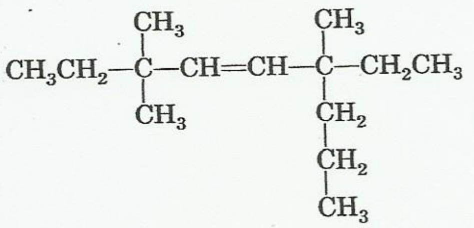
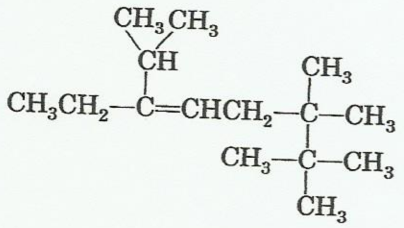
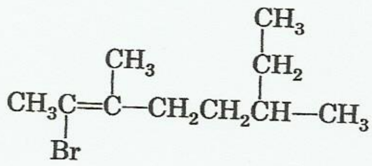
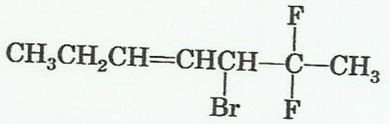
Problem 3.1 Write the structural formulas for these compounds.
(a) 2-Methyl-2-butene
(b) 4,5-Dimethyl-3-isopropyl-2-hexene
(c) 2-Chloro-4-methyl-2-pentene
(d) 3-Bromo-2-chloro-3-methyl-1-pentene
(e) 1,3-Dimethylcyclohexene
(f) 1-Bromo-3-chlorocyclobutene

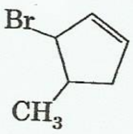
Problem 3.2 Name the following compounds.

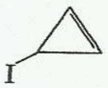
(a) 

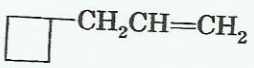
(b) 

(c) 

(d) 

(e) 

(f) 

(g) 

Problem 3.3 The names in this list are incorrect. Give the correct name and structure for each compound listed.

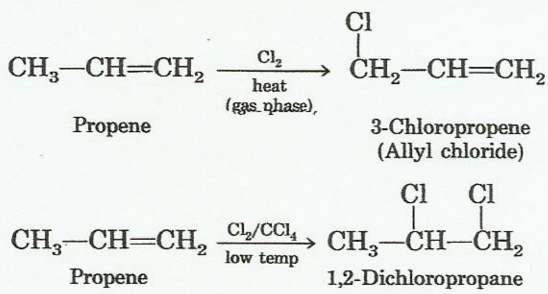
(a) 2,2-Dimethyl-4-pentene
(b) 4,5-Dimethyl-2-isopropyl-2-hexene
(c) 4-*n*-Butyl-5-hexene
(d) 2-Chloro-6-methylcyclohexene
(e) 1,2-Dimethyl-3-cyclopentene

Now that we know how to recognize and name alkenes, let us look into how a carbon–carbon double bond is formed, and also into its geometry.

3.2 Geometry of the Carbon–Carbon Double Bond: sp^2 Hybridization

In alkanes carbon is always bonded to four atoms. As a consequence, the singly bonded carbon uses sp^3-hybridized orbitals that are directed toward the corners of a regular tetrahedron. In alkenes, on the other hand, the doubly bonded carbon is always attached to only three other atoms. As a consequence, the doubly bonded carbon *must* use a different kind of hybridization and *must* assume a different shape. Let us look at the type of hybrid orbitals in and the shape of the simplest alkene, ethylene. In ethylene the carbons are **sp^2 hybridized** ($\frac{1}{3}s$ and $\frac{2}{3}p$ characteristics). These orbitals are formed in the following manner: As with sp^3 hybridization (Sec. 1.10), the ground-state carbon proceeds to its excited state, but this time the 2*s* orbital and only two of the three 2*p* orbitals hybridize. The result is three equivalent sp^2 hybrid orbitals and one unhybridized $2p_z$ orbital (Fig. 3.1). The three sp^2 orbitals get as far away from each other as possible by assuming a *planar* arrangement with an angle of 120° between the hybrid orbitals. This type of arrangement is also known as trigonal planar geometry. The remaining unhybridized $2p_z$ orbital is perpendicular to the plane of the sp^2 orbitals (Fig. 3.2).

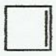
of chlorine with propene in the liquid phase at low temperature, in the dark, yields only 1,2-dichloropropane, an addition product.

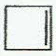


Problem 3.25 Write the structure of the major product expected in each reaction.

(a) $CH_3CH=CHCH_3 + Cl_2 \xrightarrow{\text{heat}}$

(b) $CH_3CH=CHCH_3 + Cl_2 \xrightarrow[\text{low temp}]{CCl_4}$

(c)  $+ Br_2 \xrightarrow[\text{low temp}]{CCl_4}$

(d)  $+ Br_2 \xrightarrow{\text{heat}}$

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n double bond,
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ssible number.
[Sec. 3.1]
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[Sec. 3.2]
metric isomers
[Sec. 3.3]
[Sec. 3.6]
[Sec. 3.10]
[Sec. 3.12]
[Sec. 3.15]
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[Sec. 3.17]
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[Sec. 3.18]
Baeyer's test).
[Sec. 3.22]
[Sec. 3.23]
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[Sec. 3.25]
d is to work
[Sec. 3.26]

Key Terms

unsaturated
alkenes (olefins)
C_nH_{2n}
alkynes
C_nH_{2n-2}
dienes
polyenes
vinyl group
allyl group
sp^2 hybridized
π (pi) bond

geometric isomers
E,Z system
elimination
Saytzeff's rule
carbocation
dehydrohalogenation
addition reaction
catalytic hydrogenation
electrophile
nucleophile
rate-determining step

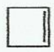
electrophilic addition
hydrohalogenation
Markovnikov's rule
hydration
vicinal dihalide
halohydrin
Baeyer test
polymers
monomer
addition polymerization
vinyl polymers

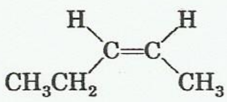
Exercises

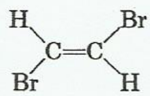
Structure, Nomenclature, and Geometric Isomerism [Secs. 3.1, 3.3]

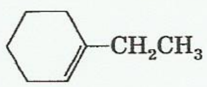
3.1 Give the IUPAC names for the following structures. Use *cis* and *trans* designations where pertinent for geometric isomers.

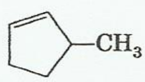
(a) $CH_2{=}CH{-}CH_2{-}C(CH_3)_2{-}CH_3$

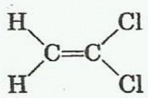
(b) 

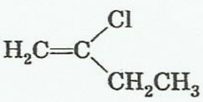
(c) 

(d) 

(e) 

(f) 

(g) 

(h) 

3.2 Write formulas for the following named compounds.
(a) 3-Methyl-1-butene
(b) 5-Bromo-2-methyl-2-hexene
(c) 4-Chlorocyclohexene
(d) Vinylcyclopropane
(e) Allylcyclopentane
(f) *cis*-3-Hexene
(g) *trans*-2-Heptene
(h) *trans*-1,2-Dicyclopropylethene
(i) *Z*-2-Bromo-1-chloropropene
(j) *E*-1-Bromo-1-chloro-2-fluoroethene

3.3 State what is wrong with the following names and give the correct name for each molecule.
(a) 2-Ethyl-2-pentene
(b) 2-*n*-Propyl-2-butene
(c) 3-Methyl-2-butene
(d) 3-*n*-Butyl-1-hexene
(e) 1-Methyl-2-cyclobutene
(f) 2,5-Dimethylcyclohexene

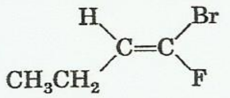
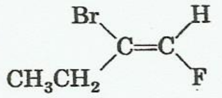
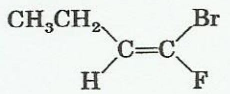
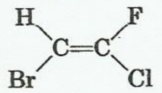
3.4 Which of the following compounds can exist as *cis* and *trans* isomers? Draw the structures of the geometric isomers.
(a) 1-Butene
(b) 2-Pentene

(c) 1-Bromo-3-hexene (d) 1-Chloro-2-methylpropene
(e) 1,1-Dichloroethene (f) 2-Methyl-2-pentene

3.5 There are three compounds with molecular formula $C_2H_2Cl_2$. Draw the structure of each compound and indicate which isomer(s) is (are) structural (constitutional) and which is (are) geometric (*cis-trans*).

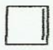
3.6 Including geometric isomers, there are sixteen alkenes of formula C_6H_{12}. Draw and name each structure, and indicate which are geometric isomers.

3.7 Name the following structures using the *E,Z* system of nomenclature.

(a) 
(b) 
(c) 
(d) 

Hybridization and Shapes of Molecules [Secs. 1.10, 3.2]

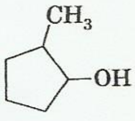
3.8 Indicate the type of hybridization and the shape about each carbon in the following structures.

(a) $CH_3CH{=}CH_2$ (b)  (c) $CH_3CH{=}CHCH_2OH$ (d) $CH_3\underset{O}{\overset{\|}{C}}CH_2\underset{O}{\overset{\|}{C}}OH$

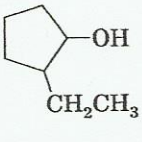
Preparation of Alkenes [Secs. 3.6–3.9]

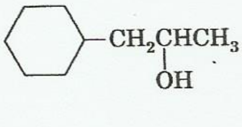
3.9 Which of the products named for each reaction is the major product according to Saytzeff's rule?

(a) $CH_3CH_2CH_2\underset{OH}{CH}CH_3 \xrightarrow{\text{dehydration}}$ 1-pentene and 2-pentene

(b)  $\xrightarrow{\text{dehydration}}$ 1-methylcyclopentene and 3-methylcyclopentene

3.10 Using Saytzeff's rule write the structure of the *main* product obtained on dehydration of each of the following alcohols.

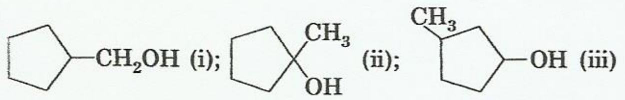
(a) $CH_3\overset{CH_3}{CH}\underset{OH}{CH}CH_3$ (b) 

(c) $CH_3CH_2\overset{CH_3}{CH}\underset{OH}{CH}CH_2CH_3$ (d) 

3.11 Dehydration of 2-butanol, $CH_3\overset{OH}{CH}CH_2CH_3$, yields 2-butene (major product) and 1-butene (minor product). Write a mechanism that accounts for the formation of these two products.

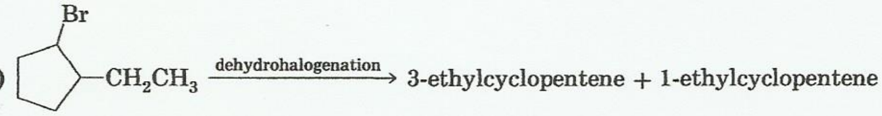
3.12 Arrange the alcohols in each group in order of ease of dehydration.

(a) $CH_3CH_2CH_2CH_2OH$ (i); $CH_3CH_2\underset{OH}{C}HCH_3$ (ii); $CH_3\overset{CH_3}{\underset{OH}{C}}CH_3$ (iii)

(b) 

3.13 Which of the products named for each reaction is the major product according to Saytzeff's rule?

(a) $CH_3\overset{CH_3}{C}H\underset{Br}{C}HCH_3 \xrightarrow{\text{dehydrohalogenation}}$ 2-methyl-2-butene + 3-methyl-1-butene

(b) 

3.14 Using Saytzeff's rule write the structure of the *main* product obtained on dehydrohalogenation of each of the following compounds.
(a) 2-Bromopentane
(b) 2-Bromo-2-methylpentane
(c) 3-Bromo-2-methylpentane
(d) 3-Bromo-2,3-dimethylpentane

Reactions of Alkenes [Secs. 3.11–3.24]

3.15 Draw the structure of the product expected on treatment of 2-butene with each of the following.
(a) H_2/Pd
(b) HCl
(c) Cold, concentrated H_2SO_4
(d) H_2O, H^+
(e) Br_2, H_2O
(f) Br_2 in CCl_4
(g) Cold, dilute $KMnO_4$
(h) O_3 followed by Zn, H_2O

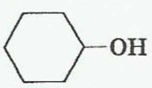
3.16 Draw the structures of the major product(s) expected on treatment of 1-butene with the reagents listed in Exercise 3.15.

3.17 Draw the structures of the products, A through N.

(a) $CH_3CH{=}CH_2 + Br_2 \xrightarrow[\text{heat}]{} A \xrightarrow{H_2/Pd} B$

(b) $CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{H^+} C \xrightarrow{HCl} D$

(c) $CH_3CH_2CH_2Br \xrightarrow[\text{heat}]{\text{KOH/alcohol}} E \xrightarrow[(2)\ Zn,\ H_2O]{(1)\ O_3} F + G$

(d)  $\xrightarrow[\text{heat}]{H^+} H \xrightarrow{Br_2/CCl_4} I$

(e) $CH_3CH_2CH_2Cl \xrightarrow[\text{heat}]{\text{KOH/alcohol}} J \xrightarrow[\text{heat}]{Cl_2} K \xrightarrow{Cl_2,\ H_2O} L$

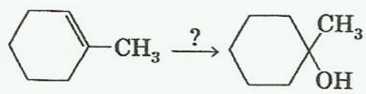
(f) $CH_3CH_2CH_2Br \xrightarrow[\text{heat}]{\text{KOH/alcohol}} M \xrightarrow{H_2O,\ H^+} N$

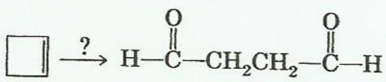
3.18 For each reaction, fill in the missing reagent(s) and, where pertinent, the reaction conditions.

(a) $CH_3CH{=}CH_2 \xrightarrow{?} CH_3CH_2CH_3$

(b) $CH_3CH{=}CH_2 \xrightarrow{?} CH_3CHO + CH_2O$

(c) $CH_3CH{=}CH_2 \xrightarrow{?} CH_3CHBrCH_2Br$

(d) 

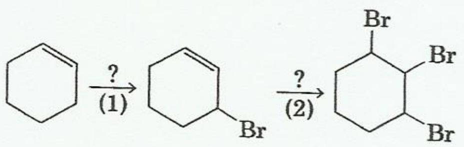
(e) 

(f) $CH_3CH{=}CH_2 \xrightarrow[(1)]{?} BrCH_2CH{=}CH_2 \xrightarrow[(2)]{?} BrCH_2CHOHCH_3$

(g) $CH_3CH_2CH_2Br \xrightarrow[(1)]{?} CH_3CH{=}CH_2 \xrightarrow[(2)]{?} CH_3CHOHCH_2Cl$

(h) $CH_3CH_2CH_2OH \xrightarrow[(1)]{?} CH_3CH{=}CH_2 \xrightarrow[(2)]{?} CH_3CHBrCH_3$

(i) $CH_2{=}CH_2 \xrightarrow[(1)]{?} CH_3CH_3 \xrightarrow[(2)]{?} CH_3CH_2Cl$

(j) 

Identification and Structural Determination [Secs. 3.22, 3.23]

3.19 *n*-Hexane and 1-hexene are both colorless liquids with similar boiling points. What three simple tests would distinguish the two compounds? Indicate what you would see.

3.20 Give the structure of an alkene that would give each of the following product(s) on ozonolysis.

(a) $H_2C{=}O$ and $CH_3CH_2C(CH_3){=}O$ (b) $2\ CH_3CH_2C(CH_3){=}O$

(c) $CH_3CH_2CH{=}O$ and $CH_3CH{=}O$ (d) $O{=}CHCH_2CH_2CH_2CH{=}O$

3.21 Compound **A**, C_4H_9Br, on treatment with alcoholic KOH, gave compound **B**, C_4H_8. Treatment of **B** with ozone followed by zinc and water yields $CH_3CH_2CH{=}O$ and $O{=}CH_2$. What are the structures of **A** and **B**?

3.22 A compound C_4H_9Br (**A**), on treatment with alcoholic KOH, gave compound **B**, C_4H_8. Treatment of **B** with ozone followed by zinc and water yielded $CH_3CH{=}O$ as the only product. What two possible structures for **B** account for these facts? What is the structure for **A**?

3.23 A compound **A**, C_4H_9Br, on treatment with alcoholic KOH, gave compound **B**, C_4H_8. Treatment of **B** with ozone followed by zinc and water yielded $(CH_3)_2C{=}O$ and $O{=}CH_2$. What two possible structures for **B** account for these facts? What is the structure for **A**?