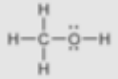
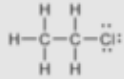
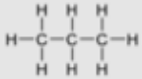
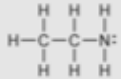
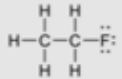
Chapter 1

1.35 Write a structural formula for each of the following compounds, using a line to represent each single bond and dots for any unshared electron pairs:

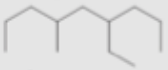
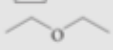
a. CH_3OH b. CH_3CH_2Cl c. C_3H_8
d. $CH_3CH_2NH_2$ e. C_2H_3F f. CH_2O

1.35 a.  b.  c. 

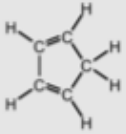
d.  e.  f. 

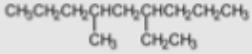
1.41 Write structural formulas that correspond to the following abbreviated structures, and show the correct number of hydrogens on each carbon:

a.  b.  c. 

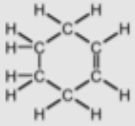
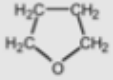
d.  e.  f. 

g.  h. 

1.41 a. $CH_3CH_2C(CH_3)=CH_2$ b. 

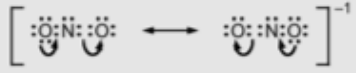
c. $(CH_3)_3CCH(CH_3)_2$ d. 

e. $CH_3CH_2OCH_2CH_3$ f. $(CH_3)_2CHCH_2CH_2CH_3$

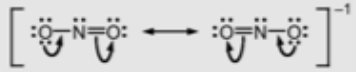
g.  h. 

1.46 Draw electron-dot formulas for the two contributors to the resonance hybrid structure of the nitrite ion, NO_2^-. (Each oxygen is connected to the nitrogen.) What is the charge on each oxygen in each contributor and in the hybrid structure? Show by curved arrows how the electron pairs can relocate to interconvert the two structures.

~~1.47~~ 1.46 There are 18 valence electrons (6 from each of the oxygens, 5 from the nitrogen, and 1 from the negative charge).

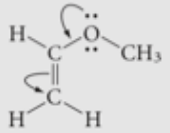


or



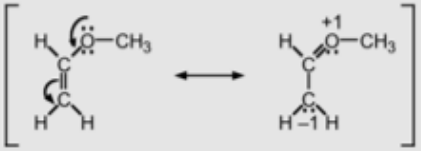
The negative charge in each contributor is on the singly bonded oxygen [6 – (6 + 1) = –1. The other oxygen and the nitrogen have no formal charge. In the resonance hybrid, the negative charge is spread equally over the two oxygens; the charge on each is –1/2.

1.47 Write the structure obtained when electrons move as indicated by the curved arrows in the following structure:

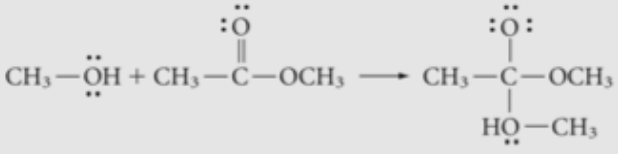


Does each atom in the resulting structure have a complete valence shell of electrons? Locate any formal charges in each structure.

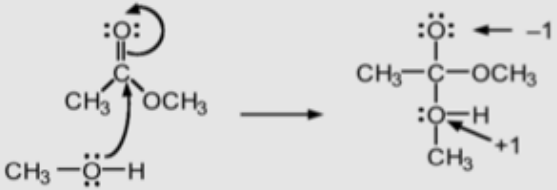
~~1.48~~ 1.47 Each atom in both structures has a complete valence shell of electrons. There are no formal charges in the first structure, but in the second structure the oxygen is formally positive and the nitrogen formally negative.



1.50 Add curved arrows to show how electrons must move to form the product from the reactants in the following equation, and locate any formal charges.

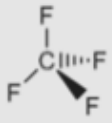


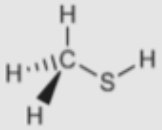
1.50



1.54 Use lines, dashed wedges, and solid wedges to show the geometry of CF_4 and CH_3SH.

1.54



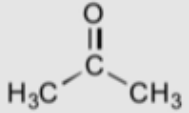


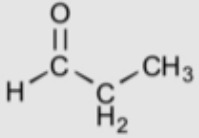
1.57 Write a structural formula that corresponds to the molecular formula C_3H_6O and is

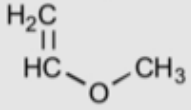
a. acyclic **b.** carbocyclic **c.** heterocyclic

1.57 Many correct answers are possible; a few are given here for part (a).

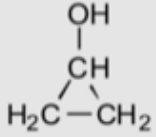
a.



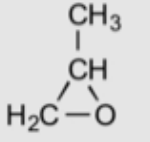


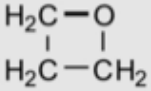


b.

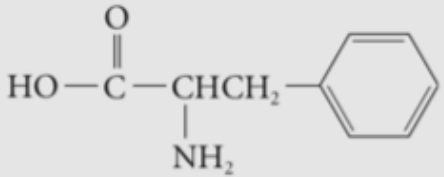


c.





1.61 Many organic compounds contain more than one functional group. An example is phenylalanine (shown below), one of the simple building blocks of proteins (Chapter 17).



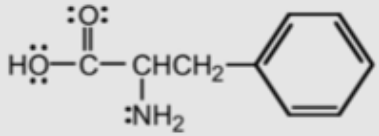
phenylalanine

a. What functional groups are present in phenylalanine?
b. Redraw the structure, adding all unshared electron pairs.
c. What is the molecular formula of phenylalanine?
d. Draw another structural isomer that has this formula. What functional groups does this isomer have?

~~1.60~~ 1.61

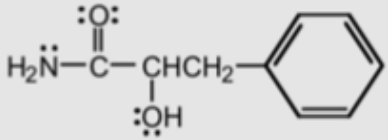
a. carbonyl group (carboxylic acid), amino group (amine), aromatic group (arene)

b.



c. $C_9H_{11}NO_2$

d. The isomer of phenylalanine shown below is both an alcohol and an amide.

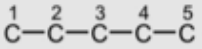


Chapter 2

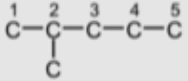
2.26 Write structural formulas for the following compounds:

a. 2-methylhexane
b. 2,3-dimethylbutane
c. 4-ethyl-2,2-dimethylheptane
d. 2-bromo-4-methyloctane
e. 1,1-diiodocyclobutane
f. 2-chlorobutane
g. 1-isopropyl-1,3-dimethylcyclohexane
h. 1,1,2-trifluoropropane
i. 1,1,3,3-tetrachlorocyclopropane

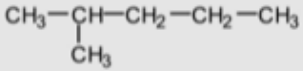
2.26 a. 2-methylpentane: First, note the root of the name (in this case, pent) and write down and number the carbon chain.

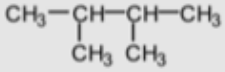


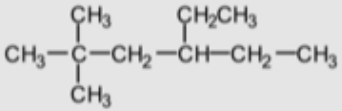
Next, locate the substituents (2-methyl).

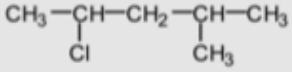


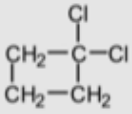
Finally, fill in the remaining hydrogens.

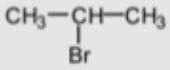


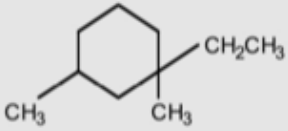
b. 

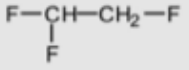
c. 

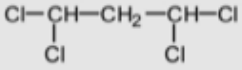
d. 

e. 

f. 

g. 

h. 

i. 

2.31 Write the structural formulas for all isomers of each of the following compounds, and name each isomer by the IUPAC system. (The number of isomers is indicated in parentheses.)

a. C_4H_{10} (2)
b. C_4H_9Cl (4)
c. C_3H_6FCl (5)
d. $C_3H_6Br_2$ (4)
e. $C_2H_2ClBr_3$ (3)
f. C_5H_{12} (3)

2.31 a.

$CH_3(CH_2)_2CH_3$	butane
$(CH_3)_3CH$	2-methylpropane

b.

$CH_3CH_2CH_2CH_2Cl$	1-chlorobutane
$CH_3CH(Cl)CH_2CH_3$	2-chlorobutane
$(CH_3)_2CHCH_2Cl$	1-chloro-2-methylpropane
$(CH_3)_3Cl$	2-chloro-2-methylpropane

c.

$CHFClCH_2CH_3$	1-chloro-1-fluoropropane
$CH_2FCHClCH_3$	2-chloro-1-fluoropropane
$CH_2FCH_2CH_2Cl$	3-chloro-1-fluoropropane
$CH_2ClCHFCH_3$	1-chloro-2-fluoropropane
$CH_3CFClCH_3$	2-chloro-2-fluoropropane

d.

$CH_3CH_2CHBr_2$	1,1-dibromopropane
$CH_3CHBrCH_2Br$	1,2-dibromopropane
$CH_2BrCH_2CH_2Br$	1,3-dibromopropane
$CH_3CBr_2CH_3$	2,2-dibromopropane

e. The two hydrogens can be on either the same or different carbon atoms:

CH_2ClCBr_3	2-chloro-1,1,1-tribromoethane
$CH_2BrCClBr_2$	1-chloro-1,1,2-tribromoethane
$CHBrClCHBr_2$	2-chloro-1,1,2-tribromoethane

f.

$CH_3(CH_2)_3CH_3$	pentane
$CH_3CH(CH_3)CH_2CH_3$	2-methylbutane
$CH_3C(CH_3)_2CH_3$	2,2-dimethylpropane

2.35 Without referring to tables, arrange the following five hydrocarbons in order of increasing boiling point. (*Hint:* Draw structures or make models of the five hydrocarbons to see their shapes and sizes.)

a. 2-methylhexane **b.** heptane **c.** 3,3-dimethylpentane
d. hexane **e.** 2-methylpentane

Explain your answer in terms of intermolecular interactions.

2.35

~~2.34~~ See Sec. 2.7 for a discussion of underlying principles. When comparing a series of alkanes, in general, the lower the molecular weight, the lower the intermolecular contact, the lower the van der Waals attractions, the less energy required to separate molecules from one another and the lower the boiling point. Thus, the hexane isomers (e and d) are expected to have lower boiling points than the heptane isomers (a, b, and c). Within a series of isomeric compounds, the greater the branching, the lower the intermolecular contact and the lower the boiling point. On these grounds, the expected order from the lowest to highest boiling point should be e, d, c, a, b. The actual boiling points are as follows: e, 2-methylpentane (60°C); c, 3,3-dimethylpentane (86°C); d, *n*-hexane (69°C); a, 2-methylhexane (90°C); b, *n*-heptane (98.4°C).

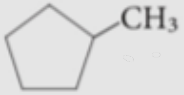
2.47 How many monobromination products can be obtained from each of the following polycyclic alkanes?

a. 

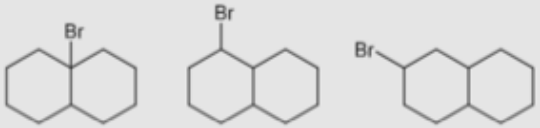
b. 

c. 

d. $CH_3CH_2CH_2CH_3$

e. 

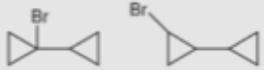
2.47 a. Three monobrominated structural isomers are possible.



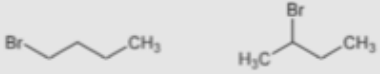
Several stereoisomers (not shown here) are possible for each structural isomer.

b. Three structural isomers

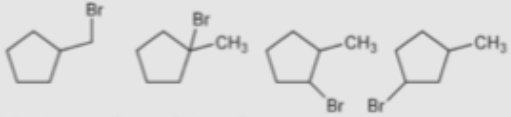
c. Two structural isomers



d. Two structural isomers



e. Four structural isomers



The latter two can have *cis-trans* isomers.

2.48 Using structural formulas, write equations for each of the following combustion reactions (see Reaction Summary 1.a, p. 63):

a. the complete combustion of propane
b. the complete combustion of pentane
c. the complete combustion of butane

2.48 a. $CH_3CH_2CH_3 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$

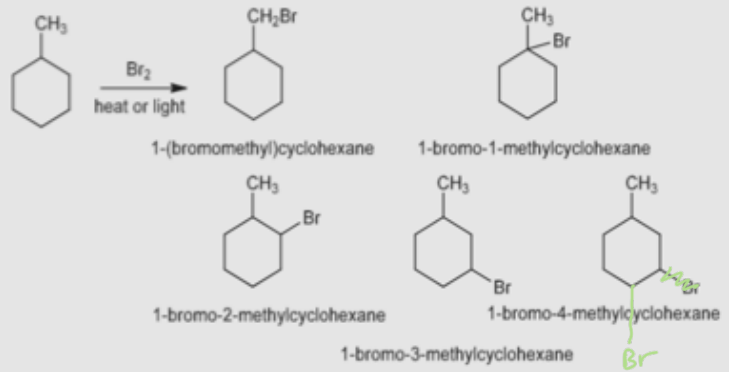
b. $CH_3(CH_2)_3CH_3 + 8O_2 \longrightarrow 5CO_2 + 6H_2O$

c. $2CH_3CH_2CH_2CH_3 + 13O_2 \longrightarrow 8CO_2 + 10H_2O$

2.50 Using structural formulas, write equations for the following halogenation reactions (see Reaction Summary 1.b, p. 63), and name each organic product:

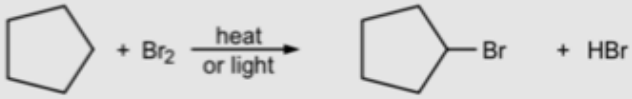
a. the monochlorination of propane
b. the monobromination of cyclopentane
c. the complete chlorination of butane
d. the monobromination of methylcyclohexane

d.



2.50 a. $CH_3CH_2CH_3 + Cl_2 \xrightarrow[\text{or light}]{\text{heat}} CH_3CH_2CH_2Cl + CH_3CH(Cl)CH_3 + HCl$

1-chloropropane 2-chloropropane

b. 

bromocyclopentane

c. $CH_3CH_2CH_2CH_3 + 10\,Cl_2 \xrightarrow[\text{or light}]{\text{heat}} CCl_3CCl_2CCl_2CCl_3 + 10HCl$

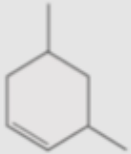
decachlorobutane

Chapter 3

3.34 Name the following compounds by the IUPAC system:

a. $CH_3CH{=}C(CH_2CH_2CH_3)_2$

b. $(CH_3)_2CHCH{=}CHCH_3$

c. 

d. $CH_3C{\equiv}CCH(Cl)CH_2CH_3$

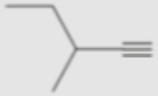
e. $CH_3{-}C{\equiv}C{-}CH_2{-}CH{=}CHCH_3$

f. $CH_2{=}CH{-}C(Br){=}CH_2$

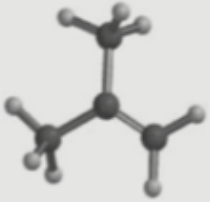
g. $CH_3{-}C{\equiv}C{-}CH{=}CH_2$

h. 

i. 

j. 

k. 

l. 

3.34

a. 3-propyl-2-hexene (number the chain such that the double bond carbons get the lowest numbers possible)

b. 4-methyl-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. 4-chloro-2-hexyne

e. 2-hepten-5-yne (the double bond receives the lowest number)

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

g. 1-penten-3-yne (the double bond receives the lowest number)

h. *cis*-2-pentene

i. *trans*-2-pentene

j. 3-methylpentyne

k. cyclobutene

l. 2-methylpropene

3.36 Explain why the following names are incorrect and give a correct name in each case:

a. 5-octyne
b. 3-pentene
c. 3-buten-1-yne
d. 1-methyl-2-pentene
e. 2-methylcyclopentene
f. 2-propyl-1-propene
g. 3-pentyne-1-ene
h. 3-ethyl-1,3-butadiene

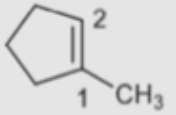
3.36

a. $\overset{8}{CH_3}\overset{7}{CH_2}\overset{6}{CH_2}\overset{5}{CH_2}-\overset{4}{C}\equiv\overset{3}{C}-\overset{2}{CH_2}\overset{1}{CH_3}$ — 3-octyne; number the chain from the other end.

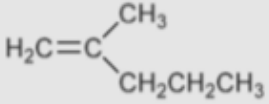
b. $\overset{1}{CH_3}\overset{2}{CH}=\overset{3}{CH}\overset{4}{CH_2}\overset{5}{CH_3}$ — 2-pentene; use the lower of the two numbers for the double bond.

c. $\overset{1}{H_2C}=\overset{2}{CH}-\overset{3}{C}\equiv\overset{4}{CH}$ — 1-buten-3-yne; use the lower of the two numbers for the double bond.

d. $CH_3CH_2CH=CHCH_2CH_3$ — 3-hexene; the "1-methyl" substituent lengthens the chain.

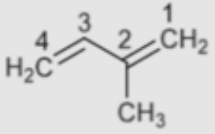
e. 

1-methylcyclopentene

f. 

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

g. $\overset{1}{H_2C}=\overset{2}{CH}-\overset{3}{C}\equiv\overset{4}{C}\overset{5}{CH_3}$ — 1-penten-3-yne; name as an enyne, *not* an ynene

h. 

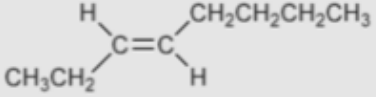
2-methyl-1,3-butadiene; number to give the substituent the lowest possible number.

3.38 Which of the following compounds can exist as *cis–trans* isomers? If such isomerism is possible, draw the structures in a way that clearly illustrates the geometry.

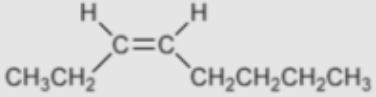
a. 3-octene
b. 3-chloropropene
c. 1-hexene
d. 1-bromopropene
e. 4-methylcyclohexene
f. 1,3,5,7-octatetraene
g. 2,3-difluoro-2-butene

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

a.



trans-3-octene



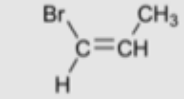
cis-3-octene

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

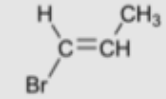
$H_2C{=}CHCH_2Cl$

c. Only one structure: $H_2C{=}CHCH_2CH_2CH_2CH_3$

d.

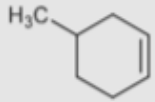


cis-1-bromopropene



trans-1-bromopropene

e.

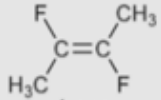


Only one structure is possible.

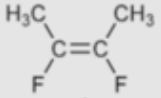
f.

Only one structure is possible.

g.



trans



cis

3.41 Write the structural formula and name of the product when each of the following reacts with one mole of bromine.

a. $CH_3CH_2CH{=}CHCH_2CH_3$ **b.** $CH_2{=}CHCH_2Cl$ **c.** 

d.  **e.** 

f. $CH_3CH{=}C(CH_3)CH_2CH_3$

3.41 a.

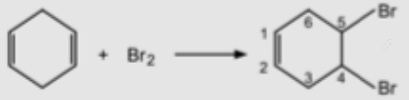
$$CH_3CH_2CH{=}CHCH_2CH_3 + Br_2 \longrightarrow CH_3CH_2CH(Br)CH(Br)CH_2CH_3$$

3,4-dibromohexane

b.

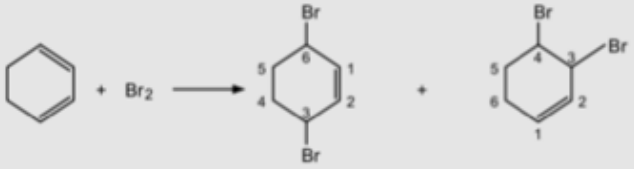
$$H_2C{=}CHCH_2Cl + Br_2 \longrightarrow H_2C(Br)CH(Br)CH_2Cl$$

1,2-dibromo-3-chloropropane

c. 

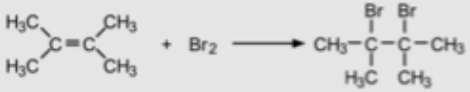
4,5-dibromocyclohexene

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

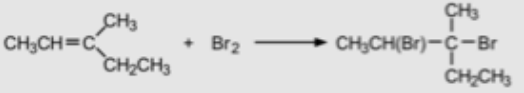
d. 

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. 

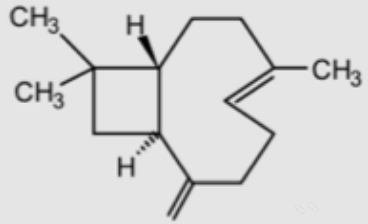
2,3-dibromo-2,3-dimethylbutane

f. 

2,3-dibromo-3-methylpentane

3.46 *Caryophyllene* is an unsaturated hydrocarbon mainly responsible for the odor of oil of cloves. It has the molecular formula $C_{15}H_{24}$. Hydrogenation of caryophyllene gives a saturated hydrocarbon $C_{15}H_{28}$. Does caryophyllene contain any rings? How many? What else can be learned about the structure of caryophyllene from its hydrogenation?

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:



3.56 Give the structural formulas of the alkenes that, on ozonolysis, give:

a. $(CH_3)_2C{=}O$ and $CH_2{=}O$
b. only $(CH_3CH_2)_2C{=}O$
c. $CH_3CH{=}O$ and $CH_3CH_2CH{=}O$
d. $O{=}CHCH_2CH_2CH_2CH{=}O$

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:

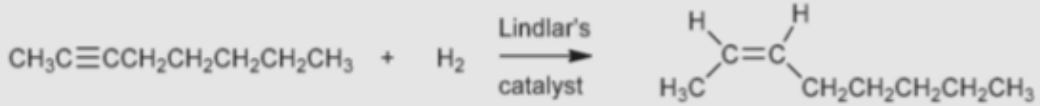
a. $(CH_3)_2C{=}CH_2$
b. $(CH_3CH_2)_2C{=}C(CH_2CH_3)_2$
c. $CH_3CH{=}CHCH_2CH_3$
d. cyclopentene

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

3.58 Write equations for the following reactions:

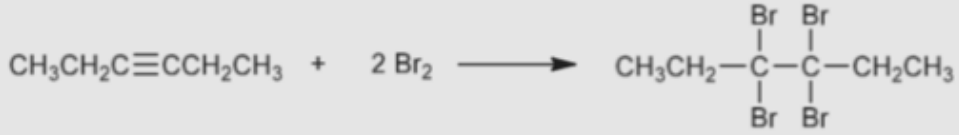
a. 2-octyne + H_2 (1 mole, Lindlar's catalyst)
b. 3-hexyne + Br_2 (2 moles)
c. 1-hexyne + sodium amide in liquid ammonia
d. 1-butyne + H_2O (H^+, Hg^{2+} catalyst)

3.58 a.



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

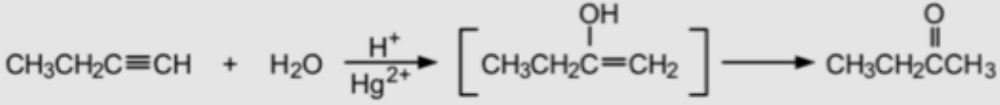
b.



c.

Compare with eq. 3.53, where R = $CH_3CH_2CH_2CH_2$.

d.

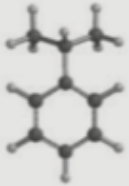


Compare with eq. 3.52, where R = CH_3CH_2.

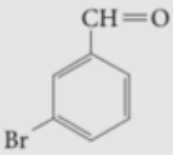
Chapter 4

4.21 Name the following compounds:

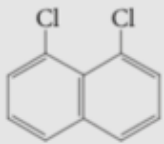
a.



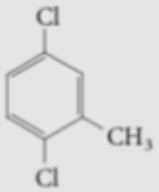
b.



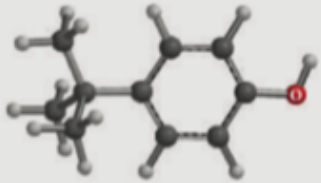
c.



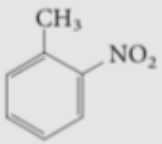
d.



e.

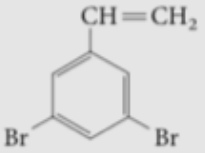


f.

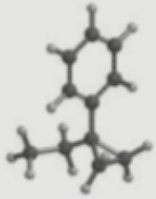


g.

h.



i.



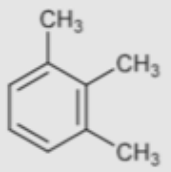
4.21

a. isopropylbenzene (or 2-phenylpropane)
b. *m*-bromobenzaldehyde
c. 1,8-dichloronaphthalene
d. 2,5-dichlorotoluene (start numbering with the carbon bonded to the methyl group and go around the ring such that substituents get the lowest possible numbers)
e. *p*-(*t*-butyl)phenol or 4-(1,1-dimethylethyl)phenol
f. *o*-nitrotoluene
g. hexafluorobenzene
h. 3,5-dibromostyrene
i. 1-ethyl-1-phenylcyclopropane (substituents in alphabetical order)

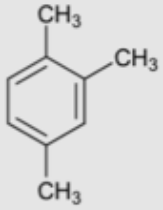
4.22 Give the structures and names for all possible

a. trimethylbenzenes
b. dibromobenzoic acids
c. dinitroanisoles
d. dichloronitrobenzenes

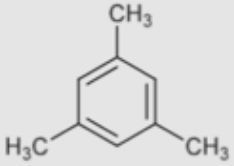
4.22 a.



1,2,3-trimethylbenzene

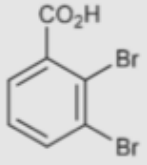


1,2,4-trimethylbenzene

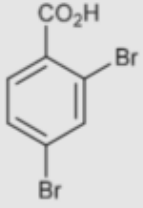


1,3,5-trimethylbenzene

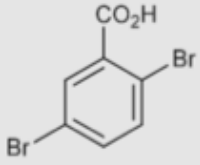
b.



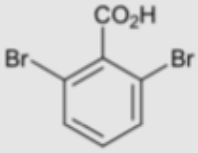
2,3-dibromobenzoic acid



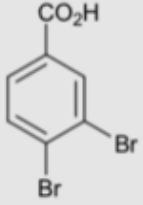
2,4-dibromobenzoic acid



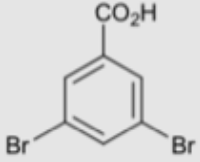
2,5-dibromobenzoic acid



2,6-dibromobenzoic acid



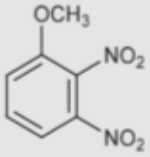
3,4-dibromobenzoic acid



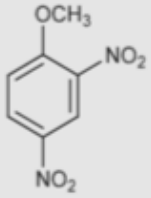
3,5-dibromobenzoic acid

4.22 Give the structures and names for all possible

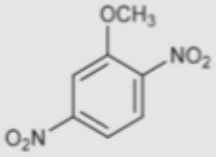
c.



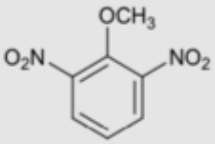
2,3-dinitroanisole



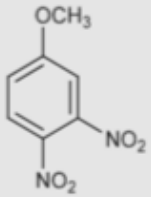
2,4-dinitroanisole



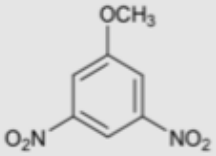
2,5-dinitroanisole



2,6-dinitroanisole

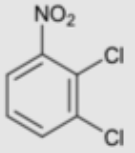


3,4-dinitroanisole

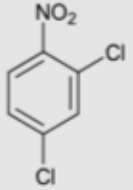


3,5-dinitroanisole

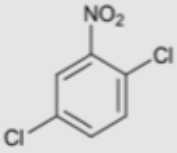
d.



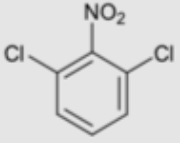
2,3-dichloronitrobenzene



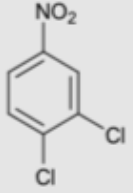
2,4-dichloronitrobenzene



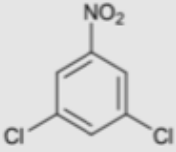
2,5-dichloronitrobenzene



2,6-dichloronitrobenzene



3,4-dichloronitrobenzene



3,5-dichloronitrobenzene

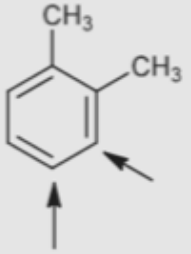
b. dibromobenzoic acids
d. dichloronitrobenzenes

4.24 Give the structure and name of each of the following aromatic hydrocarbons:

a. C_8H_{10}; has two possible ring-substituted monobromo derivatives
b. C_9H_{12}; can give only one mononitro product after nitration
c. C_9H_{12}; can give four mononitro derivatives after nitration

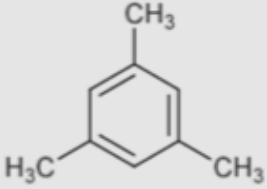
4.24 In each case, six carbons are required for the benzene ring; the remaining carbons must be present as alkyl substituents:

a.



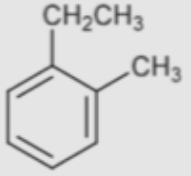
Only *o*-xylene gives two monobromo derivatives, as shown by the arrows.

b.



The structure is symmetrical, and all three positions for aromatic substitution are equivalent.

c.

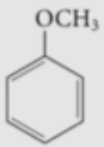


Substitution at each unoccupied ring position gives a different product.

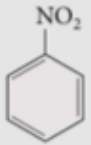
The compound in part b is 1,3,5-trimethylbenzene and that in part c is *o*-ethyltoluene or 2-ethyltoluene.

4.38 For each of the monosubstituted benzenes shown below,

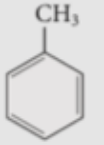
(1) indicate whether the substituent is *ortho,para* directing or *meta* directing.
(2) draw the structure of the main *mono*substitution product for each of the reactions indicated.

a. 

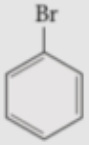
+ chlorine (Fe catalyst)

b. 

+ bromine (Fe catalyst)

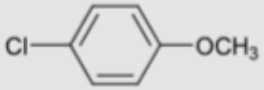
c. 

+ bromine (Fe catalyst)

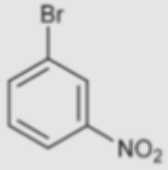
d. 

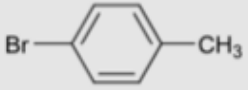
+ concentrated sulfuric acid (heat) + SO_3

4.38 See Sec. 4.11 for a discussion of the orienting influence of substituents.

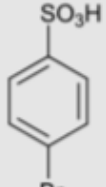
a. 

(and *ortho*)

b. 

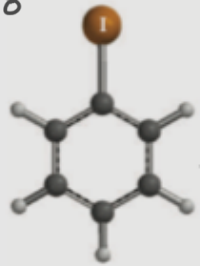
c. 

(and *ortho*)

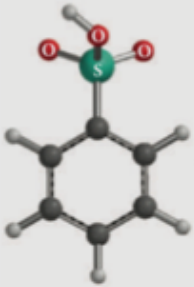
d. 

(and *ortho*)

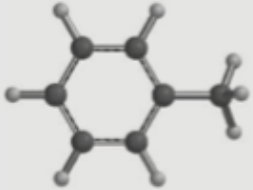
4·38

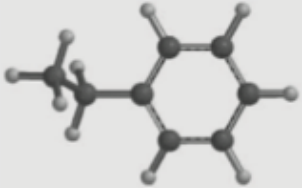
e. 

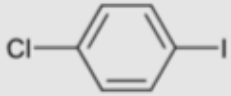
+ chlorine (Fe catalyst)

f. 

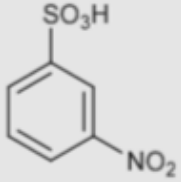
+ concentrated nitric acid (heat) (H_2SO_4 catalyst)

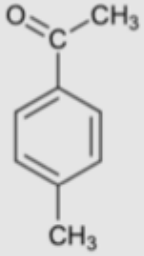
g. 
+ acetyl chloride ($AlCl_3$ catalyst)

h. 
+ concentrated nitric acid (H_2SO_4 catalyst)

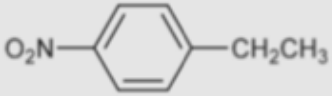
e. 

(and *ortho*)

f. 

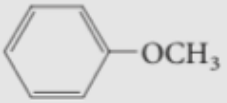
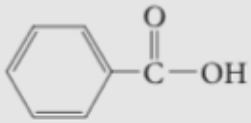
g. 

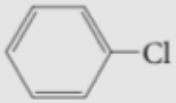
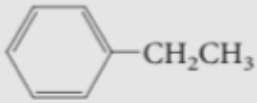
(and *ortho*)

h. 

(and *ortho*)

4.40 Which compound is more reactive toward electrophilic substitution (for example, nitration)?

a.  or 

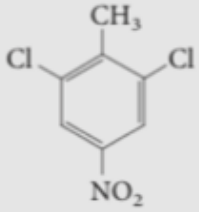
b.  or 

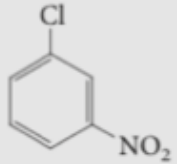
4.40

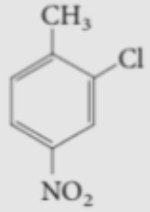
a. Anisole; the $-OCH_3$ group is ring-activating, whereas the $-CO_2H$ group is ring-deactivating.

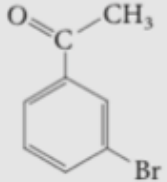
b. Ethylbenzene; although both substituents ($-CH_2CH_3$ and $-Cl$) are *ortho,para*-directing, the ethyl group is ring-activating, whereas the chlorine is ring-deactivating.

4.44 Using benzene or toluene as the only aromatic organic starting material, devise a synthesis for each of the following compounds. Name the product.

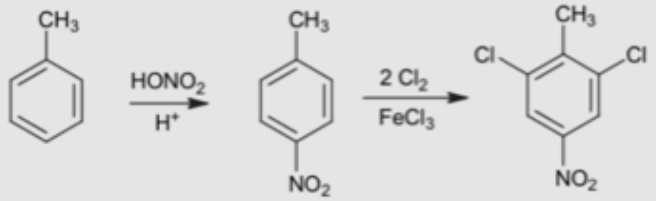
a. 

b. 

c. 

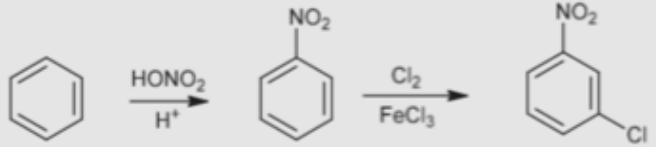
d. 

4.44 a. The nitro substituent must be introduced first, to block the *para* position from the chlorination.

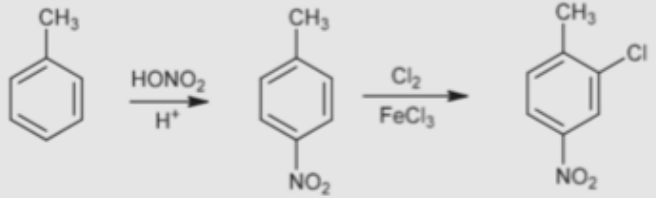


+ some *ortho* isomer

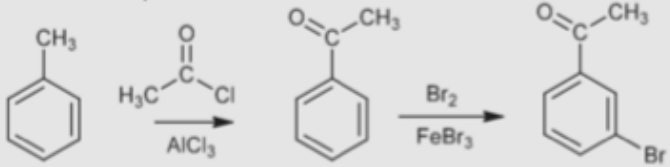
b. The nitration must be performed first. The nitro group is a *m*-director while a chloro group is an *o*,*p*-director.



c. If the chlorination were performed first, a considerable portion of product would have the chlorine *para* to the methyl group. Also, note that in the second step, both substituents direct the chlorine to the desired position (–CH_3 is *o*,*p*-directing, –NO_2 is *m*-directing).



d. If the bromination were performed first, the Friedel–Crafts acylation would occur at the 2 and 4 positions.

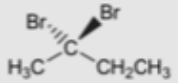


Chapter 5

5.27 Which of the following substances contain stereogenic centers? (*Hint:* Drawing the structures will help you answer this question.)

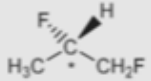
a. 2,2-dibromobutane
b. 3-methylcyclopentene
c. 1,2-difluoropropane
d. 2,3-dimethylheptane
e. methylcyclobutane
f. 1-deuteriopropanol (CH_3CH_2CHDOH)

5.27 a. The molecule has a plane of symmetry and has no stereogenic centers.

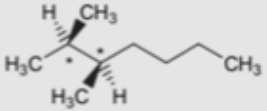


b. The carbon marked with an asterisk is a stereogenic center.

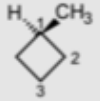
c. Carbon-2 is a chiral center, with four different groups attached.



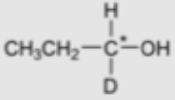
d. There are two carbons (marked with an asterisk) which are stereogenic centers.



e. This molecule has a plane of symmetry perpendicular to the four-membered ring, through carbon-1 and carbon-3.



f. The carbon marked with an asterisk is a stereogenic center, with four different groups attached. Even isotopes of the same element are sufficiently different to lead to optical activity.



5.29 What would happen to the observed and to the *specific* rotation if, in measuring the optical activity of a solution of sugar in water, we

a. doubled the concentration of the solution?
b. doubled the length of the sample tube?

5.29 In each case the *observed* rotation would be doubled, but the specific rotation would remain constant. For example, if c is doubled, α will also double, but the fraction α/c in the formula for specific rotation will remain constant.

5.30 The observed rotation for 100 mL of an aqueous solution containing 1 g of sucrose (ordinary sugar), placed in a 2-decimeter sample tube, is +1.33° at 25°C (using a sodium lamp). Calculate and express the specific rotation of sucrose.

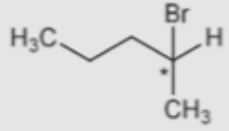
5.30
$$[\alpha]_D^{25} = \frac{1.33}{0.5 \times \frac{1}{100}} = 66.5^\circ \text{ (water)}$$

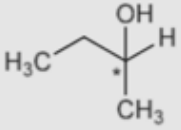
5.32 Draw a structural formula for an optically active compound with the molecular formula

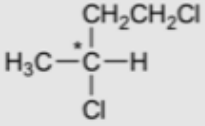
a. C_6H_{14} **b.** $C_5H_{11}Br$
c. $C_4H_{10}O$ **d.** $C_4H_8Cl_2$

5.32 The following are examples. There may be other possibilities.

a. $CH_3CH_2\overset{*}{C}HCH_2CH_2CH_3$ (with CH_3 on the starred carbon)

b. 

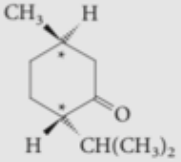
c. 

d. 

In each case the stereogenic carbon atom is marked with an asterisk.

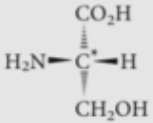
5.36 Tell whether the stereogenic centers marked with an asterisk in the following structures have the *R* or the *S* configuration:

a.



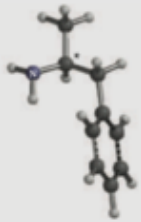
(−)-menthone
(found in peppermint)

b.



(−)-serine
(an amino acid found in proteins)

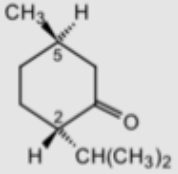
c.



(+)-amphetamine
(central nervous system stimulant)

5.36 In each case, write down the groups in the proper priority order. Then view the stereogenic center from the face opposite the lowest-priority group and determine whether the remaining array is clockwise (*R*) or counterclockwise (*S*). If you have difficulty, construct and examine molecular models.

a.



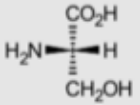
Carbon-5

$-CH_2C(=O) > -CH_2CH_2 > -CH_3 > -H$
therefore *R*

Carbon-2

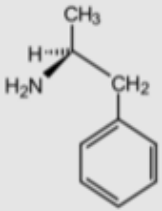
$-C(=O) > -CH(CH_3)_2 > -CH_2 > -H$
therefore *S*

b.



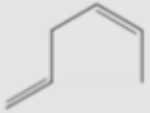
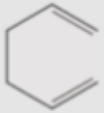
$-NH_2 > -CO_2H > -CH_2OH > -H$
therefore *S*

c.

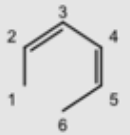


$-NH_2 > -CH_2C_6H_5 > -CH_3 > -H$
therefore *S*

5.39 Name the following compounds, using *E*-*Z* notation:

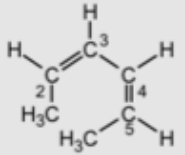
a.  **b.**  **c.**  **d.** 

5.39 a.



(*Z*,*Z*)-2,4-hexadiene or more precisely, (2*Z*,4*Z*)-2,4-hexadiene

If you have difficulty, draw the full structure:

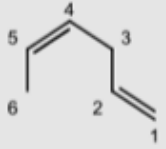


At the double bond between C-2 and C-3, the priority order is CH_3 > H and $CH_3CH{=}CH{-}$ > H. The two high-priority groups, CH_3 and $CH_3CH{=}CH{-}$, are *Z* or *zusammen*. The same is true at the double bond between C-4 and C-5.

b.

(*E*,*E*)-2,4-hexadiene

c.



(*Z*)-1,4-hexadiene; there is no stereochemistry at the double bond joining C-1 and C-2 because both substituents at C-1 are identical (=CH_2).

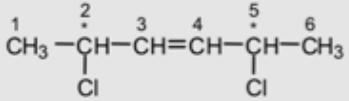
d.

There is no stereochemistry at either double bond. The IUPAC name is 1,5-hexadiene.

5.42 How many stereoisomers are possible for each of the following structures? Draw them, and name each by the *R*-*S* and *E*-*Z* conventions. (See Problem 5.41.)

a. 2,5-dichloro-3-hexene
b. 2-chloro-5-fluoro-3-hexene
c. 3-methyl-1,4-pentadiene
d. 3-methyl-1,4-heptadiene

5.42 a.



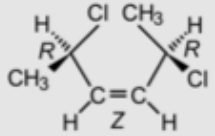
Compare with part b. In this case, both stereogenic centers are identical. Therefore, two *meso* forms are possible, and the total number of isomers is reduced to six:

R, *Z*, *R*
R, *Z*, *S* (meso)
R, *E*, *R*
R, *E*, *S* (*meso*)
S, *Z*, *S*
S, *E*, *S*

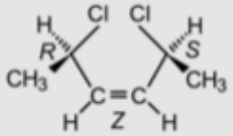
There are two sets of enantiomers:

R, *Z*, *R* and *S*, *Z*, *S*
R, *E*, *R* and *S*, *E*, *S*

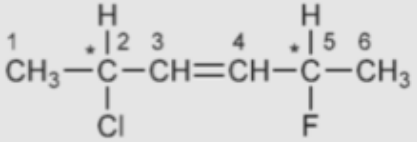
And there are two optically inactive, *meso* forms: *R*, *Z*, *S* and *R*, *E*, *S*. The *R*, *Z*, *R* isomer is shown below.



The other five structures can be derived from this one by interchanging groups. For example, the *R*, *Z*, *S meso* form is:



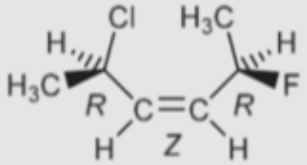
b.



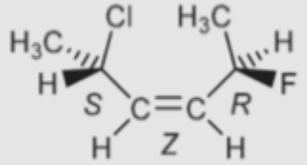
There are two stereogenic centers, marked with asterisks. Each can be either *R* or *S*. Also, the double bond joining C-3 and C-4 can be *E* or *Z*. Thus eight isomers are possible:

R, *Z*, *R*	*S*, *Z*, *R*
R, *Z*, *S*	*S*, *Z*, *S*
R, *E*, *R*	*S*, *E*, *R*
R, *E*, *S*	*S*, *E*, *S*

The first of these is shown below:

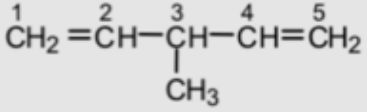


The other seven isomers can be drawn by interchanging one or more groups, using this structure as a guide. For example, the *S*, *Z*, *R* isomer is



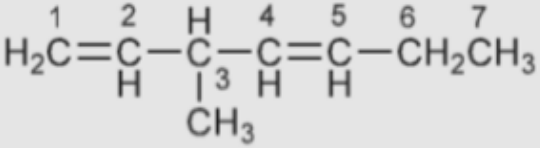
and so on.

c.

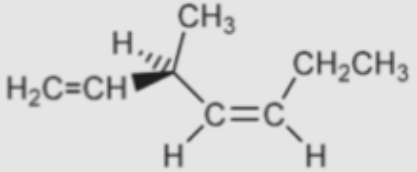


There are no stereogenic centers and no *cis–trans* possibilities at either double bond. Only one structure is possible.

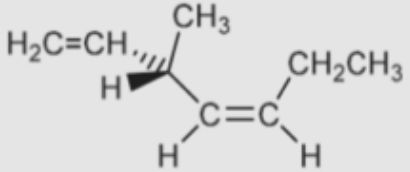
d.



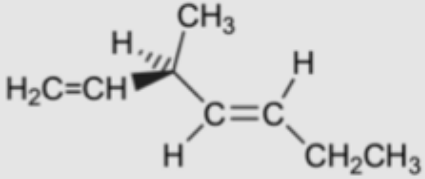
Carbon-3 is a stereogenic center, and *cis–trans* isomers are possible at the double bond between C-4 and C-5. Therefore, four structures are possible (*R* or *S* at C-3, and *E* or *Z* at the double bond).



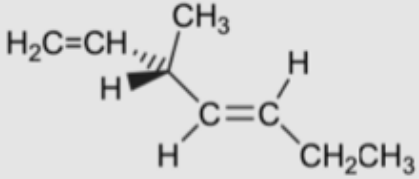
(*R*,*Z*)-3-methyl-1,4-heptadiene



(*S*,*Z*)-3-methyl-1,4-heptadiene



(*R*,*E*)-3-methyl-1,4-heptadiene



(*S*,*E*)-3-methyl-1,4-heptadiene

Chapter 6

6.13 Select an alkyl halide and a nucleophile that will give each of the following products:

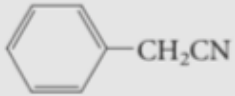
a. $CH_3OCH_2CH_2CH_2CH_3$

b. $HC{\equiv}CCH_2CH_2CH_3$

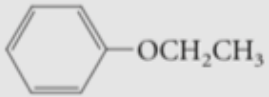
c. $CH_3CH_2CH_2NH_2$

d. $CH_3CH_2CH_2SCH_2CH_2CH_3$

e.



f.



6.13 Use the equations in Table 6.1 as a guide.

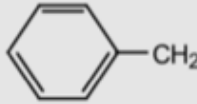
a. $CH_3CH_2CH_2CH_2Br + NaOCH_3$ (item 2)

b. $CH_3CH_2CH_2Br + HC{\equiv}C^- Na^+$ (item 15)

c. $CH_3CH_2CH_2Br + NH_3$ (item 6)

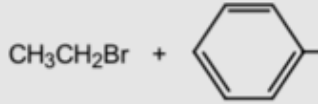
d. $CH_3CH_2CH_2Br + CH_3CH_2CH_2SNa$ (item 11)

e.



(item 14)

f.



(item 2)

6.14 Draw each of the following equations in a way that shows clearly the stereochemistry of the reactants and products.

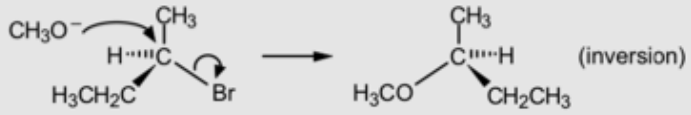
a. (*R*)-2-bromobutane + sodium methoxide (in methanol) $\xrightarrow{S_N2}$ 2-methoxybutane

b. (*S*)-3-bromo-3-methylhexane + methanol $\xrightarrow{S_N1}$ 3-methoxy-3-methylhexane

c. *cis*-1-bromo-4-methylcyclohexane + NaSH $\longrightarrow$ 4-methylcyclohexanethiol

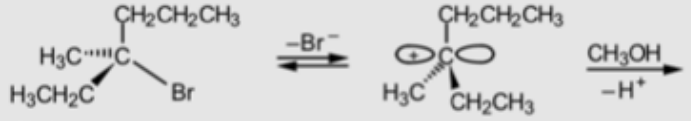
6.14 The configuration inverts if the reaction occurs by an S_N2 mechanism, but if the S_N1 mechanism prevails, considerable racemization occurs.

a. The nucleophile is methoxide ion, CH_3O^-. The alkyl halide is secondary, and the mechanism is S_N2.



(*R*)-2-bromobutane (*S*)-2-methoxybutane

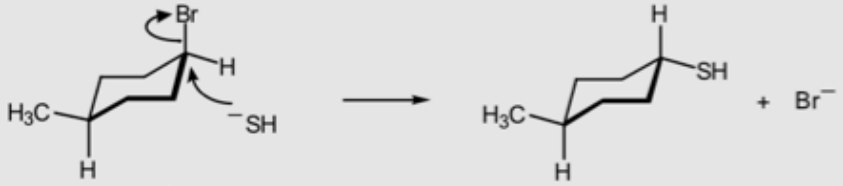
b. The alkyl halide is tertiary and the nucleophile is methanol (a weaker nucleophile than methoxide ion). The mechanism is S_N1, and the product is a mixture of *R* and *S* isomers.



(*S*)-3-bromo-3-methylhexane

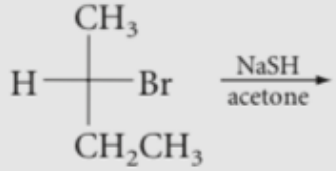
(*R*)-3-methoxy-3-methylhexane (*S*)-3-methoxy-3-methylhexane

c. The alkyl halide is secondary, and the HS^- ion is a strong nucleophile. The mechanism is S_N2.

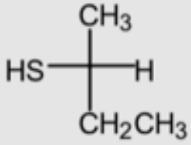


(*cis*) (*trans*)

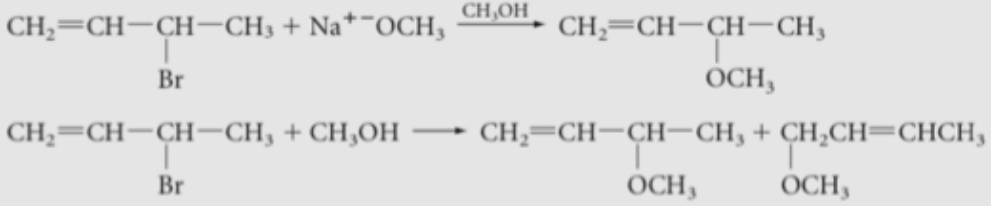
6.18 Draw a Fischer projection formula for the product of this S_N2 reaction:



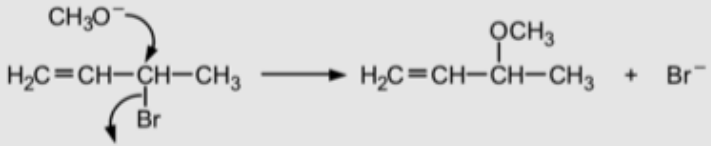
6.18 The reaction involves a good nucleophile and a polar solvent (acetone). These conditions favor an S_N2 mechanism with inversion of configuration.



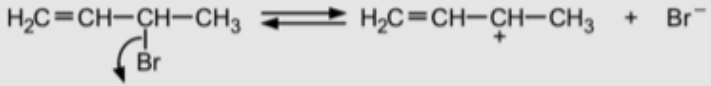
6.24 Explain the different products of the following two reactions by considering the mechanism by which each reaction proceeds. As part of your explanation, use the curved arrow formalism to draw a mechanism for each reaction.



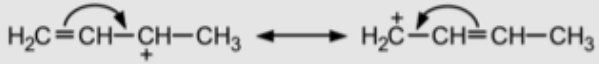
6.24 The first reaction involves a strong nucleophile (CH_3O^-), and the S_N2 mechanism is favored. Therefore, only one product is obtained.



The second reaction involves a weak nucleophile (CH_3OH) that is also a fairly polar solvent, favoring the S_N1 mechanism:



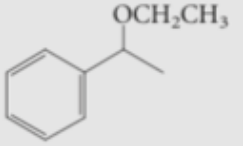
The carbocation is a resonance hybrid:



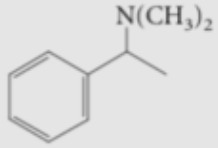
It can react with methanol at either positively charged carbon, giving the two observed products.

6.25 Provide equations for the synthesis of the following compounds from 1-bromo-1-phenylethane.

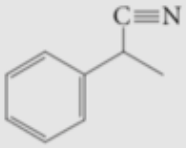
a.



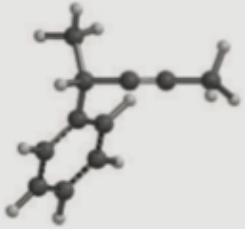
b.



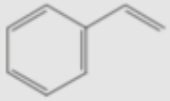
c.



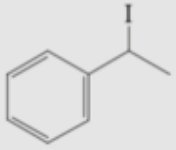
d.



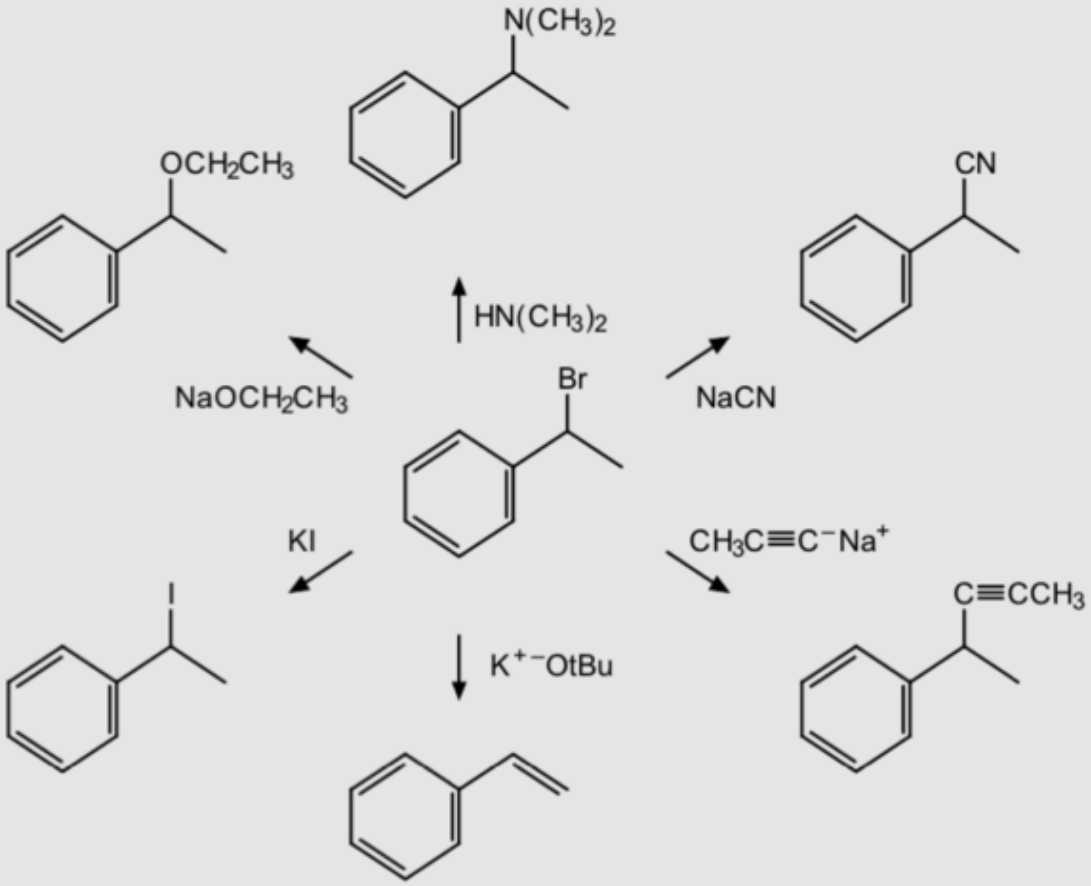
e.



f.



6.25


N(CH3)2
OCH2CH3
CN
HN(CH3)2
NaOCH2CH3
Br
NaCN
KI
CH3C≡C−Na+
C≡CCH3
K+ −OtBu

Chapter 7

7.27 Name each of the following alcohols:

a. $CH_3CH(Cl)CH(OH)CH_2CH_3$
b. $CH_3CH(OH)CH_2CH_3$
c. $(CH_3)_2C(Cl)CH(OH)CH_2CH_3$
d. $CH_3CH(Cl)CH_2CH(OH)CH_3$

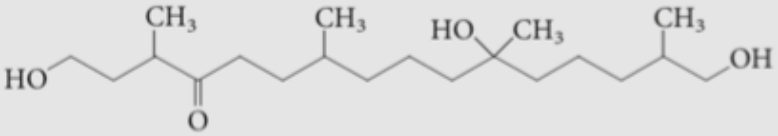
7.27
a. 2-chloro-3-pentanol
b. 2-butanol
c. 2-chloro-2-methyl-3-pentanol
d. 4-chloro-2-pentanol; the alcohol gets a lower number than the chloro group

7.29 Explain why each of the following names is unsatisfactory, and give a correct name:

a. 2-ethyl-1-propanol
b. 2,2-dimethyl-3-butanol
c. 1-propene-3-ol
d. 2-chloro-4-pentanol
e. 3,6-dibromophenol

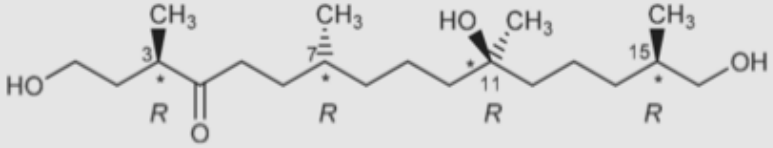
7.29
a. 2-Methyl-1-butanol; the longest chain was not selected.
b. 3,3-Dimethyl-2-butanol; the hydroxyl should get the lower number.
c. 2-Propen-1-ol (or allyl alcohol); the hydroxyl group should get the lower number.
d. 4-Chloro-2-pentanol; the hydroxyl group should get the lower number.
e. 2,5-Dibromophenol; give substituents the lowest possible numbers.

7.30 Members of the fungus-like genus *Phytophthora* are responsible for many crop diseases that threaten plants around the world. Sexual reproduction for this genus is modulated by a mating hormone, shown below:



a. How many stereogenic centers are present in this compound?
b. Draw structures for the unique stereoisomers of this hormone and provide the name of each structure.

7.30 There are 4 stereogenic centers are position 3, 7, 11 and 15. The (3*R*,7*R*,11*R*,15*R*) isomer is:



There are 16 stereoisomers for all combinations of *R* and *S* at the 4 positions. The base name of the compound is 3,7,11,15-tetramethyl-4-oxo-1,11,16-hexadecanetriol.

7.34 Arrange the compounds in each of the following groups in order of increasing solubility in water, and briefly explain your answers:

a. 1-octanol; ethanol; ethyl chloride
b. $HOCH_2(CHOH)_3CH_2OH$; 1,5-pentanediol; 1-pentanol

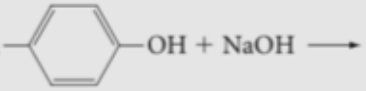
7.34 a. Ethyl chloride < 1-octanol < ethanol. Both alcohols can hydrogen bond with water and will be more soluble than the alkyl chloride. The lower molecular weight alcohol will be more soluble (it has a shorter hydrophobic carbon chain).

b. 1-Pentanol < 1,5-pentanediol < 1,2,3,4,5-pentanepentol. All three compounds have the same number of carbon atoms. Water solubility will therefore increase with increasing numbers of hydroxyl groups (that is, as the ratio of hydroxyl groups to carbon atoms increases).

7.38 Complete each of the following equations:

a. $CH_3CH(OH)CH_2CH_3 + K \longrightarrow$

b. $(CH_3)_2CHOH + NaH \longrightarrow$

c.  $+ NaOH \longrightarrow$

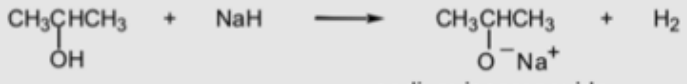
d.  $+ NaOH \longrightarrow$

e. $CH_3CH{=}CHCH_2SH + NaOH \longrightarrow$

7.38 a. Use eq. 7.12 as a guide.

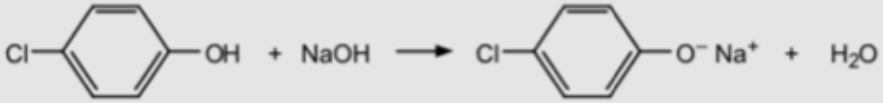
potassium 2-butoxide

b. Use eq. 7.13 as a guide.



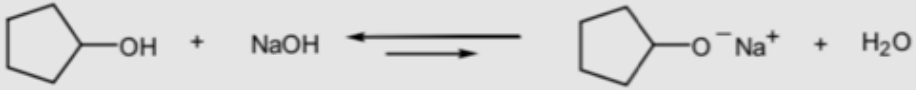
sodium isopropoxide
(or 2-propoxide)

c. Use eq. 7.15 as a guide.



sodium *p*-chlorophenoxide

d. Use eq. 7.14 as a guide. The equilibrium lies on the side of the weakest acid (cyclopentanol) and weakest base (sodium hydroxide).



e. Use eq. 7.48 as a guide. The equilibrium lies on the side of the weakest acid (the alcohol) and the weakest base (the thiolate salt).

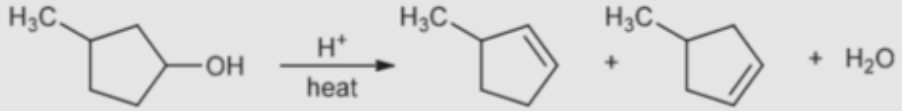
$$CH_3CH{=}CHCH_2SH + NaOH \longrightarrow CH_3CH{=}CHCH_2S^-Na^+ + H_2O$$

7.40 Show the structures of all possible acid-catalyzed dehydration products of the following. If more than one alkene is possible, predict which one will be formed in the largest amount.

a. 3-methylcyclopentanol
b. 1-methylcyclopentanol
c. 2-phenylethanol
d. 2-hexanol

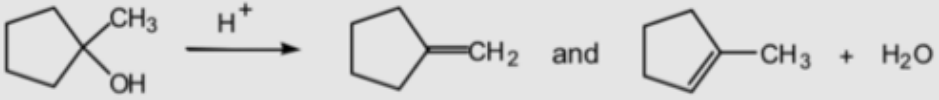
7.40 If you have any difficulty with this problem, review Sec. 7.8.

a.



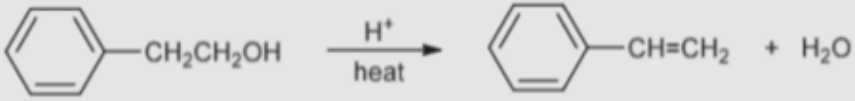
Both disubstituted alkenes will be formed in equal amounts.

b.

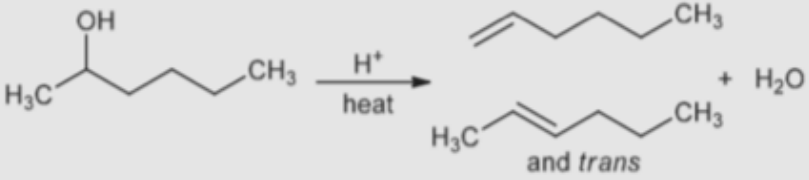


The major product is 1-methylcyclopentene as it is the more substituted (more stable) double bond.

c.



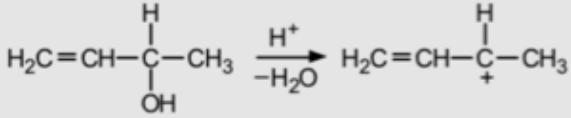
d.



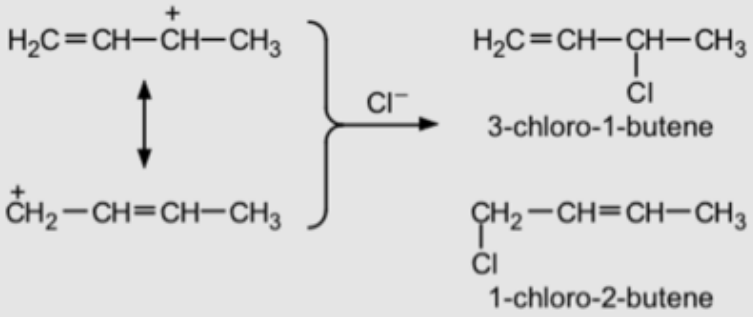
Of the three possible alkenes, the *cis* and *trans*-2-hexenes are the most stable and will predominate.

7.47 Treatment of 3-buten-2-ol with concentrated hydrochloric acid gives a mixture of two products, 3-chloro-1-butene and 1-chloro-2-butene. Write a reaction mechanism that explains how both products are formed.

7.47 The mechanism involves protonation of the hydroxyl group and loss of water to form a carbocation:



The carbocation is allylic and stabilized by resonance. This allylic ion can react with the nucleophile Cl^- at either end, giving the observed products:



7.48 Write an equation for each of the following reactions:

a. 2-methyl-2-butanol + HCl
b. 3-pentanol + Na
c. cyclohexanol + PBr_3
d. 2-phenylethanol + $SOCl_2$
e. 1-methylcyclopentanol + H_2SO_4, heat
f. ethylene glycol + $HONO_2$
g. 1-octanol + HBr + $ZnBr_2$
h. 1-pentanol + aqueous NaOH
i. 1-pentanol + CrO_3, H^+
j. 2-cyclohexylethanol + PCC

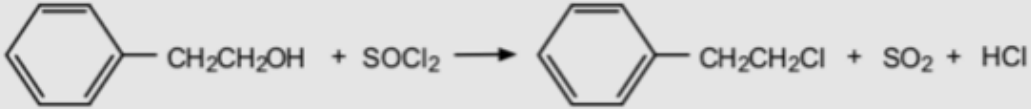
7.48 a.

b. $2\ CH_3(CH_2)_3CH_2OH + 2\ Na \longrightarrow 2\ CH_3(CH_2)_3CH_2O^-Na^+ + H_2$

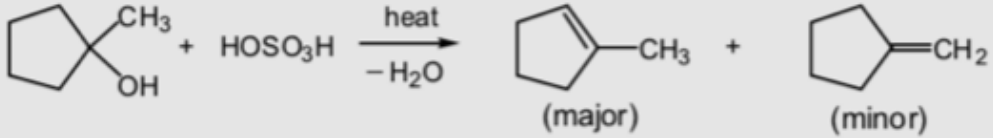
sodium pentoxide

c.

d.



e.



(major) (minor)

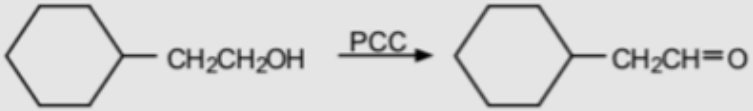
f. $HO{-}CH_2CH_2{-}OH + 2\ HONO_2 \longrightarrow O_2NO{-}CH_2CH_2{-}ONO_2 + 2\ H_2O$

g. $CH_3(CH_2)_6CH_2OH + HBr \xrightarrow{ZnBr_2} CH_3(CH_2)_6CH_2Br + H_2O$

h. $CH_3CH_2CH_2CH_2CH_2OH + NaOH \longrightarrow$ no reaction

i. $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[H^+]{CrO_3} CH_3CH_2CH_2CH_2CO_2H$

j.

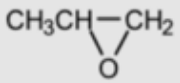


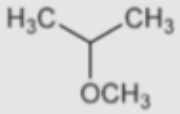
Chapter 8

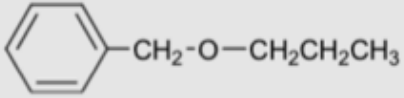
8.16 Write a structural formula for each of the following compounds:

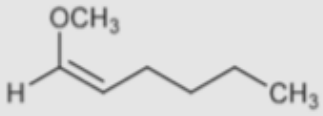
a. diethyl ether
b. propylene oxide
c. 2-methoxypropane
d. benzyl propyl ether
e. 1-methoxyhexene
f. *m*-chlorophenyl ethyl ether
g. *trans*-2-ethoxycyclohexanol
h. ethyl isopropyl ether
i. propylene glycol
j. *p*-isopropoxyanisole

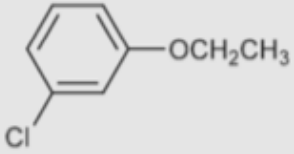
8.16 a. $CH_3CH_2–O–CH_2CH_3$

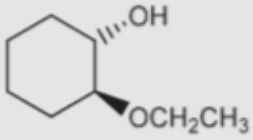
b. 

c. 

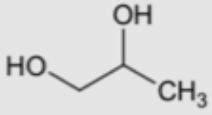
d. 

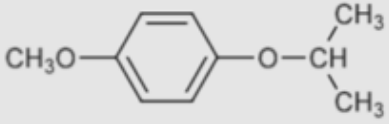
e. 

f. 

g. 

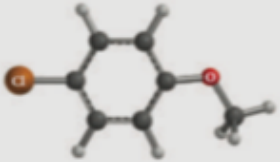
h. $CH_3CH_2–O–CH(CH_3)_2$

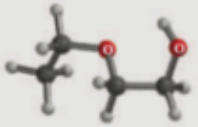
i. 

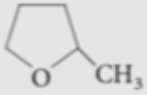
j. 

8.17 Name each of the following compounds:

a. $CH_3CH_2CH_2OCH_2CH(CH_3)_2$ **b.** $CH_3OCH_2CH(CH_3)_2$ **c.** $CH_3CH{-}CH_2$ (O)

d. 

e. $CH_3CH_2CH(OCH_3)CH_2CH_2CH_2OH$ **f.** 

g. 

h. $CH_3OCH_2CH_2C{\equiv}CH$

8.17 a. isobutyl propyl ether b. isobutyl methyl ether
c. propylene oxide (or methyloxirane)
d. *p*-chloroanisole (or *p*-chlorophenyl methyl ether)
e. 4-methoxyhexanol f. 2-ethoxyethanol
g. 2-methyltetrahydrofuran h. 4-methoxy-1-butyne

8.21 Write equations for the reaction of each of the following with (1) Mg in ether followed by (2) addition of D_2O to the resulting solution:

a. $CH_3CH_2CH_2CH_2I$ **b.** $CH_3CH_2OCH_2CH_2Br$
c. $C_6H_5CH_2Br$ **d.** allyl bromide

8.21 a.

$$CH_3CH_2CH_2CH_2I \xrightarrow[Et_2O]{Mg} CH_3CH_2CH_2CH_2MgI \xrightarrow{D_2O} CH_3CH_2CH_2CH_2D$$

b.

$$CH_3CH_2OCH_2CH_2CH_2Br \xrightarrow[ether]{Mg} CH_3CH_2OCH_2CH_2CH_2MgBr \xrightarrow{D_2O} CH_3CH_2OCH_2CH_2CH_2D$$

c.

$$C_6H_5CH_2Br \xrightarrow[Et_2O]{Mg} C_6H_5CH_2MgBr \xrightarrow{D_2O} C_6H_5CH_2D$$

d.

$$H_2C{=}CHCH_2Br \xrightarrow[Et_2O]{Mg} H_2C{=}CHCH_2MgBr \xrightarrow{D_2O} H_2C{=}CHCH_2D$$

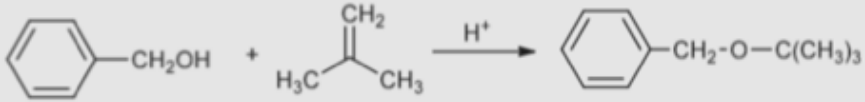
Note that the ether functional group can be tolerated in making a Grignard reagent (part b).

8.25 Provide *two* synthetic routes to prepare $C_6H_5CH_2OC(CH_3)_3$, starting from $C_6H_5CH_2OH$ in one case and $HOC(CH_3)_3$ for the other. What general mechanistic pathway (S_N1, S_N2, etc.) is being used for each of your two proposed synthetic routes?

8.25 The product (benzyl *t*-butyl ether) is primary on the benzyl side and tertiary on the *t*-butyl side. So, an S_N2 type displacement by potassium *t*-butoxide of benzyl bromide is one approach, and an acid-catalyzed (S_N1) process of benzyl alcohol with isobutylene (2-methylpropene) is another method:

$$(CH_3)_3COH + 2K \longrightarrow (CH_3)_3CO^- K^+ + H_2$$

and



8.27 Write an equation for each of the following reactions. If no reaction occurs, say so.

a. methyl propyl ether + excess HBr (hot) $\longrightarrow$

b. dibutyl ether + boiling aqueous NaOH $\longrightarrow$

c. ethyl ether + cold concentrated H_2SO_4 $\longrightarrow$

d. dipropyl ether + Na $\longrightarrow$

e. ethyl phenyl ether $\xrightarrow[2.\ H_2O]{1.\ BBr_3}$

8.27 a. $CH_3OCH_2CH_2CH_3 + 2HBr \longrightarrow CH_3Br + CH_3CH_2CH_2Br + H_2O$

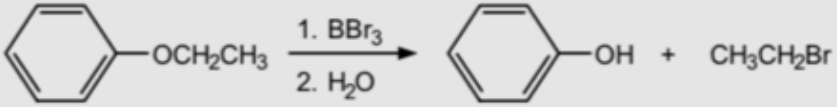
b. No reaction; ethers (except for epoxides) are inert toward base.

c. $CH_3CH_2-\ddot{\underset{\cdot\cdot}{O}}-CH_2CH_3 + H_2SO_4 \longrightarrow$

$$CH_3CH_2-\overset{H}{\overset{|}{\overset{+}{\ddot{O}}}}-CH_2CH_3 + HSO_4^-$$

The ether acts as a base and dissolves in the strong acid.

d. No reaction; ethers can be distinguished from alcohols by their inertness toward sodium metal.

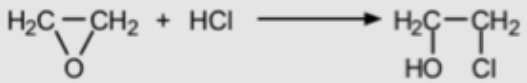
e. 

Compare with eq. 8.15.

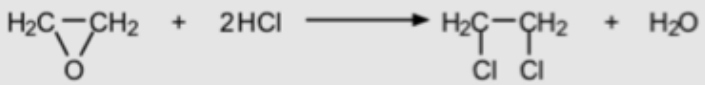
8.31 Write an equation for the reaction of ethylene oxide with

a. 1 mole of HCl
b. excess HCl
c. phenol + H^+
d. phenylmagnesium bromide

8.31 a.

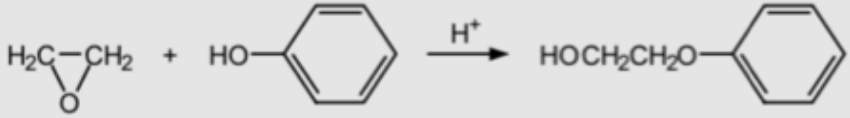


b.



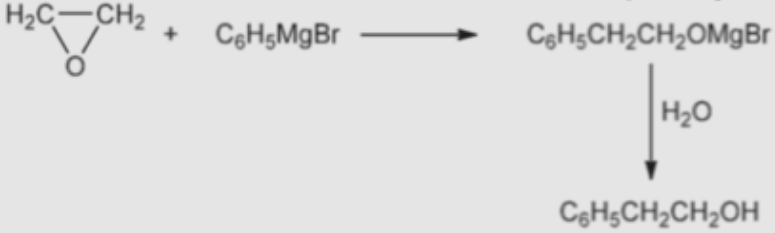
The 2-chloroethanol formed in part a reacts as an alcohol with the second mole of HCl to produce the dichloride.

c.



2-phenoxyethanol

d.

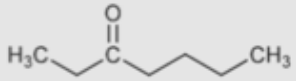


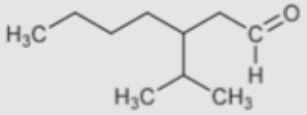
Chapter 9

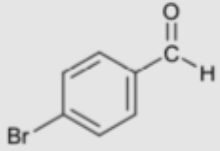
9.31 Write a structural formula for each of the following:

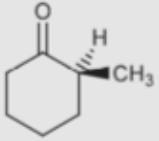
a. 3-heptanone
b. 3-isopropylheptanal
c. *p*-bromobenzaldehyde
d. (*S*)-2-methylcyclohexanone
e. 3-hexenal
f. benzyl *p*-methylphenyl ketone
g. 2,2-dichlorohexanal
h. 4-phenyl-2-butanone
i. cyclobutanone
j. *p*-tolualdehyde

9.31

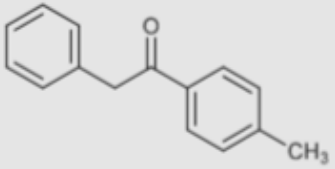
a. 

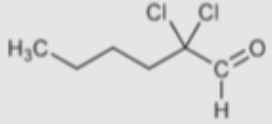
b. 

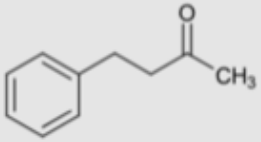
c. 

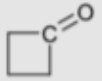
d. 

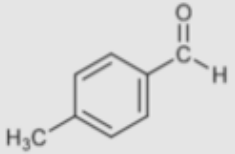
e. $CH_3CH_2CH{=}CHCH_2CHO$

f. 

g. 

h. 

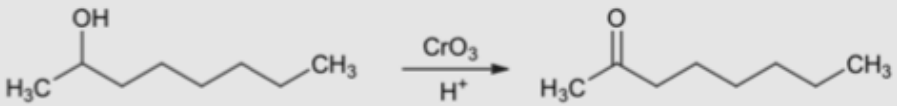
i. 

j. 

9.34 Write an equation for the synthesis of 2-octanone by

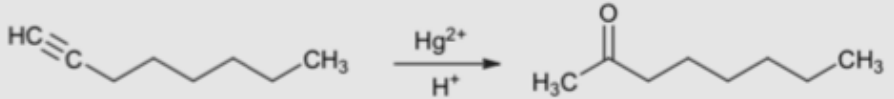
a. oxidation of an alcohol **b.** hydration of an alkyne

9.34 a.



(see eq. 7.36)

b.



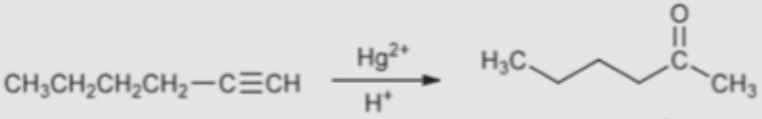
(see eq. 3.52)

9.37 Using 1-hexyne as a starting reagent, suggest a synthesis of

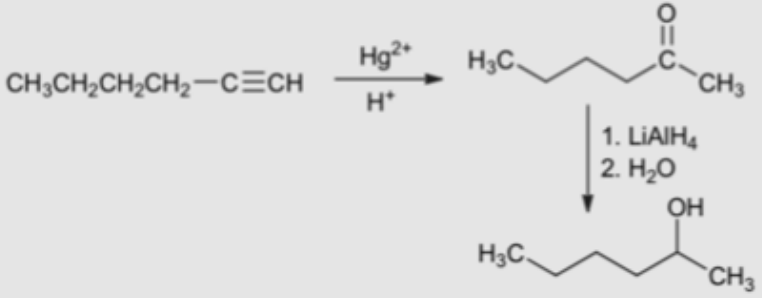
a. 2-hexanone **b.** 2-hexyl alcohol

c. a mixture of 1-hexene and 2-hexene **d.** 1-hexene (and without 2-hexene present)

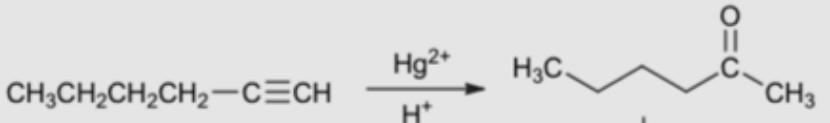
9.37 a.

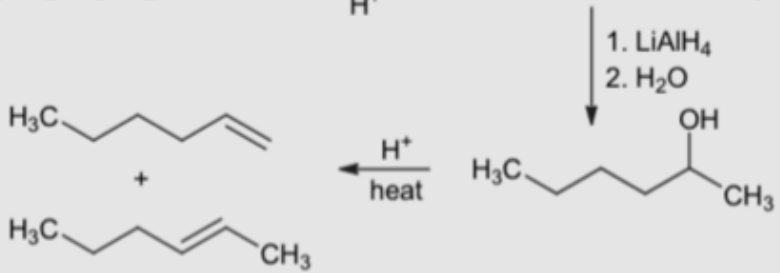


b.

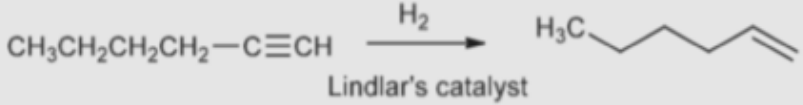


c.

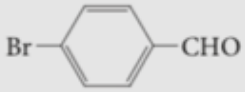




d.



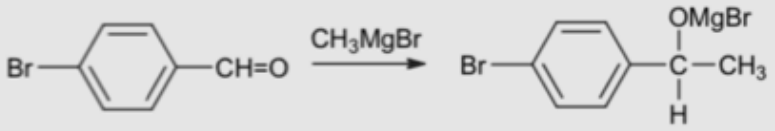
9.38 Write an equation for the reaction, if any, of *p*-bromobenzaldehyde with each of the following reagents, and name the organic product.

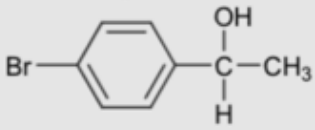


p-bromobenzaldehyde

a. methylmagnesium bromide, then H_3O^+
b. methylamine (CH_3NH_2)
c. ethylene glycol, H^+
d. phenylhydrazine
e. HCN (catalytic NaOH)
f. Tollens' reagent

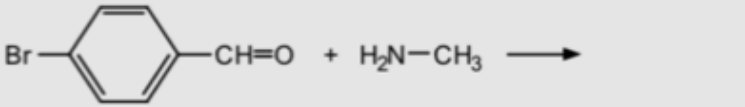
9.38 a.

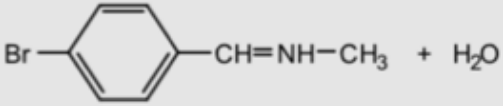




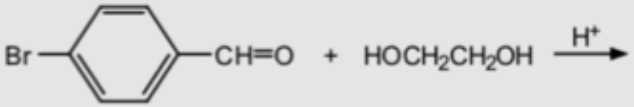
1-(*p*-bromophenyl)-1-ethanol

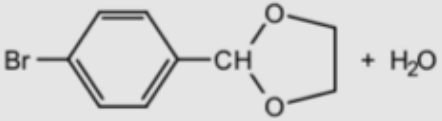
b.





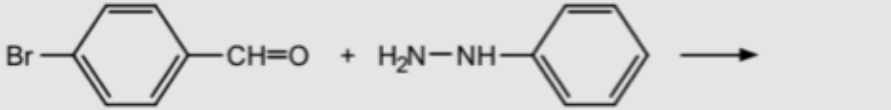
c.

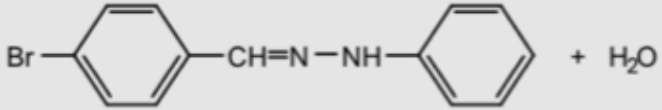




2-*p*-bromophenyl-1,3-dioxolane
(*p*-bromobenzaldehyde ethylene glycol acetal)

d.



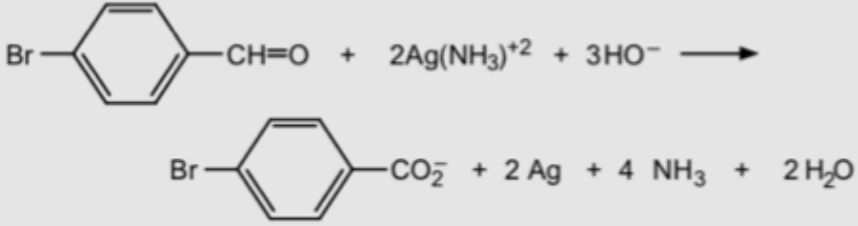


p-bromobenzaldehyde phenylhydrazone

e.

p-bromobenzaldehyde cyanohydrin

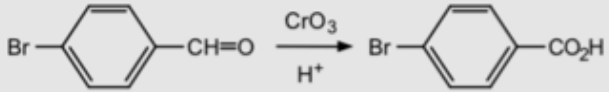
f.



p-bromobenzoate ion

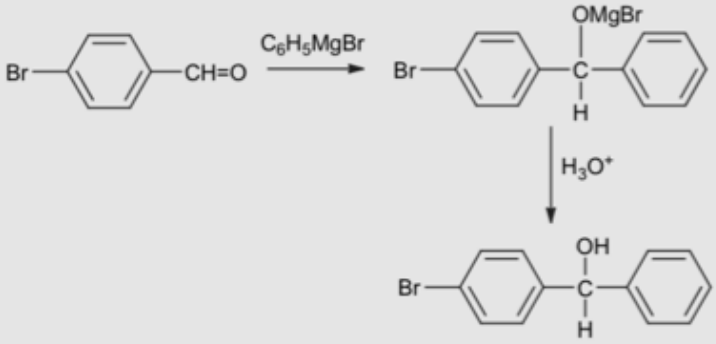
g. CrO_3, H^+
h. phenylmagnesium bromide, then H_3O^+
i. excess methanol, dry HCl
j. hydroxylamine
k. sodium borohydride

g.



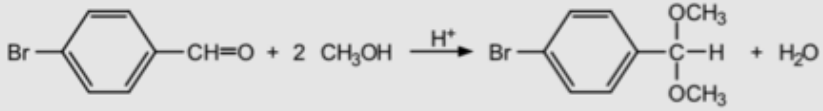
p-bromobenzoic acid

h.



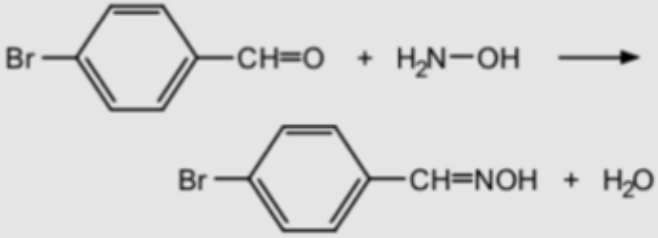
1-(*p*-bromophenyl)-1-(phenyl)-1-methanol

i.



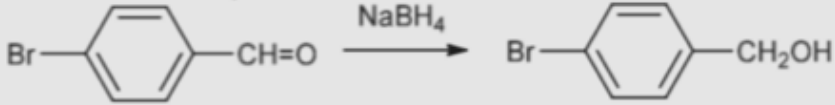
p -bromobenzaldehyde dimethylacetal

j.



p-bromobenzaldoxime

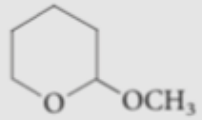
k.

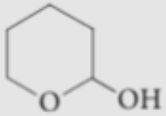


9.41 Complete each of the following equations:

a. butanal + excess methanol, $H^+ \longrightarrow$

b. $CH_3CH(OCH_3)_2 + H_2O, H^+ \longrightarrow$

c.  $+ H_2O, H^+ \longrightarrow$

d.  + excess $CH_3CH_2OH, H^+ \longrightarrow$

9.41 All parts of this problem involve the preparation or hydrolysis of hemiacetals or acetals (or the corresponding ketone derivatives). See Sec. 9.7.

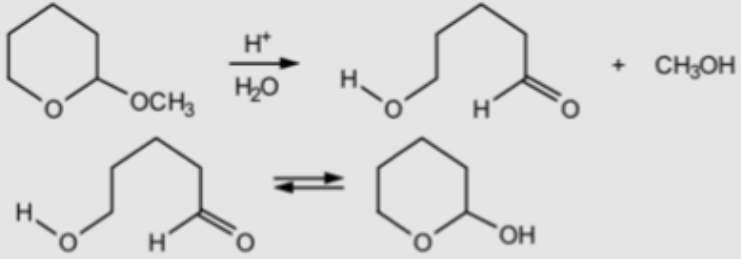
a.

$$CH_3CH_2CH_2CH{=}O + 2\ CH_3OH \xrightarrow{H^+} CH_3CH_2CH_2CH(OCH_3)_2 + H_2O$$

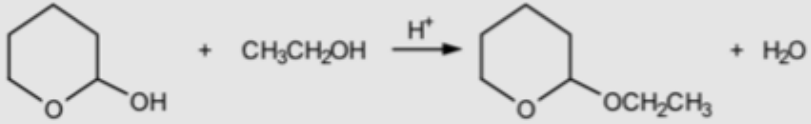
b.

$$CH_3CH(OCH_3)_2 \xrightarrow[H_2O]{H^+} CH_3CH{=}O + 2\ CH_3OH$$

c. In this case, the acetal is cyclic, and the product is a hydroxy aldehyde, which may exist in its cyclic hemiacetal form.



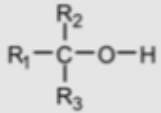
d. In this reaction, a hemiacetal is converted to an acetal.



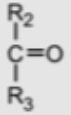
9.45 Using a Grignard reagent and the appropriate aldehyde or ketone, show how each of the following can be prepared:

a. methylcyclohexanol
b. 3-octanol
c. 2-methyl-2-pentanol
d. 1-cyclopentylcyclopentanol
e. 1-phenyl-1-propanol
f. 3-butene-2-ol

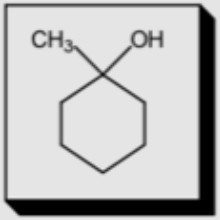
9.45 In each case, write the structure of the alcohol:

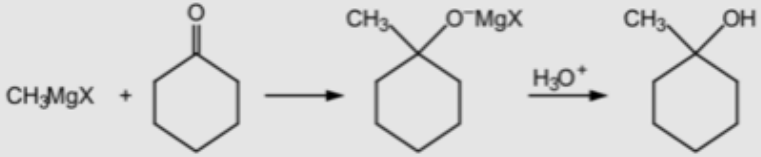


One of the R groups comes from the Grignard reagent. The rest of the molecule comes from the carbonyl compound. For example, If we select R_1 as the alkyl group to come from the Grignard reagent, then the carbonyl compound is:

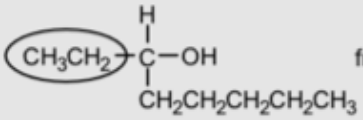


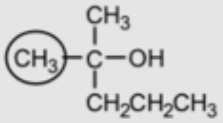
a.



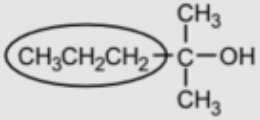


For the remaining cases, we will not write the equations, but simply show how the initial reactants are derived.

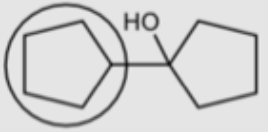
b.  from CH_3CH_2MgX + $CH_3CH_2CH_2CH_2CH_2CH{=}O$

c.  from CH_3MgX + $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH_3$

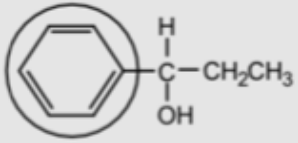
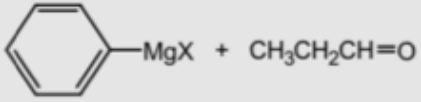
or

 from $CH_3CH_2CH_2MgX$ + $CH_3\overset{\overset{O}{\|}}{C}CH_3$

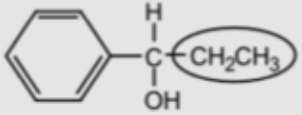
Either of these combinations of reagents will work.

d.  from 

In this case, the "free-standing" R group is selected to come from the Grignard reagent.

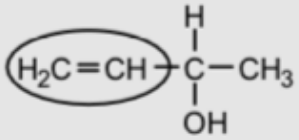
e.  from 

or

 from CH_3CH_2MgX + $O{=}CH$ 

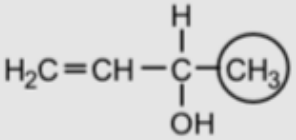
Either of these combinations of reagents will work.

f.



from $H_2C{=}CHMgX$ + $CH_3CH{=}O$

or

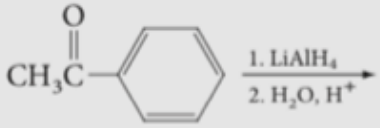


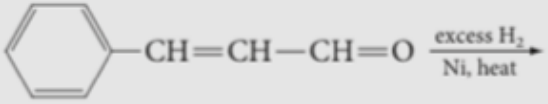
from CH_3MgX + $H_2C{=}CH{-}CH{=}O$

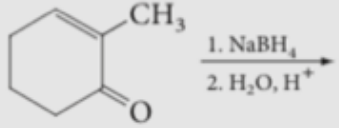
Either of these combinations of reagents will work.

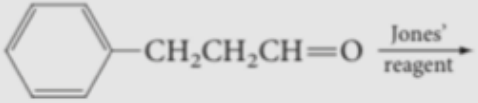
Vinyl Grignard reagents are known, although they are a bit more difficult to prepare than simple alkyl Grignard reagents. Either pair of reagents will work.

9.48 Give the structure of each product.

a. 

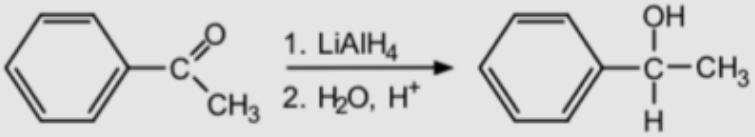
b. 

c. 

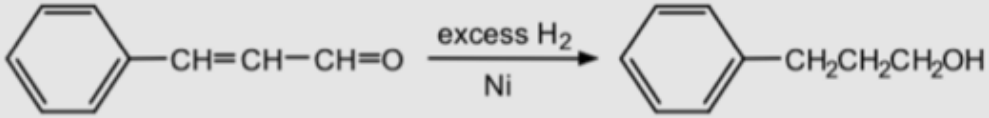
d. 

e. 

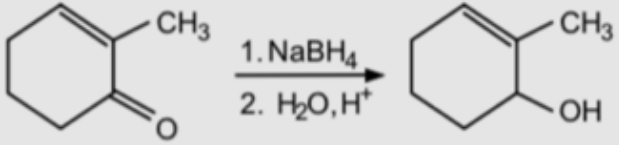
9.48 a. See Sec. 9.12.



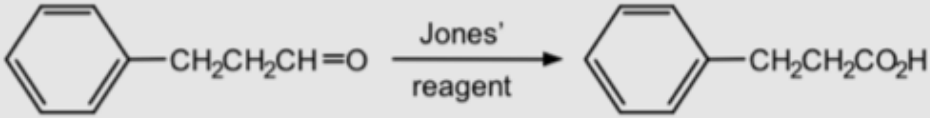
b. See Sec. 9.12. Usually the aromatic ring will not be reduced, although under certain reaction conditions even this is possible.



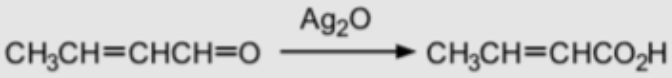
c. The carbonyl group is reduced, but the carbon–carbon double bond is not reduced.



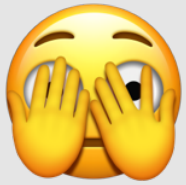
d. The carbonyl group is oxidized, but the aromatic ring is not.



e. The carbonyl group is oxidized, while the carbon–carbon double bond is not.



Chapter 10

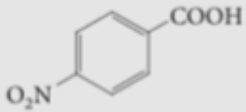
والاخييرر 

10.38 Name each of the following acids:

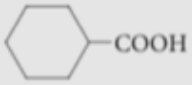
a. $(CH_3)_2C(Br)CH_2CH_2COOH$

b. $CH_3CH(OCH_3)CH(CH_3)COOH$

c.

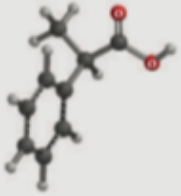


d.



e. $CH_2{=}CHCOOH$

f.



g. CH_3CF_2COOH

h. $HC{\equiv}CCH_2CO_2H$

10.38

a. 4-bromo-4-methylpentanoic acid
c. *p*-nitrobenzoic acid
e. propenoic acid (or acrylic acid)
g. 2,2-difluoropropanoic acid

b. 3-methoxy-2-methylbutanoic acid
d. cyclohexanecarboxylic acid
f. 2-phenylpropanoic acid
h. 3-butynoic acid

10.39 Which will have the higher boiling point? Explain your reasoning.

a. CH_3CH_2COOH or $CH_3CH_2CH_2CH_2OH$

b. $CH_3CH_2CH_2CH_2COOH$ or $(CH_3)_3CCOOH$

10.39 a. The molecular weights are identical (74), but acids hydrogen-bond more effectively than alcohols do.

$$CH_3CH_2CO_2H > CH_3CH_2CH_2CH_2OH$$

bp 141°C bp 118°C

b. Chain branching generally lowers the boiling point. Thus, for these isomeric acids, the order is:

$$CH_3CH_2CH_2CH_2CO_2H > (CH_3)_3CCO_2H$$

bp 187°C bp 164°C

10.40 In each of the following pairs of acids, which would be expected to be the stronger acid, and why?

a. $ClCH_2CO_2H$ and $BrCH_2CO_2H$

b. *o*-$BrC_6H_4CO_2H$ and *m*-$BrC_6H_4CO_2H$

c. Cl_3CCO_2H and F_3CCO_2H

d. $C_6H_5CO_2H$ and *p*-$CH_3OC_6H_4CO_2H$

e. $ClCH_2CH_2CO_2H$ and $CH_3CHClCO_2H$

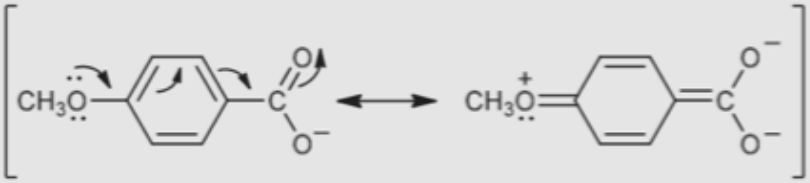
10.40 The factors that affect acidity of carboxylic acids are discussed in Sec. 10.5.

a. $ClCH_2CO_2H$; both substituents, chlorine and bromine, are approximately the same distance from the carboxyl group, but chlorine is more electronegative than bromine.

b. *o*-Bromobenzoic acid; the bromine is closer to the carboxyl group and is an electron-withdrawing substituent. Compare the pK_as of the corresponding chloro acids, given in Table 10.4.

c. CF_3CO_2H; fluorine is more electronegative than chlorine.

d. Benzoic acid; the methoxy group is an electron-releasing substituent when in the *para* position and may destabilize the anion because of the presence of resonance structures such as



which bring two negative charges near one another.

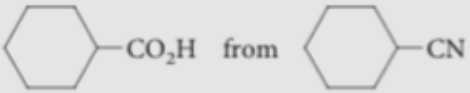
e. $CH_3CHClCO_2H$; the chlorine, which is electron-withdrawing, is closer to the carboxyl group.

10.42 Give equations for the synthesis of

a. $CH_3CH_2CH_2CO_2H$ from $CH_3CH_2CH_2CH_2OH$

b. $CH_3CH_2CH_2CO_2H$ from $CH_3CH_2CH_2OH$ (two ways)

c.  from

d. 

e. $CH_3OCH_2CO_2H$ from (two steps)

f. 

10.42 a.

$$CH_3CH_2CH_2CH_2OH \xrightarrow{Na_2Cr_2O_7} CH_3CH_2CH_2CO_2H$$

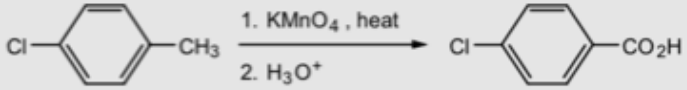
b.

$$CH_3CH_2CH_2OH \xrightarrow{HBr} CH_3CH_2CH_2Br$$

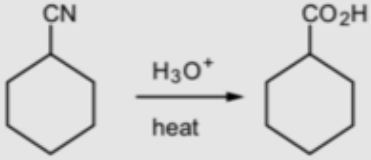
$$CH_3CH_2CH_2Br \xrightarrow{NaCN} CH_3CH_2CH_2CN \xrightarrow[\text{heat}]{H_3O^+} CH_3CH_2CH_2CO_2H$$

$$CH_3CH_2CH_2Br \xrightarrow[\text{ether}]{Mg} CH_3CH_2CH_2MgBr \xrightarrow[2.\ H_2O,\ H^+]{1.\ CO_2} CH_3CH_2CH_2CO_2H$$

c.



d.



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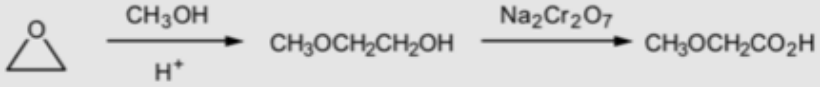

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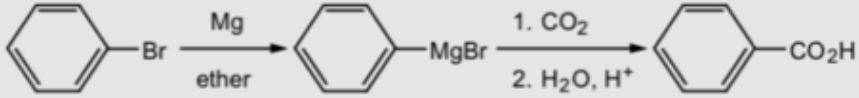
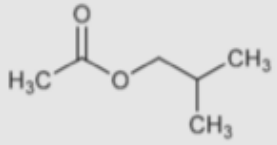


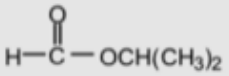
10.44 Write a structure for each of the following compounds:

a. isobutyl acetate
b. isopropyl formate
c. sodium 2-chlorobutanoate
d. calcium acetate
e. phenyl benzoate
f. *o*-toluamide
g. 2-methoxybutanoyl chloride
h. benzonitrile
i. propanoic anhydride
j. 2-acetylcyclohexanecarboxylic acid
k. α-methyl-γ-butyrolactone

10.44 a.



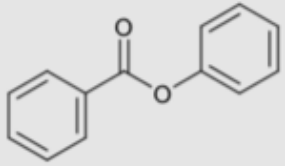
b.



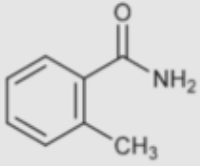
c. $CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCO_2^-Na^+$

d. $(CH_3CO_2^-)_2Ca^{+2}$

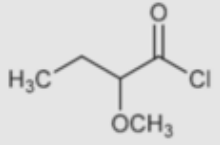
e.



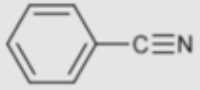
f.



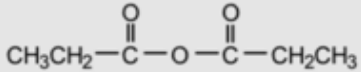
g.



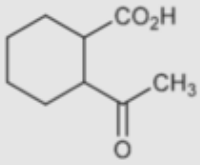
h.



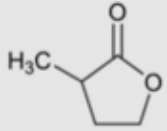
i.



j.

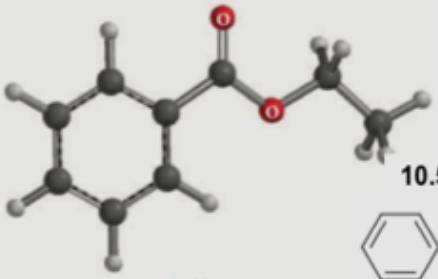


k.



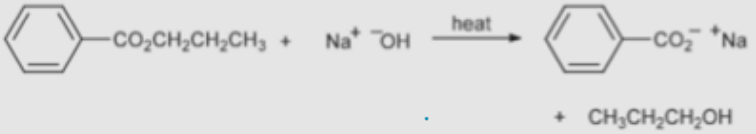
10.51 Write an equation for the reaction of propyl benzoate with

a. hot aqueous sodium hydroxide
b. ammonia (heat)
c. phenylmagnesium iodide (two equivalents), then H_3O^+
d. lithium aluminum hydride (two equivalents), then H_3O^+

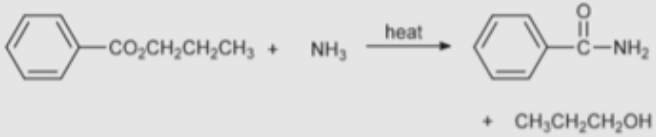


ethyl benzoate

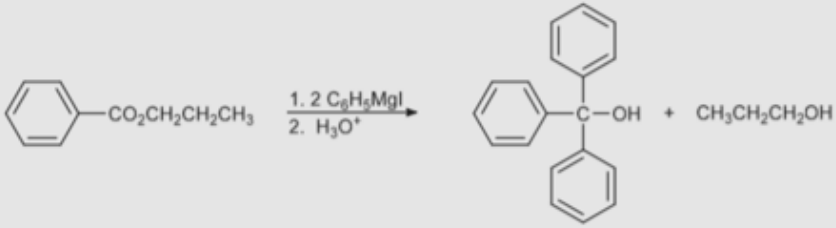
10.51 a. See eq. 10.22, where R = phenyl and R' = propyl.



b. Compare with eq. 10.25.



c. See Sec. 10.15.



d. See Sec. 10.16.