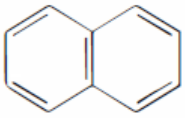
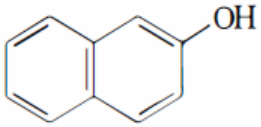
Ether as polar solvents
الايثرات كمذيبات قطبية

PROBLEM 14-1

Rank the given solvents in decreasing order of their ability to dissolve each compound.

Solutes

(a) NaOAc (b)  naphthalene (c)  2-naphthol

Solvents

ethyl ether
water
ethanol
dichloromethane

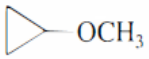
ANSWER

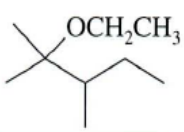
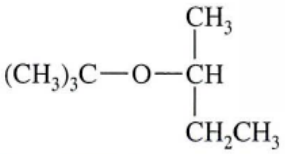
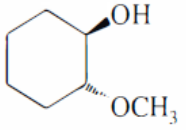
14-1
The four solvents decrease in polarity in this order: water, ethanol, ethyl ether, and dichloromethane. The three solutes decrease in polarity in this order: sodium acetate, 2-naphthol, and naphthalene. The guiding principle in determining solubility is, "Like dissolves like." Compounds of similar polarity will dissolve (in) each other. Thus, sodium acetate will dissolve in water, will dissolve only slightly in ethanol, and will be virtually insoluble in ethyl ether and dichloromethane. 2-Naphthol will be insoluble in water, somewhat soluble in ethanol, and soluble in ether and dichloromethane. Naphthalene will be insoluble in water, partially soluble in ethanol, and soluble in ethyl ether and dichloromethane. (Actual solubilities are difficult to predict, but you should be able to predict *trends*.)

Nomenclature of Ethers
تسمية من الايثرات

PROBLEM 14-4

Give a common name and a systematic name for each compound.

(a)  (b) $CH_3CH_2—O—CH(CH_3)_2$ (c) $ClCH_2CH_2OCH_3$

(d)  (e)  (f) 

ANSWER

14-4 IUPAC name first; then common name (see Appendix 1 in this Solutions Manual for a summary of IUPAC nomenclature)

(a) methoxycyclopropane; cyclopropyl methyl ether
(b) 2-ethoxypropane; ethyl isopropyl ether
(c) 1-chloro-2-methoxyethane; 2-chloroethyl methyl ether
(d) 2-ethoxy-2,3-dimethylpentane; no common name
(e) 2-*t*-butoxybutane; *sec*-butyl *t*-butyl ether
(f) *trans*-2-methoxycyclohexan-1-ol; no common name

Nomenclature of Cyclic Ethers

تسمية الايثرات الحلقية

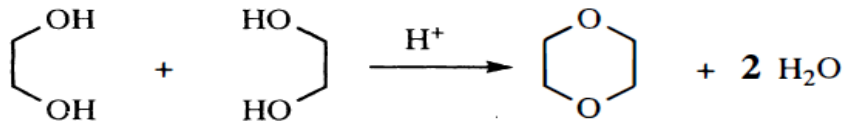
PROBLEM 14-5

1,4-Dioxane is made commercially by the acid-catalyzed dehydration of an alcohol.
(a) Show what alcohol will dehydrate to give 1,4-dioxane.
(b) Propose a mechanism for this reaction.

ANSWER

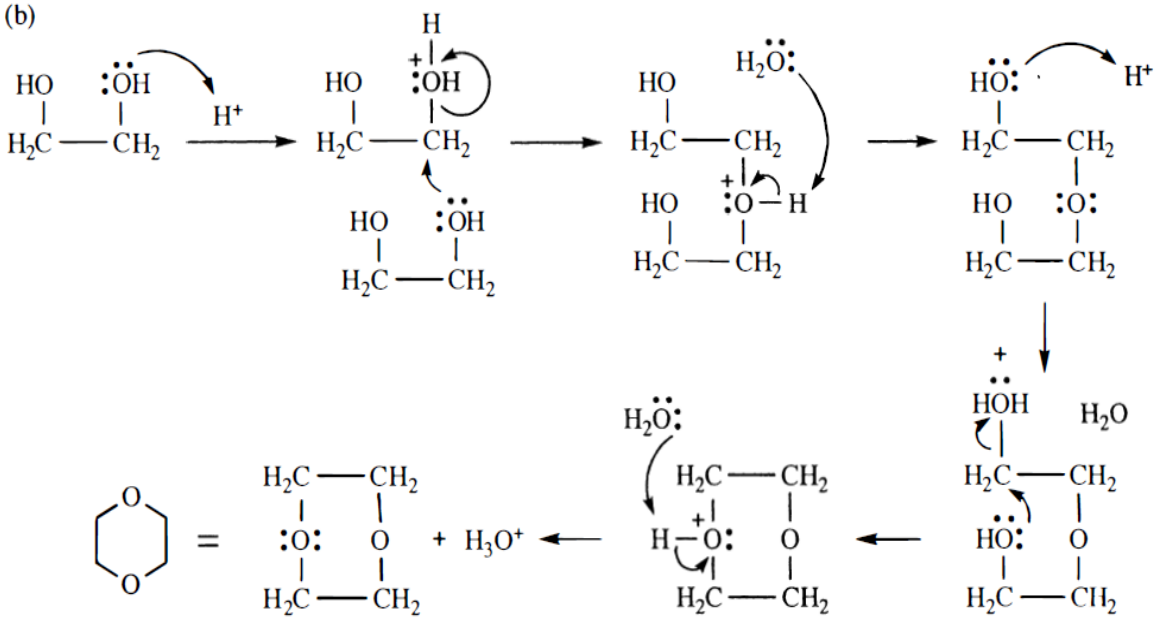
14-5

(a)



The alcohol is ethane-1,2-diol; the common name is ethylene glycol.

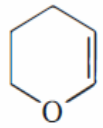
(b)

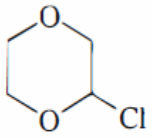


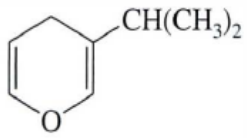
The mechanism shows that the acid catalyst is regenerated at the end of the reaction.

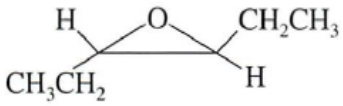
PROBLEM 14-6

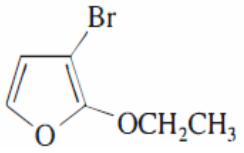
Name the following heterocyclic ethers.

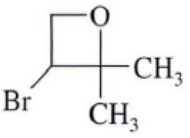
(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

ANSWER

14-6

(a) dihydropyran
(b) 2-chloro-1,4-dioxane
(c) 3-isopropylpyran
(d) *trans*-2,3-diethyloxirane; *trans*-3,4-epoxyhexane; *trans*-3-hexene oxide
(e) 3-bromo-2-ethoxyfuran
(f) 3-bromo-2,2-dimethyloxetane

Synthesis of Ethers

تحضير الايثرات

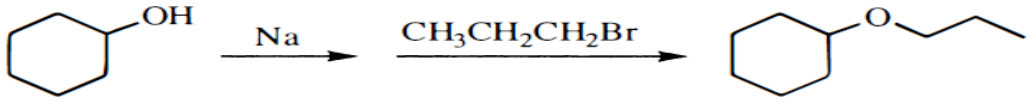
PROBLEM 14-9

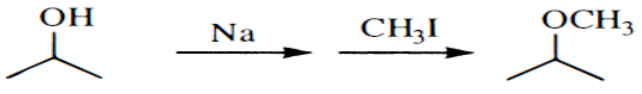
Show how you would use the Williamson ether synthesis to prepare the following ethers. You may use any alcohols or phenols as your organic starting materials.

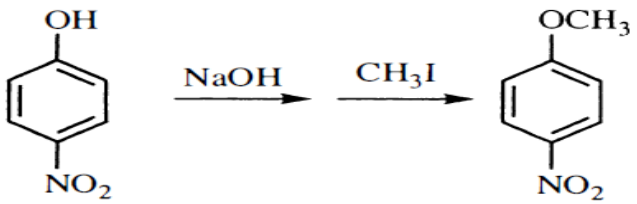
(a) cyclohexyl propyl ether
(b) isopropyl methyl ether
(c) 1-methoxy-4-nitrobenzene
(d) ethyl *n*-propyl ether (two ways)
(e) benzyl *t*-butyl ether (benzyl = Ph—CH_2—)

ANSWER

14-9

(a) 

(b) 

(c) 

14-9

(d) $CH_3CH_2CH_2OH \xrightarrow{Na} \xrightarrow{CH_3CH_2Br} CH_3CH_2CH_2OCH_2CH_3$

$CH_3CH_2OH \xrightarrow{Na} \xrightarrow{CH_3CH_2CH_2Br} CH_3CH_2CH_2OCH_2CH_3$

(e) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH \xrightarrow{Na} \xrightarrow{PhCH_2Br} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OCH_2Ph$

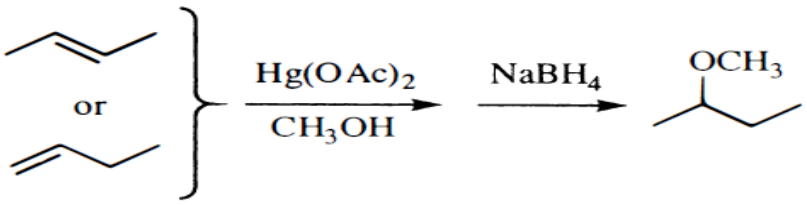
PROBLEM 14-10

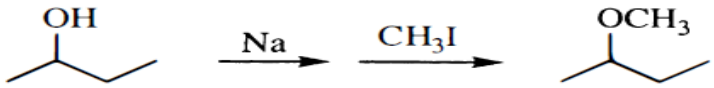
Show how the following ethers might be synthesized using (1) alkoxymercuration--demercuration and (2) the Williamson synthesis. (When one of these methods cannot be used for the given ether, point out why it will not work.)

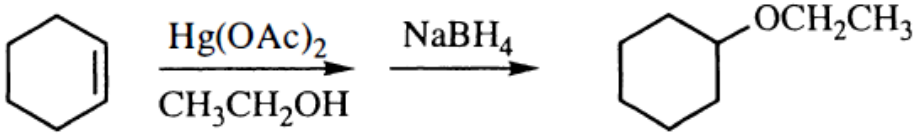
(a) 2-methoxybutane
(b) ethyl cyclohexyl ether
(c) 2-methyl-1-methoxycyclopentane
(d) 1-methyl-1-methoxycyclopentane
(e) 1-methyl-1-isopropoxycyclopentane
(f) *t*-butyl phenyl ether

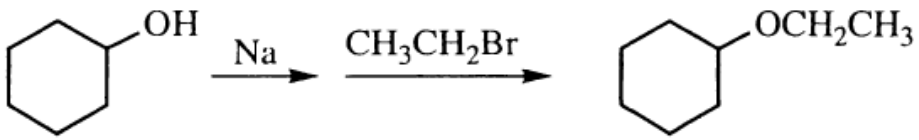
ANSWER

14-10

(a) (1) 

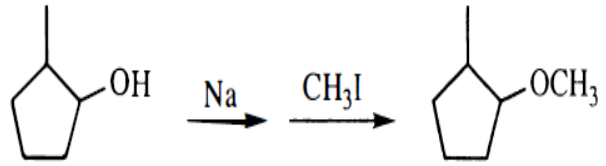
(2) 

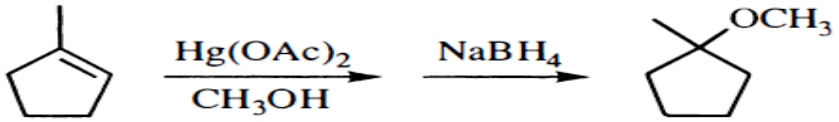
(b) (1) 

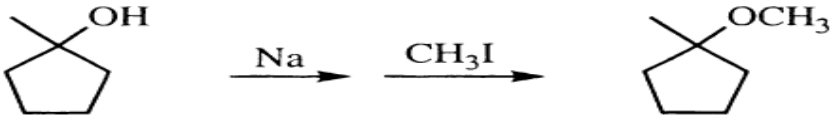
(2) 

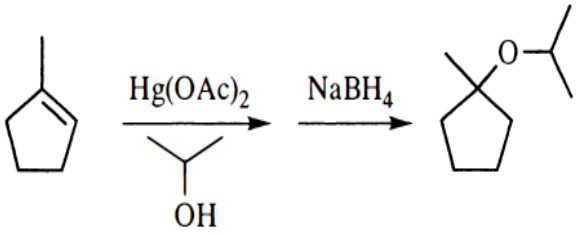
14-10 continued

(c) (1) Alkoxymercuration is not practical here; the product does not have Markovnikov orientation.

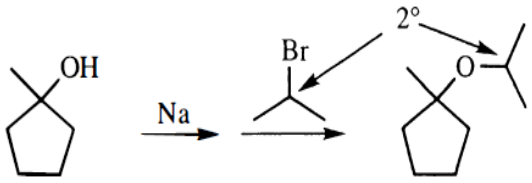
(2) 

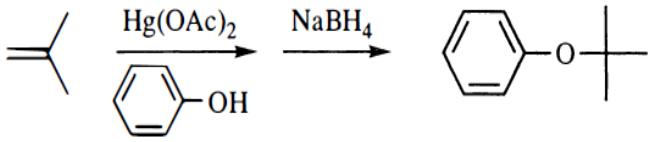
(d) (1) 

(2) 

(e) (1) 

(2) Williamson ether synthesis would give a poor yield of product as the halide is on a 2° carbon.

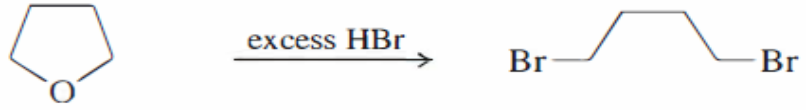


(f) (1) 

(2) Williamson ether synthesis is not feasible here. S_N2 does not work on either a benzene or a 3° halide.

PROBLEM 14-14

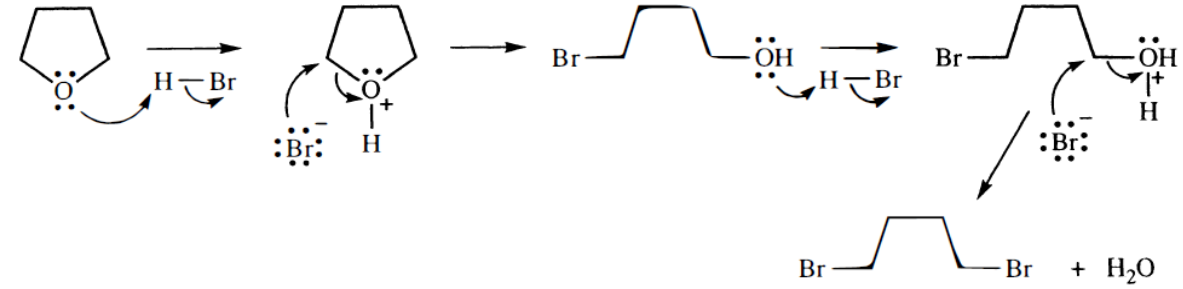
Propose a mechanism for the following reaction.



tetrahydrofuran — 1,4-dibromobutane

ANSWER

14-14



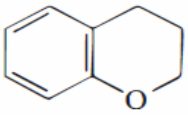
PROBLEM 14-15

Predict the products of the following reactions. An excess of acid is available in each case.

(a) ethoxycyclohexane + HBr

(b) tetrahydropyran + HI

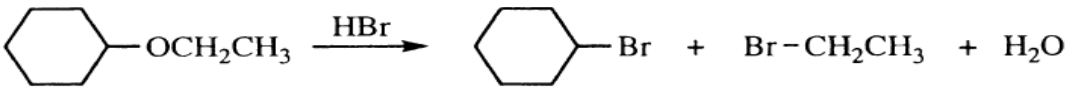
(c) anisole (methoxybenzene) + HBr

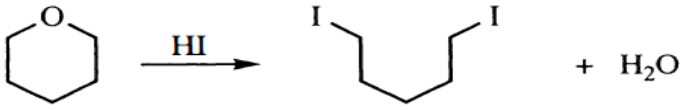
(d)  + HI

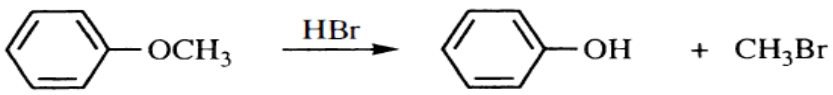
(e) $Ph-O-CH_2CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-O-CH_2CH_3$ + HBr

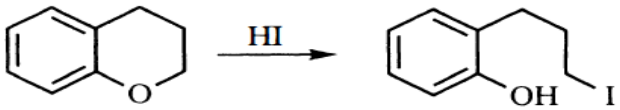
ANSWER

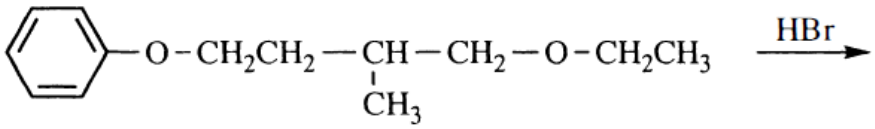
14-15

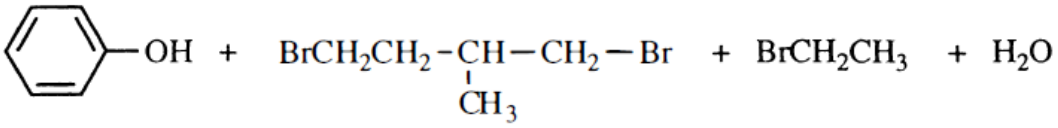
(a) 

(b) 

(c) 

(d) 

(e) 

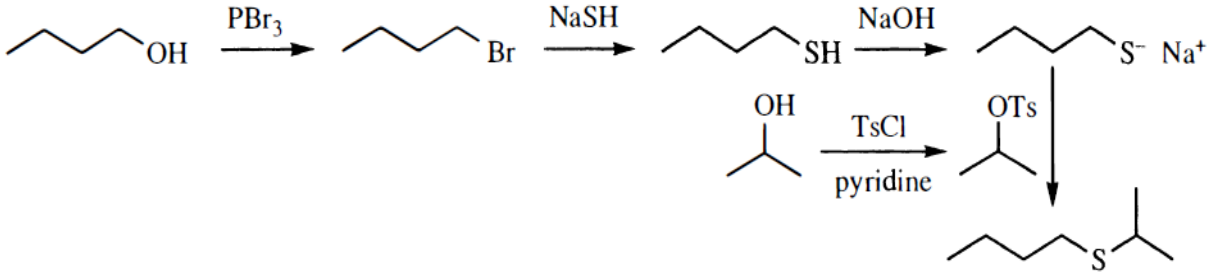


PROBLEM 14-17

Show how you would synthesize butyl isopropyl sulfide using 1-butanol, 2-propanol, and any solvents and reagents you need.

ANSWER

14-17 Begin by transforming the alcohols into good leaving groups like halides or tosylates:



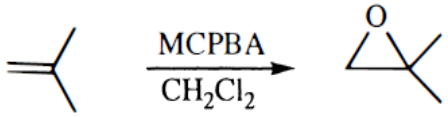
PROBLEM 14-19

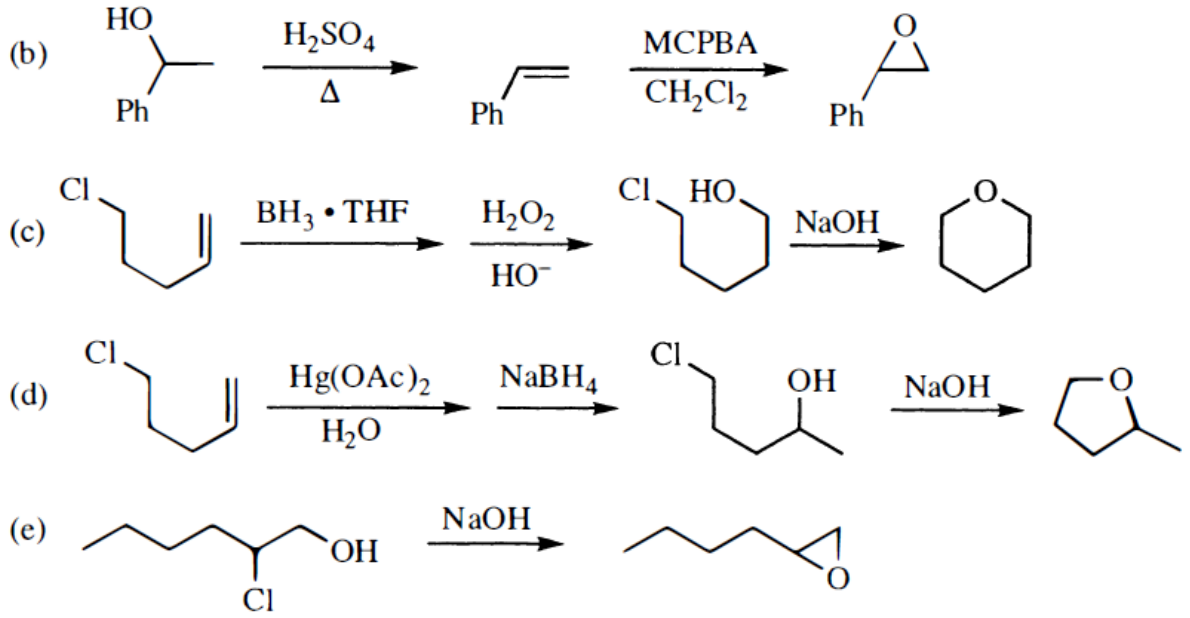
Show how you would accomplish the following transformations. Some of these examples require more than one step.

(a) 2-methylpropene → 2,2-dimethyloxirane
(b) 1-phenylethanol → 2-phenyloxirane
(c) 5-chloro-1-pentene → tetrahydropyran
(d) 5-chloro-1-pentene → 2-methyltetrahydrofuran
(e) 2-chloro-1-hexanol → 1,2-epoxyhexane

ANSWER

Generally, chemists prefer the peroxyacid method of epoxide formation to the halohydrin method. Reactions (a) and (b) show the peroxyacid method, but the halohydrin method could also be used.

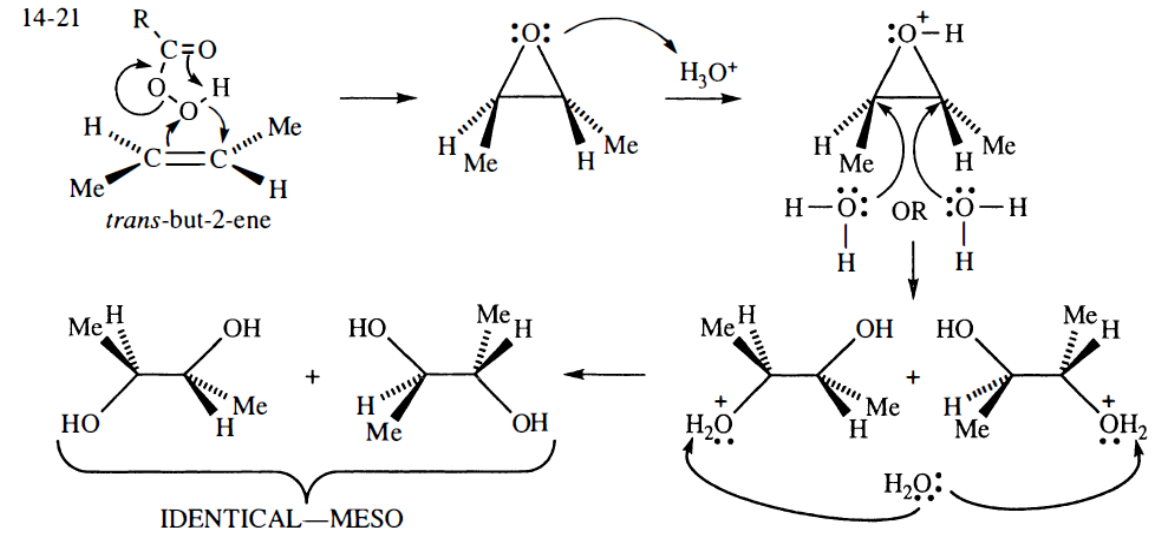
(a) 



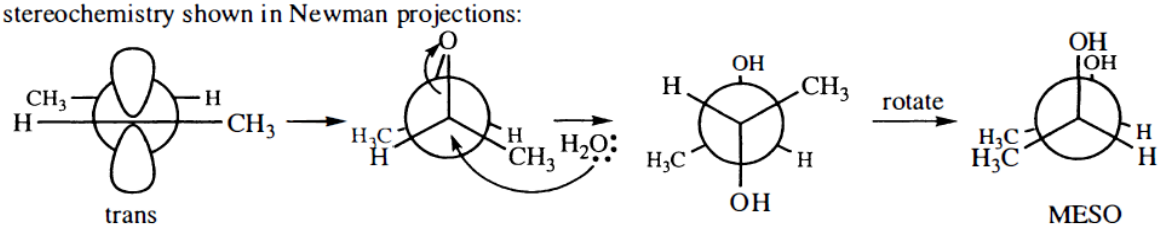
PROBLEM 14-21

Propose mechanisms for the epoxidation and ring-opening steps of the epoxidation and hydrolysis of *trans*-2-butene shown above. Predict the product of the same reaction with *cis*-2-butene.

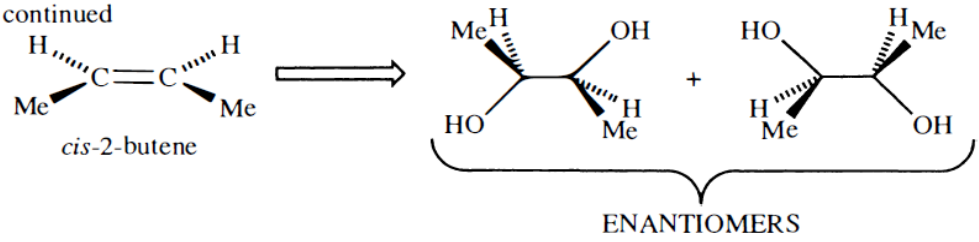
ANSWER



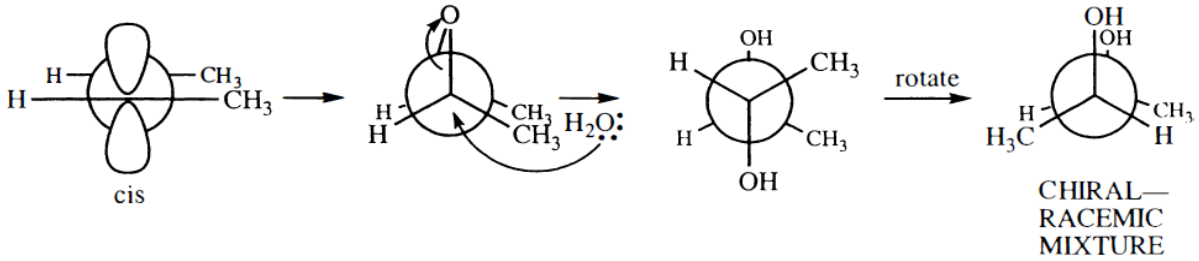
stereochemistry shown in Newman projections:



14-21 continued



stereochemistry shown in Newman projections:



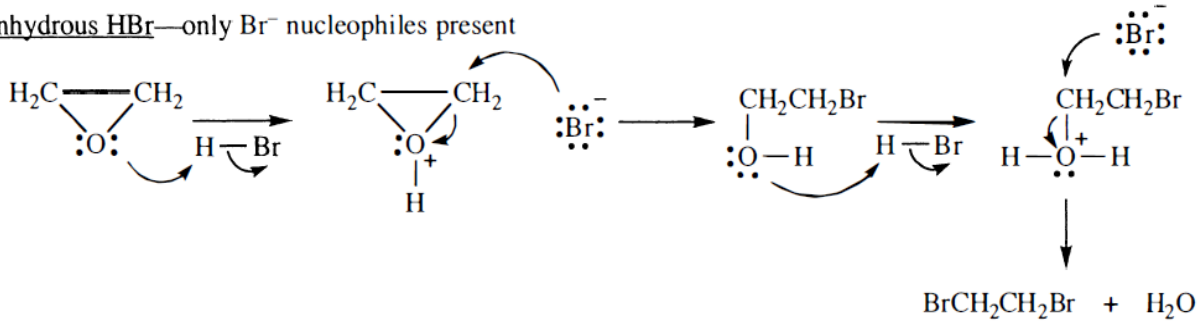
PROBLEM 14-23

When ethylene oxide is treated with anhydrous HBr gas, the major product is 1,2-dibromoethane. When ethylene oxide is treated with concentrated aqueous HBr, the major product is ethylene glycol. Use mechanisms to explain these results.

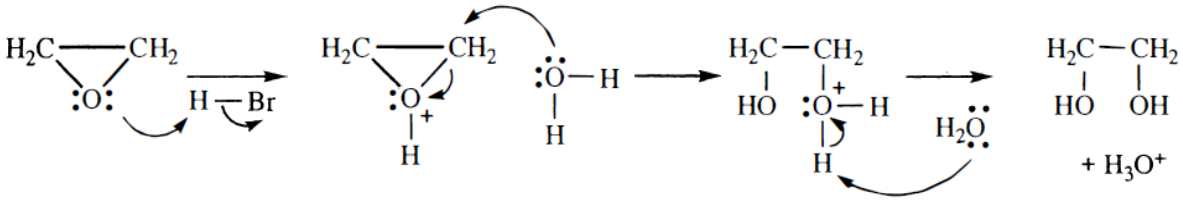
ANSWER

14-23

anhydrous HBr—only Br^- nucleophiles present



aqueous HBr—many more H_2O nucleophiles than Br^- nucleophiles

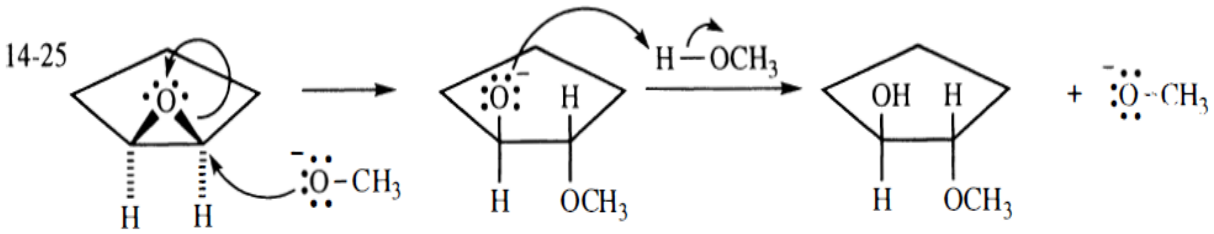


PROBLEM 14-25

Propose a complete mechanism for the reaction of cyclopentene oxide with sodium methoxide in methanol.

ANSWER

14-25



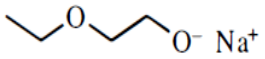
PROBLEM 14-26

Predict the major product when each reagent reacts with ethylene oxide.

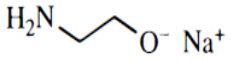
(a) $NaOCH_2CH_3$ (sodium ethoxide) **(b)** $NaNH_2$ (sodium amide)
(c) NaSPh (sodium thiophenoxide) **(d)** $PhNH_2$ (aniline)
(e) KCN (potassium cyanide) **(f)** NaN_3 (sodium azide)

14-26

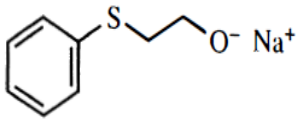
(a)



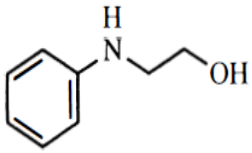
(b)



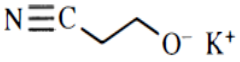
(c)



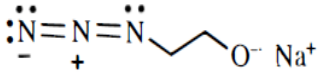
(d)



(e)



(f)



PROBLEM 14-27

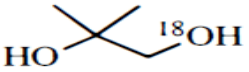
Predict the major products of the following reactions, including stereochemistry where appropriate.

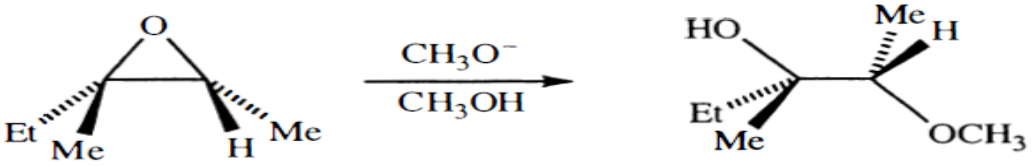
(a) 2,2-dimethyloxirane + $H^+/H_2{}^{18}O$ (oxygen-labeled water)
(b) 2,2-dimethyloxirane + $H^{18}O^-/H_2{}^{18}O$
(c) (*Z*)-2-ethyl-2,3-dimethyloxirane + CH_3O^-/CH_3OH
(d) (*Z*)-2-ethyl-2,3-dimethyloxirane + H^+/CH_3OH

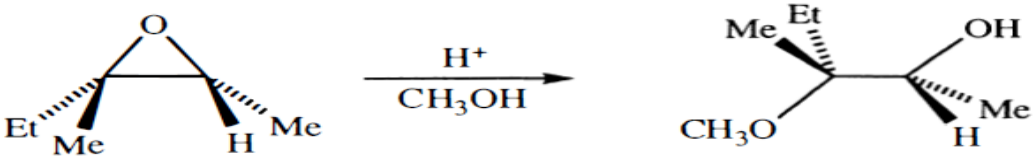
ANSWER

14-27

(a) 

(b) 

(c) 

(d) 

PROBLEM 14-28

Give the expected products of the following reactions. Include a hydrolysis step where necessary.

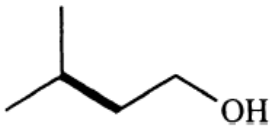
(a) ethylene oxide + isopropylmagnesium bromide

(b) 2,2-dimethyloxirane + methyllithium

(c) cyclopentyloxirane + ethyllithium

ANSWER

14-28 Newly formed bonds are shown in bold.

(a) 

(b) 

(c)