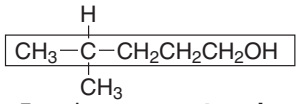
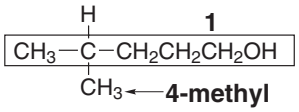
**9.38** Use the directions from Answer 9.2.

a. $(CH_3)_2CHCH_2CH_2CH_2OH$

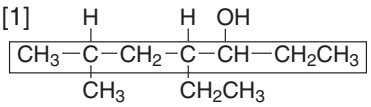
[1] 


5 carbons = **pentanol**

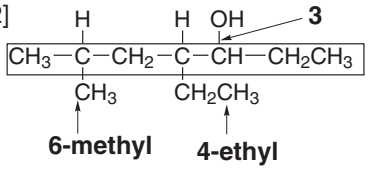
[2] 


[3] **4-methyl-1-pentanol**

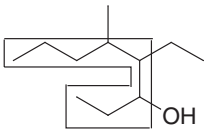
b. $(CH_3)_2CHCH_2CH(CH_2CH_3)CH(OH)CH_2CH_3$

[1] 

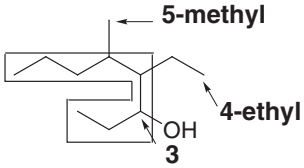

7 carbons = **heptanol**

[2] 


[3] **4-ethyl-6-methyl-3-heptanol**

c. [1] 

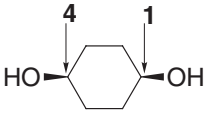

8 carbons = **octanol**

[2] 


[3] **4-ethyl-5-methyl-3-octanol**

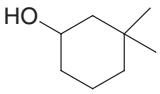
d. [1] 


**cyclohexanediol**

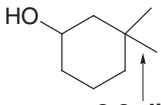
[2] 


**cis**

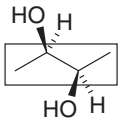
[3] ***cis*-1,4-cyclohexanediol**

e. [1] 

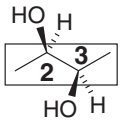

6 carbons = **cyclohexanol**

[2] 


[3] **3,3-dimethylcyclohexanol**

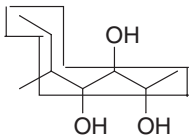
f. [1] 


4 carbons = **butanediol**

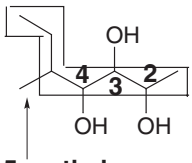
[2] 


**2*R*, 3*R***

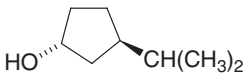
[3] **(2*R*,3*R*)-2,3-butanediol**

g. [1] 

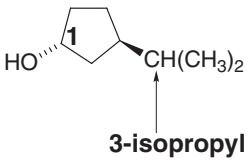

7 carbons = **heptanetriol**

[2] 


[3] **5-methyl-2,3,4-heptanetriol**

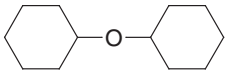
h. [1] 


5 carbons = **cyclopentanol**

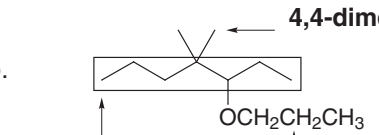
[2] 


[3] **3-isopropylcyclopentanol**

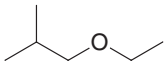
**9.39** Use the rules from Answers 9.4 and 9.5.

a. 

common name: **dicyclohexyl ether**

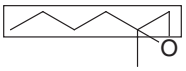
b. 


IUPAC name: **4,4-dimethyl-3-propoxyheptane**

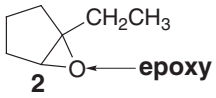
c. 

common name: **ethyl isobutyl ether**

IUPAC name: **1-ethoxy-2-methylpropane**

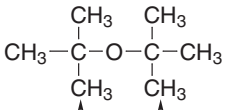
d. 

**1,2-epoxy-2-methylhexane**
or **1-butyl-1-methyloxirane**
or **2-methylhexene oxide**

e. 


5 carbons =
**cyclopentane**

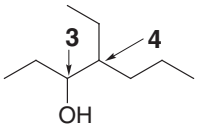
IUPAC name: **1,2-epoxy-1-ethylcyclopentane**

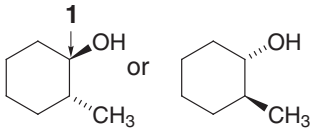
f. 

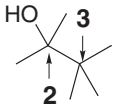
***tert*-butyl** ***tert*-butyl**

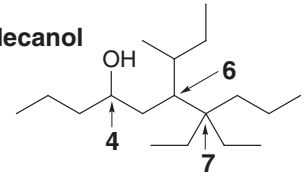
common name: **di-*tert*-butyl ether**

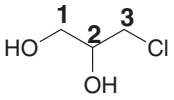
**9.40** Use the directions from Answer 9.3.

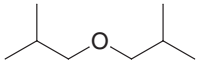
a. 4-ethyl-3-**heptanol** 

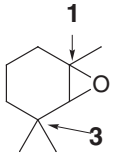
b. *trans*-2-methyl**cyclohexanol** 

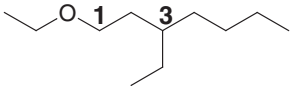

c. 2,3,3-trimethyl-2-**butanol** 

d. 6-*sec*-butyl-7,7-diethyl-4-**decanol** 

e. 3-chloro-1,2-**propanediol** 

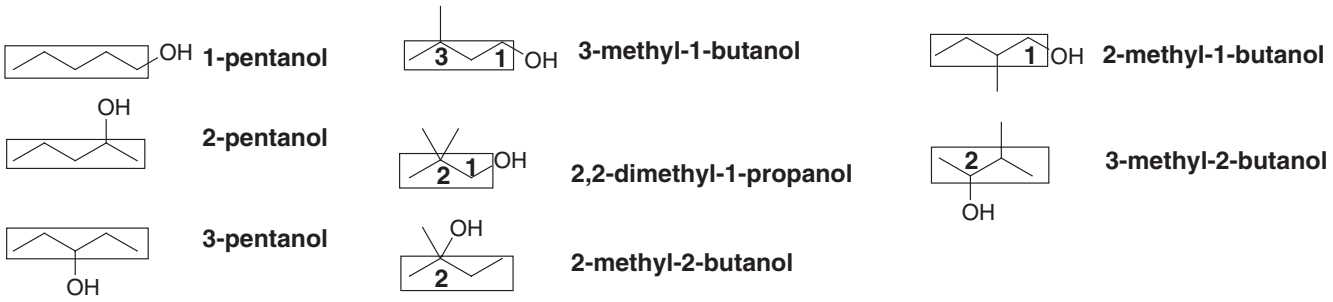
f. diisobutyl ether 

g. 1,2-epoxy-1,3,3-trimethyl**cyclohexane** 

h. 1-ethoxy-3-ethyl**heptane** 

**9.41**

Eight constitutional isomers of molecular formula $C_5H_{12}O$ containing an OH group:




**9.42** Use the boiling point rules from Answer 9.6.

a. $CH_3CH_2OCH_3$ — ether, no hydrogen bonding, **lowest bp**

$(CH_3)_2CHOH$ — 2° alcohol, hydrogen bonding, **intermediate bp**

$CH_3CH_2CH_2OH$ — 1° alcohol, hydrogen bonding, **highest bp**

b. $CH_3CH_2CH_2CH_2CH_2CH_3$ — no OH group, **lowest water solubility**

$CH_3CH_2CH_2CH_2CH_2CH_2OH$ — one OH group, **intermediate water solubility**

$HOCH_2CH_2CH_2CH_2CH_2CH_2OH$ — two OH groups, **highest water solubility**

**9.43**

a. $CH_3CH_2CH_2OH \xrightarrow{H_2SO_4} CH_3CH{=}CH_2 + H_2O$

b. $CH_3CH_2CH_2OH \xrightarrow{NaH} CH_3CH_2CH_2O^- Na^+ + H_2$

c. $CH_3CH_2CH_2OH \xrightarrow[ZnCl_2]{HCl} CH_3CH_2CH_2Cl + H_2O$

d. $CH_3CH_2CH_2OH \xrightarrow{HBr} CH_3CH_2CH_2Br + H_2O$

e. $CH_3CH_2CH_2OH \xrightarrow[pyridine]{SOCl_2} CH_3CH_2CH_2Cl$

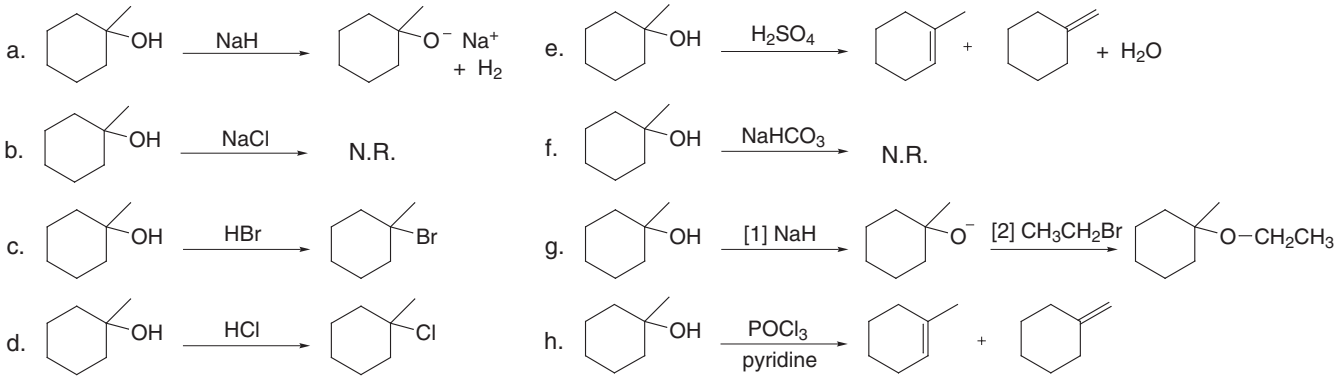
f. $CH_3CH_2CH_2OH \xrightarrow{PBr_3} CH_3CH_2CH_2Br$

g. $CH_3CH_2CH_2OH \xrightarrow[pyridine]{TsCl} CH_3CH_2CH_2OTs$

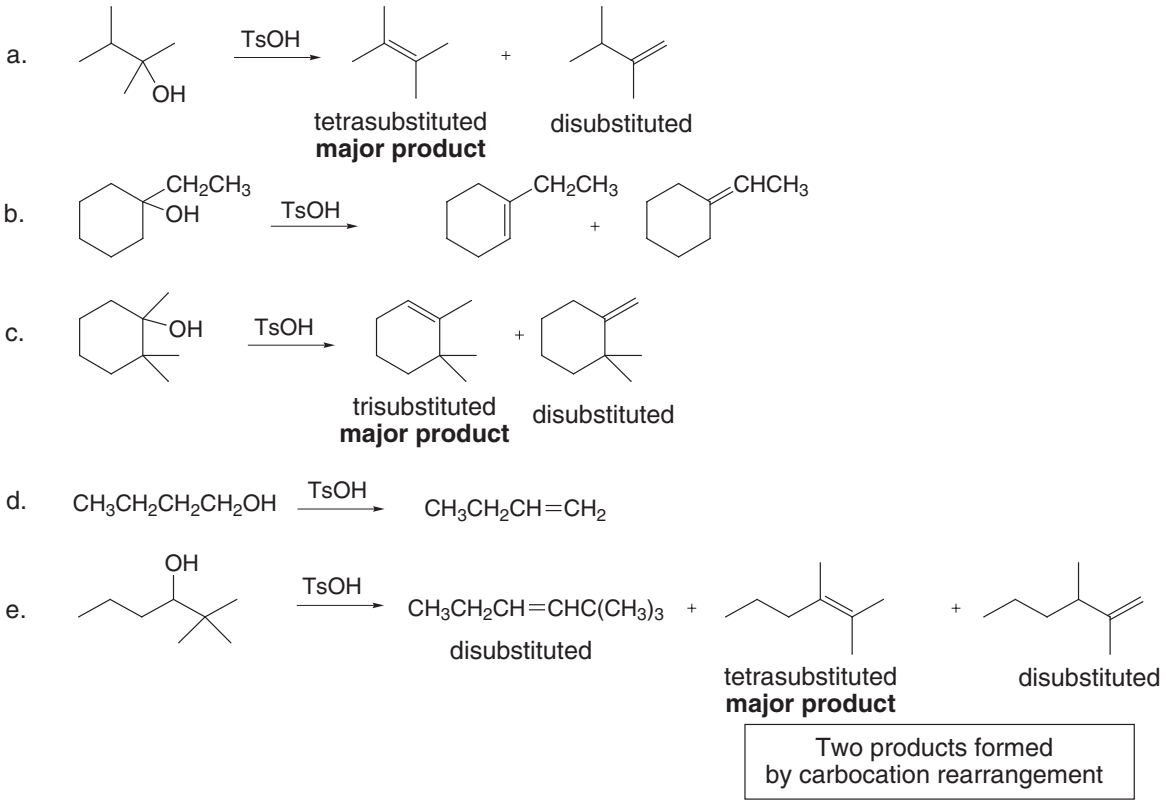
h. $CH_3CH_2CH_2OH \xrightarrow{[1]\ NaH} CH_3CH_2CH_2O^- Na^+ \xrightarrow{[2]\ CH_3CH_2Br} CH_3CH_2CH_2OCH_2CH_3$

i. $CH_3CH_2CH_2OH \xrightarrow{[1]\ TsCl} CH_3CH_2CH_2OTs \xrightarrow{[2]\ NaSH} CH_3CH_2CH_2SH$

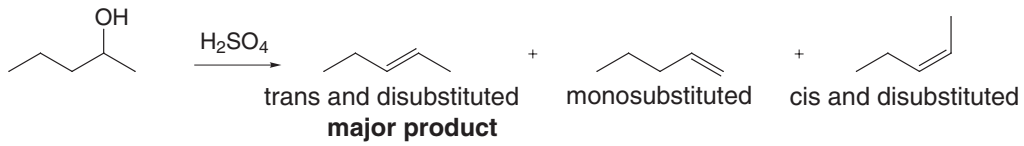
**9.44**




**9.45** **Dehydration follows the Zaitsev rule**, so the more stable, more substituted alkene is the major product.




**9.46** The more stable alkene is the major product.



**9.47** OTs is a good leaving group and will easily be replaced by a nucleophile. Draw the products by substituting the nucleophile in the reagent for OTs in the starting material.

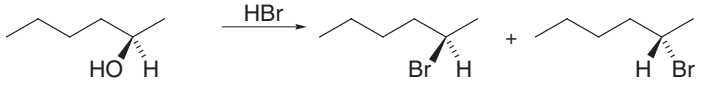
a. $CH_3CH_2CH_2CH_2-OTs \xrightarrow[\mathbf{S_N2}]{CH_3SH} CH_3CH_2CH_2CH_2-SCH_3 + HOTs$

b. $CH_3CH_2CH_2CH_2-OTs \xrightarrow[\mathbf{S_N2}]{NaOCH_2CH_3} CH_3CH_2CH_2CH_2-OCH_2CH_3 + Na^+ \ ^-OTs$

c. $CH_3CH_2CH_2CH_2-OTs \xrightarrow[\mathbf{S_N2}]{NaOH} CH_3CH_2CH_2CH_2-OH + Na^+ \ ^-OTs$

d. $CH_3CH_2CH_2CH_2-OTs \xrightarrow[\mathbf{E2}]{K^+ \ ^-OC(CH_3)_3} CH_3CH_2CH{=}CH_2 + (CH_3)_3COH + K^+ \ ^-OTs$

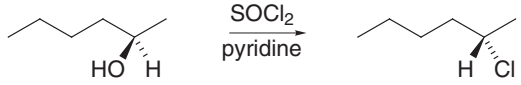
**9.48**

a. 

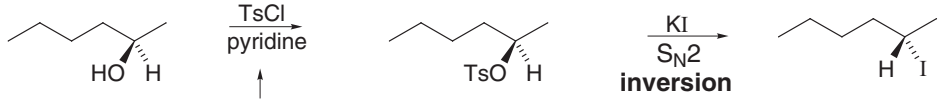
2° Alcohol will undergo $S_N1$.
**racemization**

b. 

1° Alcohol will undergo $S_N2$.
**inversion**

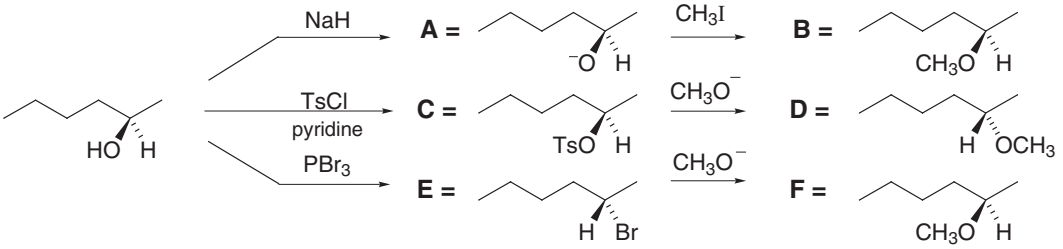
c. 

$SOCl_2$ always implies $S_N2$.
**inversion**

d. 

Configuration is maintained.
C–O bond is not broken.

**9.49**

a. 


b. **B** and **D** are enantiomers.

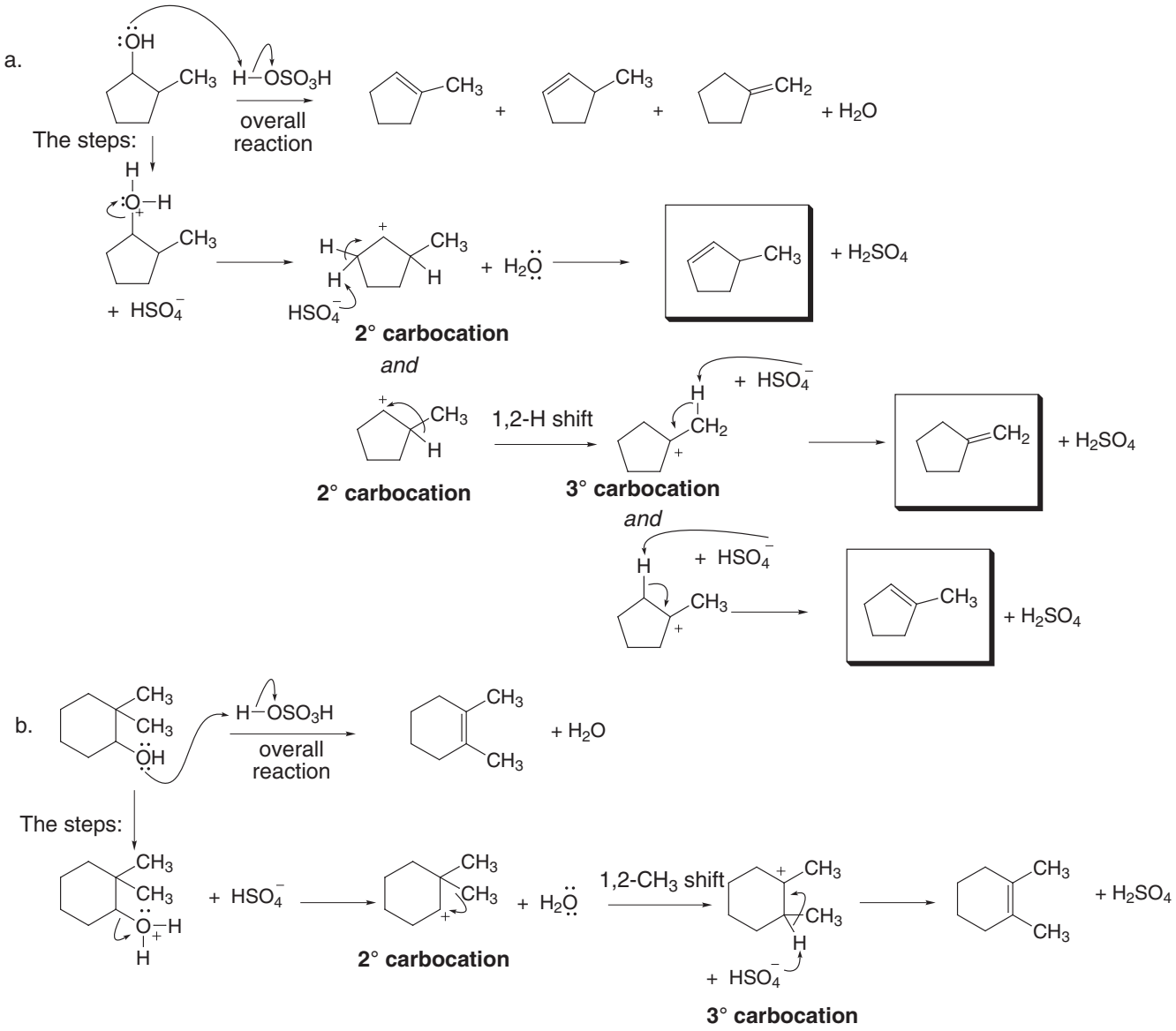
c. **B** and **F** are identical.

**9.50** Acid-catalyzed dehydration follows an E1 mechanism for 2° and 3° ROH with an added step to make a good leaving group. The three steps are:

[1] Protonate the oxygen to make a good leaving group.

[2] Break the C–O bond to form a carbocation.

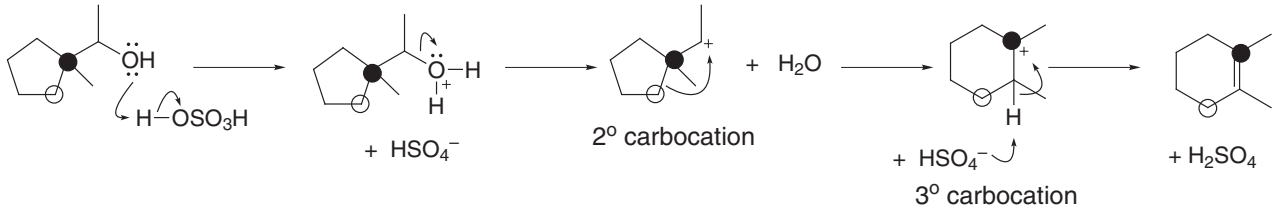
[3] Remove a β hydrogen to form the π bond.



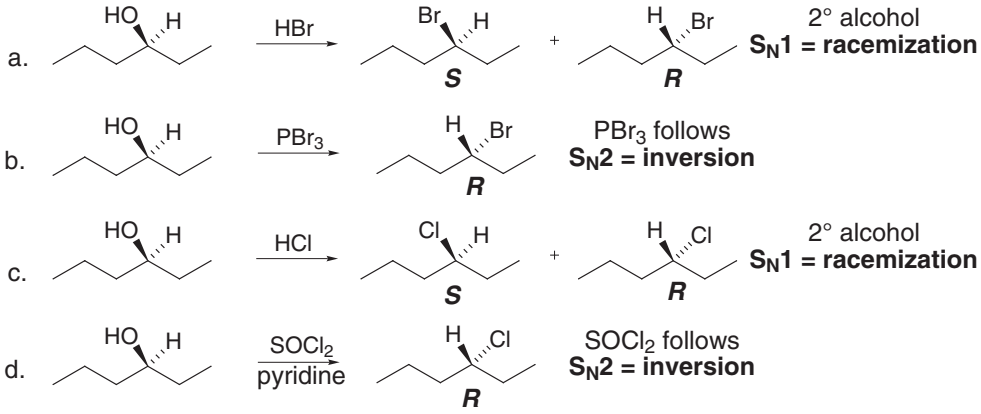

**9.51** To draw the mechanisms:

[1] Protonate the oxygen to make a good leaving group.
[2] Break the C–O bond to form a carbocation.
[3] Look for possible rearrangements to make a more stable carbocation.
[4] Remove a β hydrogen to form the π bond.

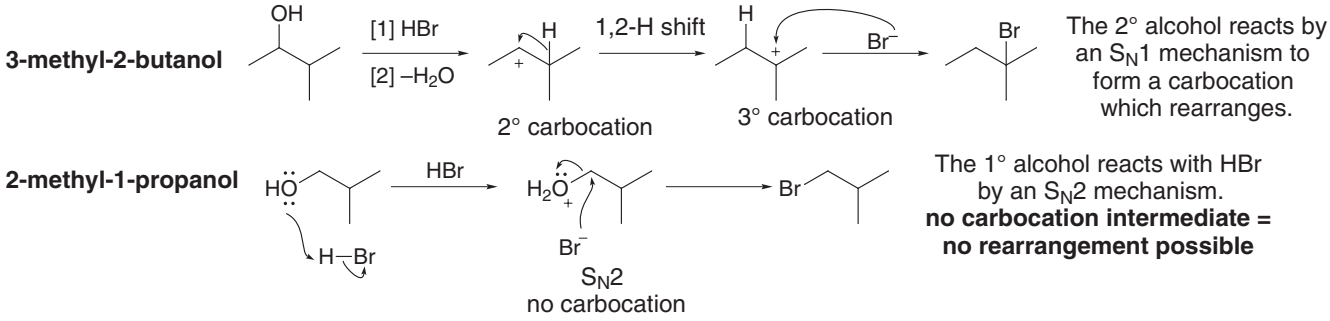
Dark and light circle are meant to show where the carbons in the starting material appear in the product.



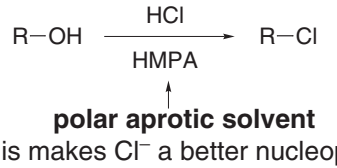
**9.52**



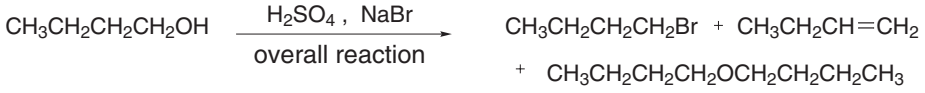

**9.53**



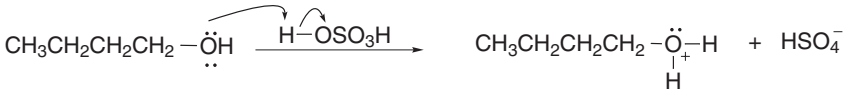

**9.54** Conversion of a 1° alcohol into a 1° alkyl chloride occurs by an $S_N2$ mechanism. $S_N2$ mechanisms occur more readily in polar aprotic solvents by making the nucleophile stronger. No added $ZnCl_2$ is necessary.



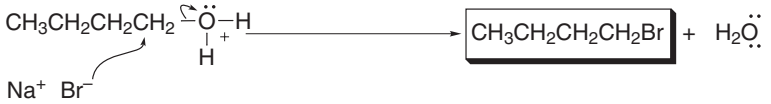
**9.55**




**Step [1] for all products: Formation a good leaving group**

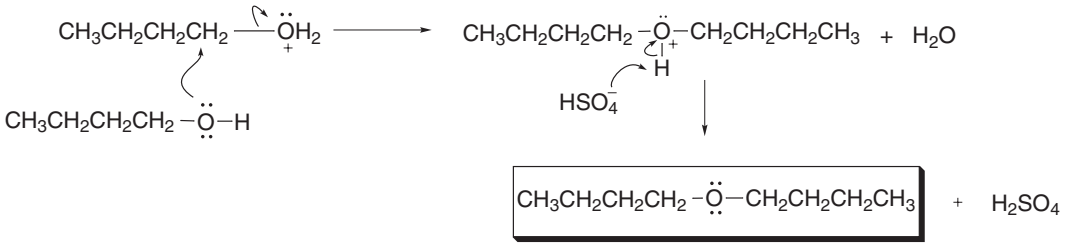



**Formation of $CH_3CH_2CH_2CH_2Br$:**

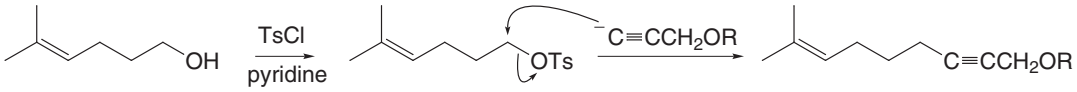



**Formation of $CH_3CH_2CH{=}CH_2$:**


**Ether forms (from the protonated alcohol):**

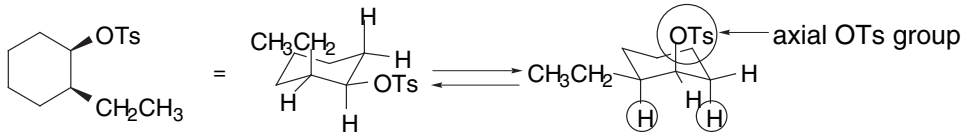



**9.56**

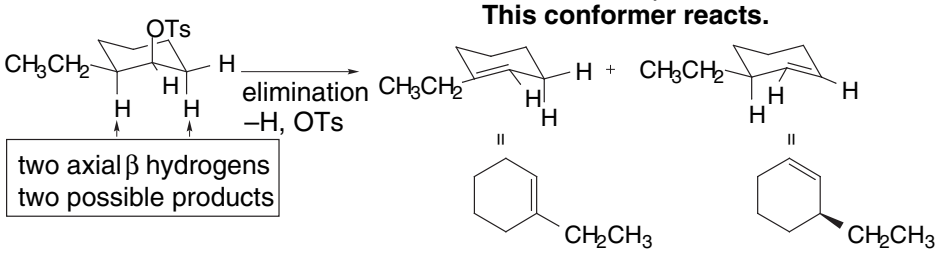



**9.57**

a.




2 anti H's
2 elimination products
**This conformer reacts.**

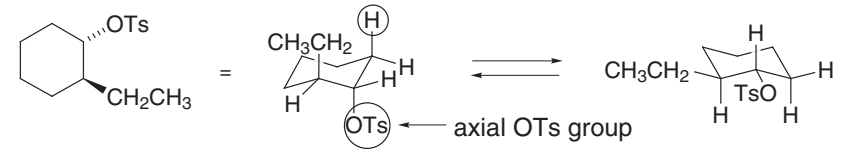



two axial β hydrogens
two possible products

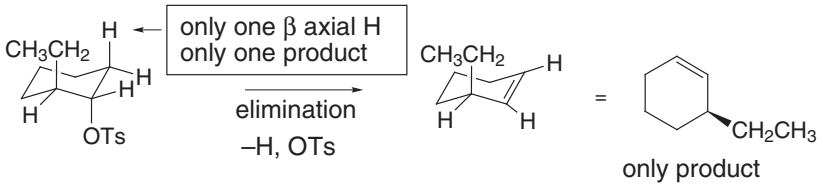
**major product**
trisubstituted

disubstituted

b.



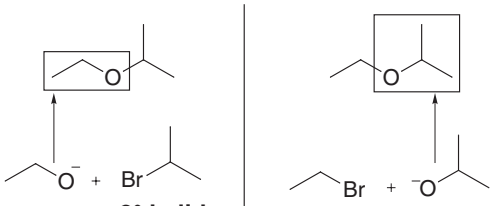

only 1 axial H
1 elimination product
**This conformer reacts.**




only product

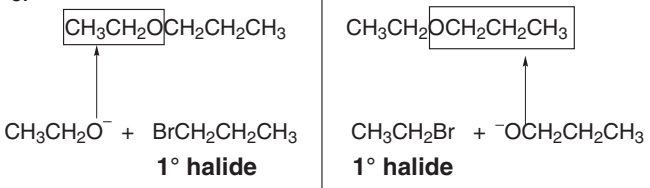
**9.58**

a.



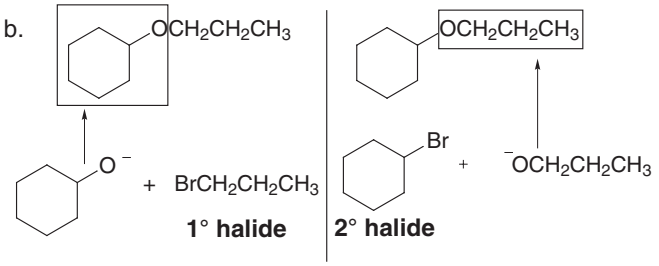

**less hindered RX**
***preferred path***

c.




**Neither path preferred.**

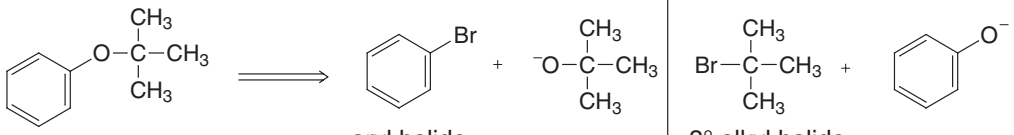
b.




**less hindered RX**
***preferred path***

**9.59** A tertiary halide is too hindered and an aryl halide too unreactive to undergo a Willamson ether synthesis.

**Two possible starting materials:**

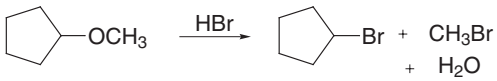


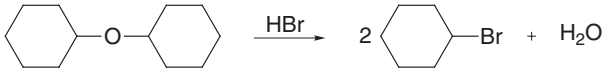

aryl halide
**unreactive in $S_N2$**

3° alkyl halide
**too sterically hindered for $S_N2$**

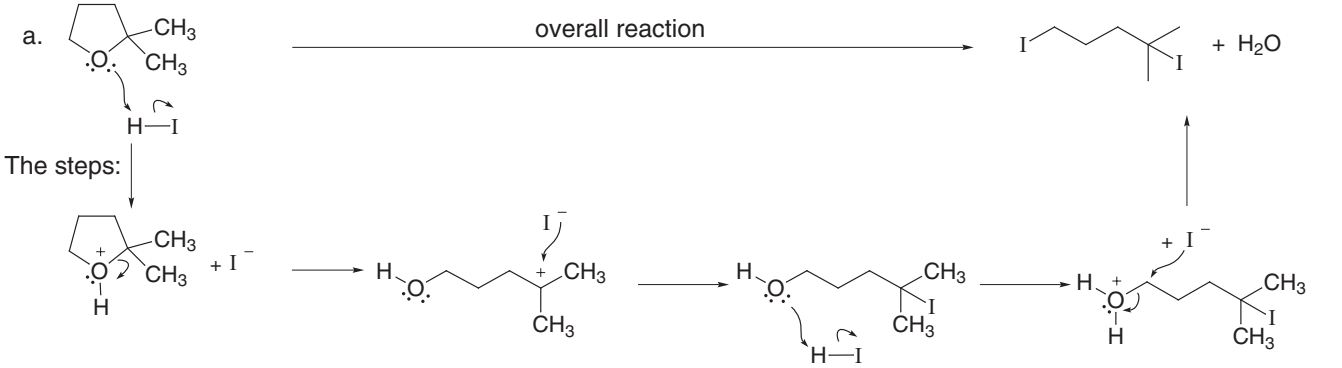
**9.60**

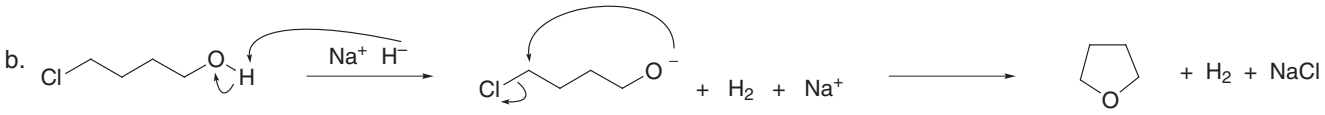
a. $(CH_3)_3COCH_2CH_2CH_3 \xrightarrow{HBr} (CH_3)_3CBr + BrCH_2CH_2CH_3 + H_2O$

c. 

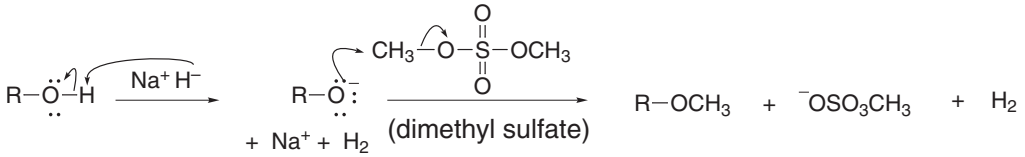
b. 

**9.61**

a. 

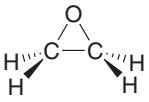

b. 

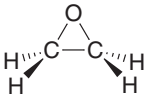

**9.62**

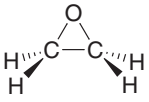


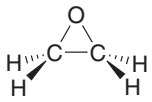

Dimethyl sulfate is a reactive methylating agent because $^-OSO_3CH_3$ is a very good leaving group; it is a resonance-stabilized, weak conjugate base. The conjugate acid of $^-OSO_3CH_3$ is $HOSO_3CH_3$, which is a strong acid, similar in acidity to $H_2SO_4$.

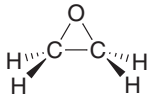
**9.63**

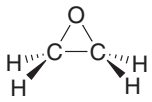
a.  $\xrightarrow{HBr}$ $BrCH_2CH_2OH$

b.  $\xrightarrow[H_2SO_4]{H_2O}$ $HOCH_2CH_2OH$

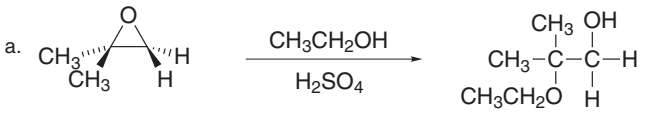
c.  $\xrightarrow[[2]\ H_2O]{[1]\ CH_3CH_2O^-}$ $CH_3CH_2OCH_2CH_2OH$

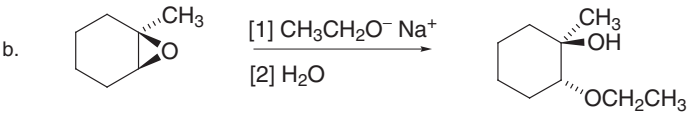
d.  $\xrightarrow[[2]\ H_2O]{[1] HC\equiv C^-}$ $HC\equiv C-CH_2-CH_2OH$

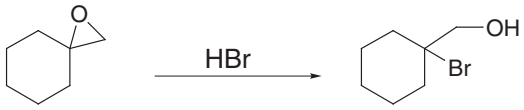
e.  $\xrightarrow[[2]\ H_2O]{[1]\ ^-OH}$ $HOCH_2CH_2OH$

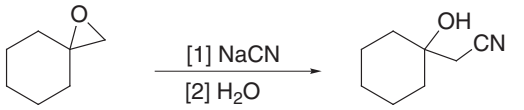
f.  $\xrightarrow[[2]\ H_2O]{[1]\ CH_3S^-}$ $CH_3SCH_2CH_2OH$

**9.64**

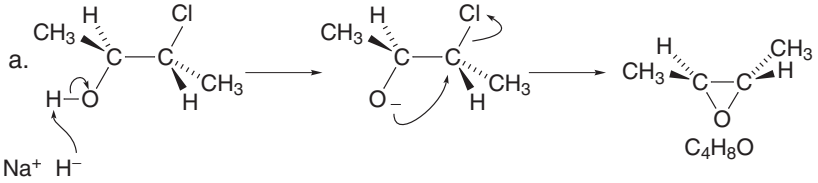
a. 


b. 

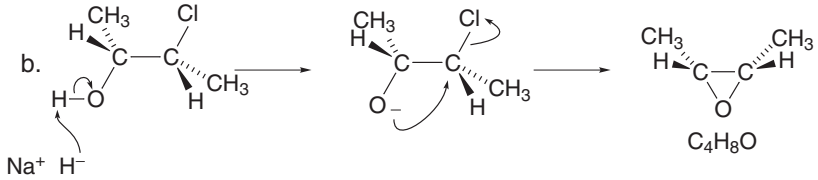

c. 


d. 


**9.65**

a. 

The 2 $CH_3$ groups are anti in the starting material, making them trans in the product.

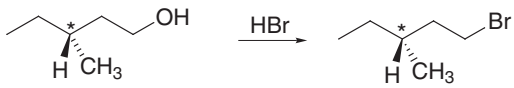
b. 

The 2 $CH_3$ groups are gauche in the starting material, making them cis in the product.

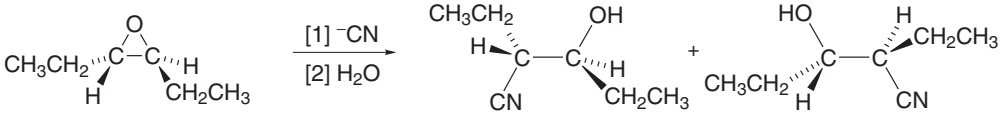
**9.66**

a. 

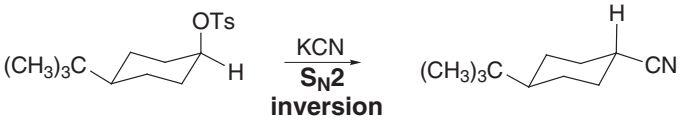
Bulky base favors E2.

b. 

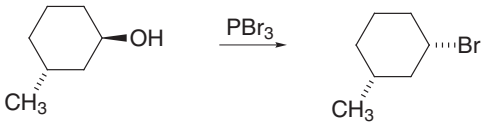
Keep the stereochemistry at the stereogenic center [*] the same here since no bond is broken to it.

c. 

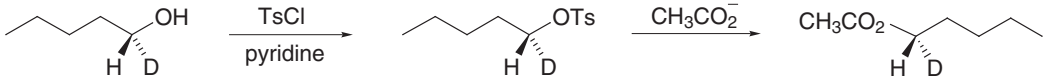
**identical**

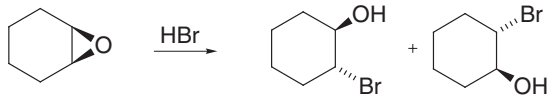
d. 

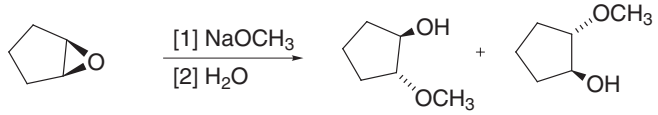
**$S_N2$ inversion**

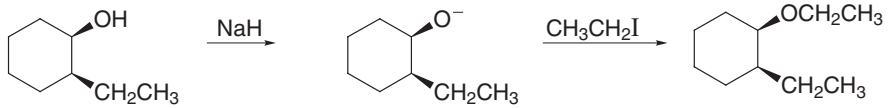
e. 

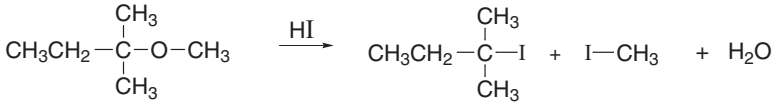
**$S_N2$ inversion**

f. 

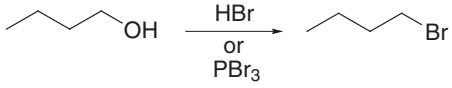
g. 

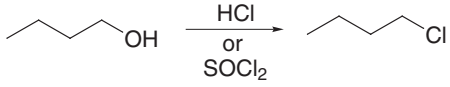

h. 

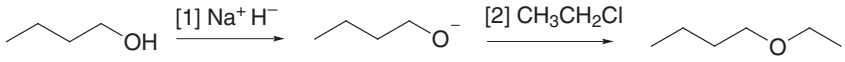

i. 

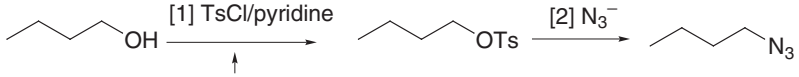

j. 


**9.67**

a. 

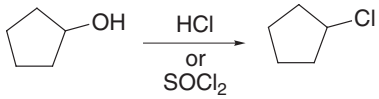

b. 

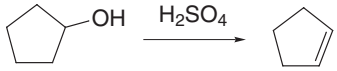

c. 

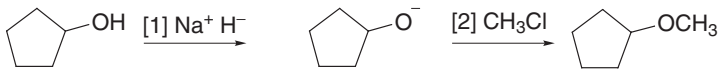

d. 

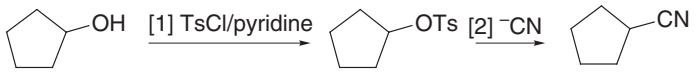

Make OH a good leaving group (use TsCl), then add $N_3^-$.

**9.68**

a. 

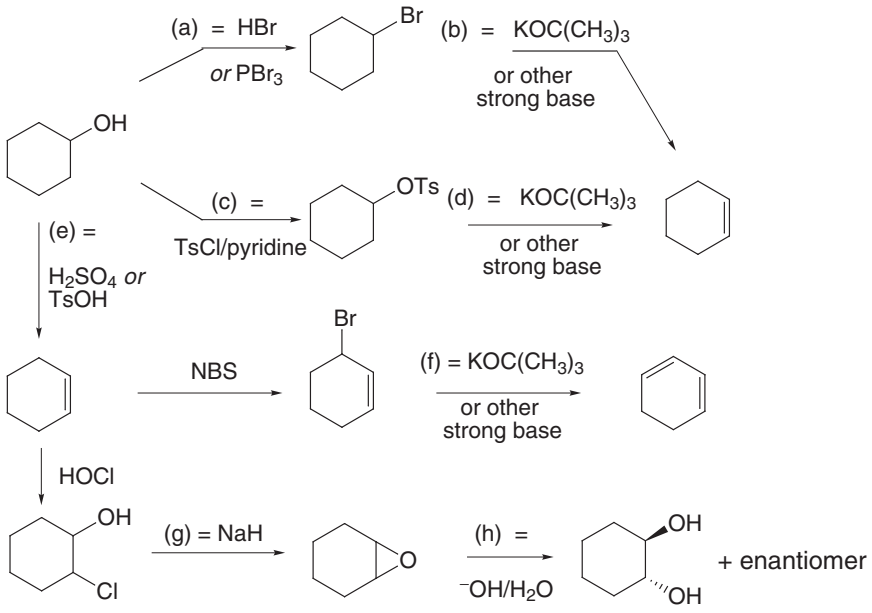

b. 


c. 

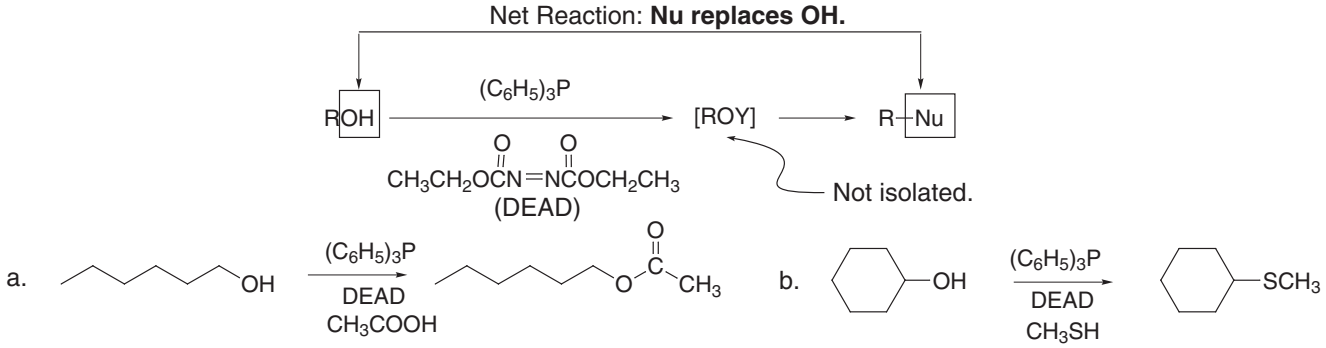

d. 


Make OH a good leaving group (use TsCl), then add $^-CN$.

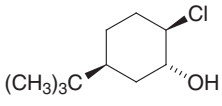
**9.69**


(a) = HBr
or PBr3
Br
(b) = KOC(CH3)3
or other
strong base
OH
(c) =
TsCl/pyridine
OTs
(d) = KOC(CH3)3
or other
strong base
(e) =
H2SO4 or
TsOH
NBS
Br
(f) = KOC(CH3)3
or other
strong base
HOCl
OH
Cl
(g) = NaH
O
(h) =
⁻OH/H2O
OH
OH
+ enantiomer

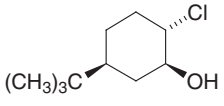
**9.70**


Net Reaction: Nu replaces OH.
ROH
(C6H5)3P
[ROY]
R—Nu
CH3CH2OCN=NCOCH2CH3
(DEAD)
Not isolated.
a.
OH
(C6H5)3P
DEAD
CH3COOH
O
C
O
CH3
b.
OH
(C6H5)3P
DEAD
CH3SH
SCH3

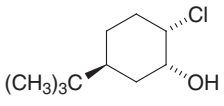
## 9.71



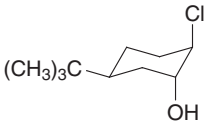

**A**



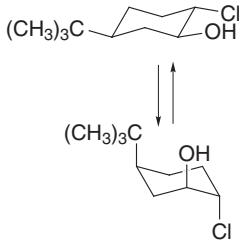

**B**



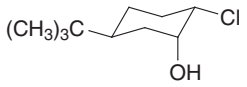

**C**




**rapid reaction**
This isomer can have the OH and Cl in the trans diaxial positions, while the larger group $C(CH_3)_3$ can be in the favorable equatorial position.

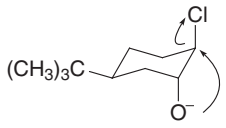



**intermediate reactivity**
This isomer can have the OH and Cl in the trans diaxial positions. But the larger group $C(CH_3)_3$ must be in the unfavorable axial position, making this reaction slower.

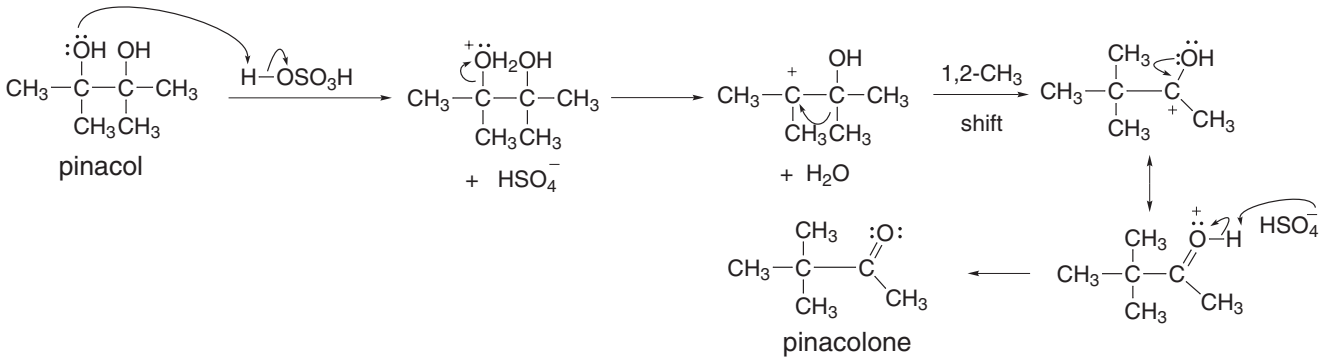



**no reaction**
This isomer has the OH and Cl in a cis position, prohibiting epoxide formation. The OH must be able to approach from the backside.

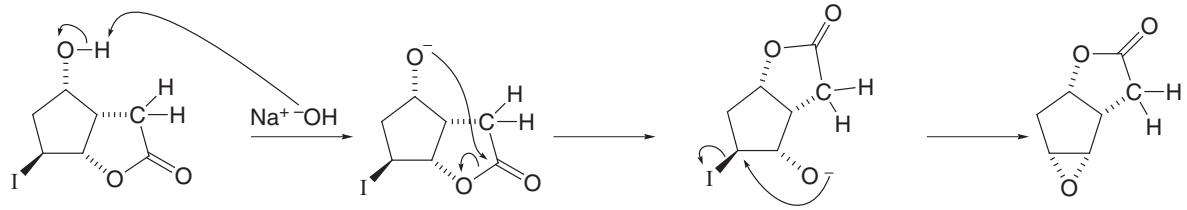
OH is in a favorable arrangement for backside attack of the nucleophile on the leaving group.



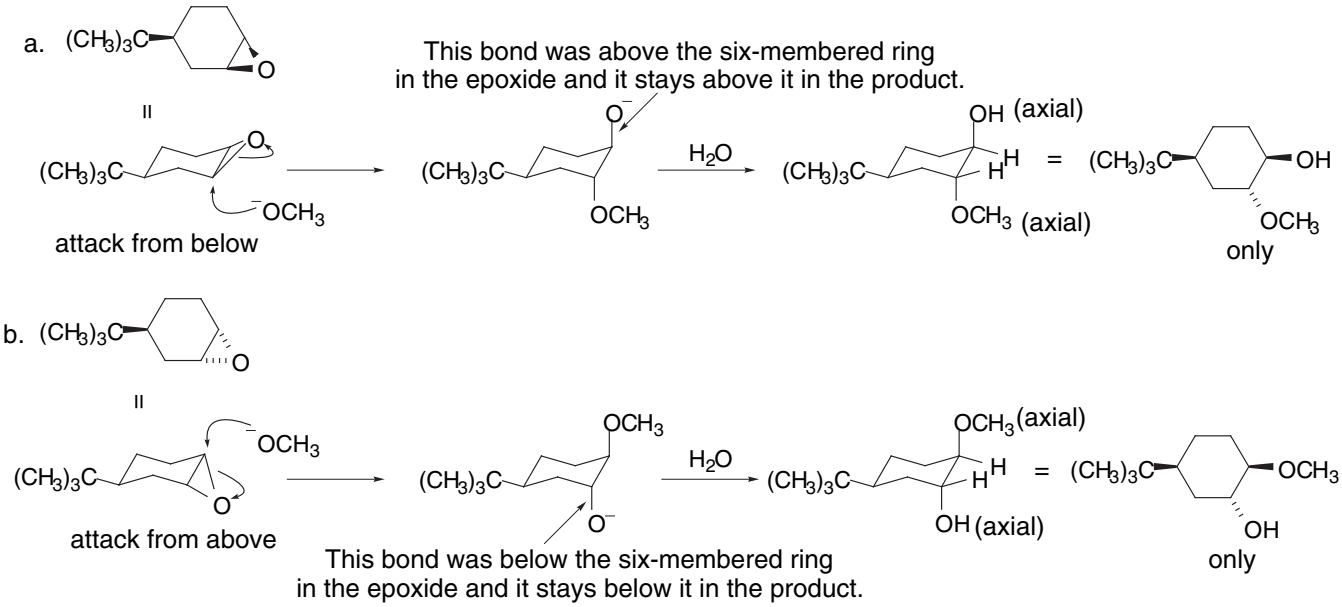

## 9.72




## 9.73



**9.74** You must draw the product that places the nucleophile and leaving group ($O^-$) trans and diaxial.




The nucleophile must always approach by backside attack; i.e. if the epoxide is drawn "up" it must attack from below. Even though both ends of the epoxide are equally substituted, nucleophilic attack occurs at only one C–O bond, the one that gives trans diaxial products, as drawn.