CHAPTER 20
UNSATURATED HYDROCARBONS

SOLUTIONS TO REVIEW QUESTIONS

1. The sigma bond in the double bond of ethene is formed by the overlap of two sp² electron orbitals and is symmetrical about a line drawn between the nuclei of the two carbon atoms. The pi bond is formed by the sidewise overlap of two p orbitals which are perpendicular to the carbon-carbon sigma bond. The pi bond consists of two electron clouds, one above and one below the plane of the carbon-carbon sigma bond.

2. \( \text{Cl} \quad \text{C} = \text{C} \quad \text{Cl} \)
   \( \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{Cl} \text{H} \text{Cl} \text{H} \text{Cl} \)

\( \textit{cis}-1,2\text{-dichloroethene} \quad \textit{trans}-1,2\text{-dichloroethene} \quad 1,2\text{-dichloroethane} \)

We are able to get \textit{cis-trans} isomers of ethene because there is no rotation around the carbon-carbon double bond, so the two structures shown are not the same. With 1,2-dichloroethane, there is free rotation of the carbon-carbon single bond. In the structure shown, exchanging the chlorine on the right with either hydrogen atom on that carbon appears to make a different isomer, but rotation makes any of the three positions equivalent.

3. Rubber products deteriorate rapidly in smog-ridden areas because ozone, which is present in smog, causes oxidation of the carbon-carbon double bonds, which changes the properties of the rubber.

4. Acetylene presents two different explosion hazards:
   (a) It can form an explosive mixture with oxygen or air;
   (b) When highly compressed or liquefied, acetylene may decompose violently, either spontaneously or from a slight shock.

5. The small molecule released in an elimination reaction can be reacted with and added to the main elimination product. For example, an alkene can be prepared by release of HX from an alkyl halide. In turn, HX can be added to an alkene to form an alkyl halide.

6. During the 10-year period from 1935 to 1945, the major source of aromatic hydrocarbons shifted from coal tar to petroleum due to the rapid growth of several industries which used aromatic hydrocarbons as raw material. These industries include drugs, dyes, detergents, explosives, insecticides, plastics, and synthetic rubber. Since the raw material
needs far exceeded the aromatics available from coal tar, another source had to be found, and processes were developed to make aromatic compounds from alkanes in petroleum. World War II, which occurred during this period, put high demands on many of these industries, particularly explosives.

7. Benzene does not undergo the typical reactions of an alkene. Benzene does not decolorize bromine rapidly and it does not destroy the purple color of permanganate ions. The reactions of benzene are more like those of an alkane. Reaction of benzene with chlorine requires a catalyst. Benzene does not readily add Cl₂, but rather a hydrogen atom is replaced by a chlorine atom.

\[
C_6H_6 + Cl_2 \xrightarrow{Fe} C_6H_5Cl + HCl
\]

8. The 11-cis isomer or retinal combines with a protein (opsin) to form the visual pigment rhodopsin. When light is absorbed, the 11-cis double bond is converted to a trans-double bond. This process initiates the mechanism of visual excitation which our brains perceive as light or light forms.

9. Polycyclic aromatic hydrocarbons are potent carcinogens.

10. Cyclohexane carbons form bond angles of about 109° in a tetrahedron; this causes the ring to be either a “boat” or a “chair” shape. Benzene carbons form bond angles of 120° in a plane. Therefore, the benzene molecule must be planar.

11. According to the mechanism, the addition of an unsymmetrical module such as HX adds to a carbon-carbon double bond. In the first step, the H adds to the carbon of the carbon-carbon double bond that has the most hydrogen atoms on it, according to Markovnikoff’s Rule. The second step completes the addition by adding the more negative element, X of the HX.

12. “Cracking” means breaking into pieces, which, according to the pyrolysis products, is what occurs in the reaction.
CHAPTER 20

SOLUTIONS TO EXERCISES

1. (a) ethane
   \[
   \begin{array}{c}
   \text{H} \\
   \text{H} \\
   \text{H} : \text{C} :: \text{C} : \text{H} \\
   \text{H} \end{array}
   \]
   (b) ethene
   \[
   \begin{array}{c}
   \text{H} \\
   \text{H} \\
   \text{H} : \text{C} :: \text{C} \end{array}
   \]
   (c) ethyne
   \[
   \begin{array}{c}
   \text{H} :: \text{C} : \text{C} : \text{H} \\
   \text{H} \end{array}
   \]

2. (a) propane
   \[
   \begin{array}{c}
   \text{H} \\
   \text{H} \\
   \text{H} \\
   \text{H} : \text{C} :: \text{C} : \text{H} \\
   \text{H} \end{array}
   \]
   (b) propene
   \[
   \begin{array}{c}
   \text{H} \\
   \text{H} \\
   \text{H} : \text{C} :: \text{C} : \text{H} \\
   \text{H} \end{array}
   \]
   (c) propyne
   \[
   \begin{array}{c}
   \text{H} :: \text{C} :: \text{C} : \text{H} \\
   \text{H} \end{array}
   \]

3. Isomeric iodobutenes, C₄H₇I
   \[
   \begin{array}{c}
   \text{H} \\
   \text{C} = \text{C} \end{array}
   \]
   (cis-1-iodo-1-butene)
   \[
   \begin{array}{c}
   \text{CH₃CH₂I} \end{array}
   \]
   2-iodo-1-butene
   \[
   \begin{array}{c}
   \text{CH₃CH₂CH₂CHCH₃} \end{array}
   \]
   4-iodo-1-butene
   \[
   \begin{array}{c}
   \text{H} \\
   \text{C} = \text{C} \end{array}
   \]
   (trans-2-iodo-2-butene)
   \[
   \begin{array}{c}
   \text{CH₃CH₃} \end{array}
   \]
   cis-2-iodo-2-butene
   \[
   \begin{array}{c}
   \text{H} \\
   \text{C} = \text{C} \end{array}
   \]
   (cis-1-iodo-2-butene)
   \[
   \begin{array}{c}
   \text{CH₃CH₃CH₂I} \end{array}
   \]
   1-iodo-2-methylpropene
   \[
   \begin{array}{c}
   \text{C} \end{array}
   \]
   (3-iodo-2-methylpropene)
4. (a) \( \text{C}_3\text{H}_5\text{Cl} \)
\[
\begin{align*}
\text{CH}_3 & \quad \text{C} = \text{C} & \quad \text{Cl} \\
\text{H} & \quad \quad & \quad \text{H} \\
\text{trans}-\text{1-chloropropene} & \quad & \quad \text{cis}-\text{1-chloropropene}
\end{align*}
\]
\( \text{CH}_3\text{CCl} = \text{CH}_2 \)
2-chloropropene
\( \text{CH}_2\text{ClCH} = \text{CH}_2 \)
3-chloropropene
(b) chlorocyclopropane

5. (a) \( \text{CH}_3\text{CHCH} = \text{CHCHCH}_3 \)
2,5-dimethyl-3-hexene
(b) \( \text{CH}_3\text{CHCH} = \text{CHCHCH}_3 \)
(c) \( \text{CH} \equiv \text{CCH} = \text{CHCH}_3 \)
3-penten-1-yne
(e) \( \text{CH} \equiv \text{CCHCH}_2\text{CH}_3 \)
3-methyl-1-pentyne
\( \text{CH}_2\text{CH}_3 \)
6. (a) \( \text{CH}_2 = \text{CHCCH}_2\text{CH}_3 \)
3-ethyl-3-methyl-1-pentene
(b) \( \text{cis}, 1,2\)-diphenylethene
7. (a) \( \text{CH}_3\text{CH}_2\text{C}==\text{CH}_2 \)
Numbering was started from the wrong end of the structure.
Correct name: 2-methyl-1-butene

(b) \( \text{CH}_3\text{CH}_2\text{C}==\text{C} \)
Numbering was started from the wrong end of the structure.
Correct name: \textit{cis}-2-pentene

(c) \( \text{CH}_3\text{CH}_2\text{C}==\text{C} \)
This compound does not have \textit{cis-trans} isomers. Correct name: 2-methyl-2-pentene

8. (a) \( \text{CH}_2==\text{CHCHCH}_3 \)
Longest chain contains five carbon atoms. Correct name: 3-methyl-1-pentene

(b) \( \text{Cl} \)
The C==C bond in cyclohexene is numbered so that substituted groups have the smallest numbers. Correct name: 1-chlorocyclohexene
Numbering was started from the wrong end of the structure.
Correct name: *trans*-2-hexene

9. (a) *trans*-3-methyl-3-hexene  
   (b) 3-phenyl-1-propyne  
   (c) 4,5-dibromo-2-hexyne

10. (a) *cis*-4-methyl-2-hexene  
     (b) 2,3-dimethyl-2-butene  
     (c) 3-isopropyl-1-pentene

11. All the hexynes, C_6H_{10}  
    CH_3CH_2CH_2CH_2C≡CH  
    1-hexyne  
    CH_3CH_2CH_2C≡CCH_3  
    2-hexyne  
    CH_3CH_2C≡CCH_3  
    3-hexyne  
    CH_3CHCH_3  
    3-methyl-1-pentyne  
    CH_3CH_2C≡CCH_3  
    4-methyl-1-pentyne  
    CH_3CH_2C≡CCH_3  
    3-methyl-1-butyn  
    CH_3CHCH_3  
    3,3-dimethyl-1-butyn

12. All the pentynes, C_5H_8  
    CH_3CH_2CH_2C≡CH  
    1-pentyne  
    CH_3CH_2C≡CCH_3  
    2-pentyne  
    CH_3CH_2C≡CH  
    3-methyl-1-butyn

13. Only structure (b) will show *cis-trans* isomers. CH_3CH≡CHCl

14. Only structure (c) will show *cis-trans* isomers. CH_2ClCH≡CHCH_2Cl
15. (a) \[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH} \equiv \text{C} = \text{H} + \text{Br}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHBrCH}_2\text{Br}
\]

(b) \[
\text{CH}_3\text{CH}_2\text{C} = \text{CHCH}_3 + \text{HI} \rightarrow \text{CH}_3\text{CH}_2\text{CCH}_2\text{CH}_3
\]

(c) \[
\text{CH}_3\text{CH}_2\text{CH} \equiv \text{C} = \text{H} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{CH}_2\text{CHCH}_3
\]

(d) \[
\text{CH} = \text{CH} + \text{H}_2 \xrightarrow{\text{Pt, } 25^\circ \text{C}, 1 \text{ atm}} \text{CH}_2\text{CH}_3
\]

(e) \[
\text{CH}_3\text{CH} = \text{CHCH}_3 + \text{KMnO}_4 \xrightarrow{\text{H}_2\text{O}} \text{CH}_2\text{CHCHCH}_3
\]

16. (a) \[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH} \equiv \text{C} = \text{H} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_3
\]

(b) \[
\text{CH}_3\text{CH}_2\text{CH} = \text{CHCH}_3 + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{CHBrCH}_2\text{CH}_3 + \text{CH}_3\text{CH}_2\text{CH}_2\text{CHBrCH}
\]

(c) \[
\text{CH}_2 = \text{CHCl} + \text{Br}_2 \rightarrow \text{CH}_2\text{BrCHClBr}
\]

(d) \[
\text{CH} = \text{CH} + \text{HCl} \rightarrow \text{CHClCH}_3
\]

(e) \[
\text{CH}_2 = \text{CHCHCH}_3 + \text{KMnO}_4 \xrightarrow{\text{H}_2\text{O}, \text{cold}} \text{CH}_2\text{CHCHCH}_3
\]

17. (a) ethyne
\[
\text{CH} \equiv \text{CH}
\]

(b) 2-butyne
\[
\text{CH}_3\text{C} \equiv \text{CCH}_3
\]

(c) propyne
\[
\text{CH}_3\text{C} \equiv \text{CH}
\]
18. (a) 1-butyne
\[ CH≡CCH₂CH₃ \]
(b) propyne
\[ CH≡CCH₃ \]
(c) 2-pentyne
\[ CH₃C≡CCH₂CH₃ \]

19. (a) \[ CH₃C≡CCH₃ + Br₂ (1 mole) \rightarrow CH₃CBr≡CBrCH₃ \]
(b) Two-step reaction:
\[ CH≡CH + HCl \rightarrow CH₂=CHCl \xrightarrow[HCl]{HCl} CH₃CHCl₂ \]
(c) \[ CH₃CH₂CH₂C≡CH + H₂ (1 mole) \xrightarrow[Pt_{25°C}]{25°C} CH₃CH₂CH₂CH=CH₂ \]

20. (a) \[ CH₃C≡CH + H₂ (1 mol) \xrightarrow[Pt, 25°C]{1 atm} CH₃CH=CH₂ \]
(b) \[ CH₃C≡CCH₃ + Br₂ (2 mol) \rightarrow CH₃CBr₂CBr₂CH₃ \]
(c) Two step reaction:
\[ CH₃C≡CH + HCl \rightarrow CH₃C≡CHH₂ \xrightarrow[HCl]{HCl} CH₃C≡CHH₂ \]

21. When cyclohexene, \[ \text{\includegraphics{cyclohexene}} \] reacts with:

(a) \[ Br₂, \text{ the product is } \text{\includegraphics{1,2-dibromocyclohexane}} \]
(b) \[ HI, \text{ the product is } \text{\includegraphics{iodocyclohexane}} \]
(c) \[ H₂O, H^+, \text{ the product is } \text{\includegraphics{cyclohexanol}} \]
(d) \[ \text{KMnO}_4(aq), \text{ the product is } \text{\includegraphics{cyclohexene glycol or 1,2-dihydroxycyclohexane}} \]
22. When cyclopentene, \( \text{C}_5\text{H}_5\cdot \) reacts with:

(a) \( \text{Cl}_2 \), the product is \( \text{C}_5\text{H}_5\text{Cl}_2 \) (1,2-dichlorocyclopentane)

(b) \( \text{HBr} \), the product is \( \text{C}_5\text{H}_5\text{Br} \) (bromocyclopentane)

(c) \( \text{H}_2, \text{Pt} \), the product is \( \text{C}_5\text{H}_{10} \) (cyclopentane)

(d) \( \text{H}_2\text{O}, \text{H}^+ \), the product is \( \text{C}_5\text{H}_{10}\text{OH} \) (cyclopentanol)

23. (a) Two possible alkenes will yield the same product, \( \text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3 \) (2-methyl-1-butene); and \( \text{CH}_2 \text{C}(\text{CH}_3)=\text{CHCH}_3 \) (2-methyl-2-butene)

(b) \( \text{CH}_2\text{C}(\text{CH}_3)\text{C}=(\text{CH})_2 \) (3,3-dimethyl-1-butene)

(c) \( \text{CH}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2 \) (2-methyl-1-propene)

(d) \( \text{H}_3\text{C} \) (3,6-dimethylcyclohexene)

24. (a) \( \text{CH}_3\text{C}=\text{CCH}_2\text{CH}_2\text{CH}_3 \) (2-hexyne)

(b) \( \text{CH}_3\text{C}(\text{CH}_3)\text{C}=\text{CCH}_3 \) (3,3-dimethyl-1-butyne)

(c) \( \text{HC}=\text{CCH}_2\text{C}(\text{CH}_3)_3 \) (4,4-dimethyl-1-pentyne)

(d) \( \text{CH}_3\text{C}=\text{CCH}_3 \) (2-butyne)

25. Reactions to convert 2-butyne to:

(a) 2,3-dibromobutane

\[
\text{CH}_3\text{C}=\text{CCH}_3 + \text{Br}_2 \text{ (1 mole)} \rightarrow \text{CH}_3\text{CBr}=\text{CBrCH}_3
\]

\[
\text{CH}_3\text{CBr}=\text{CBrCH}_3 + \text{H}_2 \text{ Pt, 25°C, 1 atm} \rightarrow \text{CH}_3\text{CHBrCHBrCH}_3
\]

(b) 2,2-dibromobutane

\[
\text{CH}_3\text{C}=\text{CCH}_3 + \text{HBr} \rightarrow \text{CH}_3\text{CH}=\text{CBrCH}_3 \xrightarrow{\text{HBr}} \text{CH}_3\text{CH}_2\text{CBr}_2\text{CH}_3
\]

(c) 2,2,3,3-tetabrromobutane

\[
\text{CH}_3\text{C}=\text{CCH}_3 + \text{Br}_2 \text{ (2 moles)} \rightarrow \text{CH}_3\text{CBr}_2\text{CBr}_2\text{CH}_3
\]
26. (a) \[ \text{CH}_3\text{C}≡\text{CCH}_2\text{CH}_3 + \text{Cl}_2 \text{ (1 mole)} \rightarrow \text{CH}_3\text{C}≡\text{CClCH}_2\text{CH}_3 \]
\[ \text{CH}_3\text{CCl}≡\text{CClCH}_2\text{CH}_3 + \text{H}_2 \rightarrow \text{Pt, 25°C, 1 atm} \rightarrow \text{CH}_3\text{CHClICHClCH}_2\text{CH}_3 \]
(b) \[ \text{CH}_3\text{C}≡\text{CCH}_2\text{CH}_3 + \text{HCl} \rightarrow \text{CH}_3\text{CCl}≡\text{CHCH}_2\text{CH}_3 \]
\[ \text{CH}_3\text{CCl}≡\text{CHCH}_2\text{CH}_3 + \text{HCl} \rightarrow \text{CH}_3\text{CCl}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]
Can also yield \( \text{CH}_3\text{CH}_2\text{CCl}_2\text{CH}_2\text{CH}_3 \) at the same time.
(c) \[ \text{CH}_3\text{C}≡\text{CCH}_2\text{CH}_3 + 2\text{Cl}_2 \rightarrow \text{CH}_3\text{CCl}_2\text{CCl}_2\text{CH}_2\text{CH}_3 \]

27. (a) ![Image of benzene]
(b) ![Image of aniline]
(c) ![Image of benzoic acid]
(d) ![Image of naphthalene]

28. (a) ![Image of toluene]
(c) ![Image of phenol]

29. (a) ![Image of 1,3,5-tribromobenzene]
(c) ![Image of tert-butylbenzene]

1,3,5-tribromobenzene

30. (a) ![Image of 1,3-dichloro-5-nitrobenzene]
(c) ![Image of 1,1-diphenylethane]

1,3-dichloro-5-nitrobenzene

1,1-diphenylethane

m-dinitrobenzene

phenylethene (styrene)
31. (a) bromodichlorobenzenes

\[ \text{Cl} \quad \text{Br} \quad \text{Cl} \quad \text{Br} \]

3-bromo-1,2-dichlorobenzene

4-bromo-1,2-dichlorobenzene

\[ \text{Cl} \quad \text{Br} \quad \text{Cl} \quad \text{Br} \]

2-bromo-1,3-dichlorobenzene

4-bromo-1,3-dichlorobenzene

\[ \text{Cl} \quad \text{Br} \quad \text{Cl} \quad \text{Br} \]

5-bromo-1,3-dichlorobenzene

2-bromo-1,4-dichlorobenzene

(b) The toluene derivatives of formula \( C_9H_{12} \):
32. (a) trichlorobenzenes

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} & \quad \text{Cl} \\
1,2,3\text{-trichlorobenzene} & \quad 1,2,4\text{-trichlorobenzene} & \quad 1,3,5\text{-trichlorobenzene}
\end{align*}
\]

(b) The benzene derivatives of formula \( \text{C}_8\text{H}_{10} \):

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
o\text{-xylene or 1,2\text{-dimethylbenzene}} & \quad m\text{-xylene or 1,3\text{-dimethylbenzene}}
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{CH}_2\text{CH}_3 & \quad \text{ethylbenzene}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{H}_3\text{C} \\
\text{CH}_3 & \quad \text{CH}_2\text{CH}_3 \\
p\text{-xylene or 1,4\text{-dimethylbenzene}} & \quad \text{ethylbenzene}
\end{align*}
\]

33. All isomers that can be written by substituting another chlorine in \( o\text{-chlorobromobenzene} \).

(a) \[
\begin{align*}
\text{Cl} & \quad \text{Br} \\
\text{Cl} & \quad \text{Cl} \\
2\text{-bromo-1,3\text{-dichlorobenzene}}
\end{align*}
\]

(b) \[
\begin{align*}
\text{Cl} & \quad \text{Br} \\
\text{Cl} & \quad \text{Cl} \\
2\text{-bromo-1,4\text{-dichlorobenzene}}
\end{align*}
\]

(c) \[
\begin{align*}
\text{Br} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
1\text{-bromo-2,4\text{-dichlorobenzene}}
\end{align*}
\]

(d) \[
\begin{align*}
\text{Br} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
1\text{-bromo-2,3\text{-dichlorobenzene}}
\end{align*}
\]
34. All isomers that can be written substituting a third chlorine atom on o-dichlorobenzene.

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} & \quad \text{Cl}
\end{align*}
\]

1,2,3-trichlorobenzene \quad 1,2,4-trichlorobenzene

35. (a) \( p \)-chloroethylbenzene \quad (d) \( p \)-bromophenol
(b) propylbenzene \quad (e) triphenylmethane
(c) \( m \)-nitroaniline

36. (a) styrene \quad (d) isopropylbenzene
(b) \( m \)-nitrotoluene \quad (e) 2,4,6-tribromophenol
(c) 2,4-dibromobenzoic acid

37. (a) 2-chloro-1,4-diiodobenzene
(b) \( o \)-dibromobenzene
(c) \( m \)-chloroaniline

38. (a) 2,3-dibromophenol
(b) 1,3,5-trichlorobenzene
(c) \( m \)-iodotoluene

39. (a) \( \begin{array}{c}
\text{Br} \\
\text{FeBr}_3
\end{array} \quad \text{Br} \\
\text{Br} + \text{HBr}
\]

\( + \) \quad \text{bromobenzene}

(b) \( \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array} \quad \text{HNO}_3 \quad \text{H}_2\text{SO}_4 \quad \text{CH}_3
\]

\( \text{CH}_3 \) + \( \text{NO}_2 \) + \( \text{H}_2\text{O} \)

1,4-dimethyl-2-nitrobenzene
40. (a) 
\[
\text{苯} + \text{CH}_3\text{CHCH}_3 \xrightarrow{\text{AlCl}_3} \text{CH}_3\text{CHCH}_3 + \text{HCl}
\]

(b) 
\[
\text{CH}_3 + \text{KMnO}_4 \xrightarrow{\text{H}_2\text{O}} \text{COOH}
\]

41. When \( \text{CH}_2=\text{CCH}_2\text{CH}_2\text{CH}_3 \) reacts with \( \text{HBr} \), two products are possible:

\[
\text{CH}_3\text{CBrCH}_2\text{CH}_2\text{CH}_3 \quad \text{and} \quad \text{CH}_2\text{BrCHCH}_2\text{CH}_2\text{CH}_3
\]

The first will strongly predominate. This is the product according to Markovnikov’s rule and forms because the tertiary carbocation intermediate formed is more stable than a primary carbocation.

42. Two tests can be used. (1) Baeyer test—hexene will decolorize \( \text{KMnO}_4 \) solution; cyclohexane will not. (2) In the absence of sunlight, hexene will react with and decolorize bromine; cyclohexane will not.

43. Methylpentenes that show geometric isomerism.

\[
\text{CH}_3\text{CH}=\text{CCH}_2\text{CH}_3 \quad \text{3-methyl-2-pentene}
\]

\[
\text{CH}_3\text{CH}=\text{CHCHCH}_3 \quad \text{4-methyl-2-pentene}
\]

44. (a) methyl carbocation

(b) propyl carbocation

(c) \( \text{t} \text{ert-} \text{butyl carbocation} \)

(d) penty carbocation
45. (a) \[ \text{Cyclohexane} + \text{Br}_2 \rightarrow \text{1,2-dibromocyclohexane} \]
(b) \[ \text{Cyclohexane} + \text{HCl} \rightarrow \text{chlorocyclohexane} \]
(c) \[ \text{1-Methylcyclohexane} + \text{HCl} \rightarrow \text{1-chloro-1-methylcyclohexane} \]
(d) \[ \text{2-Chloro-1-methylcyclohexane} + \text{3-Chloro-1-methylcyclohexane} \]

46. The reaction mechanism by which benzene is brominated in the presence of FeBr₃:
(a) \[ \text{FeBr}_3 + \text{Br}_2 \rightarrow \text{FeBr}_4^- + \text{Br}^+ \]
Formation of a bromonium ion (Br⁺), an electrophile.
(b) \[ \text{Bromonium ion} + \text{Benzene} \rightarrow \text{Carbocation intermediate} \]
The bromonium ion adds to benzene forming a carbocation intermediate.
(c) \[ \text{Carbocation intermediate} + \text{FeBr}_4^- \rightarrow \text{Bromobenzene} + \text{FeBr}_3 + \text{HBr} \]
A hydrogen ion is lost from the carbocation forming the product bromobenzene.

47. (a) \[ \text{CH}_3\text{CHClCH}_2\text{CH}_3 \xrightarrow{\text{HCl}} \text{CH}_2=\text{CHCH}_2\text{CH}_3 + \text{CH}_3\text{CH}=\text{CHCH}_3 \]
(b) \[ \text{CH}_2\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{HCl}} \text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3 \]
(c) \[ \text{1-Chlorocyclohexane} \xrightarrow{\text{HCl}} \text{Cyclohexane} \]
48. Yes, there will be a color change (loss of Br₂ color). The fact that there is no HBr formed indicates that the reaction is not substitution but addition. Therefore, C₄H₈, must contain a carbon-carbon double bond. Three structures are possible.

\[
\begin{align*}
\text{CH₃CH₂CH} = \text{CH₂} & \quad \text{CH₃CH} = \text{CHCH₃} & \quad \text{CH₃C} = \text{CH₂} \\
\text{CH₃CH₂CH} = \text{CH₂} & \quad \text{CH₃CH} = \text{CHCH₃} & \quad \text{CH₃C} = \text{CH₂}
\end{align*}
\]

49. Baeyer test: Add KMnO₄ solution to each sample. The KMnO₄ will lose its purple color with 1-heptene. There will be no reaction (no color change) with heptane.

50. The carbon-carbon bonds in the three molecules are different. Ethane has a single bond between carbon atoms formed from the overlap of two sp³ hybridized orbitals. Ethene has a double bond between carbon atoms. One bond is a sigma bond formed by the overlap of two sp² hybridized orbitals, the other is a pi bond formed by the sidewise overlap of two p orbitals. Ethyne has a triple bond between carbon atoms—one sigma bond formed from the overlap of two sp hybridized orbitals and two pi bonds formed from the sidewise overlap of p orbitals.

51. Other possibilities are

- Cyclopentane
- CH₃
- CH₂CH₃
- CH₃CH₃
- CH₃
- CH₃
- CH₃
52. Benzene compounds of formula $\text{C}_8\text{H}_9\text{Cl}$

53. (a) $\text{CH}_2\text{CH} = \text{CH} - \text{C} - \text{CH}_2 - \text{CH}_3$

(b) $\text{HC} = \text{C} - \text{CH}_3$

(c) $\text{H}_3\text{C} - \text{sp}^3$

all $\text{sp}^2$
54. (a) Four isomers:  
\[ \text{CH}_2=\text{CHCH}_2\text{CH}_3 \] 1-butene  
\[ \text{CH}_3\text{CH}==\text{CH}_3 \] 2-butene (cis and trans)  
\[ \text{CH}_2=\text{C(CH}_3)_2 \] 2-methyl-1-propene  
\[ \text{C}_4\text{H}_8 \]

(b) One isomer  
\[ \text{C}_5\text{H}_8 \]

55. (b) is the correct structure. (a) is an incorrect structure because the carbons where the two rings are fused have five bonds, not four bonds to each carbon.

56. Carbon-2 has two methyl groups on it. The configuration of two of the same groups on a carbon of a carbon-carbon double bond does not show cis-trans isomerism.

57. (a) alkyne or cycloalkene  
(b) alkene  
(c) alkane  
(d) alkyne or cycloalkene

58. Chemically distinguishing between benzene, 1-hexene, and 1-hexyne  
Step 1. Add KMnO\textsubscript{4} solution to a sample of each liquid. Benzene is the only one in which the KMnO\textsubscript{4} does not lose its purple color.  
Step 2. To 0.5 mL samples of 1-hexene and 1-hexyne add bromine solution dropwise until there is no more color change of the bromine (from reddish-brown to colorless). 1-hexyne (with a triple bond) will decolor about twice as many drops of bromine as 1-hexene. Thus the three liquids are identified.

59. (a) \[ \text{CH}_3\text{C}==\text{CH} \xrightarrow{\text{HCl}} \text{CH}_3\text{C}==\text{Cl} \xrightarrow{\text{HBr}} \text{CH}_3\text{CCIBrCH}_3 \]

(b) \[ \text{CH}_3\text{C}==\text{CH} \xrightarrow{\text{Br}_2} \text{CH}_3\text{C}==\text{Br} \xrightarrow{\text{HCl}} \text{CH}_3\text{CCIBrCH}_2\text{Br} \]

(c) \[ \text{CH}_3\text{C}==\text{CH} \xrightarrow{2\text{Cl}_2} \text{CH}_3\text{CCl}_2\text{CHCl}_2 \]