3

Alkenes and Alkynes

Chapter Summary

Alkenes have a carbon-carbon double bond and **alkynes** have a carbon–carbon triple bond. Nomenclature rules are given in Sec. 3.2. Each carbon of a double bond is **trigonal**, and connected to only *three* other atoms, all of which lie in a plane with bond angles of 120°. Ordinarily, rotation around double bonds is restricted. All six atoms of **ethylene** lie in a single plane. The C=C bond length is 1.34 Å, shorter than a C–C bond (1.54 Å). These facts can be explained by an orbital model with three sp^2 hybrid orbitals (one electron in each) and one *p* orbital perpendicular to these (containing the fourth electron). The double bond is formed by end-on overlap of sp^2 orbitals to form a σ bond and lateral overlap of aligned *p* orbitals to form a π **bond** (Figures 3.4 and 3.5). Since rotation around the double bond is restricted, ***cis–trans* isomerism** is possible if each carbon atom of the double bond has two different groups attached to it.

Alkenes react mainly by **addition.** Typical reagents that add to the double bond are halogens, hydrogen (metal catalyst required), water (acid catalyst required), and various acids. If either the alkene or the reagent is **symmetrical** (Table 3.2), only one product is possible. If *both* the alkene and reagent are unsymmetrical, however, two products are possible, in principle. In this case, **Markovnikov's rule** (Secs. 3.8–3.10) allows us to predict the product obtained.

Electrophilic additions occur by a two-step mechanism. In the first step, the **electrophile** adds in such a way as to form the most stable **carbocation** (the stability order is tertiary > secondary > primary). Then the carbocation combines with a **nucleophile** to give the product.

The energetics of electrophilic additions, and all other reactions, can be described using **energy reaction diagrams** (Figures 3.10–3.12). Such diagrams show each step in the reaction mechanism, and indicate the relative energies of **reactants, products, intermediates**, and **transition states.** They indicate whether the **enthalpy** of a step in a reaction is **exothermic** or **endothermic**, or whether the step has a high or low **energy of activation**. In general, reactions that are exothermic and have low energies of activation proceed at relatively fast rates (Secs. 3.11 and 3.12).

Conjugated dienes have alternating single and double bonds. They may undergo **1,2-** or **1,4-addition**. **Allylic carbocations**, which are stabilized by resonance, are intermediates in both the 1,2- and 1,4-additions (Sec. 3.15a). Conjugated dienes also undergo cycloaddition reactions with alkenes (**Diels–Alder reaction**), a useful synthesis of six-membered rings (Sec. 3.15b).

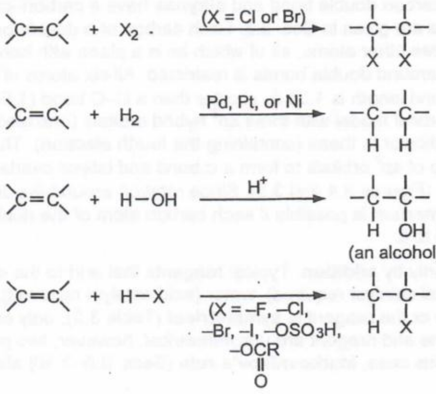
Addition to double bonds may also occur by a **free-radical mechanism.** Polyethylene can be made in this way from the **monomer** ethylene.

Alkenes undergo a number of other reactions, such as **hydroboration**, permanganate oxidation, and **ozonolysis**.

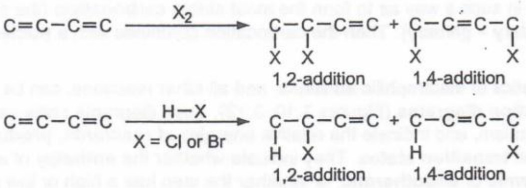
Triple bonds are **linear** and the carbons are ***sp*-hybridized** (Figure 3.16). Alkynes, like alkenes, undergo addition reactions. A hydrogen connected to a triply bonded carbon is weakly acidic and can be removed by a very strong base such as **sodium amide**, $NaNH_2$, to give acetylides.

Reaction Summary

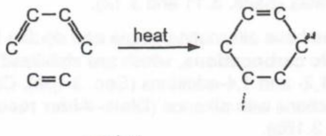
Additions to the Double Bond



Conjugated Dienes



Cycloaddition (Diels–Alder)



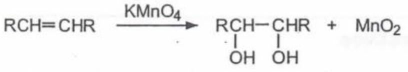
Polymerization of Ethylene

$$n\ H_2C{=}CH_2 \xrightarrow{\text{catalyst}} \text{-(}CH_2-CH_2\text{)-}_n$$

Hydroboration–Oxidation

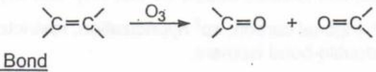
$$3\ R{-}CH{=}CH_2 \xrightarrow{BH_3} (RCH_2CH_2)_3B \xrightarrow[HO^-]{H_2O_2} 3\ RCH_2CH_2OH$$

Permanganate Oxidation

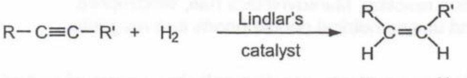


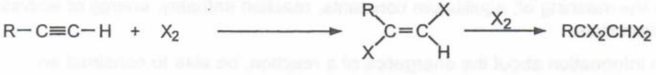
$$RCH{=}CHR \xrightarrow{KMnO_4} \underset{OH}{RCH}{-}\underset{OH}{CHR} + MnO_2$$

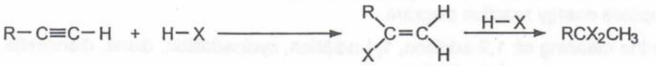
Ozonolysis

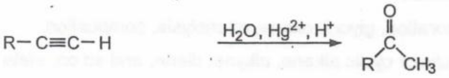


Additions to the Triple Bond







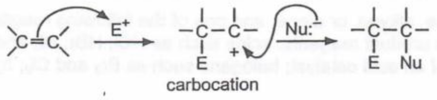


Alkyne Acidity

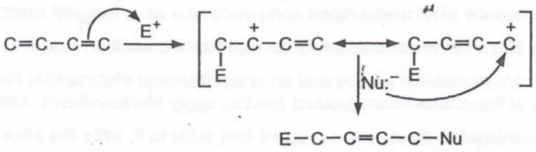
$$RC{\equiv}CH + NaNH_2 \xrightarrow{NH_3} RC{\equiv}C^-\,Na^+ + NH_3$$

Mechanism Summary

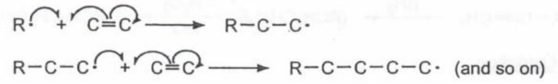
Electrophilic Addition (E^+ = electrophile and Nu :$^-$ = nucleophile)



1,4-Addition



Free-Radical Polymerization of Ethylene



Learning Objectives

1. Know the meaning of: saturated and unsaturated; alkene, alkyne, and diene; conjugated, cumulated, and isolated double bonds; vinyl and allyl groups.
2. Know the meaning of: trigonal carbon, sp^2 hybridization, restricted rotation, σ and π bonds, *cis* and *trans* double-bond isomers.
3. Know the meaning of: addition reaction, Markovnikov's rule, electrophile, nucleophile, symmetrical and unsymmetrical double bonds and reagents, carbocation.
4. Know the meaning of: equilibrium constants, reaction enthalpy, energy of activation, transition state.
5. Given information about the energetics of a reaction, be able to construct an appropriate energy reaction diagram.
6. Know the meaning of: 1,2-addition, 1,4-addition, cycloaddition, diene, dienophile, polymer, monomer, polymerization.
7. Know the meaning of: hydroboration, glycol, ozone, ozonolysis, combustion.
8. Given the structure of an acyclic or cyclic alkene, alkyne, diene, and so on, state the IUPAC name.
9. Given the IUPAC name of an alkene, alkyne, diene, and so on, write the structural formula.
10. Given the molecular formula of a hydrocarbon and the number of double bonds, triple bonds, or rings, draw the possible structures.
11. Given the name or abbreviated structure of an unsaturated compound, tell whether it can exist in *cis* and *trans* isomeric forms and, if so, how many. Draw them.
12. Given an alkene, alkyne, or diene, and one of the following reagents, draw the structure of the product reagents: acids such as HCl, HBr, HI, and H_2SO_4; water in the presence of an acid catalyst; halogens such as Br_2 and Cl_2; hydrogen and Pd, Pt or Ni.
13. Given the structure or name of a compound that can be prepared by an addition reaction, deduce what unsaturated compound and what reagent react to form it.
14. Write the steps in the mechanism of an electrophilic addition reaction.
15. Given an unsymmetrical alkene and an unsymmetrical electrophilic reagent, give the structure of the predominant product (that is, apply Markovnikov's rule).
16. Given a conjugated diene and a reagent that adds to it, write the structures of the 1,2-and 1,4-addition products.

17. Given a diene and dienophile, write the structure of the resulting cycloaddition (Diels–Alder) adduct.

18. Given the structure of a cyclic compound that can be synthesized by the Diels–Alder reaction, deduce the structures of the required diene and dienophile.

19. Given an alkyne, write the structures of products obtained by adding one or two moles of a particular reagent to it.

20. Write the steps in the mechanism of ethylene polymerization catalyzed by a free radical.

21. Write the structure of the alcohol produced from the hydroboration–oxidation sequence when applied to a particular alkene.

22. Given an alkene or cycloalkene (or diene, and so on), write the structures of the expected ozonolysis products.

23. Given the structures of ozonolysis products, deduce the structure of the unsaturated hydrocarbon that produced them.

24. Draw orbital pictures for a double bond and a triple bond.

25. Draw conventional structures for the contributors to the resonance hybrid of an allyl cation.

26. Describe simple chemical tests that can distinguish an alkane from an alkene or alkyne.

27. Know the meaning of: cracking, alkylation, isomerization, platforming, and octane number as applied to petroleum refining.

ANSWERS TO PROBLEMS

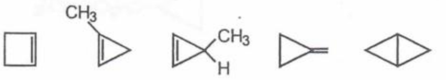
Problems Within the Chapter

3.1 The formula C_4H_6 corresponds to C_nH_{2n-2}. The possibilities are one triple bond, two double bonds, one double bond and one ring, or two rings.

$HC{\equiv}CCH_2CH_3$ $CH_3C{\equiv}CCH_3$

(Acrylic)

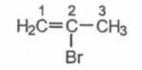
$H_2C{=}CH{-}CH{=}CH_2$ $H_2C{=}C{=}CHCH_3$



(Cyclic)

3.2 Compounds a and c have alternating single and double bonds, and are conjugated. In b and d, the double bonds are isolated.

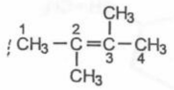
3.3 a.



$$\overset{1}{H_2C}{=}\underset{\displaystyle Br}{\overset{2}{C}}{-}\overset{3}{CH_3}$$

2-bromopropene

b.



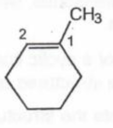
$$\overset{1}{CH_3}{-}\underset{\displaystyle CH_3}{\overset{2}{C}}{=}\overset{\displaystyle CH_3}{\underset{3}{C}}{-}\underset{4}{CH_3}$$

2,3-dimethyl-2-butene

c. $Cl\overset{1}{C}H=\overset{2}{C}H\overset{3}{C}H_3$

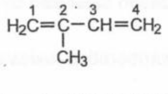
1-chloropropene

d.



1-methylcyclohexene

e.



$\overset{1}{H_2C}=\underset{CH_3}{\overset{2}{C}}-\overset{3}{C}H=\overset{4}{C}H_2$

2-methyl-1,3-butadiene (also called isoprene)

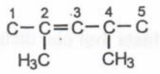
f. $H\overset{1}{C}\equiv\overset{2}{C}\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_3$

1-hexyne

3.4 a. First write out the five-carbon chain, with a double bond between carbon-2 and carbon-3:

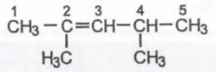
$\overset{1}{C}-\overset{2}{C}=\overset{3}{C}-\overset{4}{C}-\overset{5}{C}$

Add the substituents:



$\overset{1}{C}-\underset{H_3C}{\overset{2}{C}}=\overset{3}{C}-\underset{CH_3}{\overset{4}{C}}-\overset{5}{C}$

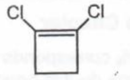
Fill in the hydrogens:



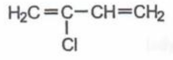
$\overset{1}{CH_3}-\underset{H_3C}{\overset{2}{C}}=\overset{3}{C}H-\underset{CH_3}{\overset{4}{C}H}-\overset{5}{C}H_3$ or $(CH_3)_2C=CHCH(CH_3)_2$

b. $CH_3CH_2\equiv CCH_2CH_3$

c.

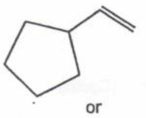


d.

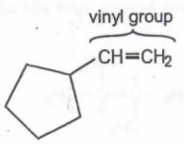


$H_2C=\underset{Cl}{C}-CH=CH_2$

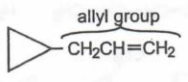
3.5 a.



or



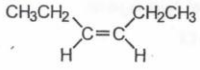
b.



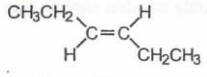
3.6 Compounds a and c have only one possible structure because in each case one of the carbons of the double bond has two identical substituents:

a. $H_2C{=}CHCH_3$

b.



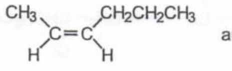
and



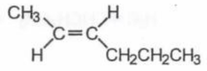
cis-3-hexene *trans*-3-hexene

c. $(CH_3)_2C{=}CHCH_3$

d.



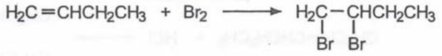
and



cis-2-hexene *trans*-2-hexene

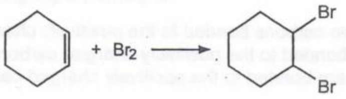
3.7 The electron pair in a σ bond lies directly between the nuclei it joins. In a π bond, the electron pair is further from the two nuclei that it joins. Therefore more energy is required to break a σ bond than a π bond.

3.8 a. One bromine atom adds to each doubly bonded carbon, and the double bond in the starting material becomes a single bond in the product:

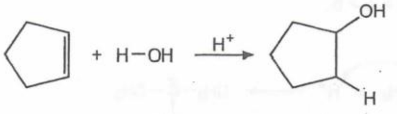


$$H_2C{=}CHCH_2CH_3 + Br_2 \longrightarrow \underset{Br}{H_2C}-\underset{Br}{C}HCH_2CH_3$$

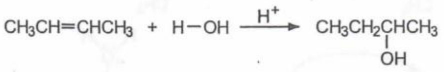
b.



3.9 a.

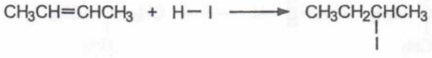


b.



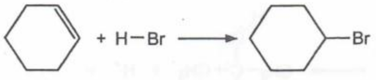
$$CH_3CH{=}CHCH_3 + H{-}OH \xrightarrow{H^+} CH_3CH_2\underset{OH}{C}HCH_3$$

3.10 a.



$$CH_3CH{=}CHCH_3 + H{-}I \longrightarrow CH_3CH_2\underset{I}{C}HCH_3$$

b.



3.11 a. $H_2C{=}CHCH_2CH_3$

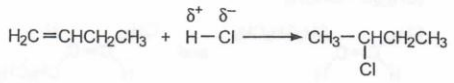
↑

This doubly bonded carbon has the most hydrogens.

$H-Cl$

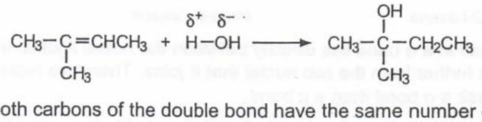
↑

This is the more electropositive part of the reagent.



$$H_2C{=}CHCH_2CH_3 + \overset{\delta^+}{H}-\overset{\delta^-}{Cl} \longrightarrow CH_3-\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2CH_3$$

b.



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCH_3 + \overset{\delta^+}{H}-\overset{\delta^-}{OH} \longrightarrow CH_3-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2CH_3$$

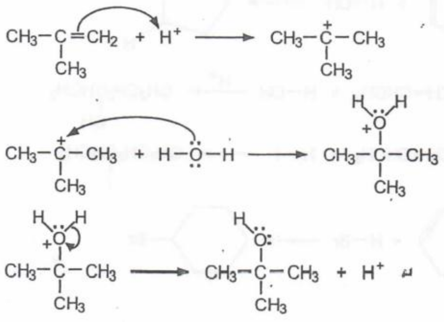
3.12 Since both carbons of the double bond have the same number of attached hydrogens (one), application of Markovnikov's rule is ambiguous. Both products are formed, and the reaction is not regiospecific.

$$CH_3CH{=}CHCH_2CH_3 + HCl \longrightarrow \begin{array}{c} CH_3CH_2CH(Cl)CH_2CH_3 \\ + \\ CH_3CH(Cl)CH_2CH_2CH_3 \end{array}$$

3.13 a. Secondary; there are two carbons bonded to the positively charged carbon.
b. Primary; one carbon is bonded to the positively charged carbon.
c. Tertiary; three carbons are bonded to the positively charged carbon.

3.14 The order of stability is c > a > b.

3.15 eq. 3.15:

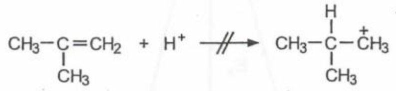


$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 + H^+ \longrightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{+}{C}}}-CH_3$$

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{+}{C}}}-CH_3 + H-\ddot{O}-H \longrightarrow CH_3-\overset{\displaystyle H\overset{+}{\ddot{O}}H}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$$

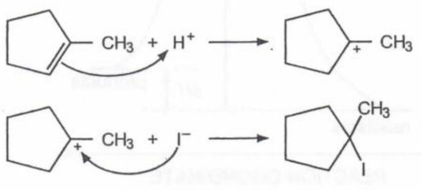
$$CH_3-\overset{\displaystyle H\overset{+}{\ddot{O}}H}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3 \longrightarrow CH_3-\overset{\displaystyle H\ddot{O}:}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3 + H^+$$

The intermediate carbocation is tertiary. If, in the first step, the proton had added to the other carbon of the double bond, the carbocation produced would have been primary:

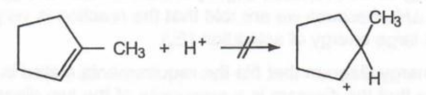


$$CH_3-\underset{CH_3}{C}=CH_2 + H^+ \not\longrightarrow CH_3-\overset{H}{\underset{CH_3}{C}}-\overset{+}{C}H_3$$

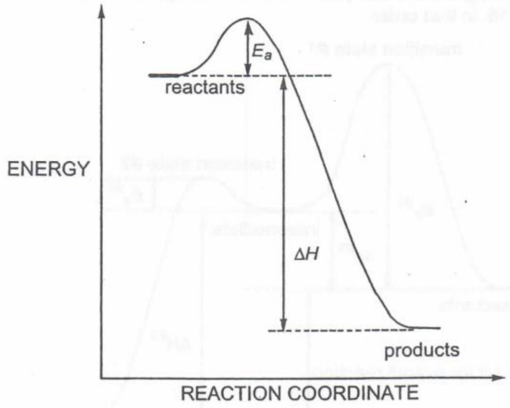
eq. 3.16:



The intermediate carbocation is tertiary. Had the proton added to the methyl-bearing carbon, the intermediate carbocation would have been secondary:

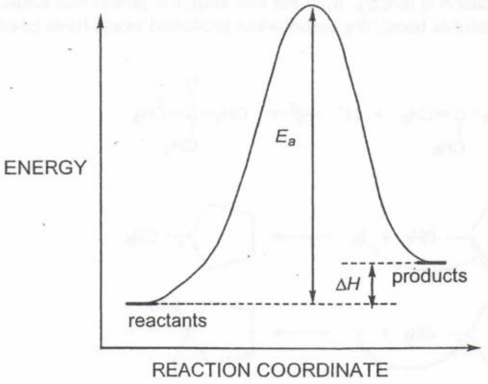


3.16



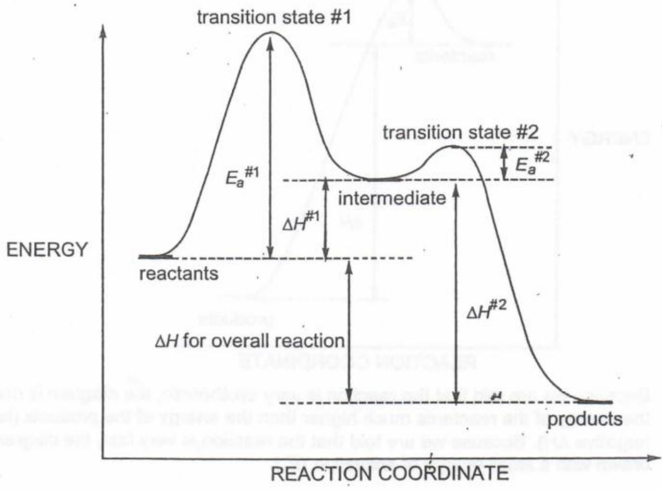
Because we are told that the reaction is very exothermic, the diagram is drawn with the energy of the reactants much higher than the energy of the products (large and negative ΔH). Because we are told that the reaction is very fast, the diagram is drawn with a small energy of activation (E_a).

3.17

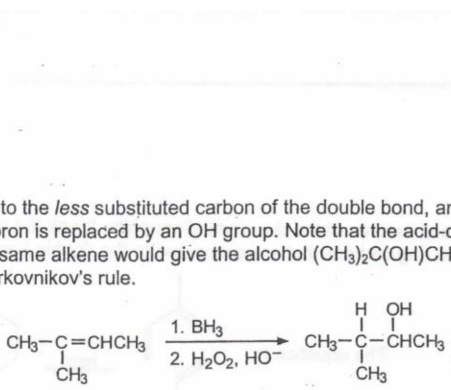


Because we are told that the reaction is slightly endothermic, the diagram is drawn with the energy of the reactants slightly lower than the energy of the products (small and positive ΔH). Because we are told that the reaction is very slow, the diagram is drawn with a large energy of activation (E_a).

3.18 A reaction energy diagram that fits the requirements stated in the problem is shown below. Notice that the diagram is a composite of the two diagrams drawn for Problems 3.17 and 3.16, in that order.

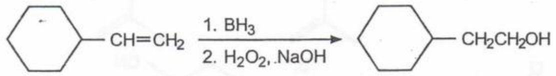


3.19 The boron adds to the *less* substituted carbon of the double bond, and, in the oxidation, the boron is replaced by an OH group. Note that the acid-catalyzed hydration of the same alkene would give the alcohol $(CH_3)_2C(OH)CH_2CH_3$ instead, according to Markovnikov's rule.

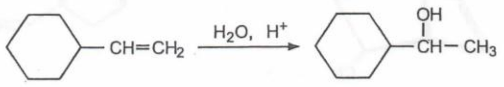


$$CH_3-\underset{CH_3}{C}=CHCH_3 \xrightarrow[\text{2. } H_2O_2,\ HO^-]{\text{1. } BH_3} CH_3-\underset{CH_3}{\overset{H}{C}}-\overset{OH}{C}HCH_3$$

3.20

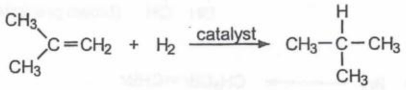


Acid-catalyzed hydration of vinylcyclohexane occurs in the Markovnikov sense:



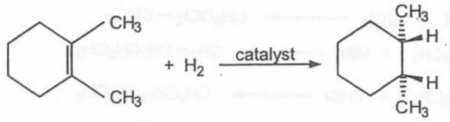
vinylcyclohexane

3.21 a.

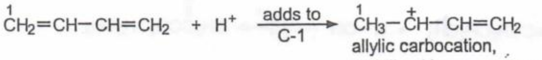


$$(CH_3)_2C=CH_2 + H_2 \xrightarrow{\text{catalyst}} CH_3-\underset{CH_3}{\overset{H}{C}}-CH_3$$

b.

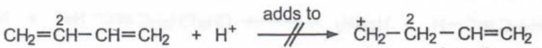


3.22



$$\overset{1}{C}H_2=CH-CH=CH_2 + H^+ \xrightarrow[\text{C-1}]{\text{adds to}} \overset{1}{C}H_3-\overset{+}{C}H-CH=CH_2$$

allylic carbocation, stabilized by resonance

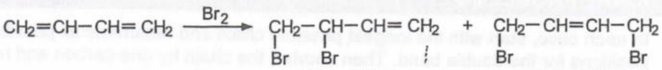


$$CH_2=\overset{2}{C}H-CH=CH_2 + H^+ \xrightarrow[\text{C-2}]{\text{adds to}} \overset{+}{C}H_2-\overset{2}{C}H_2-CH=CH_2$$

primary carbocation, much less stable than the allylic carbocation

3.23

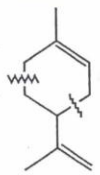
3.24



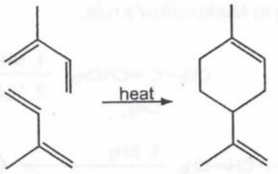
$$CH_2=CH-CH=CH_2 \xrightarrow{Br_2} \underset{Br}{C}H_2-\underset{Br}{C}H-CH=CH_2 + \underset{Br}{C}H_2-CH=CH-\underset{Br}{C}H_2$$

1,2-addition 1,4-addition

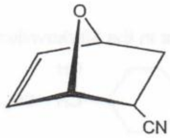
3.25 To find the structures of the diene and dienophile, break the cyclohexene ring just beyond the ring carbons that are connected to the double bond (the allylic carbons):



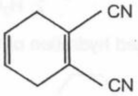
The equation is:



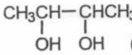
3.26 a.



b.



3.27 $CH_3CH{=}CHCH_3$ + $KMnO_4$ ⟶



$$CH_3\underset{OH}{CH}-\underset{OH}{CH}CH_3$$

+ MnO_2 (brown precipitate)

3.28 $(CH_3)_2C{=}C(CH_3)_2$

3.29 a. $CH_3C{\equiv}CH + Br_2 \longrightarrow CH_3CBr{=}CHBr$

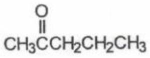
b. $CH_3C{\equiv}CH + 2Cl_2 \longrightarrow CH_3CCl_2-CHCl_2$

c. $HC{\equiv}CCH_2CH_3 + HBr \longrightarrow CH_2{=}CBrCH_2CH_3$

$HC{\equiv}CCH_2CH_3 + 2HBr \longrightarrow CH_3CBr_2CH_2CH_3$

d.

$HC{\equiv}CCH_2CH_2CH_3 + H{-}OH \xrightarrow[H^+]{Hg^{++}}$



$$CH_3\overset{\overset{\Large O}{\|}}{C}CH_2CH_2CH_3$$

3.30 Follow eq. 3.53 as a guideline:

$$CH_3(CH_2)_3C{\equiv}C{-}H + NaNH_2 \longrightarrow CH_3(CH_2)_3C{\equiv}C^-\,Na^+ + NH_3$$

3.31 $HC{\equiv}C^-\,Na^+ + H_2O \longrightarrow HC{\equiv}CH + NaOH$

3.32 2-Butyne has no hydrogens on the triple bond:

$$CH_3C{\equiv}CCH_3$$

Therefore, it does not react with sodium amide.

ADDITIONAL PROBLEMS

3.33 In each case, start with the longest possible chain and determine all possible positions for the double bond. Then shorten the chain by one carbon and repeat, and so on.

a.

$HC{\equiv}CCH_2CH_2CH_3$	1-pentyne
$CH_3C{\equiv}CCH_2CH_3$	2-pentyne
$HC{\equiv}CCH(CH_3)_2$	3-methyl-1-butyne

b.	$CH_2=CHCH_2CH_3$	1-butene
	$CH_3CH=CHCH_3$	2-butene (*cis* and *trans*)
	$CH_2=C(CH_3)CH_3$	2-methylpropene
c.	$CH_2=C=CHCH_2CH_3$	1,2-pentadiene
	$CH_2=CH-CH=CHCH_3$	1,3-pentadiene
	$CH_2=CHCH_2CH=CH_2$	1,4-pentadiene
	$CH_3CH=C=CHCH_3$	2,3-pentadiene
	$CH_2=C=C(CH_3)_2$	3-methyl-1,2-butadiene
	$CH_2=C(CH_3)CH=CH_2$	2-methyl-1,3-butadiene

3.34 a. 3-ethyl-2-pentene (number the chain such that the double bond carbons get the lowest numbers possible)

b. 2-pentene

c. 3,5-dimethylcyclohexene (number the ring starting with the double bond such that the substituent methyl group get the lowest numbers possible)

d. 2-hexyne

e. 2-bromo-1,3-butadiene (number from the end nearest the bromine substituent)

f. 1-penten-4-yne (the double bond receives the lowest number)

g. *cis*-2-pentene

h. *trans*-2-pentene

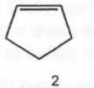
i. 3-methylpentyne

j. cyclobutene

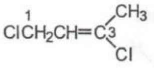
k. 2-methylpropene

3.35 a. $H_2C=CHCH_2CH_2CH_2CH_3$

b.



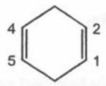
c.



$\overset{1}{ClC}H_2CH=\overset{3}{C}(CH_3)Cl$

d. $CH_3\overset{2}{C}\equiv C\overset{4}{C}H(CH_3)CH_2CH_3$

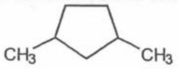
e.



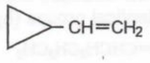
f. $H_2C=CH-Br$

($H_2C=CH-$ is vinyl)

g.



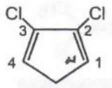
h.



i. $H_2C=CHCH_2-Cl$

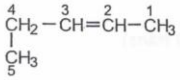
($H_2C=CHCH_2-$ is allyl)

j.



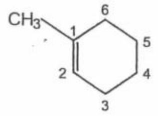
3.36 a. $H\overset{1}{C}\equiv\overset{2}{C}\overset{3}{C}H_2\overset{4}{C}H_3$ 1-butyne; number the chain from the other end.

b. $\overset{1}{C}H_3\overset{2}{C}H=\overset{3}{C}H\overset{4}{C}H_2\overset{5}{C}H_3$ 2-pentene; use the lower of the two numbers for the double bond.

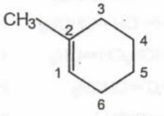
c. 

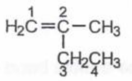
$\underset{\underset{5}{CH_3}}{\overset{4}{C}H_2}-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}H_3$

2-pentene; the "1-methyl" substituent lengthens the chain.

d. 

1-methylcyclohexene, *not*



e. 

$H_2\overset{1}{C}=\underset{\underset{3\ \ 4}{CH_2CH_3}}{\overset{2}{C}}-CH_3$

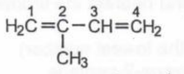
2-methyl-1-butene; number the longest chain.

f. $H_2\overset{1}{C}=\overset{2}{C}H-\overset{3}{C}\equiv\overset{4}{C}\overset{5}{C}H_3$

1-penten-3-yne; name as an enyne, *not* an ynene

g. $H_2\overset{1}{C}=\overset{2}{C}H-\overset{3}{C}\equiv\overset{4}{C}H$

1-buten-3-yne; use the lower of the two numbers for the double bond.

h. 

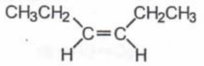
$H_2\overset{1}{C}=\underset{CH_3}{\overset{2}{C}}-\overset{3}{C}H=\overset{4}{C}H_2$

2-methyl-1,3-butadiene; number to give the substituent the lowest possible number.

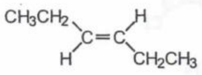
3.37 a. The average values are 1.54 Å, 1.34 Å, and 1.21 Å, respectively.

b. These single bonds are shorter than the usual 1.54 Å because they are between sp^2-sp^2 (1.47 Å), and sp^2-sp (1.43 Å), and sp-sp (1.37 Å) hybridized carbons. The more *s*-character the orbitals have, the more closely the electrons are pulled in toward the nuclei and the shorter the bonds.

3.38 Review Sec. 3.5 if you have difficulty with this question.

a. 

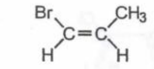
cis-3-hexene



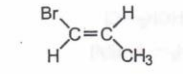
trans-3-hexene

b. Only one structure is possible since one of the doubly bonded carbons has two identical groups (hydrogens):

$H_2C=CHCH_2CH_2CH_3$

c. 

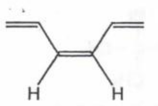
cis-1-bromopropene



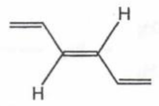
trans-1-bromopropene

d. Only one structure: $H_2C=CHCH_2Br$

e.



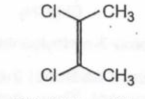
cis-1,3,5-hexatriene



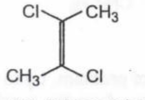
trans-1,3,5-hexatriene

Only the central double bond has two different groups (a vinyl group and a hydrogen) attached to each carbon.

f.

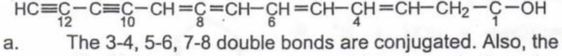


cis-2,3-dichloro-2-butene



trans-2,3-dichloro-2-butene

3.39



$$\overset{13}{HC}\equiv\underset{12}{C}-\overset{11}{C}\equiv\underset{10}{C}-\overset{9}{CH}=\underset{8}{C}=\overset{7}{CH}-\underset{6}{CH}=\overset{5}{CH}-\underset{4}{CH}=\overset{3}{CH}-\overset{2}{CH_2}-\underset{1}{\overset{O}{\overset{\|}{C}}}-OH$$

a. The 3-4, 5-6, 7-8 double bonds are conjugated. Also, the 8-9, 10-11, and 12-13 multiple bonds are conjugated (alternate single and multiple bonds).

b. The 7-8 and 8-9 double bonds are cumulated.

c. Only the C=O bond is isolated (separated from the nearest multiple bond by two single bonds).

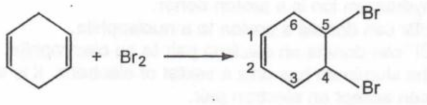
3.40 a. $CH_3CH{=}CHCH_3 + Br_2 \longrightarrow CH_3CHBrCHBrCH_3$

2,3-dibromobutane

b. $H_2C{=}CHCl + Br_2 \longrightarrow CH_2BrCHBrCl$

1,2-dibromo-1-chloroethane

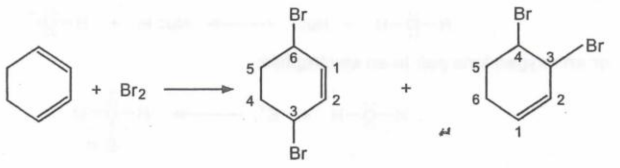
c.



4,5-dibromocyclohexene

The double bonds are not conjugated, so only 1,2-addition is possible.

d.

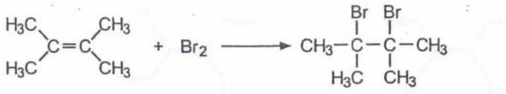


3,6-dibromocyclohexene
(1,4-addition)

3,4-dibromocyclohexene
(1,2-addition)

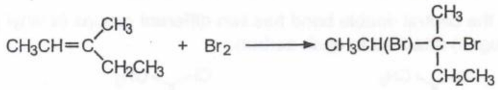
Compare with eqs. 3.31–3.33. The 1,4-addition product predominates.

e.



2,3-dibromo-2,3-dimethylbutane

f.



2,3-dibromo-3-methylpentane

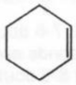
3.41 To work this kind of problem, try to locate (on adjacent carbons) the atoms or groups that must have come from the small molecule or reagent. Then remove them from the structure and insert the multiple bond appropriately.

a. $CH_3CH{=}CHCH_3 + Br_2$

b. $CH_2{=}CHCH_3 + H{-}OSO_3H$

c. $CH_2{=}C(CH_3)_2 + HOH + H^+$

d.

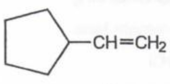


$+ H{-}Cl$

e. $CH_2{=}CH{-}CH{=}CH_2 + H{-}Cl$ (1,4-addition)

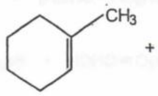
f. $CH_3CH_2C{\equiv}CCH_3 + 2Cl_2$

g.



$+ H{-}Br$

h.



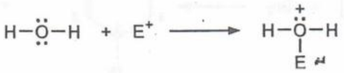
$+ H_2O + H^+$

3.42
a. Electrophile; hydronium ion is a proton donor.
b. Electrophile; HBr can donate a proton to a nucleophile.
c. Nucleophile; Cl^- can donate an electron pair to an electrophile.
d. Electrophile; the aluminum has only a sextet of electrons. It is electron-deficient and can accept an electron pair.
e. Nucleophile; the negatively charged oxygen reacts with electrophiles.

3.43 Water can donate a proton to a nucleophile:

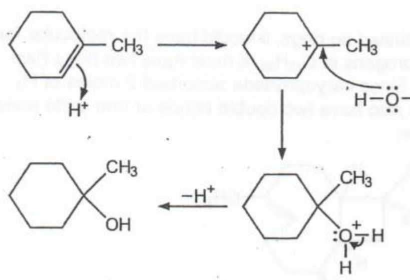
$$H{-}\ddot{\underset{\cdot\cdot}{O}}{-}H + Nu{:}^- \longrightarrow Nu{:}H + H{-}\ddot{\underset{\cdot\cdot}{O}}{:}^-$$

or an oxygen lone pair to an electrophile:



$$H{-}\ddot{\underset{\cdot\cdot}{O}}{-}H + E^+ \longrightarrow H{-}\overset{+}{\underset{E}{\ddot{O}}}{-}H$$

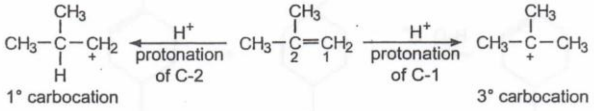
3.44



The oxygen carries a formal +1 charge

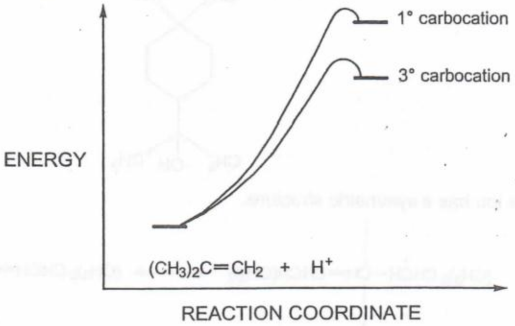
In the first step, the proton adds in such a way as to give the tertiary carbocation intermediate.

3.45 a.



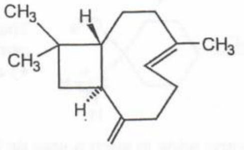
The 3° carbocation is more stable than the 1° carbocation.

b. Both protonations are endothermic, but the protonation which gives the tertiary carbocation is less endothermic, and thus energetically more favorable than the reaction leading to the primary carbocation.

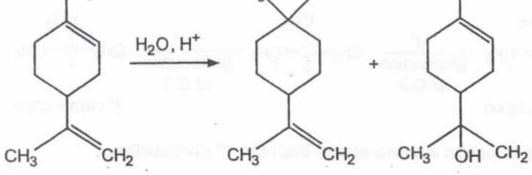


The tertiary carbocation then reacts with water to give $(CH_3)_3C{-}OH$ (2-methyl-2-propanol).

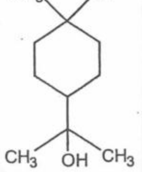
3.46 If the saturated hydrocarbon contained no rings, it would have the molecular formula $C_{15}H_{32}$. Since there are fewer hydrogens in $C_{15}H_{28}$, it must have two rings (two hydrogens are deleted per ring). Since caryophyllene absorbed 2 moles of H_2 ($C_{15}H_{24} + 2\ H_2 \rightarrow C_{15}H_{28}$), it must also have two double bonds or one triple bond. The structure of caryophyllene follows:



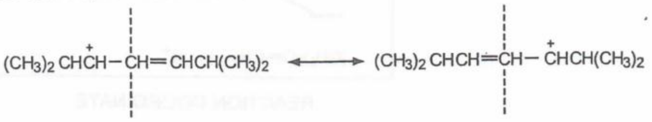
3.47



In each case, water adds according to Markovnikov's rule (via a tertiary carbocation). The diol is:

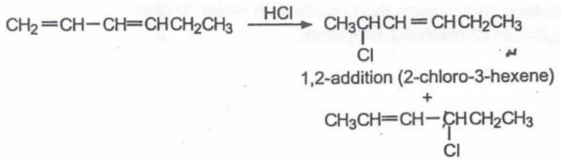


3.48 The ion has a symmetric structure.



$$(CH_3)_2\,\overset{+}{C}HCH-CH=CHCH(CH_3)_2 \longleftrightarrow (CH_3)_2\,CHCH=CH-\overset{+}{C}HCH(CH_3)_2$$

3.49



$$CH_2=CH-CH=CHCH_2CH_3 \xrightarrow{HCl} CH_3\underset{\displaystyle Cl}{C}HCH=CHCH_2CH_3$$

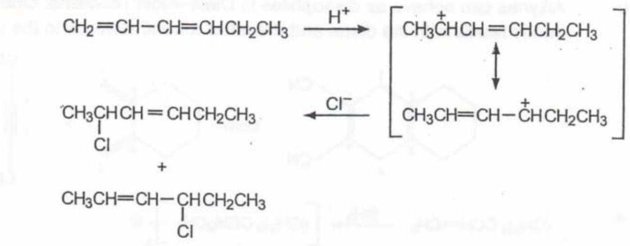
1,2-addition (2-chloro-3-hexene)

+

$$CH_3CH=CH-\underset{\displaystyle Cl}{C}HCH_2CH_3$$

1,4-addition (4-chloro-2-hexene)

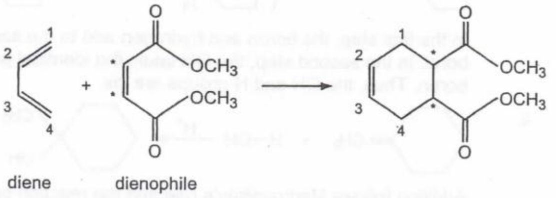
Mechanism:



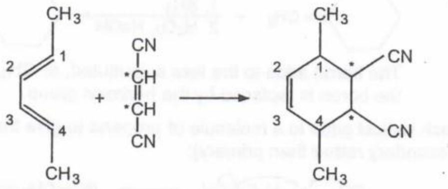
$$CH_2{=}CH{-}CH{=}CHCH_2CH_3 \xrightarrow{H^+} \left[CH_3\overset{+}{C}HCH{=}CHCH_2CH_3 \longleftrightarrow CH_3CH{=}CH{-}\overset{+}{C}HCH_2CH_3 \right] \xrightarrow{Cl^-} CH_3\underset{Cl}{C}HCH{=}CHCH_2CH_3 + CH_3CH{=}CH{-}\underset{Cl}{C}HCH_2CH_3$$

In the final step, the nucleophile Cl^- can react with the allylic carbocation at either of the two positive carbons.

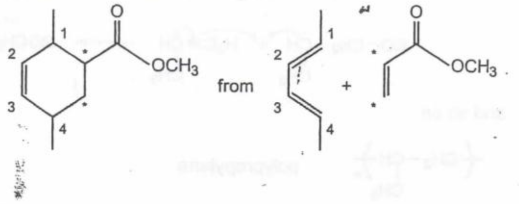
3.50 a. The product of a Diels–Alder reaction is a cyclohexene. The terminal carbons of the diene (C-1 and C-4) form single bonds with the doubly bonded carbons of the dienophile (marked with an asterisk). The double bond of the dienophile becomes a single bond. The double bond in the product forms between the carbons that originated as C-2 and C-3 of the diene.



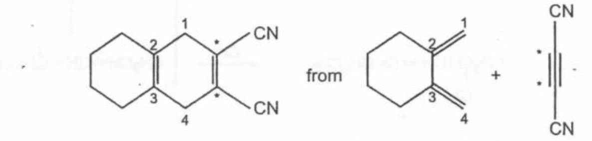
b. The methyl groups at the ends of the 1,3-diene simply come along for the ride.



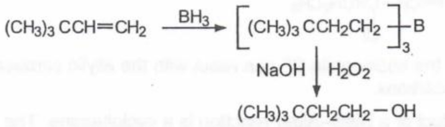
3.51 a. Use the reverse of the strategy used in Problem 3.50:



b. Alkynes can behave as dienophiles in Diels–Alder reactions. One of the π bonds reacts with the diene and the other π bond remains in the product.

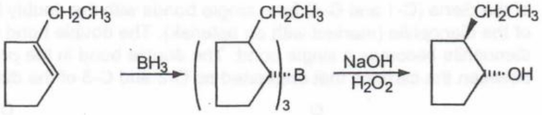


3.52 a.



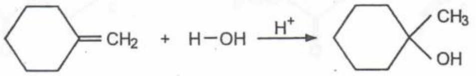
$$(CH_3)_3CCH{=}CH_2 \xrightarrow{BH_3} [(CH_3)_3CCH_2CH_2]_3B \xrightarrow{NaOH,\ H_2O_2} (CH_3)_3CCH_2CH_2{-}OH$$

b.



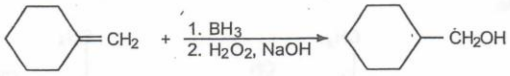
In the first step, the boron and hydrogen add to the same face of the double bond. In the second step, the OH takes the identical position occupied by the boron. Thus, the OH and H groups are *cis*.

3.53 a.



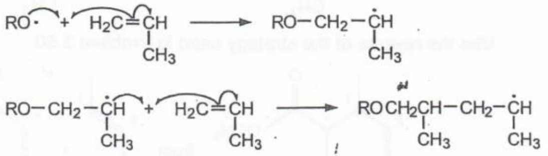
Addition follows Markovnikov's rule and the reaction proceeds *via* a tertiary carbocation intermediate.

b.



The boron adds to the less substituted, or CH_2, carbon. In the second step, the boron is replaced by the hydroxyl group.

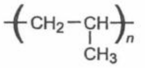
3.54 Each radical adds to a molecule of propene to give the more stable radical (secondary rather than primary):



$$RO\cdot + H_2C{=}CH(CH_3) \longrightarrow RO{-}CH_2{-}\dot{C}H(CH_3)$$

$$RO{-}CH_2{-}\dot{C}H(CH_3) + H_2C{=}CH(CH_3) \longrightarrow ROCH_2CH(CH_3){-}CH_2{-}\dot{C}H(CH_3)$$

and so on



$$\left(CH_2{-}CH(CH_3)\right)_n$$

polypropylene

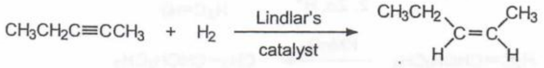
3.55 Cyclohexene will rapidly decolorize a dilute solution of bromine in carbon tetrachloride (Sec. 3.7a) and will be oxidized by potassium permanganate, resulting in a color change from the purple of $KMnO_4$ to the brown solid MnO_2 (Sec. 3.17a). Cyclohexane, being saturated, does not react with either of these reagents.

3.56 The alkene that gave the particular aldehyde or ketone can be deduced by joining the two carbons attached to oxygens by a C=C double bond:

a.	$(CH_3)_2C{=}CH_2$	b.	$(CH_3)_2C{=}C(CH_3)_2$
c.	$CH_3CH{=}CHCH_2CH_3$	d.	cyclopentene

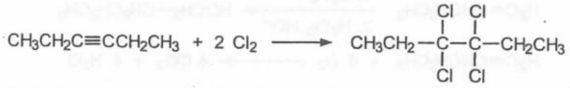
In the case of compound a, where *cis* and *trans* are possible, either isomer gives the same ozonolysis products.

3.57 a.



This catalyst limits the addition to 1 mole of H_2, which adds to the same face of the double bond.

b.

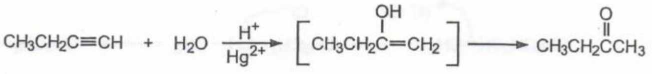


$$CH_3CH_2C\equiv CCH_2CH_3 + 2\,Cl_2 \longrightarrow CH_3CH_2-\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}-CH_2CH_3$$

c. $CH_3CH_2\equiv CH + NaNH_2 \longrightarrow CH_3CH_2\equiv C^-Na^+ + NH_3$

Compare with eq. 3.53, where R = CH_3CH_2.

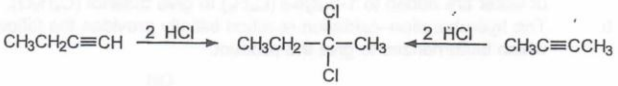
d.



$$CH_3CH_2C\equiv CH + H_2O \xrightarrow[Hg^{2+}]{H^+} \left[CH_3CH_2\overset{OH}{C}{=}CH_2\right] \longrightarrow CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3$$

Compare with eq. 3.52, where R = CH_3CH_2.

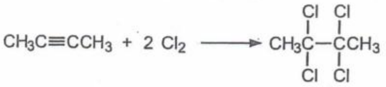
3.58 a.



$$CH_3CH_2C\equiv CH \xrightarrow{2\ HCl} CH_3CH_2-\underset{Cl}{\overset{Cl}{C}}-CH_3 \xleftarrow{2\ HCl} CH_3C\equiv CCH_3$$

Either 1- or 2-butyne will add HCl to give the same product.

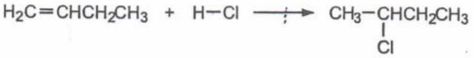
b.



$$CH_3C\equiv CCH_3 + 2\,Cl_2 \longrightarrow CH_3\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}CH_3$$

The triple bond must be between C-2 and C-3 if the chlorines are to be attached to those carbons in the product.

3.59 a. Follow Markovnikov's rule:



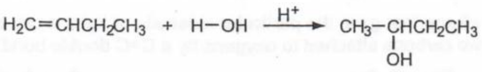
$$H_2C{=}CHCH_2CH_3 + H{-}Cl \longrightarrow CH_3-\underset{Cl}{C}HCH_2CH_3$$

b.

$$H_2C{=}CHCH_2CH_3 + Br_2 \longrightarrow \underset{Br}{C}H_2-\underset{Br}{C}HCH_2CH_3$$

c. $H_2C{=}CHCH_2CH_3 + H_2 \xrightarrow{Pt} CH_3{-}CH_2CH_2CH_3$

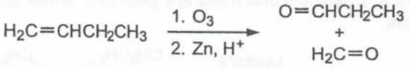
d. Follow Markovnikov's rule:



$$H_2C{=}CHCH_2CH_3 + H{-}OH \xrightarrow{H^+} CH_3{-}\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_3$$

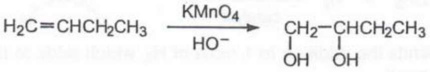
The product is the regioisomer of that obtained by the hydroboration–oxidation sequence (part g).

e.



$$H_2C{=}CHCH_2CH_3 \xrightarrow[2.\ Zn,\ H^+]{1.\ O_3} \begin{array}{c} O{=}CHCH_2CH_3 \\ + \\ H_2C{=}O \end{array}$$

f.

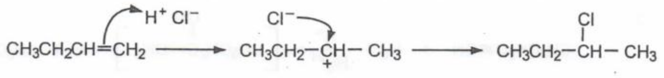


$$H_2C{=}CHCH_2CH_3 \xrightarrow[HO^-]{KMnO_4} \underset{\displaystyle OH}{\underset{|}{C}}H_2{-}\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_3$$

g. $H_2C{=}CHCH_2CH_3 \xrightarrow[2.\ H_2O_2,\ HO^-]{1.\ B_2H_6} HOCH_2{-}CH_2CH_2CH_3$

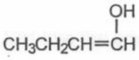
h. $H_2C{=}CHCH_2CH_3 + 6\ O_2 \longrightarrow 4\ CO_2 + 4\ H_2O$

3.60 This is an electrophilic addition. The double bond is protonated in the first step to give the secondary carbocation, which reacts with chloride ion in the second step to provide the product.



3.61 a. This reaction is similar to a hydroboration–oxidation reaction. The elements of water are added to 1-butyne (C_4H_6) to give butanol (C_4H_8O).

b. The hydroboration–oxidation reaction initially provides the following enol, which tautomerizes to give the product.



$$CH_3CH_2CH{=}\overset{\displaystyle OH}{\overset{|}{C}}H$$