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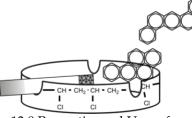
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Chapter 2: Unsaturated Hydrocarbons

CHAPTER OUTLINE

12.1 The Nomenclature of Alkenes12.2 The Geometry of Alkenes12.3 Properties of Alkenes12.4 Addition Polymers 12.5 Alkynes12.6 Aromatic Compounds and the Benzene Structure12.7 The Nomenclature of Benzene Derivatives



12.8 Properties and Uses of Aromatic Compounds

LEARNING OBJECTIVES/ASSESSMENT

When you have completed your study of this chapter, you should be able to:

- 1. Classify unsaturated hydrocarbons as alkenes, alkynes, or aromatics. (Section 12.1; Exercise 12.2)
- 2. Write the IUPAC names of alkenes from their molecular structures. (Section 12.1; Exercise 12.4)
- 3. Predict the existence of geometric (cis-trans) isomers from formulas of compounds. (Section 12.2; Exercise 12.18)
- 4. Write the names and structural formulas for geometric isomers. (Section 12.2; Exercise 12.20)
- 5. Write equations for addition reactions of alkenes, and use Markovnikov's rule to predict the major products of certain reactions. (Section 12.3; Exercise 12.26)
- 6. Write equations for addition polymerization, and list uses for addition polymers. (Section 12.4; Exercise 12.36)
- 7. Write the IUPAC names of alkynes from their molecular structures. (Section 12.5; Exercise 12.44)
- 8. Classify organic compounds as aliphatic or aromatic. (Section 12.6; Exercise 12.48)
- 9. Name and draw structural formulas for aromatic compounds. (Section 12.7; Exercises 12.52 and 12.54)
- 10. Recognize uses for specific aromatic compounds. (Section 12.8; Exercise 12.66)

LECTURE HINTS AND SUGGESTIONS

- 1. Explain the term "unsaturated" as the ability of a hydrocarbon to pick up smaller molecules. Describe how smaller molecules can be added to the double bond. The students have heard of the term "unsaturated" as it applies to fats. Explain that unsaturated fats have double bonds as part of their structure.
- 2. Use molecular models in class to illustrate the different types of isomerism. Students are easily confused as to when structures are equivalent or non-equivalent. Models are essential at this point to illustrate the differences. Two models which represent equivalent rather than isomeric structures can be shown to superimpose upon turning or upon rotation about single bonds.

3. When explaining the formation of addition polymers, first show with structural formulas how ethylene changes into polyethylene. Then show how by replacing one or more hydrogens in the ethylene with another group (e.g., chlorine, a benzene ring), essentially the same reaction can lead to a variety of different polymers. In each case be sure to give common examples of uses for the polymer.

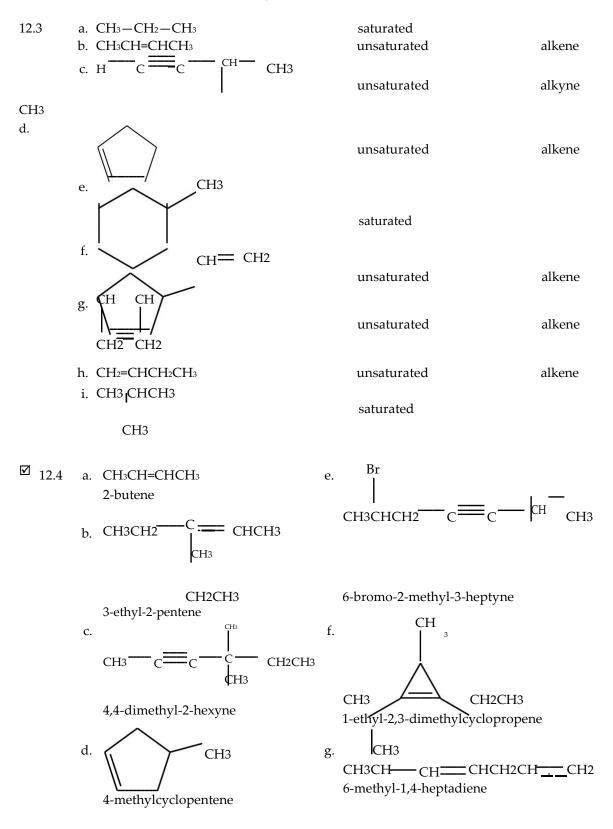
SOLUTIONS FOR THE END OF CHAPTER EXERCISES

THE NOMENCLATURE OF ALKENES (SECTION 12.1) AND ALKYNES (SECTION 12.5)

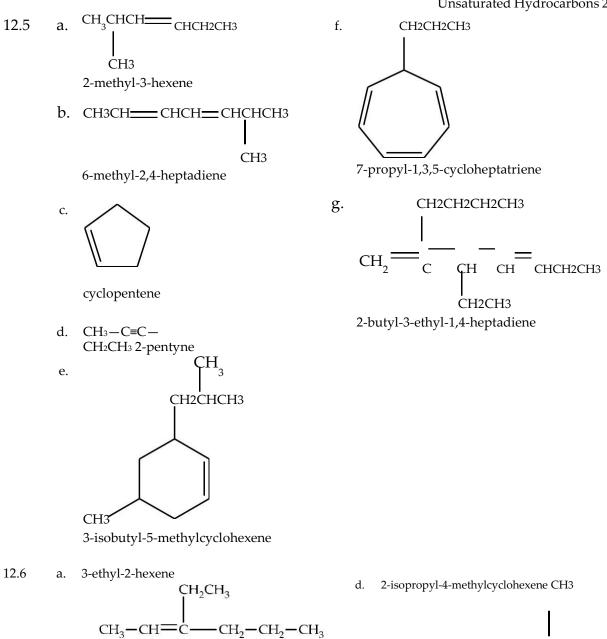
12.1 An unsaturated hydrocarbon is a hydrocarbon containing one or more multiple bonds.

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☑ 12.2 An alkene is a hydrocarbon that contains at least one carbon-carbon double bond. An alkyne is a hydrocarbon that contains at least one carbon-carbon triple bond. An aromatic hydrocarbon is a compound that contains a benzene ring or other similar feature.



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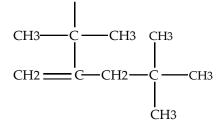


- b. 3,4-dimethyl-1-pentene ÇH3 CH3 $CH2 \equiv CH - CH - CH - CH3$
 - c. 3-methyl-1,3-pentadiene CH3 $CH2 \equiv CH$ -С СН - СН3
- CH3. CH СН3
- e. 1-butylcyclopropene CH2CH2CH2CH3

- 12.7 a. 4,4,5-trimethyl-2-heptyne CH3 CH3 - C = C - CH - CH2 - CH3CH3 CH3 - C
 - b. 1,3-cyclohexadiene



c. 2-t-butyl-4,4-dimethyl-1-pentene CH3



d. 4-isopropyl-3,3-dimethyl-1,5-octadiene CH3

СН3 СН—СН3

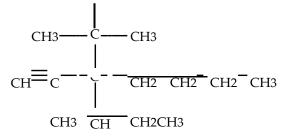


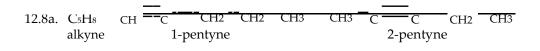
СН2 — СН3

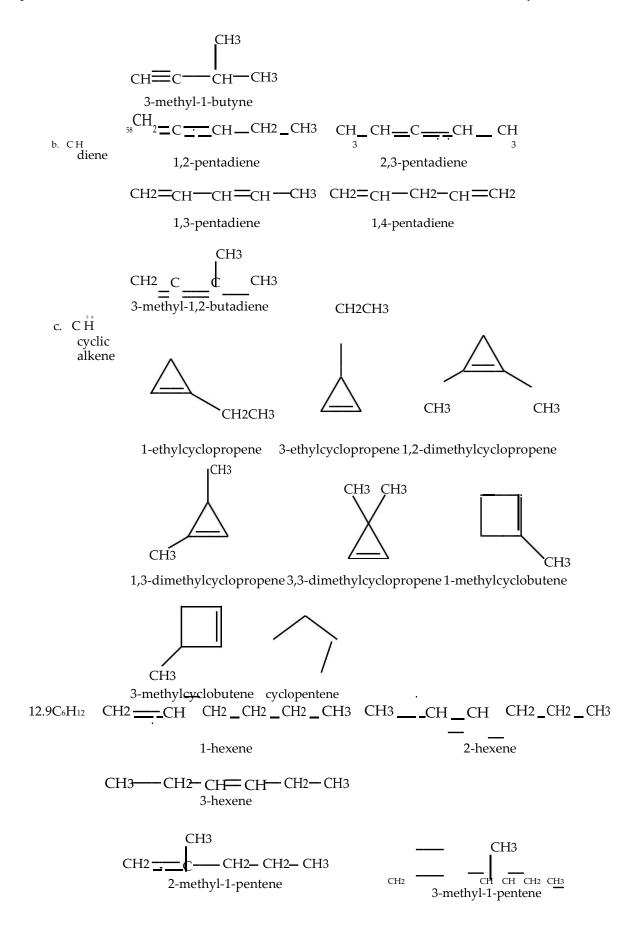
— СН

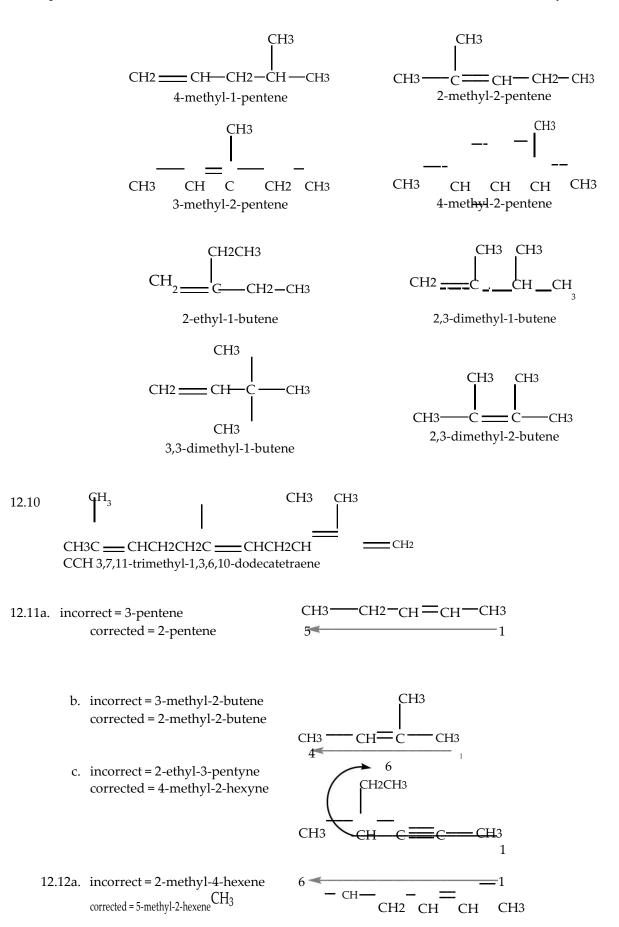
- —

- CH3 e. 2-methyl-1,3-cyclopentadiene CH3
- f. 3-sec-butyl-3-t-butyl-1-heptyne CH3



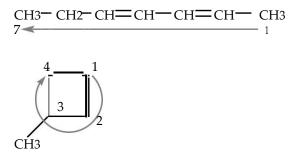






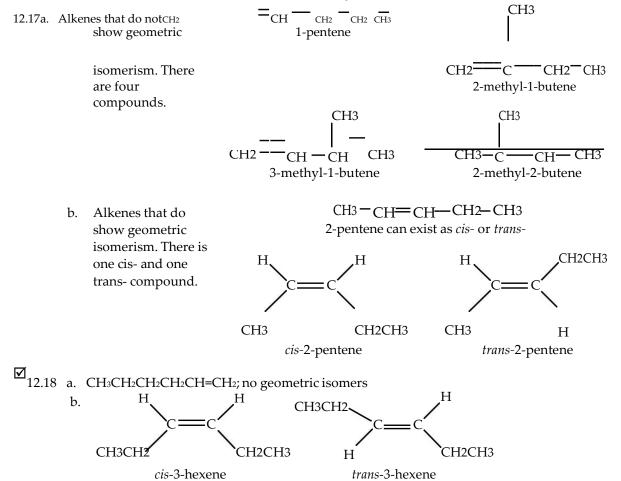
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- b. incorrect = 3,5-heptadiene corrected = 2,4-heptadiene

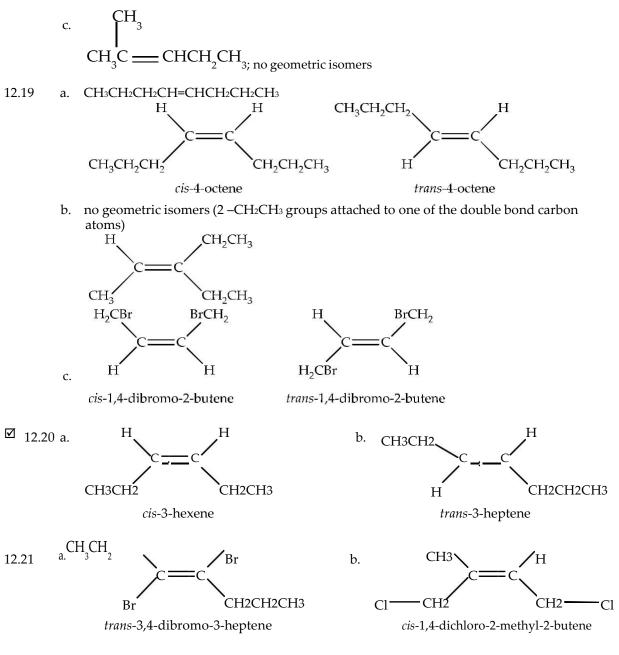


THE GEOMETRY OF ALKENES (SECTION 12.2)

- 12.13 Carbon atoms in a double bond each have 3 sp₂ hybrid orbitals as well 1 unhybridized p orbital.
- 12.14 Pi bonds are formed when unhybridized *p* orbitals overlap sideways. The pi bond is represented by π The pi bond contains 2 electrons.
- 12.15 Carbon atoms in a double bond have a trigonal planar geometry where the two atoms attached to the double bonded carbon atom as well as the other carbon atom in the double bond are in the same plane, separated by bond angles of 120°.
- 12.16 Structural isomers have a different order of linkage of atoms. Geometric isomers have the same order of linkage of atoms; however, the three dimensional structures are unique because of restricted rotation as a result of a ring or a double bond.



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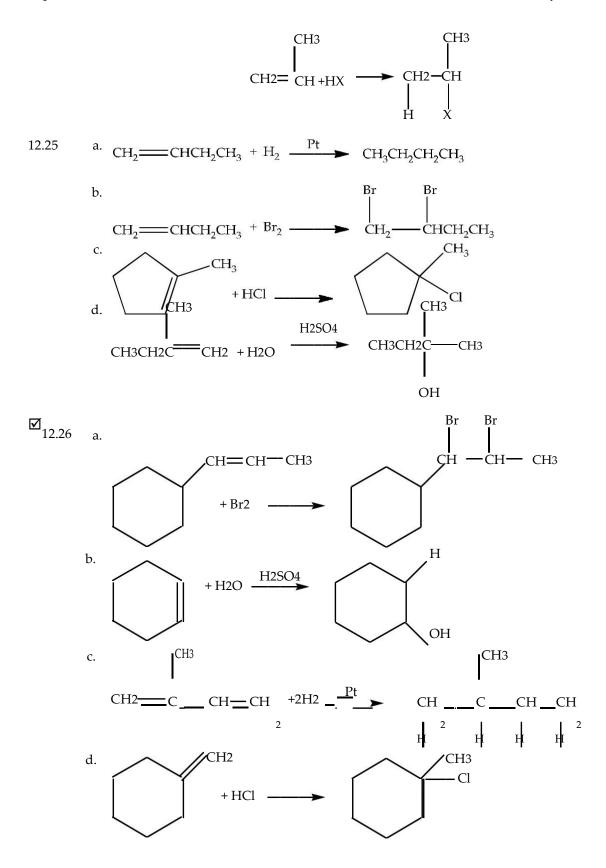


PROPERTIES OF ALKENES (SECTION 12.3)

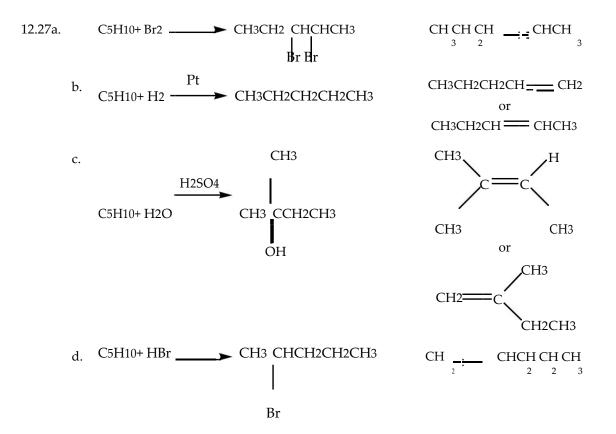
12.22 Alkenes and alkanes are both nonpolar molecules that have low solubility in water and high solubility in nonpolar solvents. They are also less dense than water.

12.23a.		$A_2 + C_3H_6 \rightarrow C_3H_6A_2$	addition
	b.	$A_2 + C_3H_6 \rightarrow C_3H_5A + HA$	not addition (substitution)
	c.	$HA + C_4H_8 \rightarrow C_4H_9A$	addition
	d.	$3O_2+C_2H_4\rightarrow 2CO_2+H_2O$	not addition (combustion)
	e.	$C_7H_{16} \rightarrow C_7H_8 + 4 H_2$	not addition (decomposition)

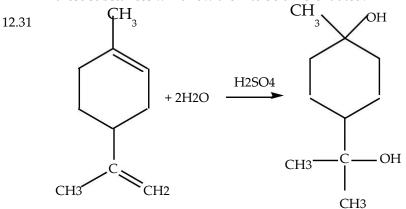
12.24 Markovnikov's rule states that when a heteroatomic compound containing hydrogen is added to a multiple bond, the hydrogen will attach to the carbon atom in the multiple bond that is directly bonded to more hydrogen atoms. The following reaction is an example of this rule:





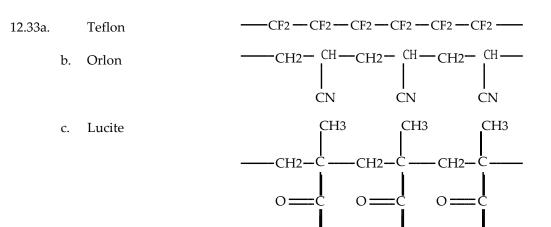


- 12.28 a. To prepare 3,4-dibromohexane from 3-hexene, I would use Br₂.
 - b. To prepare hexane from 3-hexene, I would use hydrogen gas and a platinum catalyst.
 - c. To prepare 3-chlorohexane from 3-hexene, I would use HCl.
 - d. To prepare 3-hydroxyhexane (3-hexanol) from 3-hexene, I would use water and a sulfuric acid catalyst.
- 12.29 An important commercial application of hydrogenation is the hydrogenation of liquid vegetable oils to produce a solid vegetable shortening.
- 12.30 Adding reddish-brown bromine to cyclohexane will produce a reddish-brown solution. Adding reddish-brown bromine to 2-hexene will produce a clear solution in a very short time, since the alkene undergoes an addition reaction. The differences in the chemical reactivity of these substances will allow them to be differentiated.



ADDITION POLYMERS (SECTION 12.4)

12.32 A monomer is the starting material for a polymer. It can be a small molecule.
A polymer is a large molecule made up of repeating units (often thousands of repeating units).
An addition polymer is a polymer formed by the reaction of monomers that contained multiple bonds to form the repeating units of a polymer.
A copolymer is a polymer formed by the reaction of at least two different types of monomers.



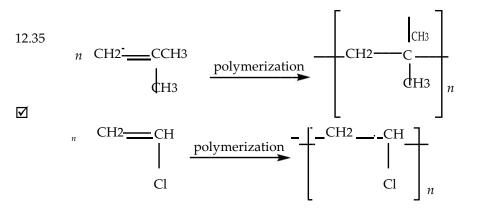
CH3

O CH3

0

CH3

12.34 All of the monomers in Table 12.3 contain one carbon-carbon double bond.



12.37a. StyrofoamFood coolers, drinking cups, insulationb. AcrilanCarpets, fabricsc. PlexiglassAirplane windows, paint, contact lenses, fiber optics

- d. PVC Synthetic leather, floor tiles, garden hoses, water pipe
- e. polypropylene Carpet fiber, pipes, bottles, artificial turf

ALKYNES (SECTION 12.5)

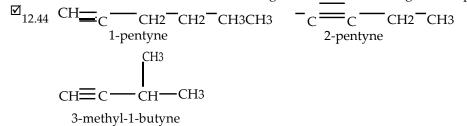
12.38 Each carbon atom bonded with a triple bond has two *sp* hybrid orbitals.

12.39 A triple bond of an alkyne is composed of 1 sigma and two pi bonds.

12.40 The geometry of a triple bond is linear.

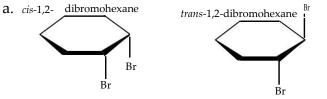
12.50

- 12.41 Geometric isomerism is not possible in alkynes because the geometry around a triple bond is linear. Each carbon atom in the triple bond only has one other attached group, unlike each carbon atom in a double bond which has two attached groups.
- 12.42 Acetylene is the simplest alkyne and it is used in torches for welding steel and in making plastics and synthetic fibers.
- 12.43 Alkynes are insoluble in water, are less dense than water, have relatively low melting and boiling points, and are flammable. They undergo addition reactions, like alkenes, but consume twice as much addition reagent for the reaction to go to completion.



AROMATIC COMPOUNDS AND THE BENZENE STRUCTURE (SECTION 12.6)

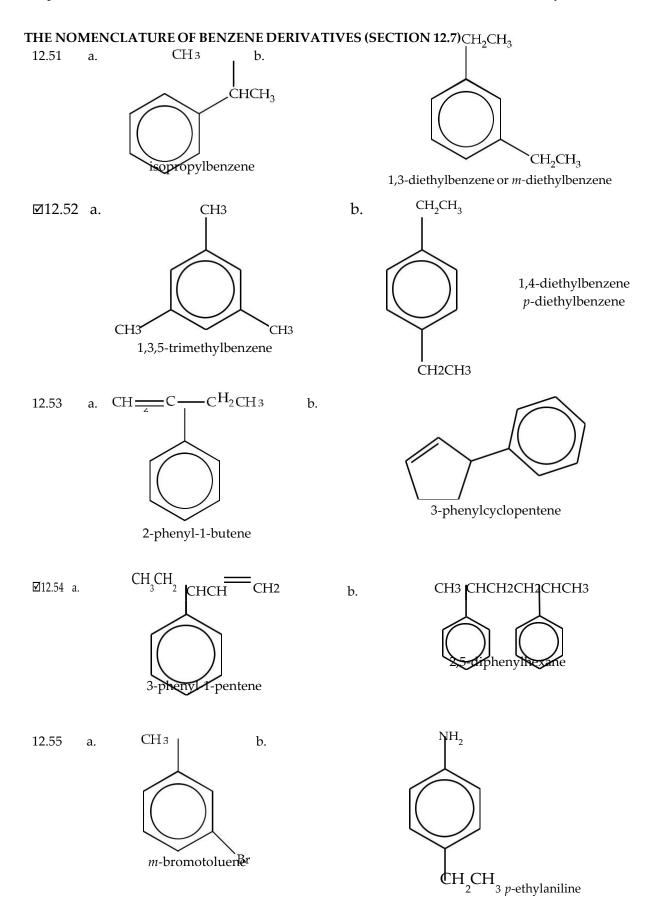
- 12.45 Carbon atoms in a benzene ring have 3 sp₂ hybridized orbitals as well as one unhybridized p orbital and each carbon atom forms 3 sigma bonds.
- 12.46 The pi bonding in a benzene ring is the result of unhybridized *p* orbitals overlapping to form a delocalized system.
- 12.47 The circle within the hexagon represents the evenly distributed electrons in the pi lobes of the six carbon atoms in the benzene ring in the structural formula for benzene.
- ✓ 12.48 Aromatic means a molecule contains a benzene ring or one of its structural relatives. Aliphatic means a molecule does not contain a benzene ring or one of its structural relatives.
- 12.49 Limonene does not contain a benzene ring; therefore, it is not considered aromatic. Aromaticity reflects structure, not the physical property of fragrance.

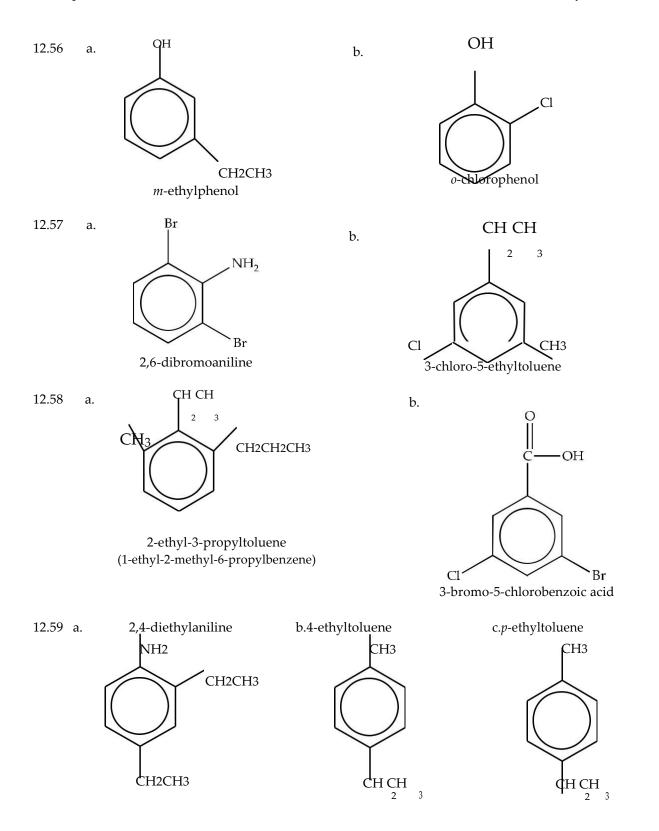


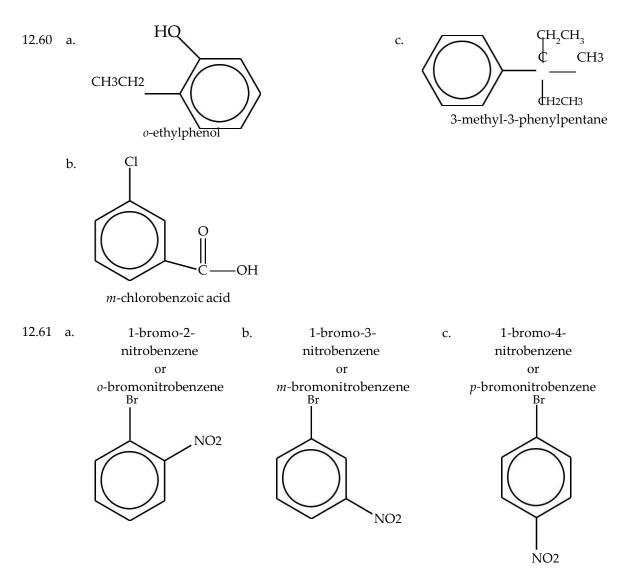
Dibromocyclohexane is not a planar molecule. Each carbon atom has two attached groups (H or another atom) in addition to two positions of

attachment in the ring. In order to maintain a tetrahedral geometry around the carbon atoms, the attached groups can be "above" or "below" the ring. Consequently, the molecule can exhibit cis-trans isomerism when it has two attached groups (other than hydrogen) on two different carbon atoms in the ring.

b. 1,2-dibromobenzene is a planar molecule because each carbon atom in the ring is only bonded to 3 other atoms. Consequently, the attached bromine atoms cannot be "above" or "below" the plane of the molecule. This in turn means the molecule cannot exhibit cistrans isomerism.







PROPERTIES AND USES OF AROMATIC COMPOUNDS (SECTION 12.8)

- 12.62 Aromatic hydrocarbons are nonpolar molecules that are insoluble in water and soluble in nonpolar solvents. They are also less dense than water.
- 12.63 Benzene does not readily undergo addition reactions characteristic of other unsaturated compounds because the delocalized pi cloud of the benzene ring makes the ring so stable that addition reactions do not occur. An addition reaction would result in the loss of one of the double bonds, and consequently, disrupt the delocalized system. This is not favored because it results in a loss of stability. Benzene, therefore, undergoes substitution reactions instead of addition reactions.
- 12.64 Cyclohexene readily undergoes addition reactions. Benzene resists addition reactions and favors substitution reactions. Both benzene and cyclohexene can undergo combustion.

aniline

12.65	a. A solvent	benzene, toluene
	b. A vitamin	riboflavin
	c. An essential amino acid	phenylalanine

d. Starting material for dyes

$\overline{\mathbf{A}}$		
-12.66	a. Used in the production of Formica®	phenol
	b. A starting material for polystyrene	styrene
	c. Used to manufacture drugs	aniline
	d. A starting material for Bakelite®	phenol

ADDITIONAL EXERCISES

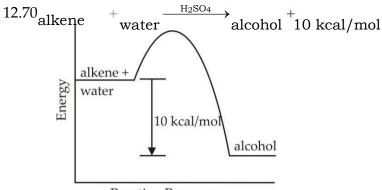
- 12.67 Alkynes have slightly higher boiling points and densities than structurally equivalent alkanes because the linear alkyne molecules can pack more closely together than the alkane molecules. This close packing allows for stronger dispersion forces, which cause the alkynes to have higher boiling points and densities than structurally equivalent alkanes.
- 12.68 Heat provides additional energy to the reactants which increases the likelihood of a "successful collision" because reactions occur when reactants collide with sufficient energy to produce the transition state. Heat also increases the number of collisions. Consequently, the reaction rate should increase as the reaction is heated.

Pressure increases the number of collisions between reactant molecules, which increases the likelihood of a "successful collision." Consequently, the reaction rate should increase as the pressure is increased.

Catalysts lower the activation energy required for a reaction to occur; therefore, the reaction rate should increase when a catalyst is added to the reaction.

12.69 Propene reacts with a diatomic molecule whose atoms have the electronic configuration of 1s22s22p63s23p5 (Cl2) to produce 1,2-dichloropropane.

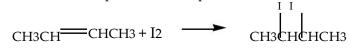
CH2 = CHCH3 + Cl2
$$\rightarrow$$
 CH2 CHCH3 CHCH3 CHCH3 CHCH3 CHCH3 CHCH3 CHCH3



Reaction Progress

This reaction is exothermic because energy is a product of the reaction.

12.71 When 25.0 g of 2-butene reacts with 25.0 g of iodine, iodine is the limiting reactant. Only 0.0985 moles of product will be produced.

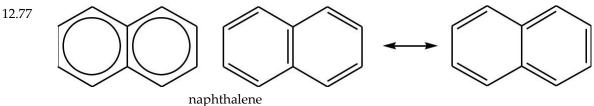


$$25.0 \text{ g C } 4 \text{ H } 8 \left(\frac{1 \text{ mole C } 4 \text{ H } 8 \text{ I2}}{56.1 \text{ g C } 4 \text{ H8}} \right) = 0.446 \text{ moles C } 4 \text{ H } 8 \text{ I2}$$
$$25.0 \text{ g I } 2 \left(\frac{1 \text{ mole C } 4 \text{ H } 8 \text{ I2}}{254 \text{ g I2}} \right) = 0.0984 \text{ moles C } 4 \text{ H } 8 \text{ I2}$$

ALLIED HEALTH EXAM CONNECTION

- 12.72 (a) Benzene and (d) phenol are aromatic compounds. (b) Ethyl alcohol and (c) methane are aliphatic compounds.
- 12.73 a. $C_n H_{2n}$ (2) an alkene with one C=C bond
 - b. $C_n H_{2n+2}$ (1) an alkane
 - c. $C_n H_{2n-2}(3)$ an alkyne with one C=C bond
- 12.74 $CH_2=CH-CH_2-CH_3$ is an example of (c) an alkene.
- 12.75 The correct structural formula for ethyne is (c) H-C=C-H.
- 12.76 Protection of the skin from the harmful effects of ultraviolet light is provided by the pigment(b) melanin, which is produced by specialized cells within the stratum germinativum.

CHEMISTRY FOR THOUGHT

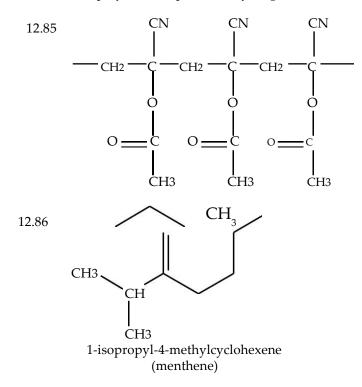


- 12.78 Propene does not exhibit geometric isomerism because one of the carbon atoms in the double bond is also bonded to two hydrogen atoms. In order to exhibit geometric isomerism, both carbon atoms in the double bond must also be bonded to two unique groups.
- 12.79 Limonene contains 10 carbon atoms, including a six membered ring and two double bonds. It is likely to be a liquid at room temperature because the structure allows the molecules to pack fairly close together.

12.80 5:0 10⁴
$$\left(\frac{1 \text{ ethylene monomer}}{28.0 \text{ u}} \right) = 1.8 \text{ $\%0^3$ ethylene monomers}$$

- 12.81 The human body gets its supply of aromatic compounds through diet. The foods humans eat contain aromatic compounds.
- 12.82 Addition polymers form a large extended structure. Polyvinyl acetate prevents the formation of sharp fragments in automobile safety glass because it holds the glass together on a flexible surface after the glass is broken. The copolymer of styrene and 1,3-butadiene allows a large flexible bubble to be formed by the girl chewing gum.

- 12.83 Alkanes can't undergo addition polymerization because they lack the reactive double bond that allows addition polymerization to occur.
- 12.84 The polymer that produces hydrogen cyanide, HCN, is polyacrylonitrile. The polymer that produces hydrogen chloride, HCl, is poly (vinyl chloride).



EXAM QUESTIONS MULTIPLE CHOICE

- 1. Name a difference between a saturated and an unsaturated hydrocarbon.
 - Saturated hydrocarbons are composed of only carbon and hydrogen, and a. unsaturated hydrocarbons include other atoms than just carbon and hydrogen.
 - Saturated hydrocarbons do not contain multiple bonds between carbons, but b. unsaturated hydrocarbons do contain multiple bonds.
 - Unsaturated hydrocarbons are flammable but saturated hydrocarbons are not. c.
 - d. Saturated hydrocarbons are essentially insoluble. Unsaturated hydrocarbons are soluble.

Answer: В

2. Which characteristic relates to alkenes, but not the other hydrocarbon families?

a. saturation c. double bonds b. halogen substitution d. triple bonds

С

Answer:

- 3. What number would be used to indicate the double bond position in the IUPAC name for CH₃CH₂CH = CHCH₃?
 - a. 1 b. 2 c. 3 d. 4 В

Answer:

4. In the IUPAC name for the following compound, the -Br group is located at what position? CH₃CHBrCH=CH₂ b. 2 d. 4 a. 1 c. 3 С Answer: ΩH2 5. What is the IUPAC name of the following compound? $\ensuremath{^{\rm CH_3}}$ CH2 CH2 С CH3 a. 3-ethyl-1-butene c. 3-ethyl-3-butene b. 2-ethyl-2-butene d. 2-ethyl-1-butene Answer: D СН3 _____С ____СН ____СН2 6. What is the IUPAC name of the following compound? CH3 a. 2-methyl-1,4-pentadiene c. 4-methyl-1,3-pentadiene b. 2-methyl-2,4-dipentene d. 4-methyl-2,4-pentadiene Answer: С Br 7. What is a correct IUPAC name of the following compound? c. 2-bromo-1,4-cyclohexadiene a. 5-bromo-1,3-cyclohexadiene b. 2-bromo-1,3-cyclohexadiene d. 3-bromo-1,5-cyclohexadiene Answer: А 8. Which of the following compounds could exist in the form of two geometric isomers? ссн — _{СН3} a. CH3 c. снз с с -CH3 CH3 **С**Н3 CH3 b. CH3 Cl Cl Cl Cl

Answer:

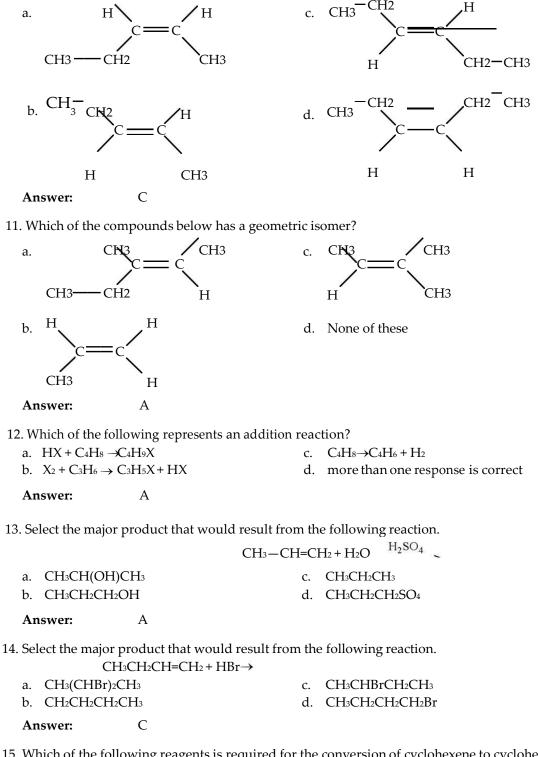
9. Which of the following can exhibit geometric isomerism?

D

a. 1-propene c. 2,3-dimethyl-2-butene b. 1,2,2-tribromoethene d. 1-bromo-1-propene

Answer: D

10. Which of the following compounds is *trans*-3-hexene?

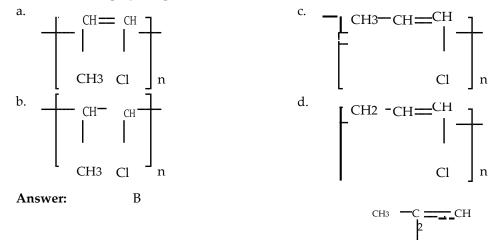


15. Which of the following reagents is required for the conversion of cyclohexene to cyclohexane?a. HClb. H2O and H2SO4c. H2 and H2SO4d. H2 and Pt

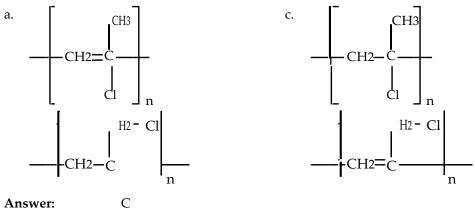
Answer: D

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16. Which addition polymer produced from CH₃-CH=CH-Cl?



17. What is the addition polymer produced from the monomer,

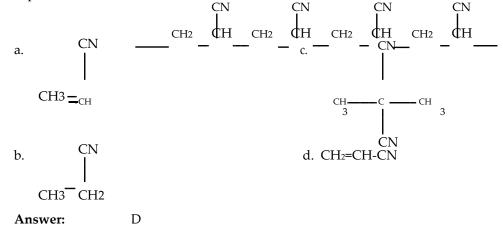


?

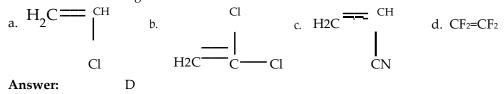
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18. A portion of the structure of Acrilan is shown. What is the structure of the monomer?

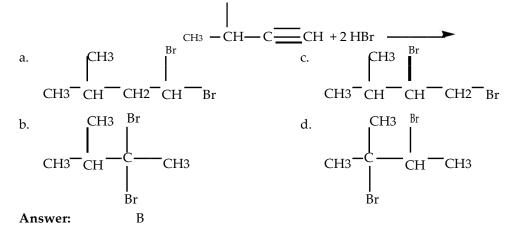


19. Which of the following is the monomer for Teflon®?



20.	20. Which is the formula for an alkene?a. CH₃CHCH₂b. CH₃CH₂CH₂		c. d.		CH3CH3CH2 There is more than one correct response.		
	An	swer:	А				
21.	a. b.	nich is the formul CH3CH2CCH2 CH3CH2CH2CH CH3CH2CH2CH	-		c. d.	CH3CH2CCH CH3CH2CCH2	
22.	Wł a. b.	nich is a differen	ce between butane a nd butene does not a double bond B	and	butene? c. d.	they are isomers the presence of a tr	iple bond
			ce between butene a	1		2	
	a. b. c. d.	They are isome Cyclobutene ha The location of carbons in bute	ers. as 2 double bonds, b the double bond is	oute terr	ne does i ninal in c	not. cyclobutene, but betw	ween interior
24	мл	nich is a differen	co hotwoon hutwno	and	cyclobut	wpo?	
۷4.	 24. Which is a difference between butyne and cyclobutyne? a. Cyclobutyne does not exist. b. Butyne's multiple bond is interior, cyclobutyne is not between interior carbons. c. Cyclobutyne burns much hotter than butyne because of the greater unsaturation. d. Both b and c are differences between the molecules. 						
	An	iswer:	А				
25.	a.	nat is the correct 4-bromopenty 1-bromo-2-pent	ne	le co	ompound c. d.		5
	An	iswer:	D				
26.	Th a.	e addition of two alkane.	o moles of hydroger b.alkene.	n me	olecules (c.	(H2) to an alkyne pro aromatic.	oduces an: d. alkyl halide.
	An	iswer:	А				

27. What is the product of the following reaction? CH3



28. Acetylene is commercially useful as a fuel for torches and as:

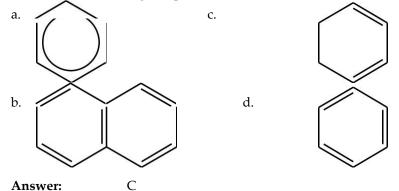
- a. a starting material for plastics.
- c. an ingredient in pesticides.
- b. an industrial solvent.
- d. a component in paint formulations.

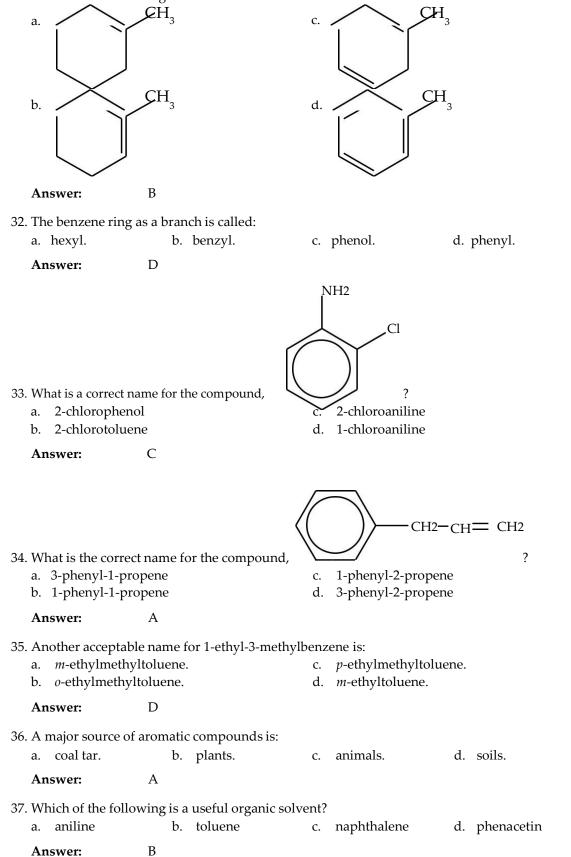
- А Answer:
- 29. What is the characteristic of aromatic compounds that is responsible for them being named aromatic compounds?
 - a. The compounds have a pleasant smell.
 - b. These compounds contain a benzene ring or structural relative.
 - c. A requirement is to contain a hydrocarbon chain that is either saturated or unsaturated and at least 3 carbons long.
 - d. There is more than one correct response.

В

Answer:

30. Which of the following compounds is not considered to be aromatic?





31. Which of the following structures violates the octet rule?

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Br,

Br

4

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38. Naphthalene is used as a(n):

a. explosive. b. moth repellent. c. pain reliever. d. solvent.

Answer:

39. Identify the statement about lycopene that is true.

a. Lycopene is known as vitamin C.

В

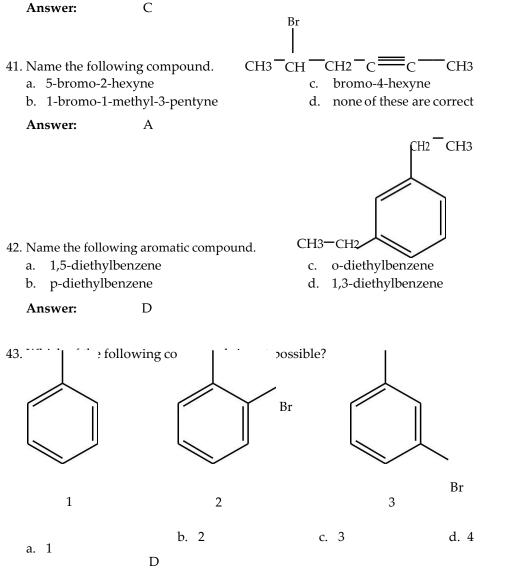
В

- b. Lycopene gives watermelon their red color.
- Raw tomatoes are a better source of lycopene than cooked tomatoes. c.
- d. Lycopene should not be eaten with fatty foods.

Answer:

- 40. Which of the following is true?
 - a. Alkynes are not flammable, the others hydrocarbons are flammable.
 - b. Alkenes all have a scent similar to the aromatic compounds, but the alkanes and alkynes have a scent that is extremely sharp.
 - Alkanes have only single bonds between carbons. c.
 - d. There is more than one correct response.

Answer:



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44. Poly (vinyl chloride), PVC, is used for water pipes and synthetic leather. What is the monomer of the PVC polymer shown on the right?



45. Lycopene has been shown to prevent certain types of cancer. Which of the following is not a good source of lycopene?

a. tomatoes		c.	guava
b. pink grapefrui	t	d.	green beans
Answer:	D		

46. The reaction of hydrogen fluoride with ethene would be an example of:

a.	hydration.	c.	hydrohalogenation.
b.	halogenation.	d.	fluorination.

С Answer:

47. Which of the following could exhibit cis/trans isomerism?

a. propene b. 1,1-dichloropropene		 1-butene 2-butene
Answer:	D	

48. What type of hybridization is associated with alkyne bonding?

a. sp	b. sp ₂	c. sp ₃	d. sp4
Answer:	А		

TRUE-FALSE

1. CH₃CH₂CH₂CH₂ is the formula for a saturated hydrocarbon.

Answer:

2. The general formula for an alkene is C_nH_{2n}.

F

Answer:

3. Alkenes must have at least two carbon atoms. Т

Т

- Answer:
- 4. Alkenes have a maximum of one double bond. F

Т

Answer:

5. The addition of bromine to an alkene results in an alkane because one bond of the multiple bond is broken.

Answer:

6. A characteristic of alkynes is a region of strong polarity caused by the multiple bond.

Answer:F

7. One of the halogenation reactions occurs when a halogen, a member of group VIIA, reacts with alkene.

Answer: T

8. Cyclic compounds do not undergo halogenation reactions.

Answer:

9. The general formula for an alkyne is C_nH_{2n} .

Т

F

Answer:F

10. Markovnikov's rule indicates that in the addition of H-X to an alkene, the hydrogen becomes attached to the carbon atom that is already bonded to more hydrogens.

Answer:

11. An alkene with one multiple bond can be converted to an alkane by hydration.

Answer:T

- 12. Polymers are compounds that are composed of repeating units chemically bound to each other.Answer: T
- 13. The physical properties of alkynes are very different from those of alkenes.

Answer:F

14. 2-butyne can exist as cis- and trans- isomers.

Т

F

Answer:F

15. The same substances which add to double bonds can add to triple bonds.

Answer:T

16. Two moles of hydrogen gas would be required to convert one mole of 2-butyne into butane.

Answer:

17. Benzene is not an alkene.

Answer:T

18. Phenyl is the name given to a benzene ring that is an attached group to a larger molecule.

Answer: T

19. Aromatic compounds dissolve well in a nonpolar solvent.

Answer:T

20. The alkynes belong to an extensive family of compounds that have a large biological significance, especially when discussing digestion.

Answer: