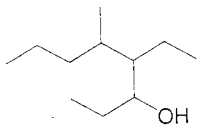
Problems

Nomenclature

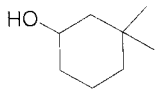
9.38 Give the IUPAC name for each alcohol.

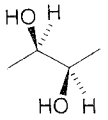
a. $(CH_3)_2CHCH_2CH_2CH_2OH$

b. $(CH_3)_2CHCH_2CH(CH_2CH_3)CH(OH)CH_2CH_3$

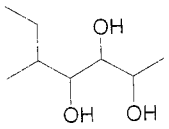
c. 

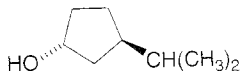
d. 

e. 

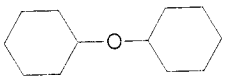
f. 

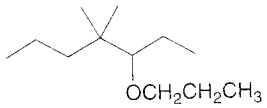
[Also label the stereogenic centers as *R* or *S*.]

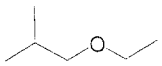
g. 

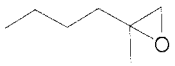
h. 

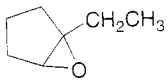
9.39 Name each ether and epoxide.

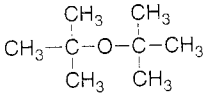
a. 

b. 

c. 

d. 

e. 

f. 

9.40 Give the structure corresponding to each name.

a. 4-ethyl-3-heptanol
b. *trans*-2-methylcyclohexanol
c. 2,3,3-trimethyl-2-butanol
d. 6-*sec*-butyl-7,7-diethyl-4-decanol
e. 3-chloro-1,2-propanediol
f. diisobutyl ether
g. 1,2-epoxy-1,3,3-trimethylcyclohexane
h. 1-ethoxy-3-ethylheptane

9.41 Draw the eight constitutional isomers with molecular formula $C_5H_{12}O$ that contain an OH group. Give the IUPAC name for each compound.

Physical Properties

9.42 Rank each group of compounds in order of:

a. increasing boiling point: $CH_3CH_2CH_2OH$, $(CH_3)_2CHOH$, $CH_3CH_2OCH_3$
b. increasing water solubility: $CH_3(CH_2)_5OH$, $HO(CH_2)_6OH$, $CH_3(CH_2)_4CH_3$

Alcohols

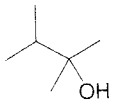
9.43 Draw the organic product(s) formed when $CH_3CH_2CH_2OH$ is treated with each reagent.

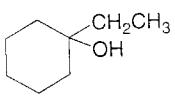
a. H_2SO_4
b. NaH
c. $HCl + ZnCl_2$
d. HBr
e. $SOCl_2$, pyridine
f. PBr_3
g. TsCl, pyridine
h. [1] NaH; [2] CH_3CH_2Br
i. [1] TsCl, pyridine; [2] NaSH

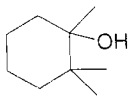
9.44 Draw the organic product(s) formed when 1-methylcyclohexanol is treated with each reagent. In some cases no reaction occurs.

a. NaH
b. NaCl
c. HBr
d. HCl
e. H_2SO_4
f. $NaHCO_3$
g. [1] NaH; [2] CH_3CH_2Br
h. $POCl_3$, pyridine

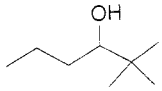
9.45 What alkenes are formed when each alcohol is dehydrated with TsOH? Label the major product when a mixture results.

a. 

b. 

c. 

d. $CH_3CH_2CH_2CH_2OH$

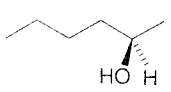
e. 

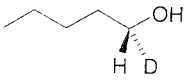
9.46 What three alkenes are formed when $CH_3CH_2CH_2CH(OH)CH_3$ is treated with H_2SO_4? Label the major product.

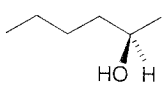
9.47 Draw the products formed when $CH_3CH_2CH_2CH_2OTs$ is treated with each reagent.

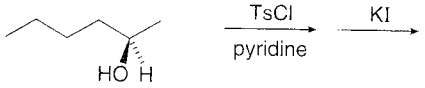
a. CH_3SH
b. $NaOCH_2CH_3$
c. NaOH
d. $KOC(CH_3)_3$

9.48 Draw the products of each reaction and indicate stereochemistry around stereogenic centers.

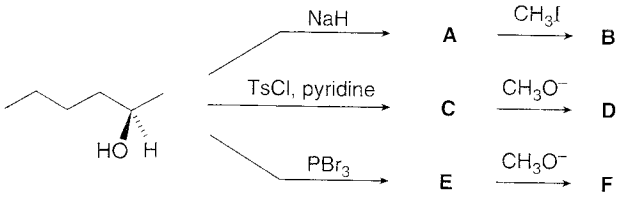
a. 

b. 

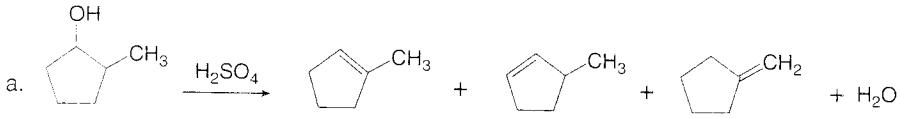
c. 

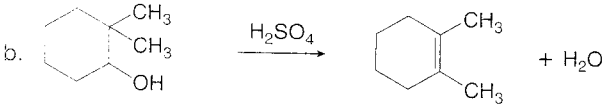
d. 

9.49 (a) Identify compounds **A**–**F** in the following reactions. (b) How are compounds **B** and **D** related? (c) How are compounds **B** and **F** related?

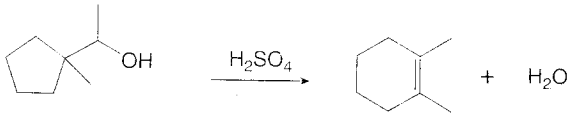


9.50 Draw a stepwise mechanism for each reaction.

a. 

b. 

9.51 Sometimes carbocation rearrangements can change the size of a ring. Draw a stepwise, detailed mechanism for the following reaction.



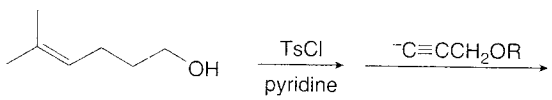
9.52 Indicate the stereochemistry of the alkyl halide formed when (*S*)-3-hexanol is treated with (a) HBr; (b) PBr_3; (c) HCl; (d) $SOCl_2$ and pyridine.

9.53 Explain the following observation. When 3-methyl-2-butanol is treated with HBr, a single alkyl bromide is isolated, resulting from a 1,2-shift. When 2-methyl-1-propanol is treated with HBr, no rearrangement occurs to form an alkyl bromide.

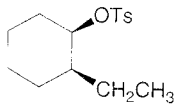
9.54 To convert a 1° alcohol into a 1° alkyl chloride with HCl, a Lewis acid such as $ZnCl_2$ must be added to the reaction mixture. Explain why it is possible to omit the Lewis acid if a polar aprotic solvent such as HMPA, $[(CH_3)_2N]_3P{=}O$, is used.

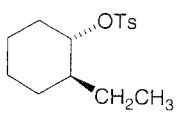
9.55 When $CH_3CH_2CH_2CH_2OH$ is treated with H_2SO_4 + NaBr, $CH_3CH_2CH_2CH_2Br$ is the major product, and $CH_3CH_2CH{=}CH_2$ and $CH_3CH_2CH_2CH_2OCH_2CH_2CH_2CH_3$ are isolated as minor products. Draw a mechanism that accounts for the formation of each of these products.

9.56 Identify the product of the following two-step reaction sequence used in the synthesis of leukotriene C_4 (Section 9.16).



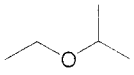
9.57 Alkyl tosylates undergo E2 elimination when treated with strong base, in exactly the same manner as alkyl halides. Thus, when the two groups removed (H and OTs) are bonded to a cyclohexane ring, they must adopt a trans diaxial arrangement. Keeping this in mind, draw the alkenes formed when each tosylate is treated with a strong base. Label the major product when a mixture results.

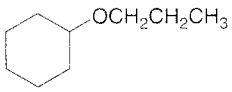
a. 

b. 

Ethers

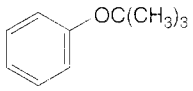
9.58 Draw two different routes to each of the following ethers using a Williamson ether synthesis. Indicate the preferred route (if there is one).

a. 

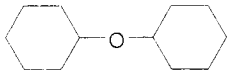
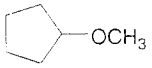
b. 

c. $CH_3CH_2OCH_2CH_2CH_3$

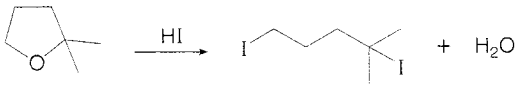
9.59 Explain why it is not possible to prepare the following ether using a Williamson ether synthesis.

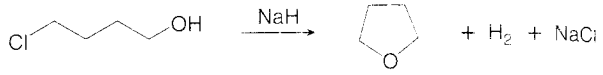


9.60 Draw the products formed when each ether is treated with HBr.

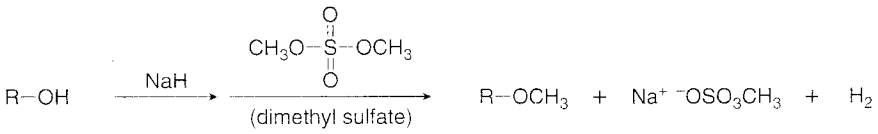
a. $(CH_3)_3COCH_2CH_2CH_3$ b.  c. 

9.61 Draw a stepwise mechanism for each reaction.

a. 

b. 

9.62 Alcohols can be converted to methyl ethers using dimethyl sulfate in the following two-step sequence. Draw a mechanism for this sequence and explain why dimethyl sulfate is a very reactive methylating agent—that is, it readily transfers a methyl group from itself to another compound.

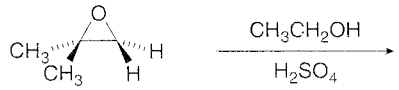


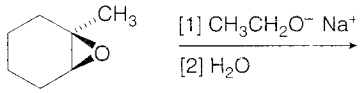
Epoxides

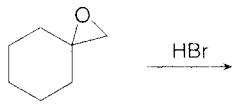
9.63 Draw the products formed when ethylene oxide is treated with each reagent.

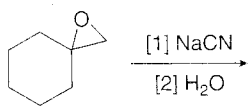
a. HBr
b. H_2O (H_2SO_4)
c. [1] $CH_3CH_2O^-$; [2] H_2O
d. [1] $HC{\equiv}C^-$; [2] H_2O
e. [1] ^-OH; [2] H_2O
f. [1] CH_3S^-; [2] H_2O

9.64 Draw the products of each reaction.

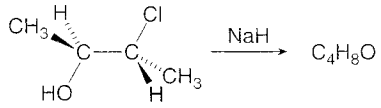
a. 

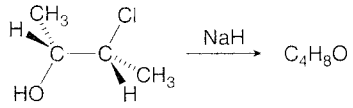
b. 

c. 

d. 

9.65 Draw the product of each reaction and indicate the stereochemistry.

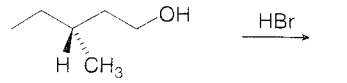
a. 

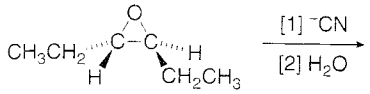
b. 

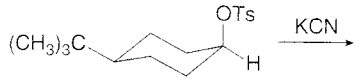
General Problems

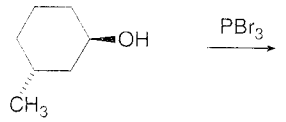
9.66 Draw the products of each reaction, and indicate the stereochemistry where appropriate.

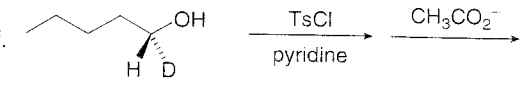
a. 

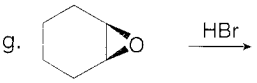
b. 

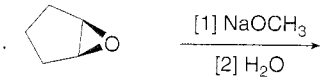
c. 

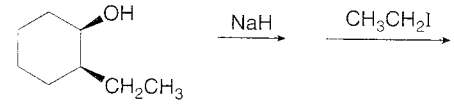
d. 

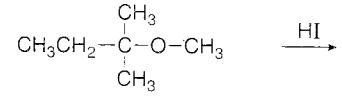
e. 

f. 

g. 

h. 

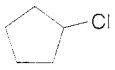
i. 

j. 

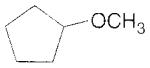
9.67 Prepare each compound from $CH_3CH_2CH_2CH_2OH$. In some cases, more than one step is needed.

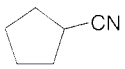
a. $CH_3CH_2CH_2CH_2Br$
b. $CH_3CH_2CH_2CH_2Cl$
c. $CH_3CH_2CH_2CH_2OCH_2CH_3$
d. $CH_3CH_2CH_2CH_2N_3$

9.68 Prepare each compound from cyclopentanol. In some cases, more than one step is needed.

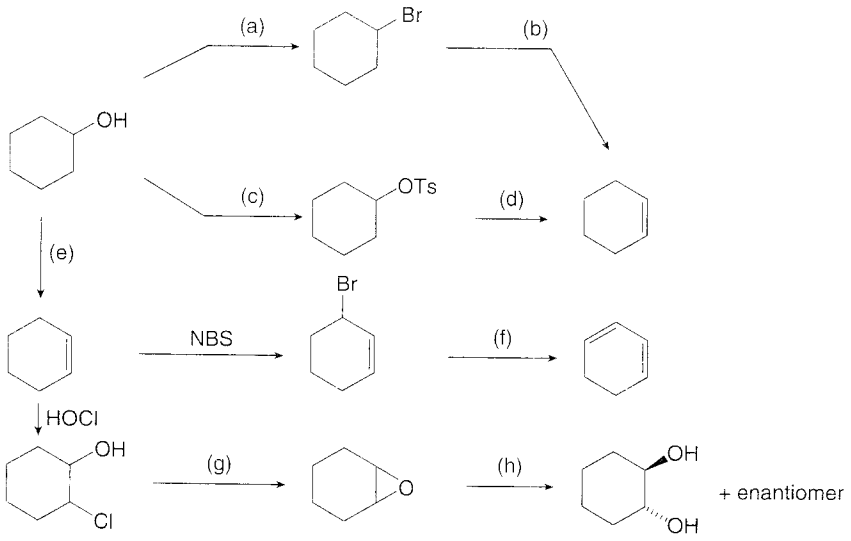
a. 

b. 

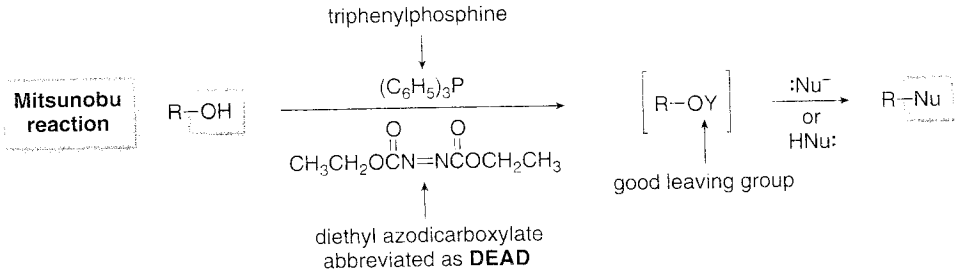
c. 

d. 

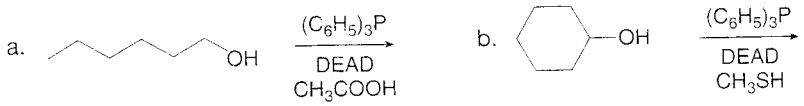
9.69 Identify the reagents (a–h) needed to carry out each reaction.



9.70 In Section 9.12, we learned that an alcohol is converted to an alkyl halide using PBr_3 because PBr_3 makes OH a better leaving group and provides the nucleophile Br^- for substitution. Mitsunobu and co-workers devised a more general variation of this reaction that converts ROH into a variety of substitution products R–Nu, using nucleophiles having the general structure H–Nu: or $:Nu^-$.

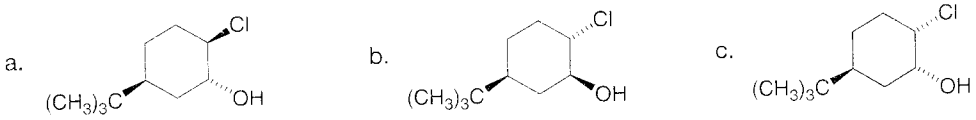


Draw the products of each Mitsunobu reaction.

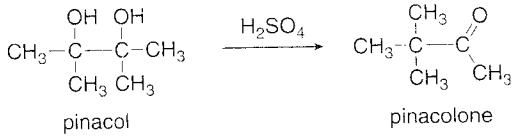


Challenge Questions

9.71 Drawn below are three isomeric halohydrins. One reacts rapidly to form an epoxide, one is intermediate in reactivity, and one does not react at all. Identify which halohydrin corresponds to each kind of reactivity and explain why.

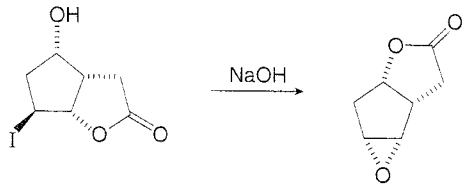


9.72 1,2-Diols are converted to carbonyl compounds when treated with strong acids, in a reaction called the *pinacol rearrangement.* Draw a stepwise mechanism for this reaction.



pinacol pinacolone

9.73 Draw a stepwise mechanism for the following reaction.



9.74 Epoxide rings bonded to six-membered rings are opened in a **trans diaxial** fashion; that is, the nucleophile attacks from the axial direction to give a leaving group that is also axial. Because of this, only one product is formed in each of the following reactions, even though both ends of the epoxide are equally substituted with alkyl groups. Draw the product of each reaction, using chair forms to indicate the stereochemistry of substituents on the cyclohexane ring.

a. $(CH_3)_3C$  $\xrightarrow[\text{[2] } H_2O]{\text{[1] } CH_3O^-}$

b. $(CH_3)_3C$  $\xrightarrow[\text{[2] } H_2O]{\text{[1] } CH_3O^-}$