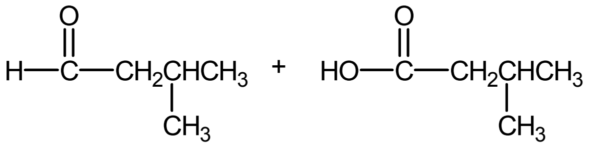
$\text{or}\ \ \overset{OH}{CH_2}{-}\overset{H}{CH_2} \xrightarrow{H^+} CH_2{=}CH_2 + H_2O$

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 excess water is reacted with the alkene. This drives the above reaction to the left making the alcohol the major organic species present. To produce the alkene, water would be removed from the reaction mixture, driving the above reaction to the right to produce the alkene.

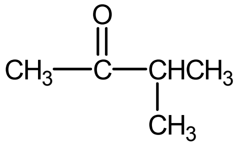
61. Primary alcohols (a, d, and f) are oxidized to aldehydes, which can be oxidized further to carboxylic acids. Secondary alcohols (b, e, and f) are oxidized to ketones, and tertiary alcohols (c and f) do not undergo this type of oxidation reaction. Note that compound f contains a primary, a secondary,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

a.



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

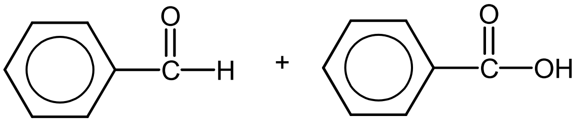
b.



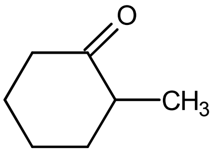
$\mathrm{CH_3{-}\overset{O}{\overset{\|}{C}}{-}\underset{CH_3}{\underset{|}{C}}HCH_3}$

c. No reaction

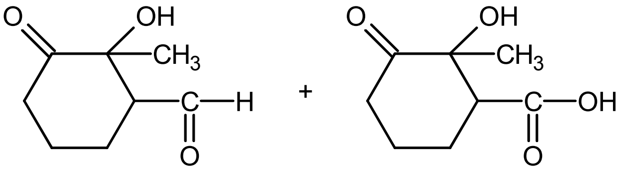
d.



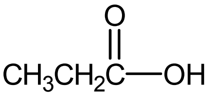
e.



f.

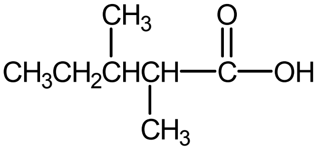


62. a.



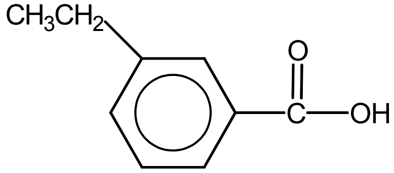
$\mathrm{CH_3CH_2\overset{O}{\overset{\|}{C}}{-}OH}$

b.



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

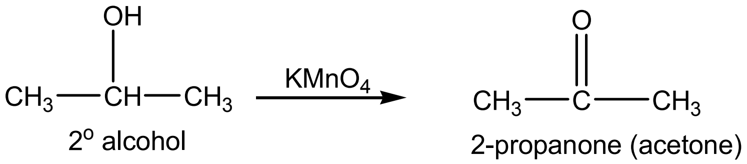
c.



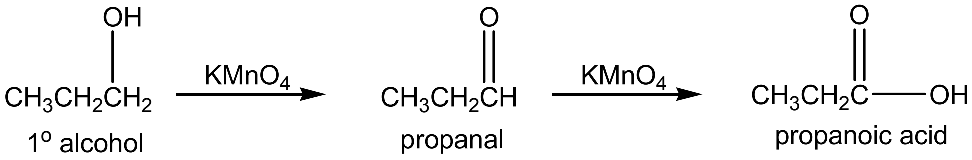
63. $KMnO_4$ will oxidize primary alcohols to aldehydes and then to carboxylic acids. Secondary alcohols are oxidized to ketones by $KMnO_4$. Tertiary alcohols and ethers are not oxidized by $KMnO_4$.

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

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



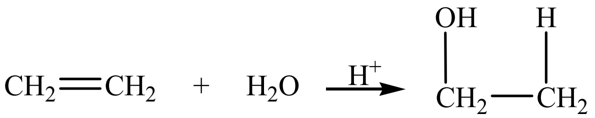
$$\underset{2^o\text{ alcohol}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_3} \xrightarrow{KMnO_4} \underset{\text{2-propanone (acetone)}}{CH_3-\overset{\overset{O}{||}}{C}-CH_3}$$



$$\underset{1^o\text{ alcohol}}{CH_3CH_2\overset{\overset{OH}{|}}{C}H_2} \xrightarrow{KMnO_4} \underset{\text{propanal}}{CH_3CH_2\overset{\overset{O}{||}}{C}H} \xrightarrow{KMnO_4} \underset{\text{propanoic acid}}{CH_3CH_2\overset{\overset{O}{||}}{C}-OH}$$

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

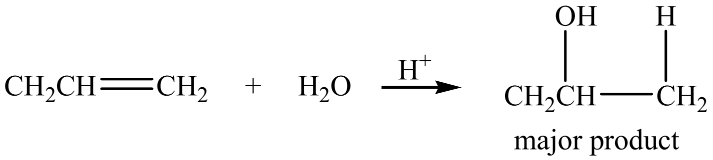
64. a.



$$CH_2{=}CH_2 + H_2O \xrightarrow{H^+} \overset{\overset{OH}{|}}{CH_2}-\overset{\overset{H}{|}}{CH_2}$$

1° alcohol

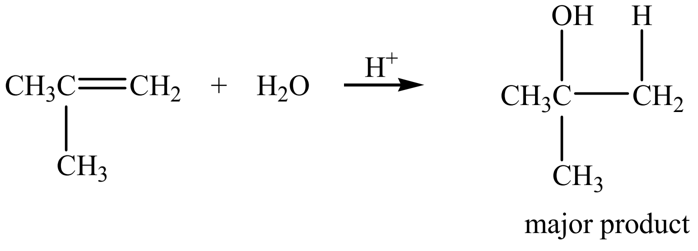
b.



$$CH_2CH{=}CH_2 + H_2O \xrightarrow{H^+} \underset{\text{major product}}{CH_2\overset{\overset{OH}{|}}{C}H-\overset{\overset{H}{|}}{CH_2}}$$

2° alcohol

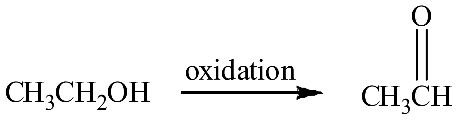
c.



$$\underset{\underset{CH_3}{|}}{CH_3C}{=}CH_2 + H_2O \xrightarrow{H^+} \underset{\text{major product}}{\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{CH_3C}}-\overset{\overset{H}{|}}{CH_2}}$$

3° alcohol

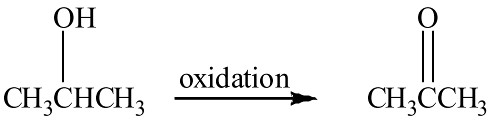
d.



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

aldehyde

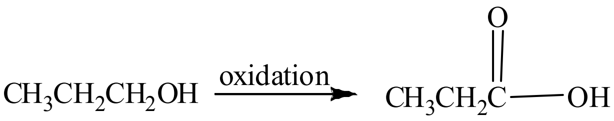
e.



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

ketone

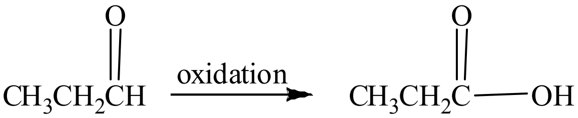
f.



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

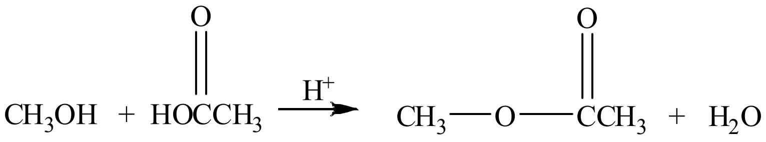
carboxylic acid

or



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

g.



$CH_3OH + HO\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{H^+} CH_3-O-\overset{\overset{O}{\|}}{C}CH_3 + H_2O$

ester

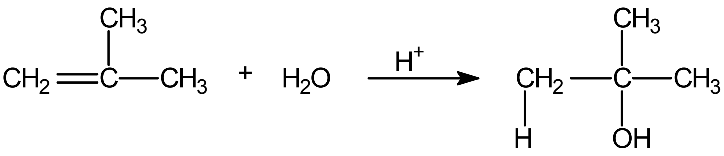
65. a. $CH_3CH = CH_2 + Br_2 \rightarrow CH_3CHBrCH_2Br$ (Addition reaction of Br_2 with propene)

b.

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

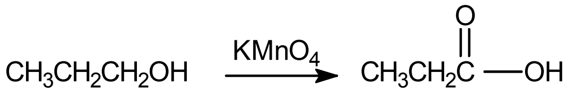
Oxidation of 2-propanol yields acetone (2-propanone).

c.



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

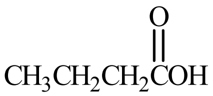
Addition of H_2O to 2-methylpropene would yield tert-butyl alcohol (2-methyl-2-propanol) as the major product.

d. 

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

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

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

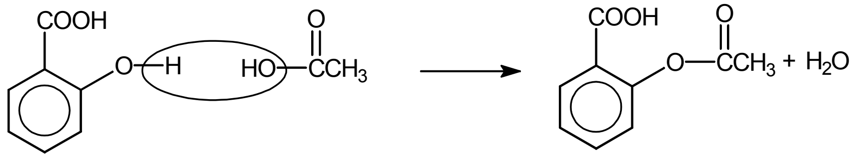


b. $CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}OH$ is an acid, so this compound should react positively with a base like $NaHCO_3$. The other compound is a ketone, which will not react with a base.

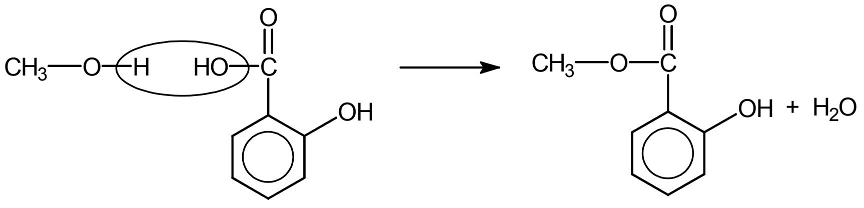
c. $CH_3CH_2CH_2OH$ can be oxidized with $KMnO_4$ to propanoic acid. 2-Propanone (a ketone) will not react with $KMnO_4$.

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.

67.



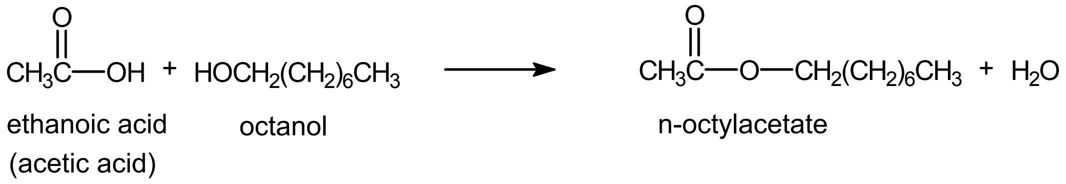
acetylsalicylic acid (aspirin)



methyl salicylate

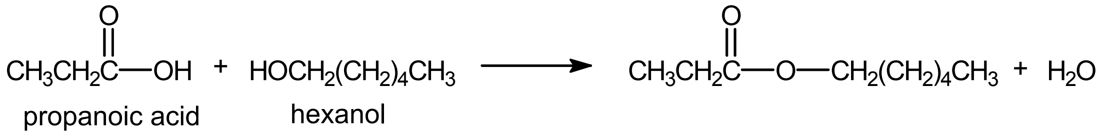
68. Reaction of a carboxylic acid with an alcohol can produce these esters.

a.



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

b.



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

Polymers

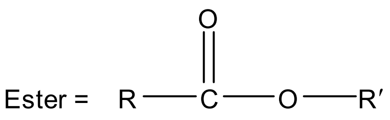
69. a. Addition polymer: a polymer that forms by adding monomer units together (usually by reacting double bonds). Teflon, polyvinyl chloride, and polyethylene are examples of addition polymers.

b. Condensation polymer: a polymer that forms when two monomers combine by eliminating a small molecule (usually H_2O or HCl). Nylon and Dacron are examples of condensation polymers.

c. Copolymer: a polymer formed from more than one type of monomer. Nylon and Dacron are copolymers.

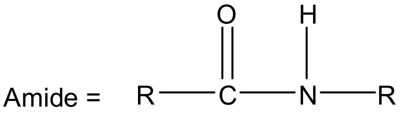
d. Homopolymer: a polymer formed from the polymerization of only one type of monomer. Polyethylene, Teflon, and polystyrene are examples of homopolymers.

e. Polyester: a condensation polymer whose monomers link together by formation of the ester functional group. Dacron is a polyester.

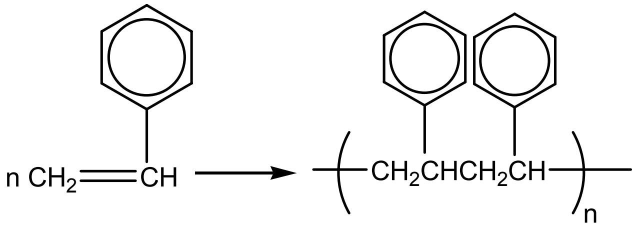


$$\text{Ester} = R-\overset{O}{\overset{\|}{C}}-O-R'$$

f. Polyamide: a condensation polymer whose monomers link together by formation of the amide functional group. Nylon is a polyamide as are proteins in the human body.



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



a. Syndiotactic polystyrene has all 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.

71. 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 a typical 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.

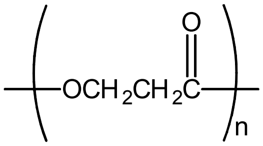
72. a.

repeating unit: monomer: $CHF{=}CH_2$

$-\!\left(CHF - CH_2 \right)_n\!-$

b.

repeating unit:

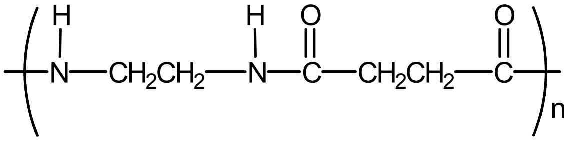


$-\!\left(OCH_2CH_2\overset{\overset{\large O}{\|}}{C} \right)_n\!-$

monomer: $HO{-}CH_2CH_2{-}CO_2H$

c.

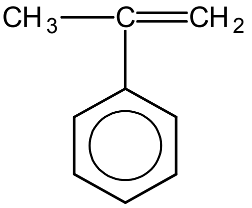
repeating unit:



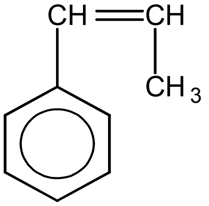
$-\!\left(\overset{\overset{\large H}{|}}{N} - CH_2CH_2 - \overset{\overset{\large H}{|}}{N} - \overset{\overset{\large O}{\|}}{C} - CH_2CH_2 - \overset{\overset{\large O}{\|}}{C} \right)_n\!-$

copolymer of: $H_2NCH_2CH_2NH_2$ and $HO_2CCH_2CH_2CO_2H$

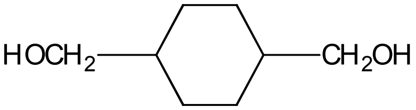
d. monomer:



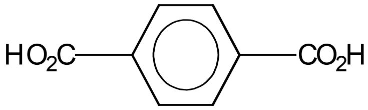
e. monomer:



f. copolymer of:

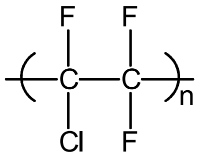


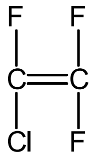
and



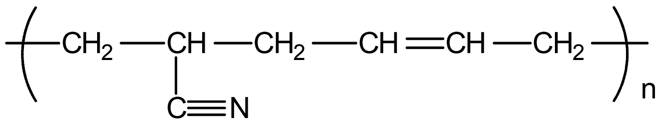
Addition polymers: a, d, and e. Condensation polymers: b, c, and f; copolymer: c and f

73. 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:



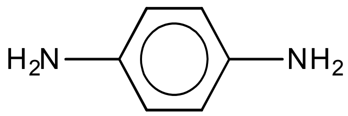


74. The monomers for nitrile are CH_2=CHCN (acrylonitrile) and CH_2=CHCH=CH_2 (butadiene). The structure of polymer nitrile is:

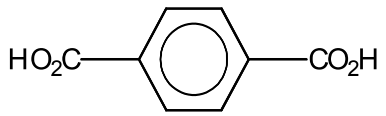


$$\left(CH_2-\underset{\displaystyle C\equiv N}{\underset{|}{CH}}-CH_2-CH=CH-CH_2 \right)_n$$

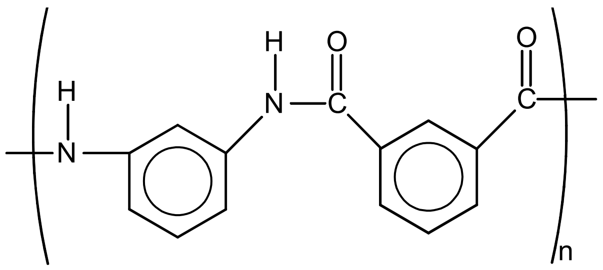
75. a.



and

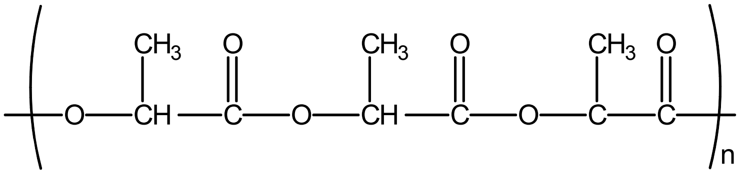


b. Repeating unit:

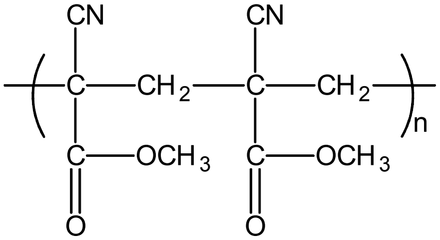


The two polymers differ in the substitution pattern on the benzene rings. The Kevlar chain is straighter, and there is more efficient hydrogen bonding between Kevlar chains than between Nomex chains.

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



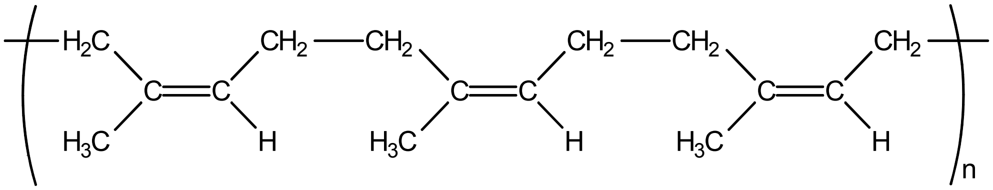
77.



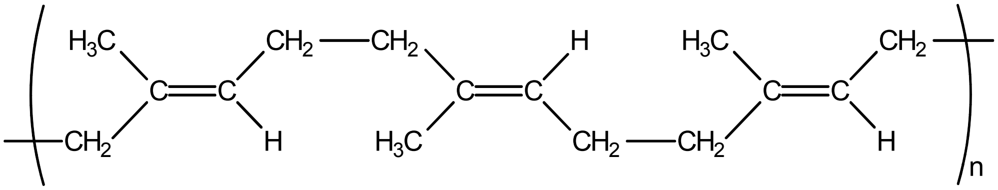
"Super glue" is an addition polymer formed by reaction of the C=C bond in methyl cyanoacrylate.

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

b.



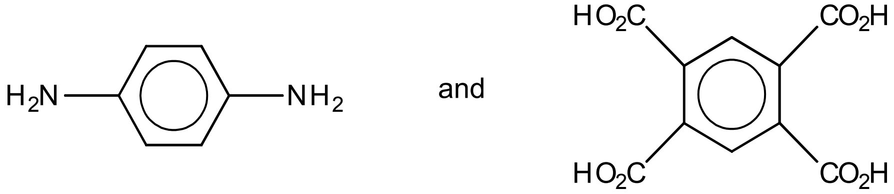
Cis-polyisoprene (natural rubber)



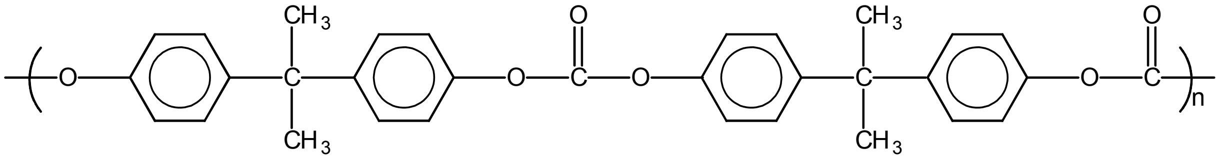
Trans-polyisoprene (gutta percha)

79. Divinylbenzene is a crosslinking agent. Divinylbenzene has two reactive double bonds that are both reacted when divinylbenzene inserts itself into two adjacent polymer chains during the polymerization process. The chains cannot move past each other because the crosslinks bond adjacent polymer chains together, making the polymer more rigid.

80. This is a condensation polymer in which two molecules of H_2O form when the monomers link together.



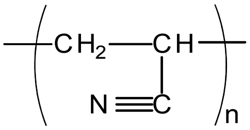
81. a.



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

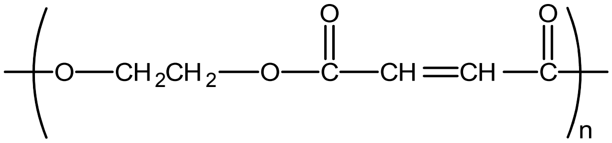
82. Polyvinyl chloride contains some polar C–Cl bonds compared with only relatively nonpolar C–H bonds in polyethylene. The stronger intermolecular forces would be found in polyvinyl chloride since there are dipole-dipole forces present in PVC that are not present in polyethylene.

83. Polyacrylonitrile:

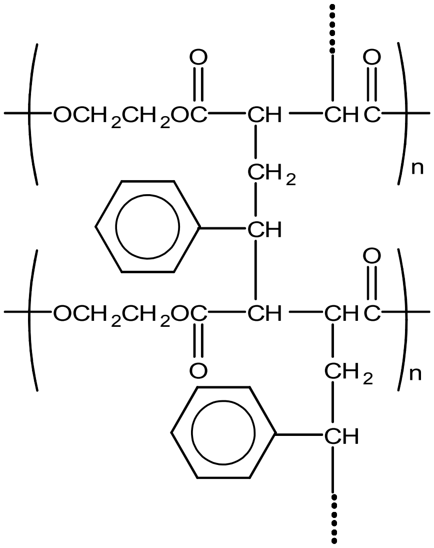


The CN triple bond is very strong and will not easily break in the combustion process. A likely combustion product is the toxic gas hydrogen cyanide, HCN(g).

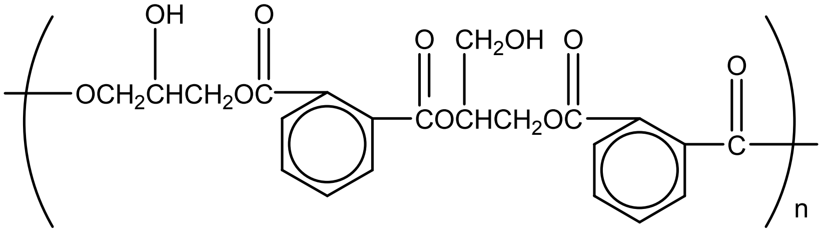
84. a.



b.



85.



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 unreacted OH groups on adjacent polymer chains can react with the acid groups of phthalic acid to form crosslinks (bonds) between various polymer chains.

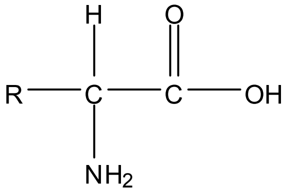
Natural Polymers

86. 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.

87.



$R-CH(NH_2)-C(=O)-OH$

= general amino acid formula

Hydrophilic ("water-loving") and hydrophobic ("water-fearing") refer to the polarity of the R group. When the R group consists of a polar group, then the amino acid is hydrophilic. When the R group consists of a nonpolar group, then the amino acid is hydrophobic.

88. Primary: The amino acid sequence in the protein. Covalent bonds (peptide linkages) are the forces that link the various amino acids together in the primary structure.

Secondary: Includes structural features known as α-helix or pleated sheet. Both are maintained mostly through hydrogen-bonding interactions.

Tertiary: The overall shape of a protein, long and narrow or globular. Maintained by hydrophobic and hydrophilic interactions, such as salt linkages, hydrogen bonds, disulfide linkages, and dispersion forces.

89. Denaturation changes the three-dimensional structure of a protein. Once the structure is affected, the function of the protein will also be affected.

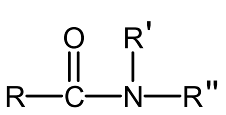
90. All amino acids can act as both a weak acid and a weak base; this is the requirement for a buffer. The weak acid is the carboxylic end of the amino acid, and the weak base is the amine end of the amino acid.

91. 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:

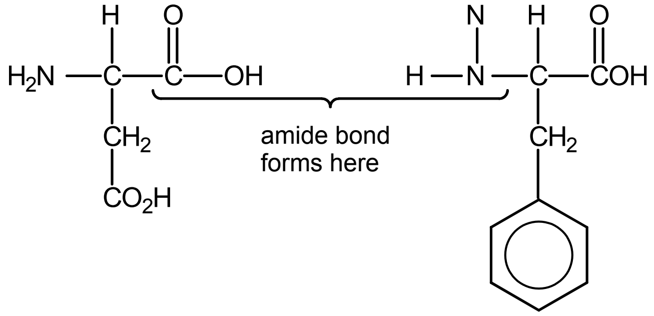


$R-C(=O)-N(R')-R''$

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.

92. Crystalline amino acids exist as zwitterions, $^{+}H_3NCHRCOO^{-}$, which are 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.

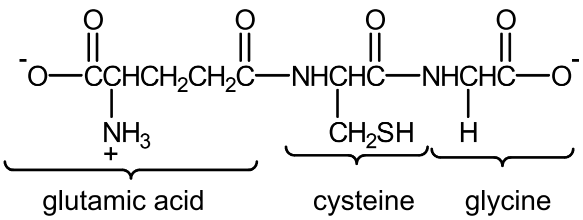
93. a. Aspartic acid and phenylalanine make up aspartame.



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

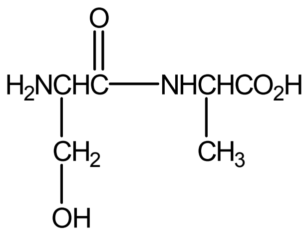
$R{-}CO_2CH_3 + H_2O \rightleftharpoons RCO_2H + HOCH_3$

94.

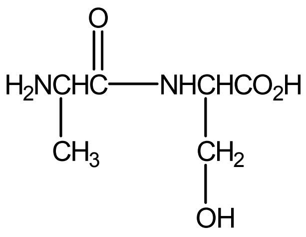

$$\underbrace{{}^{-}O-\overset{O}{\overset{\|}{C}}\underset{\underset{+}{NH_3}}{CH}CH_2CH_2\overset{O}{\overset{\|}{C}}}_{\text{glutamic acid}}-\underbrace{NH\underset{CH_2SH}{CH}\overset{O}{\overset{\|}{C}}}_{\text{cysteine}}-\underbrace{NH\underset{H}{CH}\overset{O}{\overset{\|}{C}}-O^{-}}_{\text{glycine}}$$

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.

95.

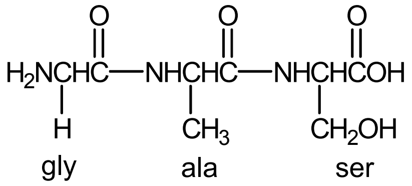

$$H_2N\underset{\underset{OH}{CH_2}}{CH}\overset{O}{\overset{\|}{C}}-NH\underset{CH_3}{CH}CO_2H$$

ser - ala

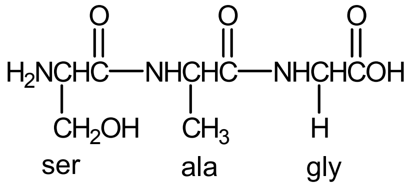

$$H_2N\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}-NH\underset{\underset{OH}{CH_2}}{CH}CO_2H$$

ala - ser

96.



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



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

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.

97. 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

98. There are five possibilities for the first amino acid, four possibilities for the second amino acid, three possibilities for the third amino acid, two possibilities for the fourth amino acid and one 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

99. a. Covalent (forms a disulfide linkage)

b. Hydrogen bonding (need N-H or O-H bond in side chain)

c. Ionic (need NH_2 group on side chain of one amino acid with CO_2H group on side chain of the other amino acid)

d. London dispersion (need amino acids with nonpolar R groups)

100. 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 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: Need amino acids with nonpolar R groups. They are:

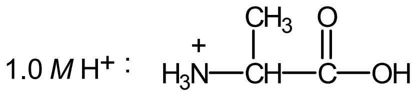
Gly, Ala, Pro, Phe, Ile, Trp, Met, Leu, and Val

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.

101. 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.

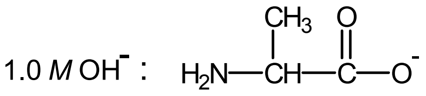
102. Alanine can be thought of as a diprotic acid. The first proton to leave comes from the carboxylic acid end with $K_a = 4.5 \times 10^{-3}$. The second proton to leave comes from the protonated amine end (K_a for $R-NH_3^+ = K_w/K_b = 1.0 \times 10^{-14}/7.4 \times 10^{-5} = 1.4 \times 10^{-10}$).

In 1.0 *M* H^+, both the carboxylic acid and the amine ends 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 since the excess OH^- will remove all acidic protons from alanine. The dibasic form of alanine follows.



1.0 *M* H^+ : $\overset{+}{H_3N}-\overset{\displaystyle CH_3}{\overset{|}{CH}}-\overset{\displaystyle O}{\overset{\|}{C}}-OH$

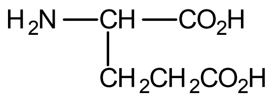
protonated form



1.0 *M* OH^- : $H_2N-\overset{\displaystyle CH_3}{\overset{|}{CH}}-\overset{\displaystyle O}{\overset{\|}{C}}-O^-$

dibasic form

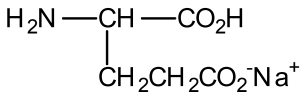
103. Glutamic acid:



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

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:

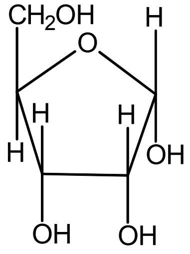


$H_2N-\underset{\displaystyle CH_2CH_2CO_2^-Na^+}{\underset{|}{CH}}-CO_2H$

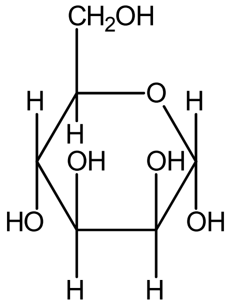
In MSG, the acidic proton from the carboxylic acid in the R group is lost, allowing formation of the ionic compound.

104. 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.

105. See Figures 21.30 and 21.31 of the text for examples of the cyclization process.

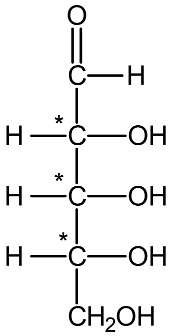


D-Ribose

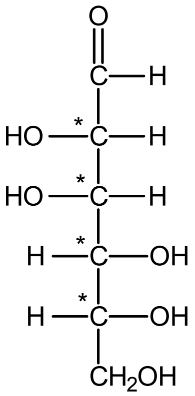


D-Mannose

106. The chiral carbon atoms are marked with asterisks.



D-Ribose



D-Mannose

Note: A chiral carbon atom has four different substituent groups attached.

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

108. This is an example of Le Chatelier's principle at work. For the equilibrium reactions between the various forms of glucose, reference Figure 21.31 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.

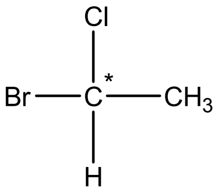
109. A disaccharide is a carbohydrate formed by bonding two monosaccharides (simple sugars) together. In sucrose, the simple sugars are glucose and fructose, and the bond formed between these two monosaccharides is called a glycoside linkage.

110. 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.

111. 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 21.31 of the text). Starch is a polymer composed of only α-D-glucose, and cellulose is a polymer composed of only β-D-glucose.

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

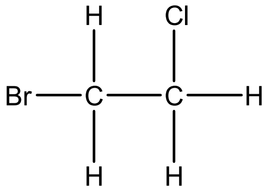
1–bromo–1–chloroethane



$$\begin{array}{ccc} & \mathrm{Cl} & \\ & | & \\ \mathrm{Br}- & \overset{*}{\mathrm{C}} & -\mathrm{CH_3} \\ & | & \\ & \mathrm{H} & \end{array}$$

The carbon with the asterisk has four different groups bonded to it (1–Br; 2–Cl; 3–CH_3; 4–H). This compound has a nonsuperimposable mirror image.

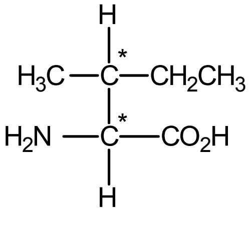
1–bromo–2–chloroethane



$$\begin{array}{cccc} & \mathrm{H} & \mathrm{Cl} & \\ & | & | & \\ \mathrm{Br}- & \mathrm{C} & -\mathrm{C} & -\mathrm{H} \\ & | & | & \\ & \mathrm{H} & \mathrm{H} & \end{array}$$

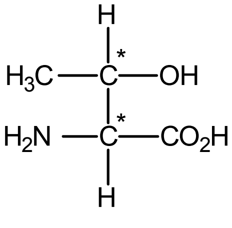
Neither of the two carbons has four different groups bonded to it The mirror image of this molecule will be superimposable (it does not exhibit optical isomerism).

113. 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).



$$\begin{array}{ccc} & \mathrm{H} & \\ & | & \\ \mathrm{H_3C}- & \overset{*}{\mathrm{C}} & -\mathrm{CH_2CH_3} \\ & | & \\ \mathrm{H_2N}- & \overset{*}{\mathrm{C}} & -\mathrm{CO_2H} \\ & | & \\ & \mathrm{H} & \end{array}$$

isoleucine

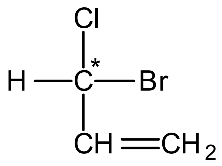


$$\begin{array}{ccc} & \mathrm{H} & \\ & | & \\ \mathrm{H_3C}- & \overset{*}{\mathrm{C}} & -\mathrm{OH} \\ & | & \\ \mathrm{H_2N}- & \overset{*}{\mathrm{C}} & -\mathrm{CO_2H} \\ & | & \\ & \mathrm{H} & \end{array}$$

threonine

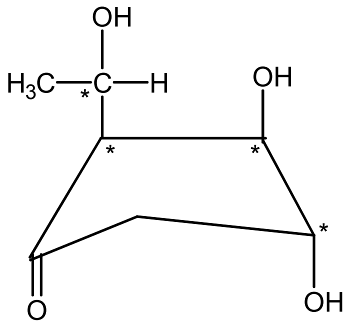
114. There is no chiral carbon atom in glycine since it does not contain a carbon atom with four different groups bonded to it.

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



$$\begin{array}{c} Cl \\ | \\ H-\overset{*}{C}-Br \\ | \\ CH=CH_2 \end{array}$$

116.



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

117. They all contain nitrogen atoms with lone pairs of electrons.

118. DNA: Deoxyribose sugar; double stranded; adenine, cytosine, guanine, and thymine are the bases.

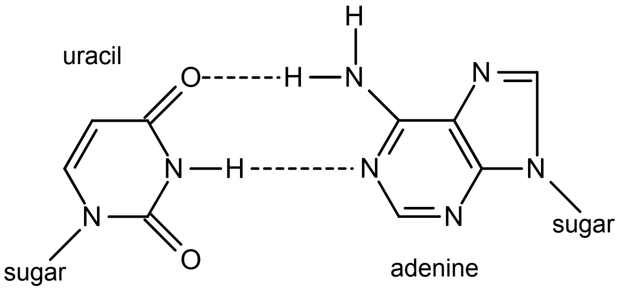
RNA: Ribose sugar; single stranded; adenine, cytosine, guanine, and uracil are the bases.

When the two strands of a DNA molecule are compared, it is found that a given base in one strand is always found paired with a particular base in the other strand. Because of the shapes and side atoms along the rings of the nitrogen bases, only certain pairs are able to approach and hydrogen bond with each other in the double helix. Adenine is always found paired with thymine; cytosine is always found paired with guanine. When a DNA helix unwinds for replication during cell division, only the appropriate complementary bases are able to approach and bond to the nitrogen bases of each strand. For example, for a guanine-cytosine pair in the original DNA, when the two strands separate, only a new cytosine molecule can approach and bond to the original guanine, and only a new guanine molecule can approach and bond to the original cytosine.

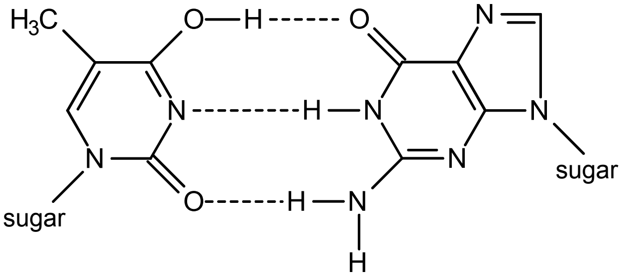
119. The complementary base pairs in DNA are cytosine (C) and guanine (G), and thymine (T) and adenine (A). The complementary sequence is C-C-A-G-A-T-A-T-G.

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

121. Uracil will hydrogen bond to adenine.



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



123. 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.

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

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

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

$$\underset{\text{Glu}}{\text{CTT}} \rightarrow \underset{\text{Val}}{\text{CAT}} \quad \text{or} \quad \underset{\text{Glu}}{\text{CTC}} \rightarrow \underset{\text{Val}}{\text{CAC}}$$

125. A deletion may change the entire code for a protein, thus giving an entirely different sequence of amino acids. A substitution will change only one single amino acid in a protein.

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

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

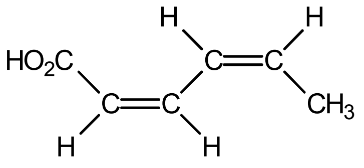
The approximate number of complete turns in a DNA molecule is:

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

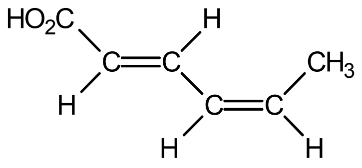
Additional Exercises

127. $CH_3CH_2CH_2CH_2CH_2CH_2CH_2COOH + OH^- \rightarrow CH_3\text{–}(CH_2)_6\text{–}COO^- + H_2O$; 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 ($R_3N + H^+ \rightarrow R_3NH^+$). By treating morphine with HCl, an ionic compound results that is more soluble in water and in the bloodstream than is the neutral covalent form of morphine.

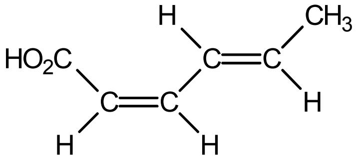
128.



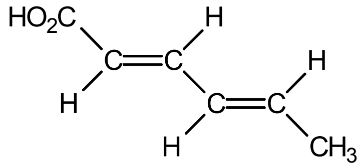
cis-2-cis-4-hexadienoic acid



trans-2-cis-4-hexadienoic acid

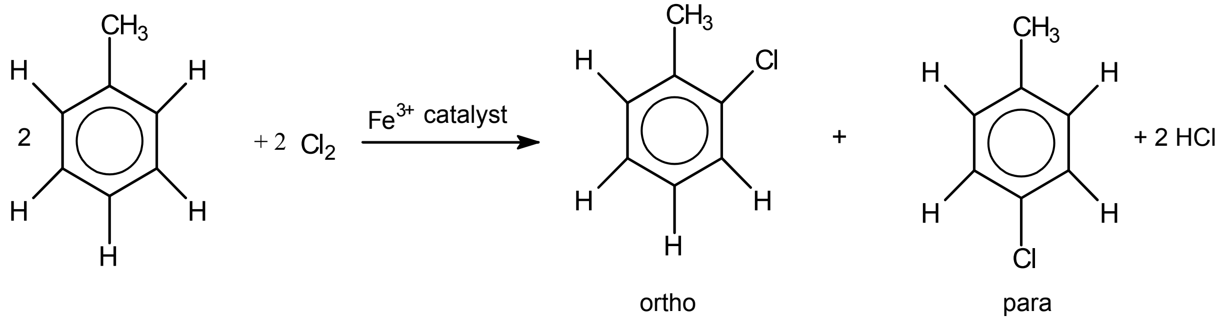


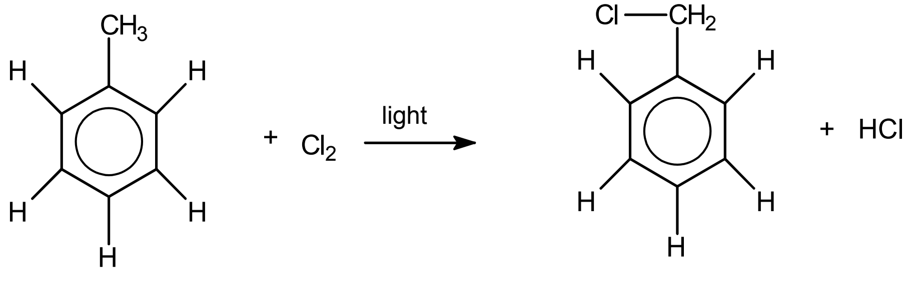
cis-2-trans-4-hexadienoic acid



trans-2-trans-4-hexadienoic acid

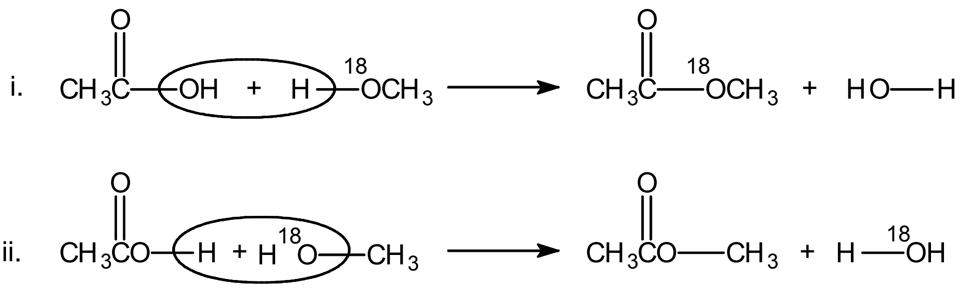
129.





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, specific wavelengths of 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.

130. 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. $CH_3\overset{O}{\overset{\|}{C}}-OH + H-\overset{18}{O}CH_3 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}-\overset{18}{O}CH_3 + HO-H$

ii. $CH_3\overset{O}{\overset{\|}{C}}O-H + H\overset{18}{O}-CH_3 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}O-CH_3 + H-\overset{18}{O}H$

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

131. $$85.63 \text{ g C} \times \frac{1 \text{ mol C}}{12.011 \text{ g C}} = 7.129 \text{ mol C};\ \ 14.37 \text{ g H} \times \frac{1 \text{ mol H}}{1.0079 \text{ g H}} = 14.26 \text{ mol H}$$

Because the moles of H to moles of C ratio is 2:1 (14.26/7.129 = 2.000), the empirical formula is CH_2. The empirical formula mass ≈ 12 + 2(1) = 14. Because 4 × 14 = 56 puts the molar mass between 50 and 60, the molecular formula is C_4H_8.

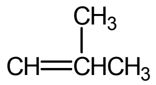
The isomers of C_4H_8 are:

$CH_2{=}CHCH_2CH_3$

1-butene

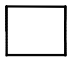
$CH_3CH{=}CHCH_3$

2-butene

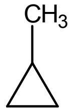


$CH{=}\overset{CH_3}{\overset{|}{C}}HCH_3$

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.

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

2° alcohol, major product

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

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.

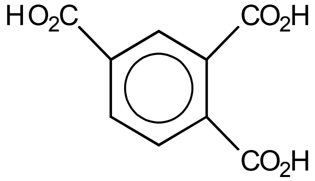
132. At low temperatures, the polymer is coiled into balls. The forces between poly(lauryl methacrylate) and oil molecules will be minimal, and the effect on viscosity will be minimal. At higher temperatures, the chains of the polymer will unwind and become tangled with the oil molecules, increasing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

133. 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 is strong electron-electron repulsions. Thus ethylene oxide is unstable (reactive).

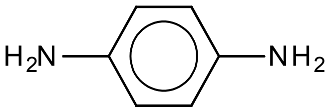
b. The ring opens up during polymerization; the monomers link together through the formation of O–C bonds.

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

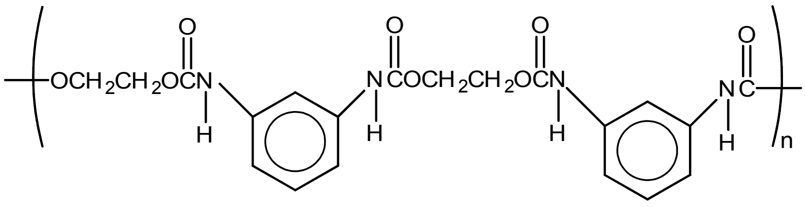
134.



and



135.



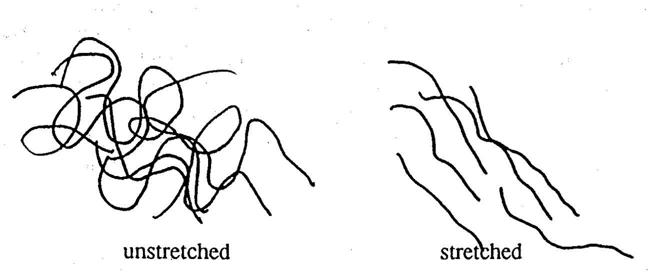
136. a. The temperature of the rubber band increases when it is stretched.

b. Exothermic since heat is released.

c. As the chains 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.

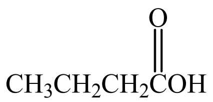
d. Stretching is not spontaneous, so ΔG is positive. ΔG = ΔH – TΔS; since ΔH is negative, ΔS must be negative in order to give a positive ΔG.

e.



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

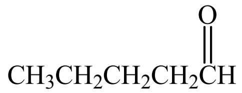
137. The structures, the types of intermolecular forces exerted, and the boiling points for the compounds are:


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

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

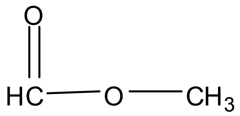
$CH_3CH_2CH_2CH_2CH_2CH_3$

n-hexane, 69°C
LD only

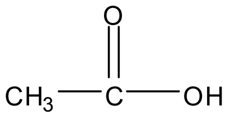
All these compounds have about the same molar mass. Therefore, the London dispersion (LD) forces in each are about the same. The other types of forces determine the boiling-point order. Because butanoic acid and 1-pentanol both exhibit hydrogen-bonding (H–bonding) interactions, these two compounds will 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.

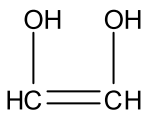
138. We would expect compounds b and d to boil at the higher temperatures because they exhibit additional dipole forces that the nonpolar compounds in a, c, and e do not exhibit. London dispersion (LD) forces are the intermolecular forces exhibited by compounds a, c, and e. Size and shape are the two 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.

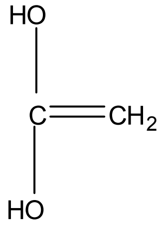
139. The isomers are:



boils at lowest temperature
(no H-bonding)

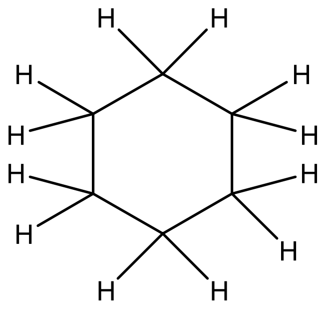






With the exception of the first isomer, the other isomers can form the relatively strong hydrogen-bonding interactions. The isomers that can hydrogen bond will boil at higher temperatures.

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

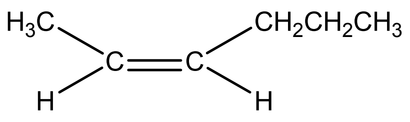


cyclohexane

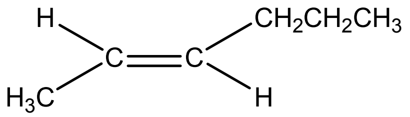
CH_2=$CHCH_2CH_2CH_2CH_3$

1-hexene

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

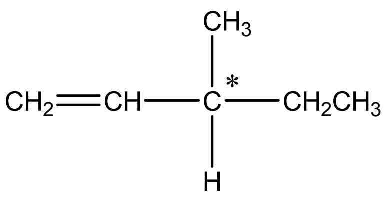


cis



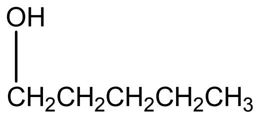
trans

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



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:



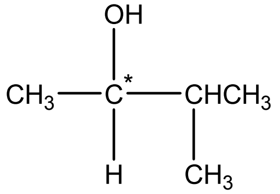
$$\overset{OH}{\overset{|}{CH_2}}CH_2CH_2CH_2CH_3$$

1-pentanol

$CH_3—O—CH_2CH_2CH_2CH_3$

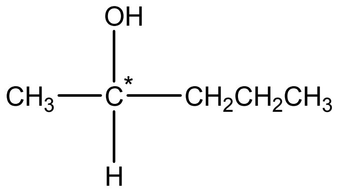
butyl methyl ether

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



$$CH_3—\underset{H}{\overset{OH}{C^*}}—\underset{CH_3}{CHCH_3}$$

3-methyl-2-butanol

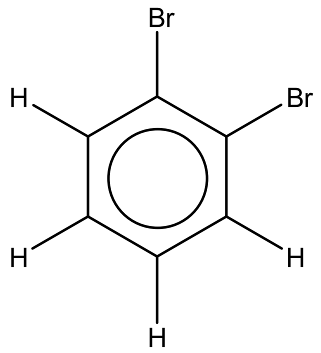


$$CH_3—\underset{H}{\overset{OH}{C^*}}—CH_2CH_2CH_3$$

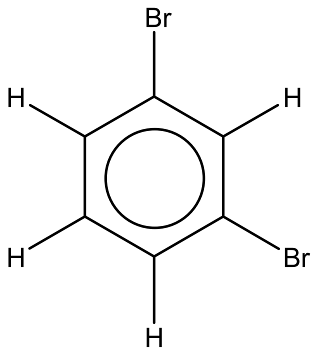
2-pentanol

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

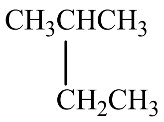


m-dibromobenzene
or 1,3-dibromobenzene

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.

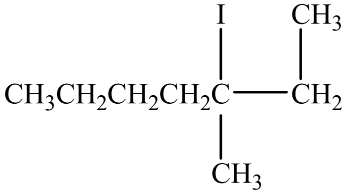
141. a.



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

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

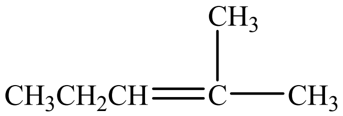
b.



$$\begin{array}{c} \qquad\qquad\qquad\quad I \quad\ CH_3 \\ \qquad\qquad\qquad\quad | \qquad | \\ CH_3CH_2CH_2CH_2C - CH_2 \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad CH_3 \end{array}$$

The longest chain is seven 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.

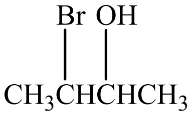
c.



$$\begin{array}{c} \qquad\qquad CH_3 \\ \qquad\qquad | \\ CH_3CH_2CH{=}C - CH_3 \end{array}$$

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.

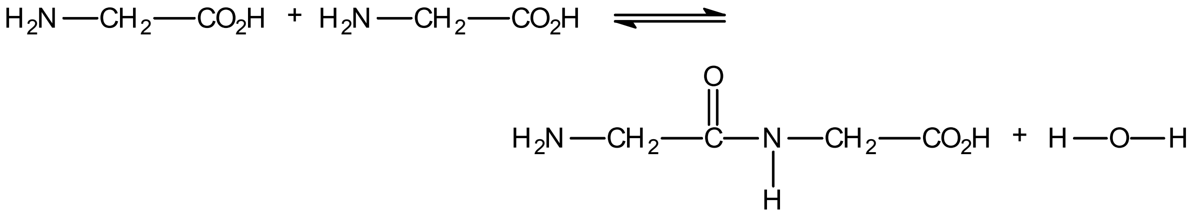
d.



$$\begin{array}{c} \quad Br\ OH \\ \quad |\ \ \ | \\ CH_3CHCHCH_3 \end{array}$$

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

142. 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

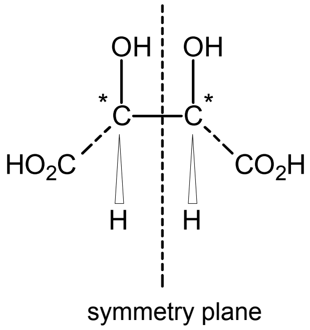
b. ΔS for this process is negative (unfavorable) since positional probability decreases.

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

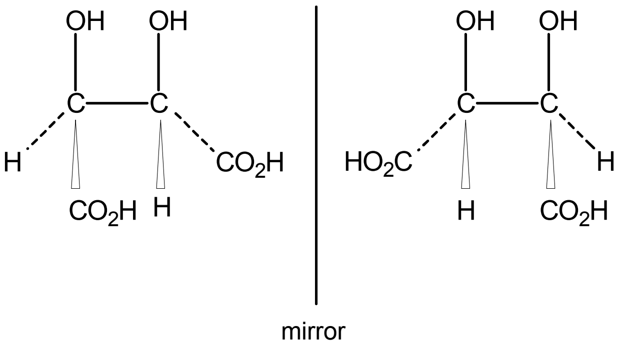
143. $\Delta G = \Delta H - T\Delta S$; for the reaction, we break a P–O and an O–H bond and form a P–O and an O–H bond. Thus $\Delta H \approx 0$. $\Delta S < 0$ because two molecules are going to form one molecule (positional probability decreases). Thus $\Delta G > 0$, and the reaction is not spontaneous.

144. 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.

145. a. Even though this form of tartaric acid contains two chiral carbon atoms (see asterisks in the following structure), the mirror image of this form of tartaric acid is superimposable. Therefore, it is not optically active. One 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 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.

146. 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. $^{+}H_3NCH_2CO_2H \rightleftharpoons 2\ H^+ + H_2NCH_2CO_2^-$

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

147. For the reaction:

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

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

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

148. 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 than in Nylon-6. Hence Nylon-46 forms a stronger polymer than Nylon-6 due to the increased hydrogen-bonding interactions.

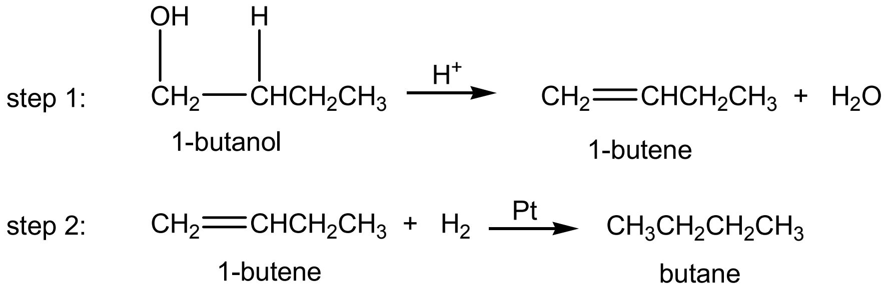
149.
$$4.2 \times 10^{-3}\ \text{g}\ K_2CrO_7 \times \frac{1\ \text{mol}\ K_2Cr_2O_7}{294.20\ \text{g}} \times \frac{1\ \text{mol}\ Cr_2O_7^{2-}}{\text{mol}\ K_2Cr_2O_7} \times \frac{3\ \text{mol}\ C_2H_5OH}{2\ \text{mol}\ Cr_2O_7^{2-}} = 2.1 \times 10^{-5}\ \text{mol}\ C_2H_5OH$$

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

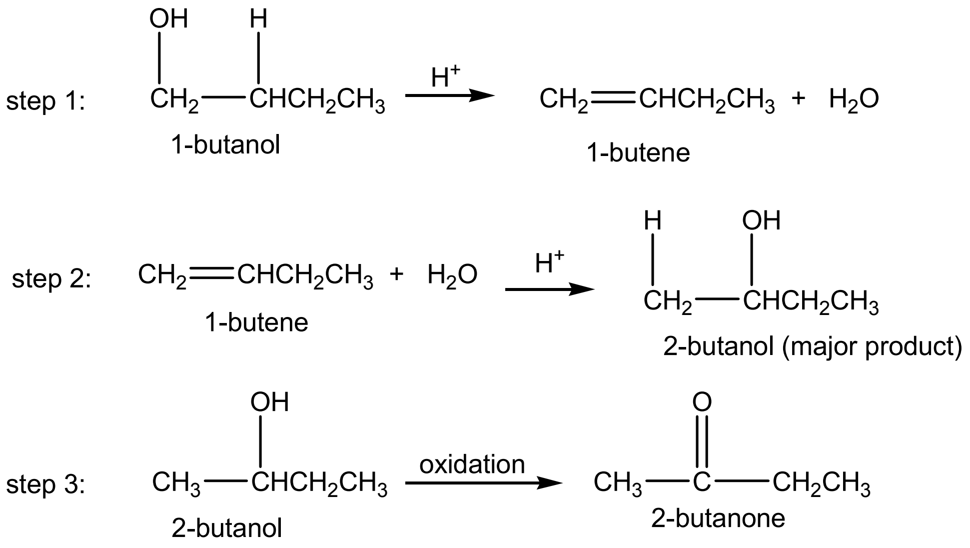
$$\text{Mol \%}\ C_2H_5OH = \frac{2.1 \times 10^{-5}\ \text{mol}\ C_2H_5OH}{0.0198\ \text{mol total}} \times 100 = 0.11\%\ \text{alcohol}$$

Challenge Problems

150. a.



b.



151. 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:

$$1.391 \text{ g/L} \times 4.000 \text{ L} = 5.564 \text{ g products}$$

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

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

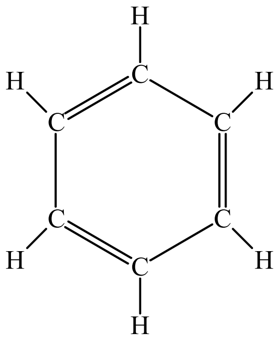
C_xH_y + oxygen $\rightarrow x\ CO_2 + y/2\ H_2O$; setting up two equations:

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

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

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

152. One of the resonance structures for benzene is:



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

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

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

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

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

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).

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

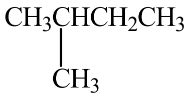
$\Delta H^\circ_{f,\,C_6H_6(g)} = 237$ kJ/mol

The experimental ΔH_f° value for $C_6H_6(g)$ is more stable (lower in energy) by 154 kJ than the ΔH_f° value 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 14.5 of the text). The large discrepancy between ΔH_f° values is due to the delocalized π electrons, whose effects were 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.

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

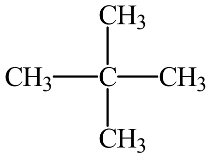
$CH_3CH_2CH_2CH_2CH_3$

n-pentane



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

2-methylbutane



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

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-methylbutane, 3-chloro-2-methylbutane (or we could name this compound as 2-chloro-3-methylbutane), and 1-chloro-3-methylbutane.

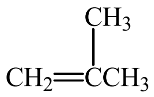
b. The isomers of C_4H_8 are:

$CH_2{=}CHCH_2CH_3$

1-butene

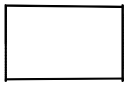
$CH_3CH{=}CHCH_3$

2-butene

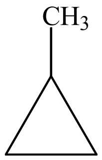


$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}CH_3$

2-methyl-1-propene or
2-methylpropene

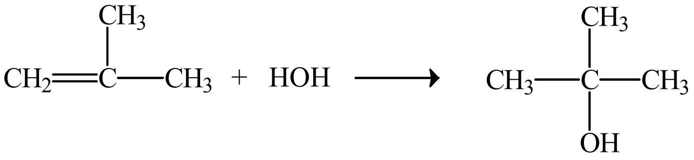


cyclobutane



methylcyclopropane

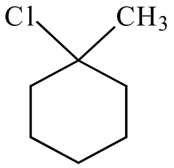
The cyclic structures will not react with H_2O; only the alkenes will add H_2O to the double bond. From Exercise 21.58, the major product of the reaction of 1-butene and H_2O is 2-butanol (a 2° alcohol). 2-Butanol is also the major (and only) product when 2-butene and H_2O react. 2-Methylpropene forms 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.



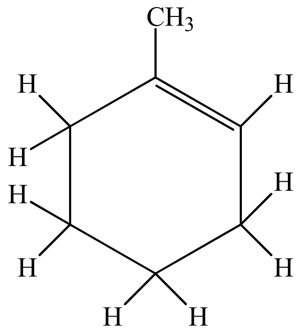
$$CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}CH_3 + HOH \longrightarrow CH_3{-}\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3$$

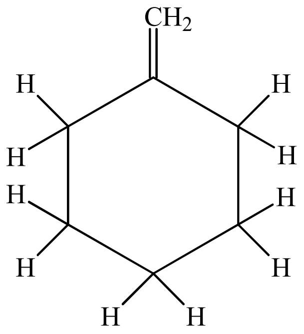
2-methyl-2-propanol (a 3° alcohol, 3 R groups)

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

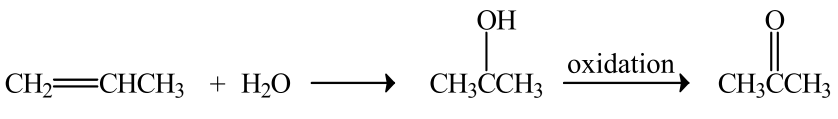


The addition reaction of HCl with an alkene is a likely choice for this reaction (see Exercise 21.58). The two isomers of C_7H_{12} that produce 1-chloro-1-methylcyclohexane as the major product are:





d. Working backwards, 2° alcohols produce ketones when they are oxidized (1° alcohols produce aldehydes, and 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).



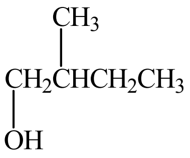
$$CH_2{=}CHCH_3 + H_2O \longrightarrow CH_3\overset{\overset{OH}{|}}{C}CH_3 \xrightarrow{\text{oxidation}} CH_3\overset{\overset{O}{\|}}{C}CH_3$$

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, and then to carboxylic acids. Therefore, we want a 1° alcohol. The 1° alcohols with formula $C_5H_{12}O$ are:

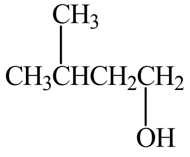
$\overset{\displaystyle OH}{\overset{|}{C}}H_2CH_2CH_2CH_2CH_3$

1-pentanol



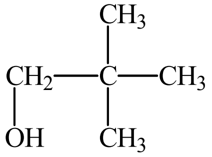
$CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2CH_3$ with $\underset{\displaystyle OH}{\underset{|}{C}}H_2$

2-methyl-1-butanol



$CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2\underset{\displaystyle OH}{\underset{|}{C}}H_2$

3-methyl-1-butanol

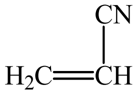


$\underset{\displaystyle OH}{\underset{|}{CH_2}}—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—CH_3$

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.

154. a.

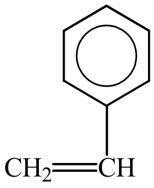


$H_2C{=}\overset{\displaystyle CN}{\overset{|}{C}}H$

acrylonitrile

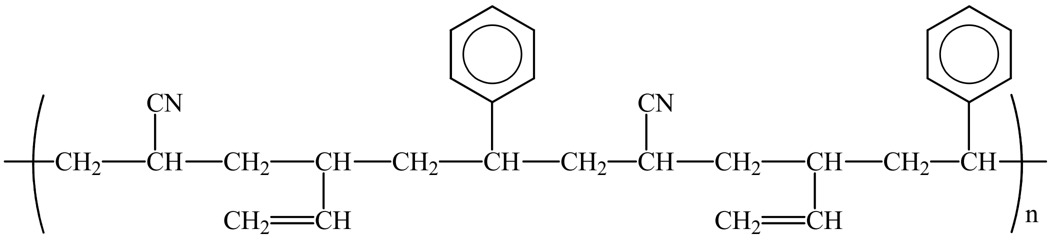
$CH_2{=}CH—CH{=}CH_2$

butadiene



styrene

The structure of ABS plastic assuming a 1:1:1 mol 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:

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

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

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 mole ratio with Br_2.

$$0.605 \text{ g } Br_2 \times \frac{1 \text{ mol } Br_2}{159.8 \text{ g } Br_2} \times \frac{1 \text{ mol } C_4H_6}{\text{mol } Br_2} \times \frac{54.09 \text{ g } C_4H_6}{\text{mol } C_4H_6} = 0.205 \text{ g } C_4H_6$$

$$\text{Mass \% } C_4H_6 = \frac{0.205 \text{ g}}{1.20 \text{ g}} \times 100 = 17.1\% \ C_4H_6$$

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:

$$33.3 \text{ g } C_3H_3N \times \frac{1 \text{ mol } C_3H_3N}{53.06 \text{ g}} = 0.628 \text{ mol } C_3H_3N$$

$$17.1 \text{ g } C_4H_6 \times \frac{1 \text{ mol } C_4H_6}{54.09 \text{ g } C_4H_6} = 0.316 \text{ mol } C_4H_6$$

$$49.6 \text{ g } C_8H_8 \times \frac{1 \text{ mol } C_8H_8}{104.14 \text{ g } C_8H_8} = 0.476 \text{ mol } C_8H_8$$

Dividing all mole values by 0.316:

$$\frac{0.628}{0.316} = 1.99; \quad \frac{0.316}{0.316} = 1.00; \quad \frac{0.476}{0.316} = 1.51$$

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

155. Treat this problem like a diprotic acid (H_2A) titration. The K_{a_1} and K_{a_2} reactions are:

$$^{+}NH_3CH_2COOH \rightleftharpoons {}^{+}NH_3CH_2COO^- + H^+ \quad K_{a_1} = \frac{[^{+}NH_3CH_2COO^-][H^+]}{[^{+}NH_3CH_2COOH]} = 4.3 \times 10^{-3}$$

$$^{+}NH_3CH_2COO^- \rightleftharpoons NH_2CH_2COO^- + H^+ \quad K_{a_2} = \frac{[NH_2CH_2COO^-][H^+]}{[^{+}NH_3CH_2COO^-]}$$

$$K_{a_2} = K_w/K_b = 1.0 \times 10^{-14}/6.0 \times 10^{-5} = 1.7 \times 10^{-10}$$

As OH^- is added, it reacts completely with the best acid present. From 0–50.0 mL of OH^- added, the reaction is:

$$^{+}NH_3CH_2COOH + OH^- \rightarrow {}^{+}NH_3CH_2COO^- + H_2O$$

At 50.0 mL OH^- added (the first equivalence point), all of the $^+NH_3CH_2COOH$ has been converted into $^+NH_3CH_2COO^-$. This is an amphoteric species. To determine the pH when an amphoteric species is the major species present, we use the formula pH = $(pK_{a_1} + pK_{a_2})/2$. From 50.1–100.0 mL of OH^- added, the reaction that occurs is:

$$^+NH_3CH_2COO^- + OH^- \rightarrow NH_2CH_2COO^- + H_2O$$

100.0 mL of OH^- added represents the second equivalence point where $H_2NCH_2COO^-$ is the major amino acid species present.

a. 25.0 mL of OH^- added represents the first halfway point to equivalence. Here, $[^+NH_3CH_2COOH] = [^+NH_3CH_2COO^-]$. This is a buffer solution where pH = pK_{a_1}.

At 25.0 mL OH^- added:

$$pH = pK_{a_1} = -\log(4.3 \times 10^{-3}) = 2.37$$

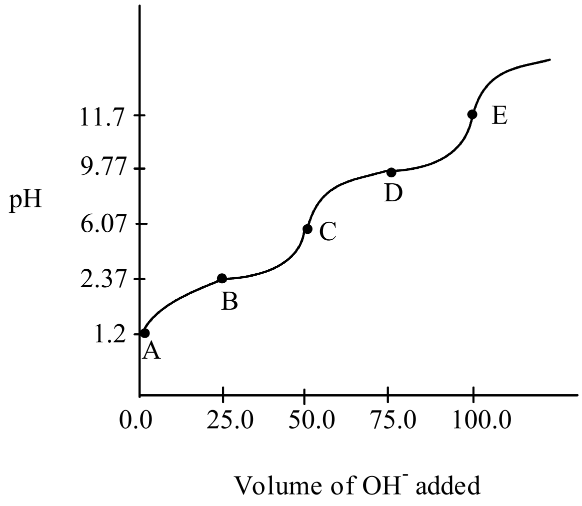
50.0 mL of OH^- added represents the first equivalence point. Here, $^+NH_3CH_2COO^-$ is the major amino acid species present. This is amphoteric species. At 50.0 mL OH^- added:

$$pH = \frac{pK_{a_1} + pK_{a_2}}{2} = \frac{2.37 - \log(1.7 \times 10^{-10})}{2} = \frac{2.37 + 9.77}{2} = 6.07$$

75.0 mL of OH^- added represents the second halfway point to equivalence. Here, $[^+NH_3CH_2COO^-] = [NH_2CH_2COO^-]$ and pH = pK_{a_2}. At 75.0 mL OH^- added:

$$pH = pK_{a_2} = -\log(1.7 \times 10^{-10}) = 9.77$$

b.



The major amino acid species present are:

point A (0.0 mL OH^-): $^+NH_3CH_2COOH$

point B (25.0 mL OH^-): $^+NH_3CH_2COOH$ and $^+NH_3CH_2COO^-$

point C (50.0 mL OH^-): $^+NH_3CH_2COO^-$

point D (75.0 mL OH^-): $^+NH_3CH_2COO^-$ and $NH_2CH_2COO^-$

point E (100.0 mL OH^-): $NH_2CH_2COO^-$

c. The various charged amino acid species are:

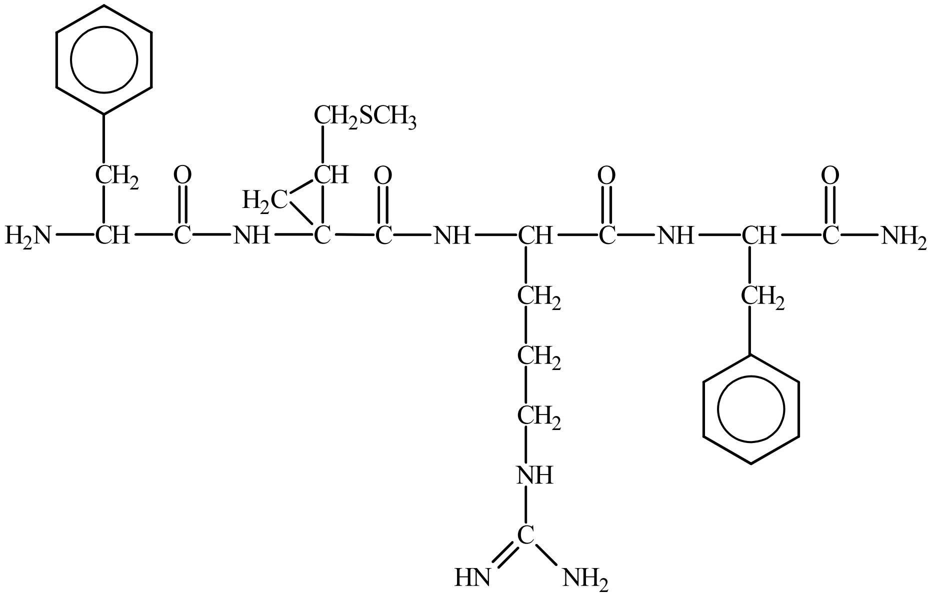
$^+NH_3CH_2COOH$	net charge = +1
$^+NH_3CH_2COO^-$	net charge = 0
$NH_2CH_2COO^-$	net charge = −1

The net charge is zero at the pH when the major amino acid species present is the $^+NH_3CH_2COO^-$ form; this happens at the first equivalence point in our titration problem. From part a, this occurs at pH = 6.07 (the isoelectric point).

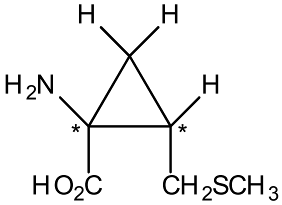
d. The net charge is +1/2 when = $[^+NH_3CH_2COOH] = [^+NH_3CH_2COO^-]$; net charge = (+1 + 0)/2 = +1/2. This occurs at the first halfway point to equivalence, where $pH = pK_{a_1} = 2.37$. The net charge is −1/2 when $[^+NH_3CH_2COO^-] = [NH_2CH_2COO^-]$; net charge = (0 − 1)/2 = −1/2. This occurs at the second halfway point to equivalence, where $pH = pK_{a_2} = 9.77$.

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

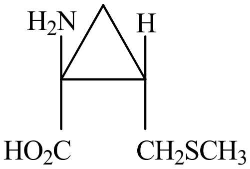
b. The new amino acid replaces methionine. The structure of the tetrapeptide is:

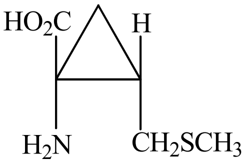


c. The chiral carbons are indicated with an asterisk.



d. Geometric isomers are possible because there are two carbons in the ring structure that each have two different groups bonded to them. The geometric isomers are:





In the first structure, CO_2H and CH_2SCH_3 are on the same side of the ring plane; in the second structure, CO_2H and CH_2SCH_3 are on opposite sides of the ring plane.