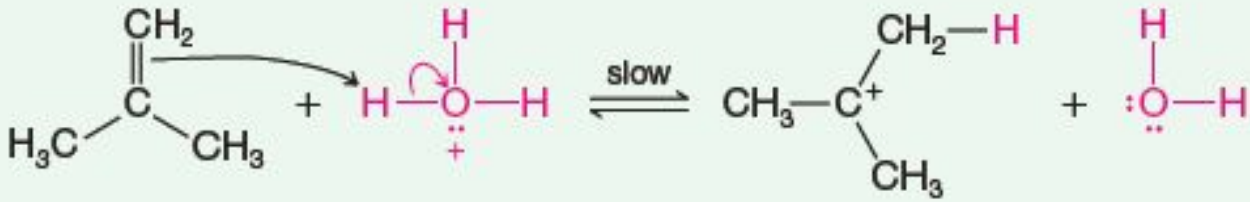
АЛКЕНЫ (часть 2)

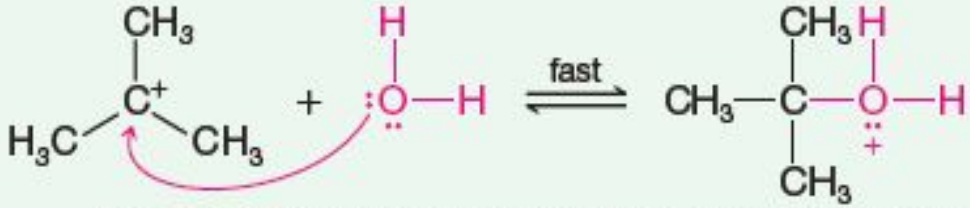
$$CH_2{=}CH_2 + HOH \xrightarrow[300\ ^\circ C]{H_3PO_4} CH_3CH_2OH$$

Step 1



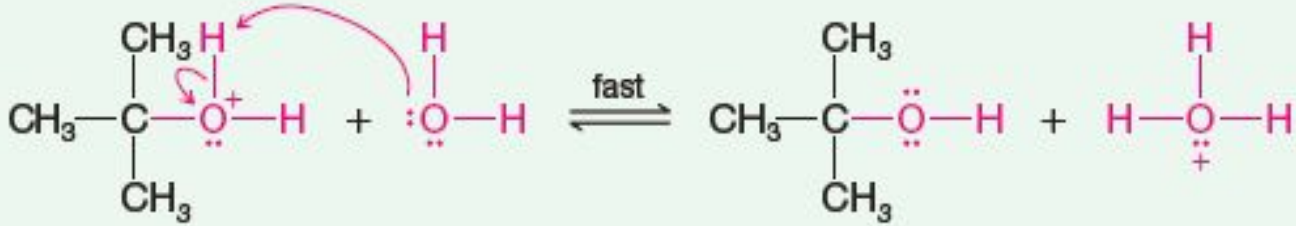
The alkene donates an electron pair to a proton to form the more stable 3° carbocation.

Step 2

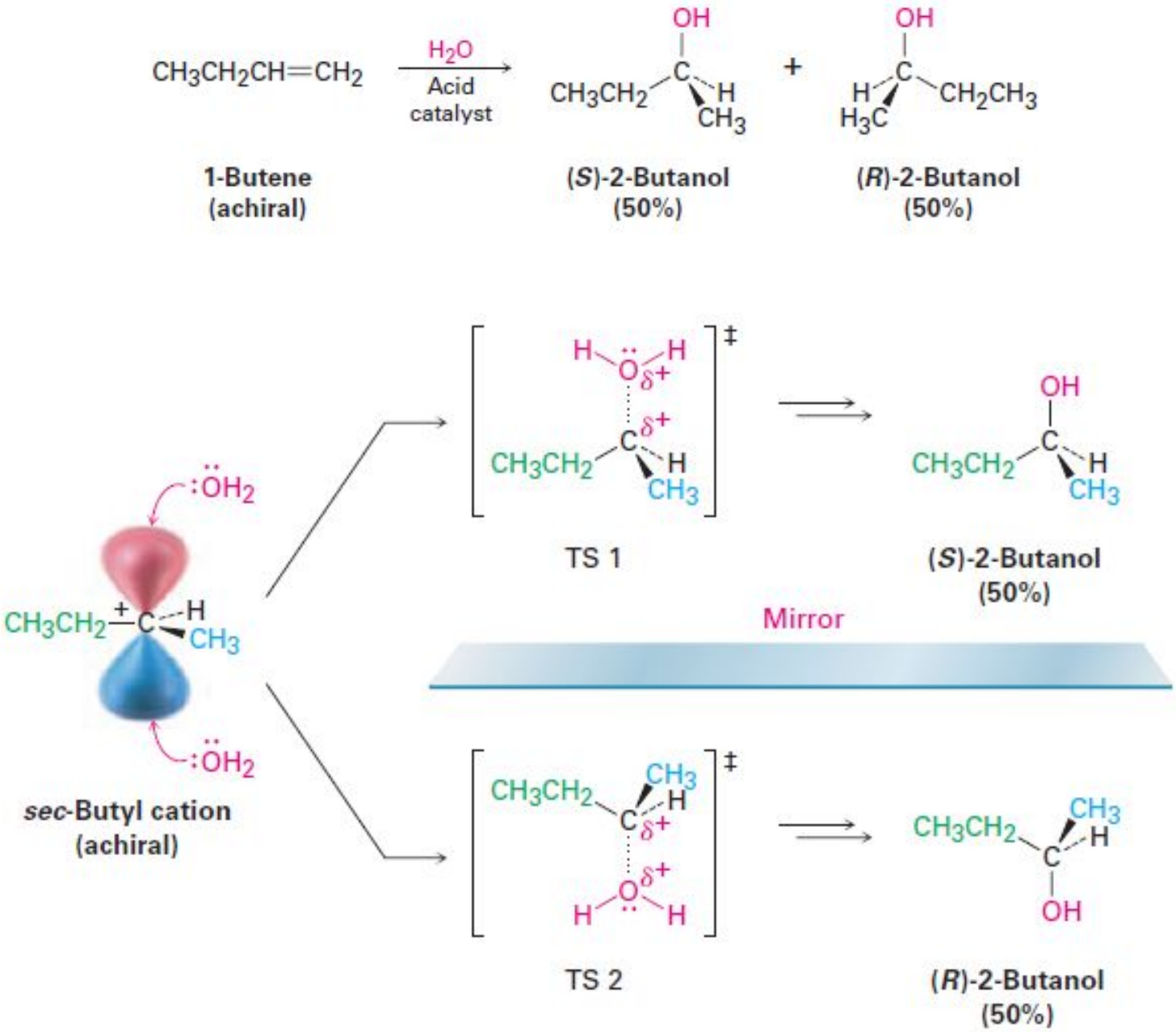


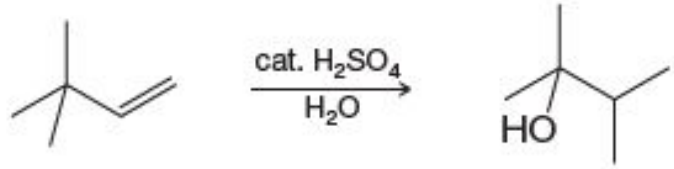
The carbocation reacts with a molecule of water to form a protonated alcohol.

Step 3



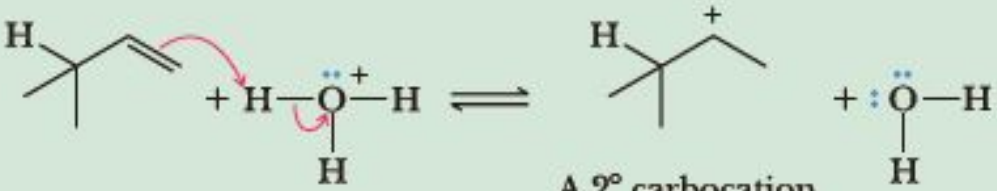
A transfer of a proton to a molecule of water leads to the product.


CH3CH2CH=CH2
H2O
Acid catalyst
OH
CH3CH2
C
H
CH3
+
OH
H
C
CH2CH3
H3C
1-Butene
(achiral)
(S)-2-Butanol
(50%)
(R)-2-Butanol
(50%)
:OH2
CH3CH2
C
H
CH3
:OH2
sec-Butyl cation
(achiral)
TS 1
(S)-2-Butanol
(50%)
Mirror
TS 2
(R)-2-Butanol
(50%)



3,3-Dimethyl-1-butene

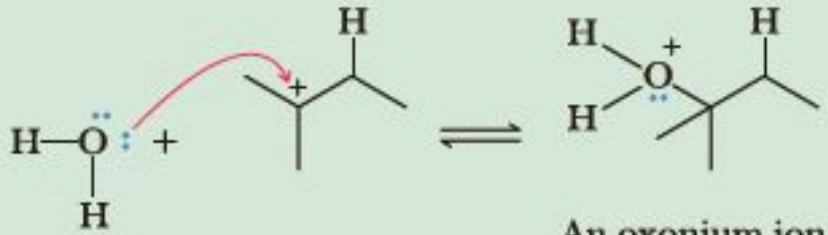
2,3-Dimethyl-2-butanol
(major product)



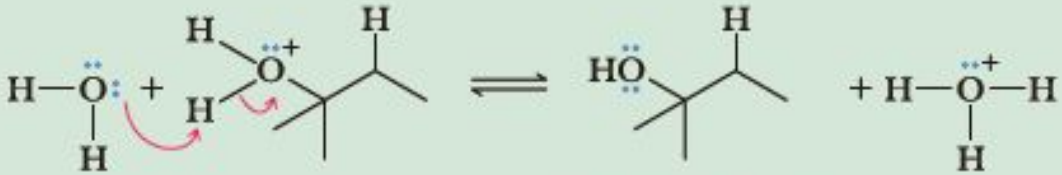
A 2° carbocation intermediate

A 2° carbocation intermediate

A 3° carbocation intermediate



An oxonium ion

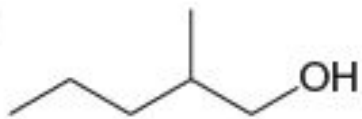


2-Methyl-2-butanol

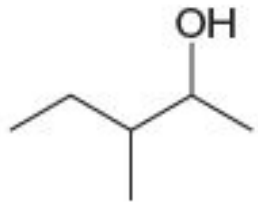
Specify the appropriate alkene and reagents for synthesis of each of the following alcohols by hydroboration–oxidation.

(a)

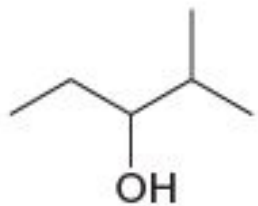
(b)



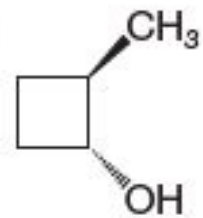
(c)



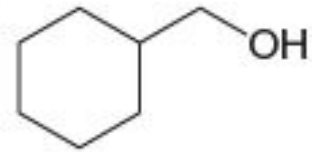
(d)



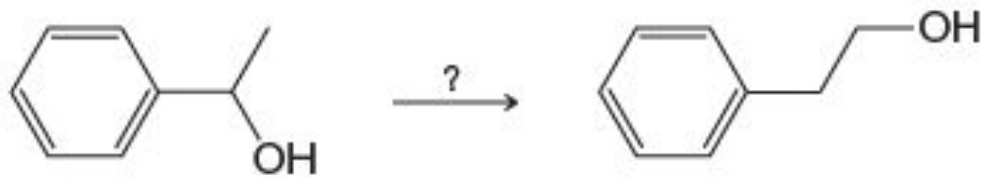
(e)



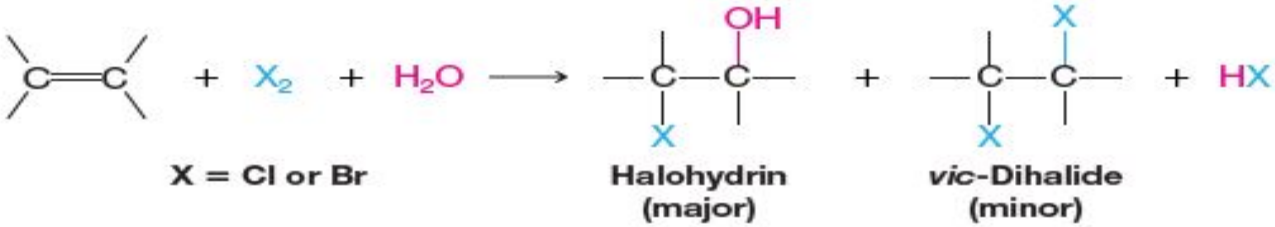
(f)

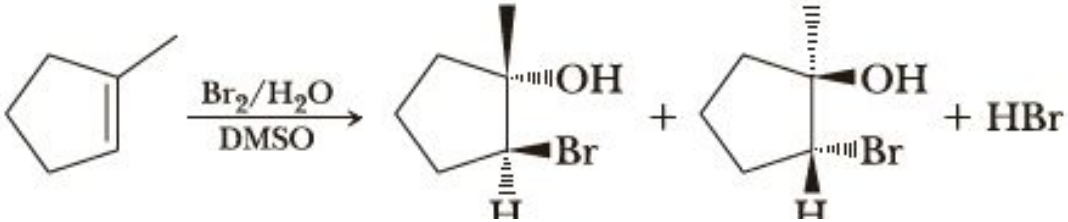


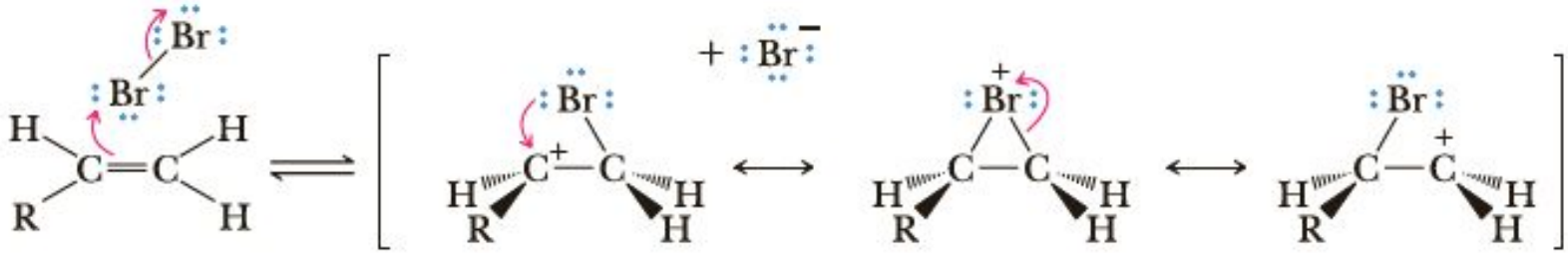
Show how you could synthesize 2-phenylethanol from 1-phenylethanol.

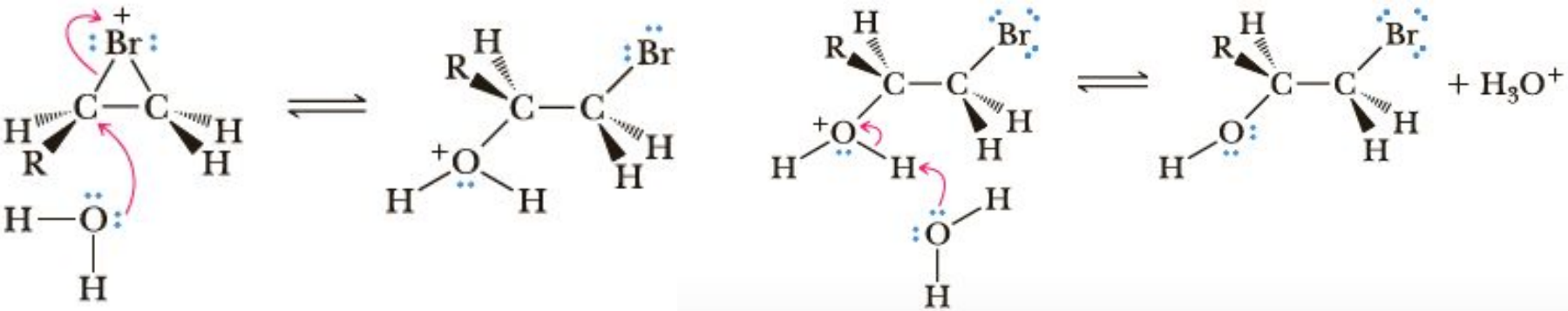


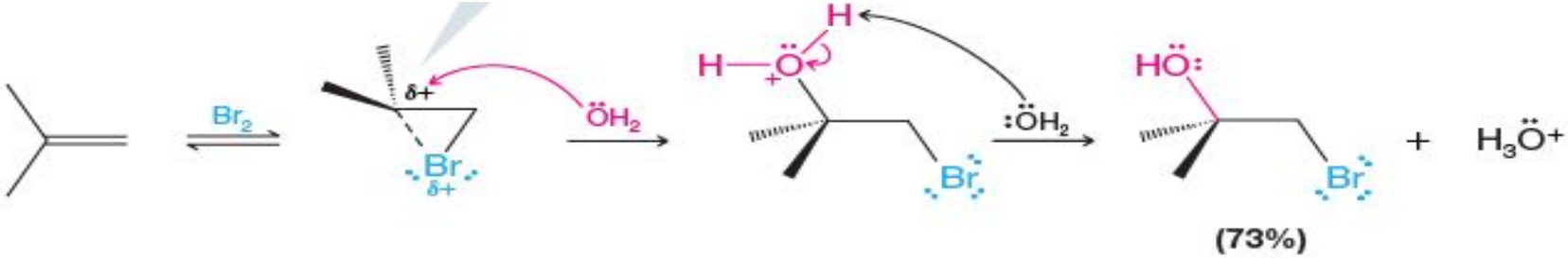
1-Phenylethanol **2-Phenylethanol**


X = Cl or Br
Halohydrin
(major)
vic-Dihalide
(minor)


Br2/H2O
DMSO
+ HBr



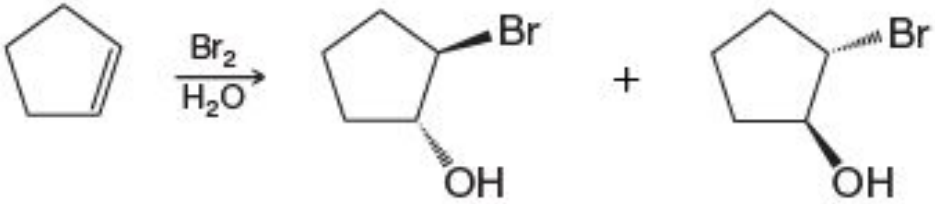

+ H3O+



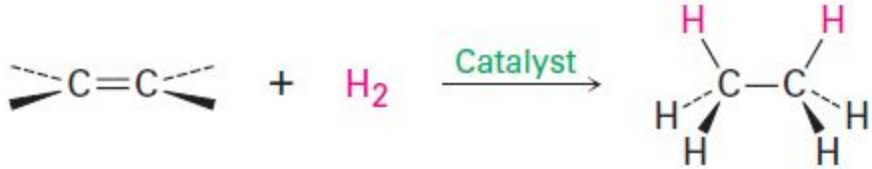
Draw the structure of the bromohydrin formed by treating 2-methylpropene with Br_2/H_2O.

Draw the structure of the chlorohydrin formed by treating 1-methylcyclohexene with Cl_2/H_2O.

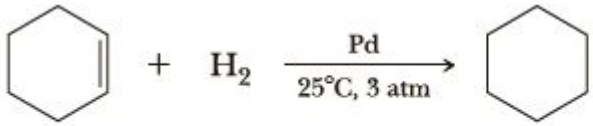
Write a mechanism to explain the following reaction.



(as a racemic mixture)

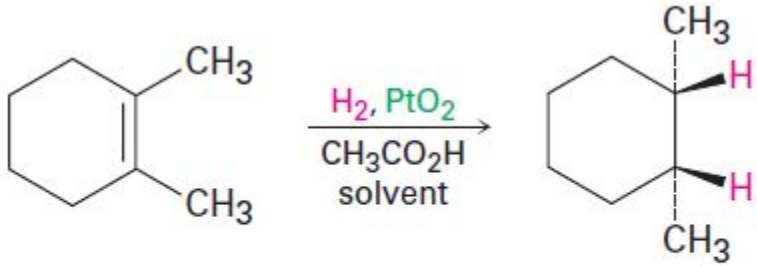


An alkene **An alkane**

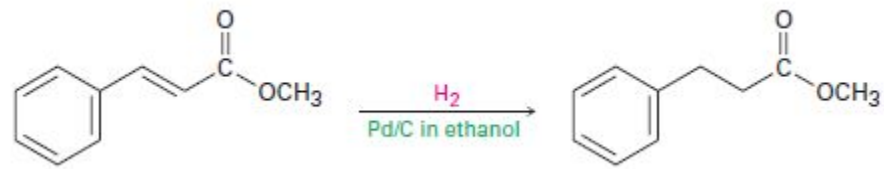


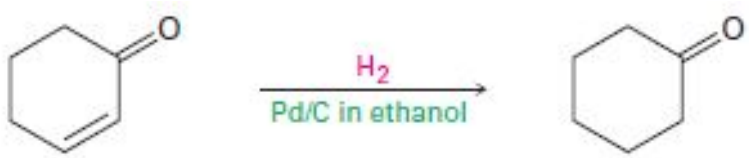
$\Delta H^0 = -119.5$ kJ $(-28.6$ kcal$)$/mol

Cyclohexene **Cyclohexane**

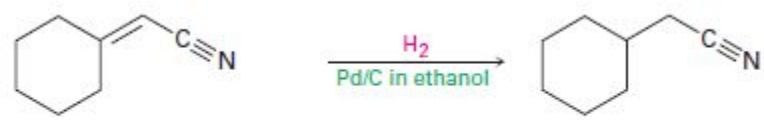


1,2-Dimethyl-cyclohexene **cis-1,2-Dimethyl-cyclohexane (82%)**

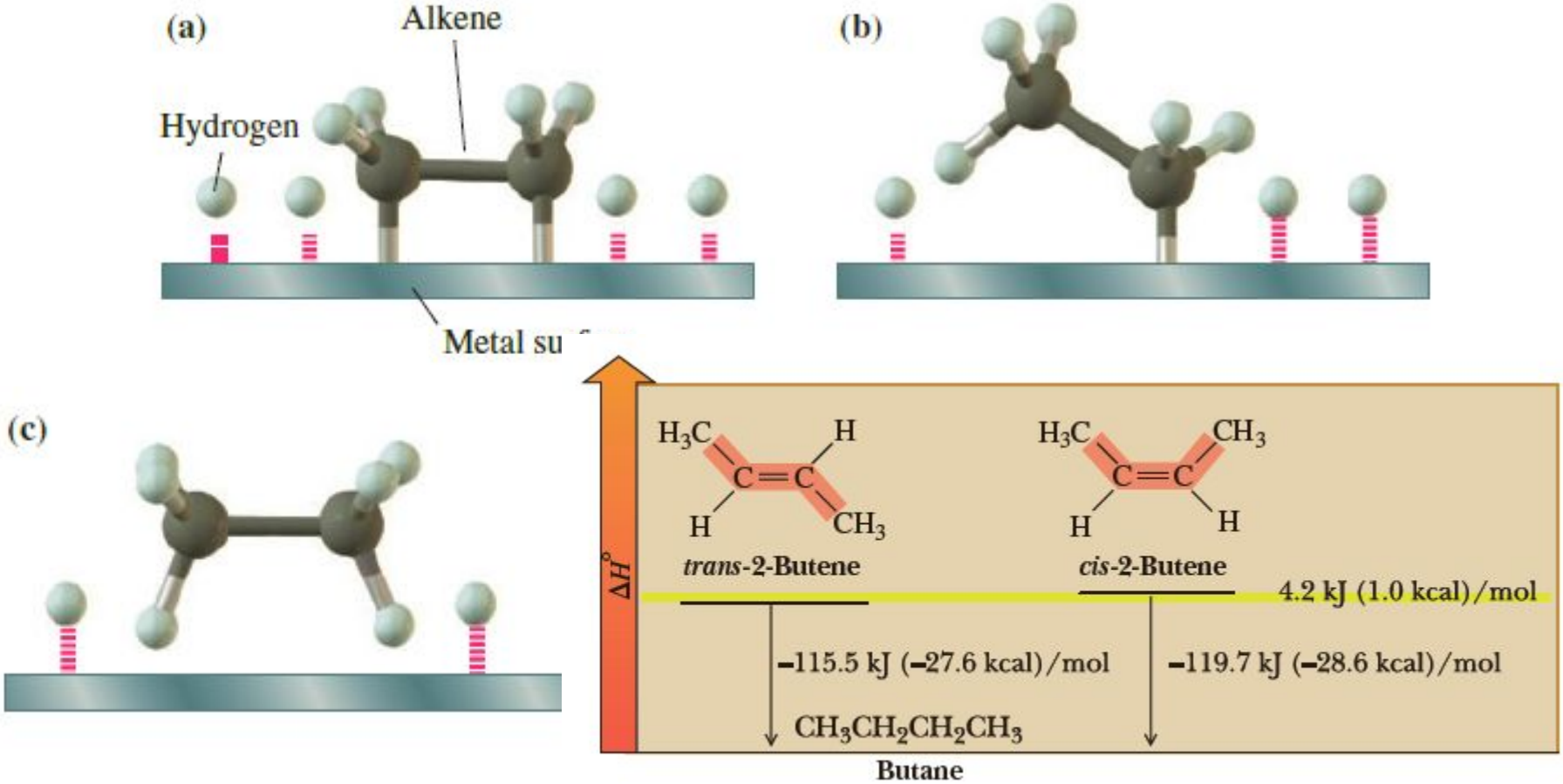


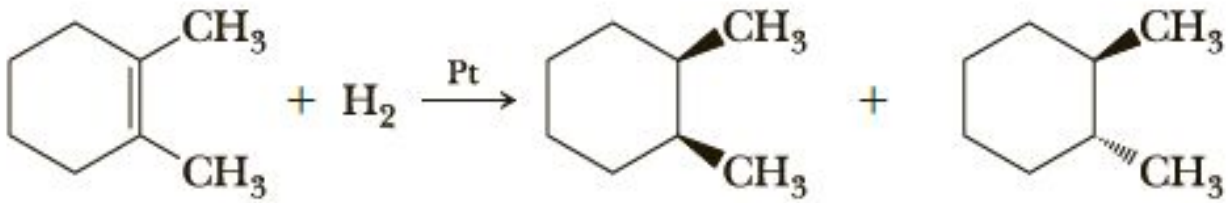


2-Cyclohexenone **Cyclohexanone (ketone not reduced)**



Cyclohexylideneacetonitrile **Cyclohexylacetonitrile (nitrile not reduced)**

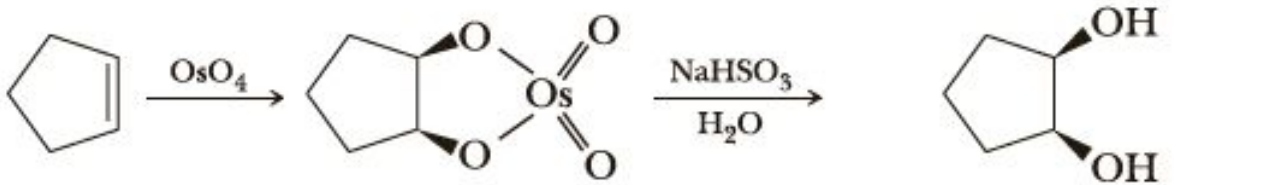


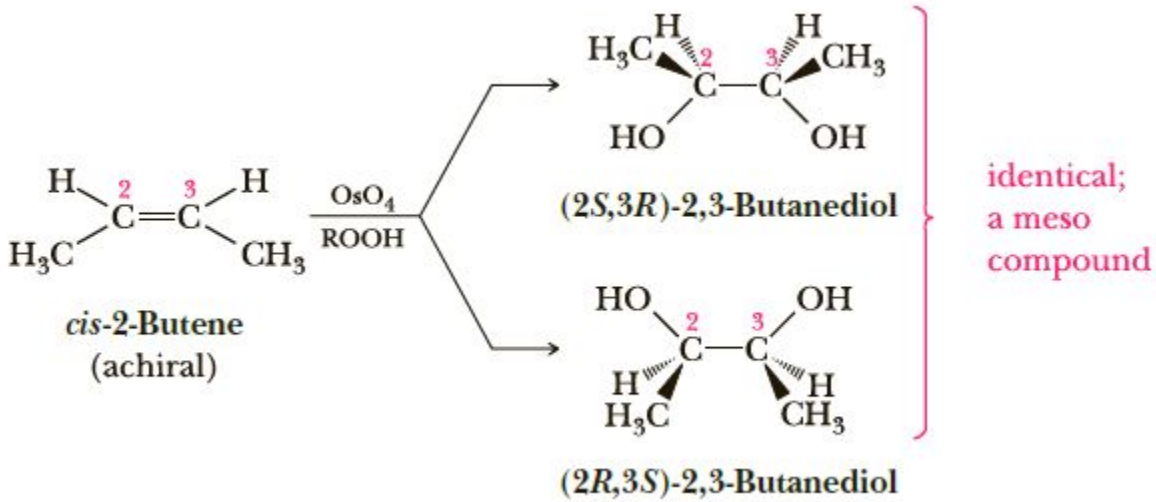


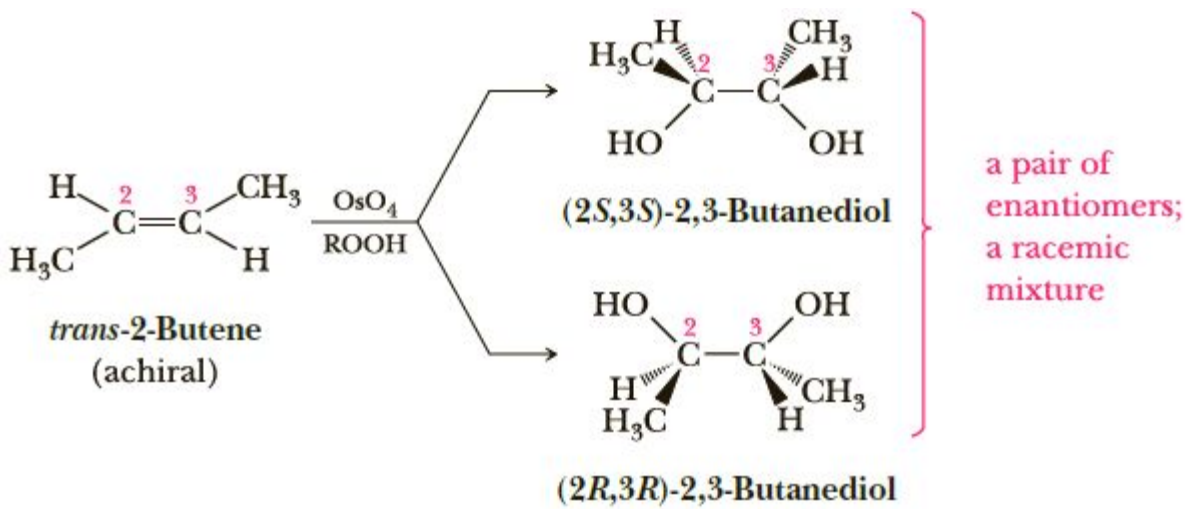
1,2-Dimethyl-cyclohexene

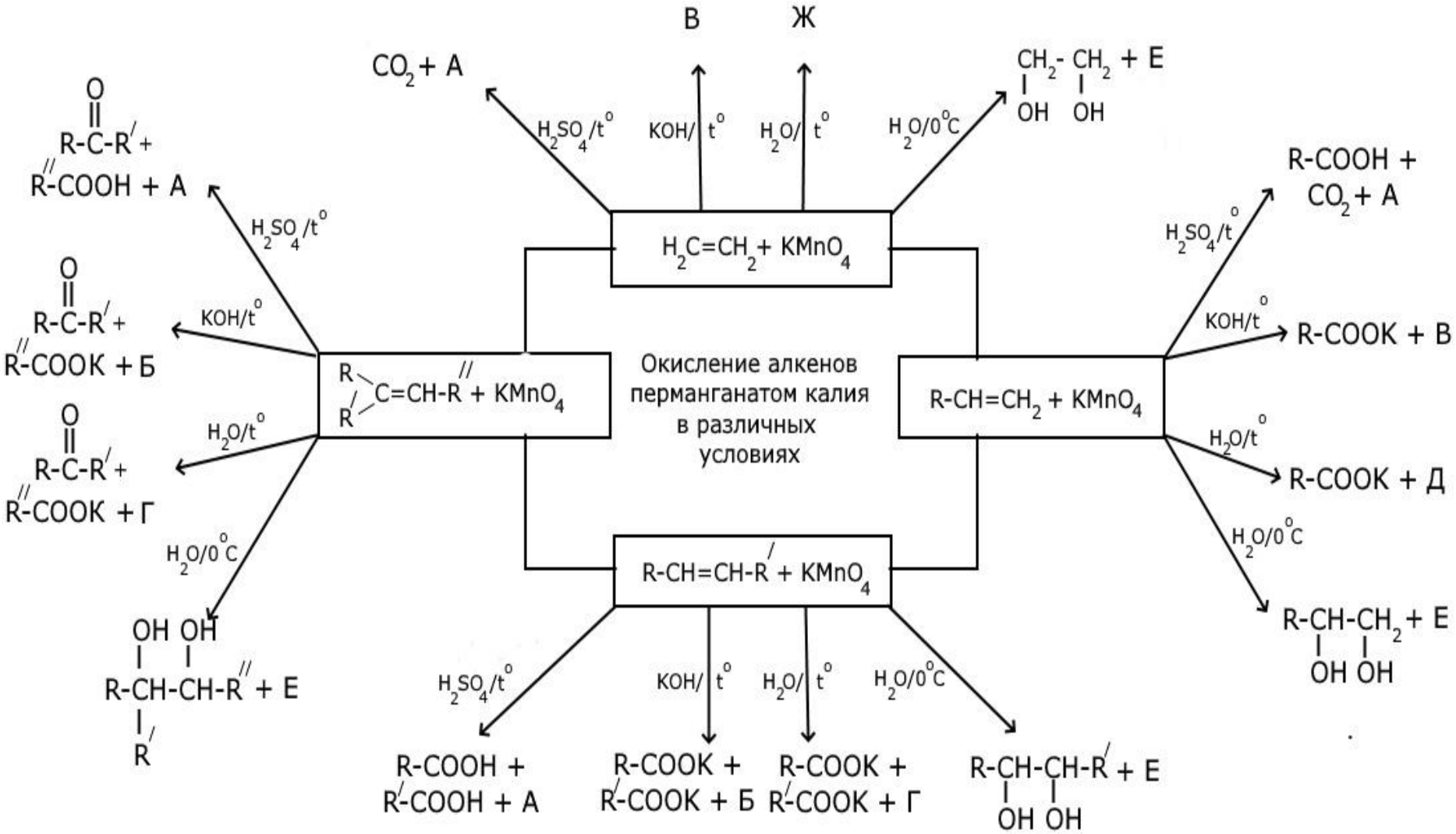
70% to 85% *cis*-1,2-Dimethyl-cyclohexane

30% to 15% *trans*-1,2-Dimethyl-cyclohexane (a racemic mixture)


OsO4
NaHSO3
H2O
A cyclic osmate
cis-1,2-Cyclopentanediol
(a cis glycol)

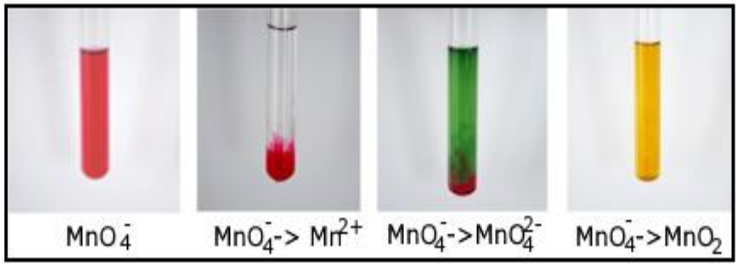

cis-2-Butene
(achiral)
OsO4
ROOH
(2S,3R)-2,3-Butanediol
(2R,3S)-2,3-Butanediol
identical;
a meso
compound

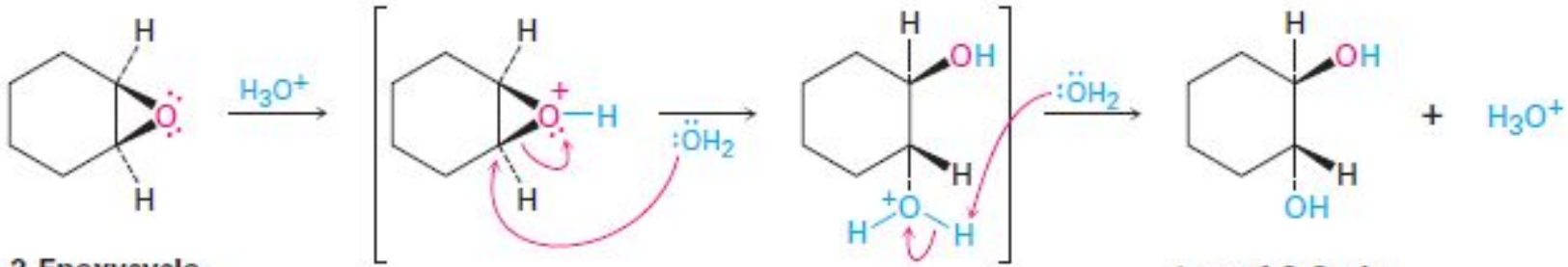

trans-2-Butene
(achiral)
OsO4
ROOH
(2S,3S)-2,3-Butanediol
(2R,3R)-2,3-Butanediol
a pair of
enantiomers;
a racemic
mixture



А: $K_2SO_4 + MnSO_4 + H_2O$
Б: $K_2MnO_4 + H_2O$
В: $K_2MnO_4 + K_2CO_3 + H_2O$
Г: $KOH + MnO_2 + H_2O$
Д: $K_2CO_3 + KOH + MnO_2 + H_2O$

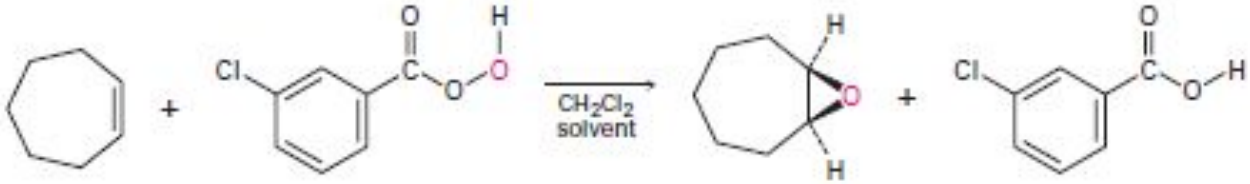
Е: $MnO_2 + KOH$
Ж: $K_2CO_3 + MnO_2 + H_2O$

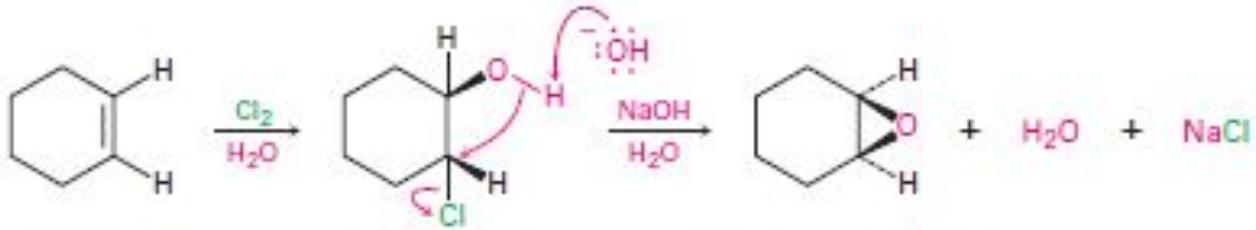




1,2-Epoxycyclohexane

trans-1,2-Cyclohexanediol (86%)

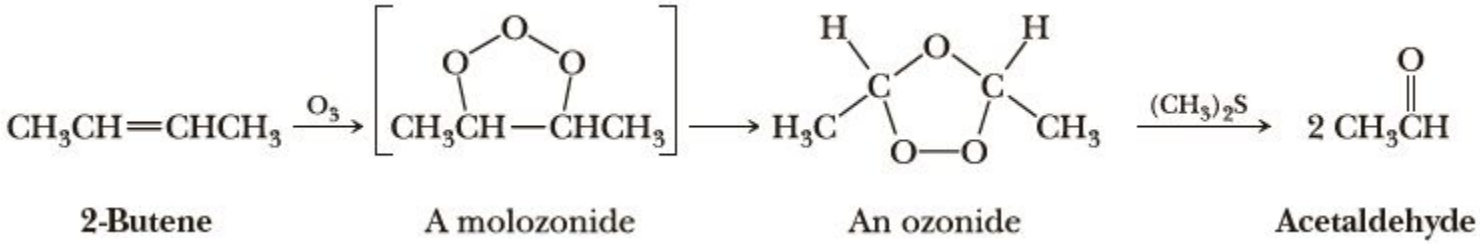




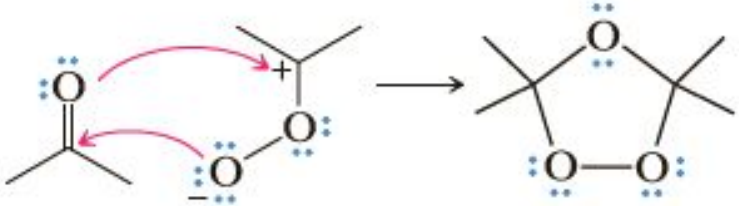
Cyclohexene

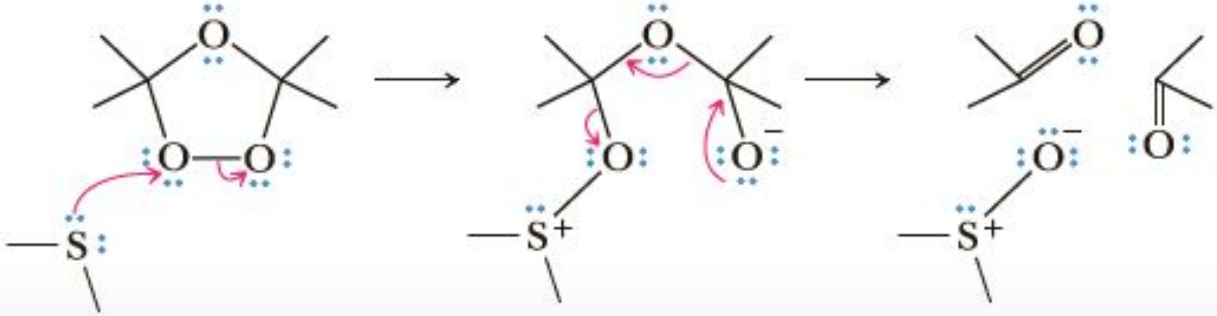
trans-2-Chlorocyclohexanol

1,2-Epoxycyclohexane (73%)

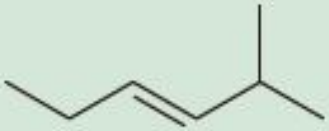


A molozonide

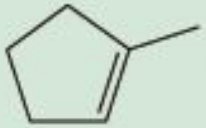




Draw structural formulas for the products of the following ozonolysis reactions and name the new functional groups formed in each oxidation.

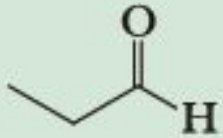
(a) 

$\xrightarrow[2.\ (CH_3)_2S]{1.\ O_3}$

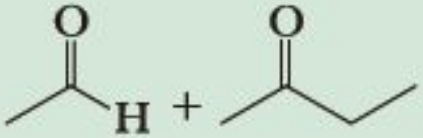
(b) 

$\xrightarrow[2.\ (CH_3)_2S]{1.\ O_3}$

What alkene with the molecular formula C_6H_{12}, when treated with ozone and then dimethyl sulfide, gives the following product(s)?

(a) 

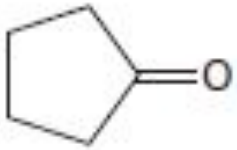
(only product)

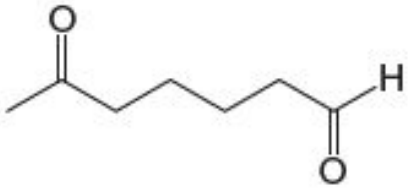
(b) 

(equal moles of each)

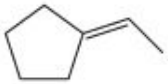
(c)

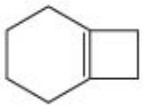
(only product)

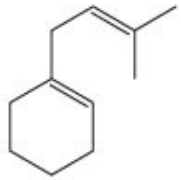
? $\xrightarrow[2.\ Zn,\ acetic\ acid]{1.\ O_3}$  + $CH_3CH_2\overset{O}{\overset{\|}{C}}H$

C_7H_{12} $\xrightarrow[(2)\ Me_2S]{(1)\ O_3,\ CH_2Cl_2,\ -78\ °C}$ 

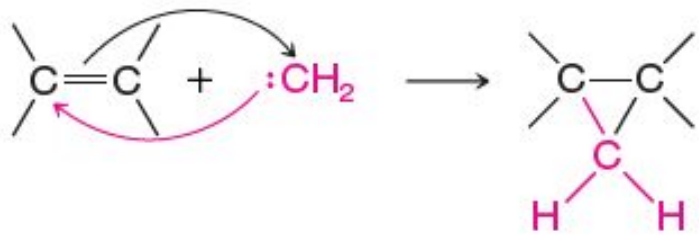
Predict the products of the following ozonolysis reactions.

(a)  $\xrightarrow[(2)\ Me_2S]{(1)\ O_3}$

(b)  $\xrightarrow[(2)\ Me_2S]{(1)\ O_3}$

(c)  $\xrightarrow[(2)\ Me_2S]{(1)\ O_3}$

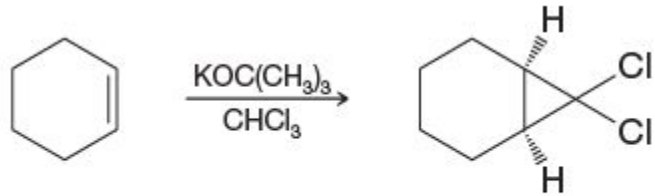
Diazomethane **Methylene** **Nitrogen**



Alkene **Methylene** **Cyclopropane**

+ enantiomer

Dichlorocarbene

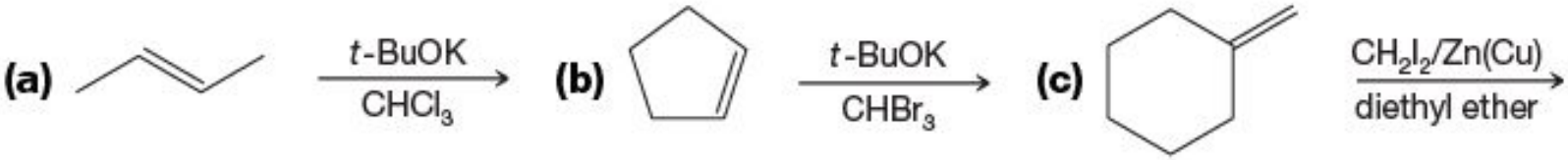


7,7-Dichlorobicyclo[4.1.0]heptane
(59%)

$$CH_2I_2 + Zn(Cu) \longrightarrow ICH_2ZnI$$

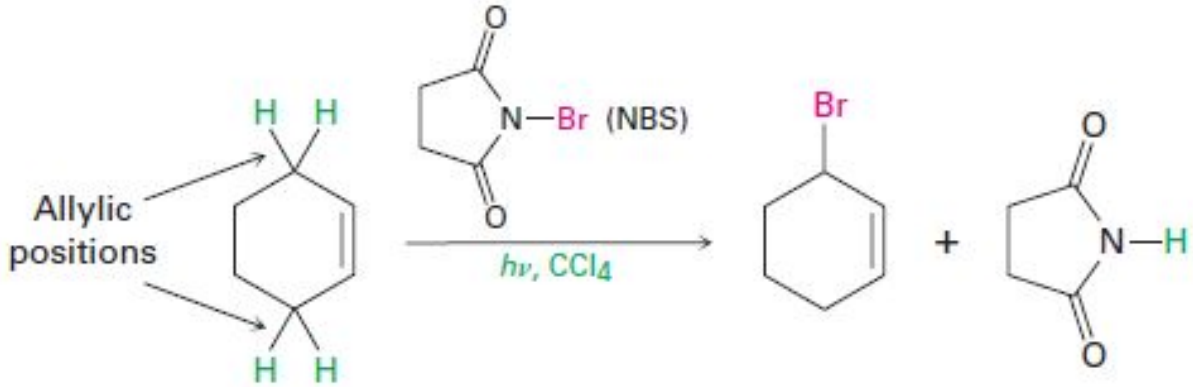
A carbenoid

What products would you expect from each of the following reactions?

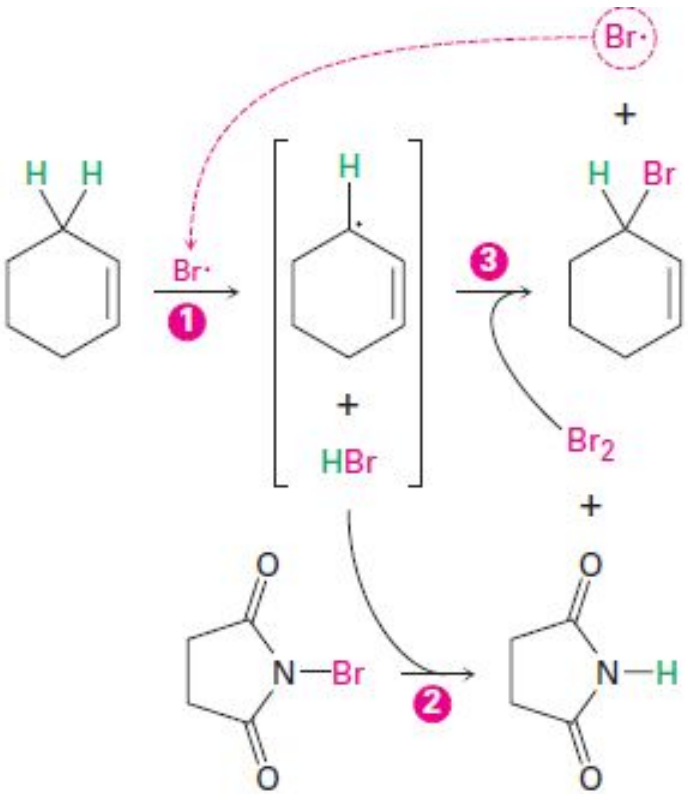


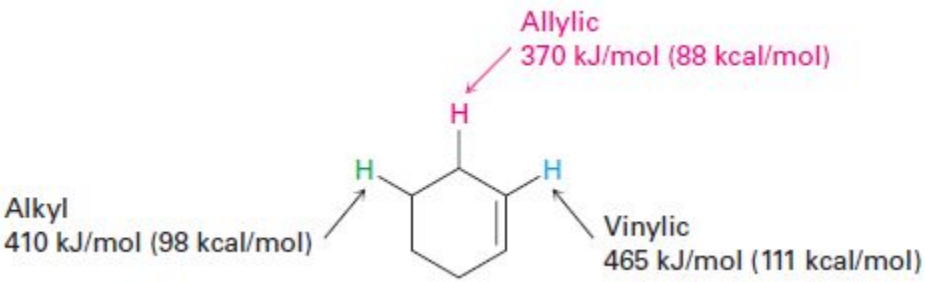
Starting with cyclohexene and using any other needed reagents, outline a synthesis of 7,7-dibromobicyclo[4.1.0]heptane.

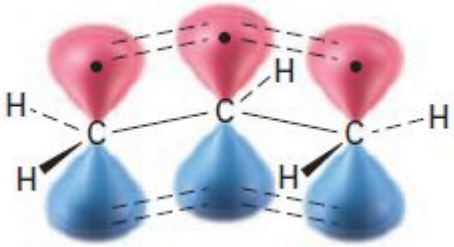
Treating cyclohexene with 1,1-diiodoethane and a zinc–copper couple leads to two isomeric products. What are their structures?

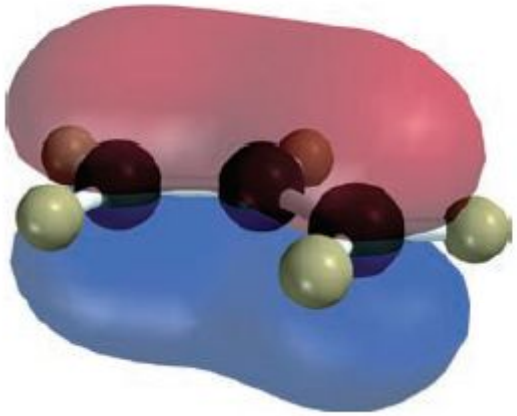


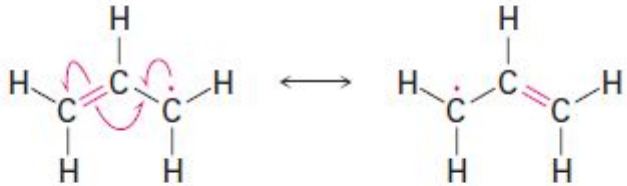
Cyclohexene **3-Bromocyclohexene (85%)**











$$CH_3CH_2CH_2CH_2CH_2CH_2CH{=}CH_2$$

1-Octene

$\downarrow$ NBS, $h\nu$, CCl_4

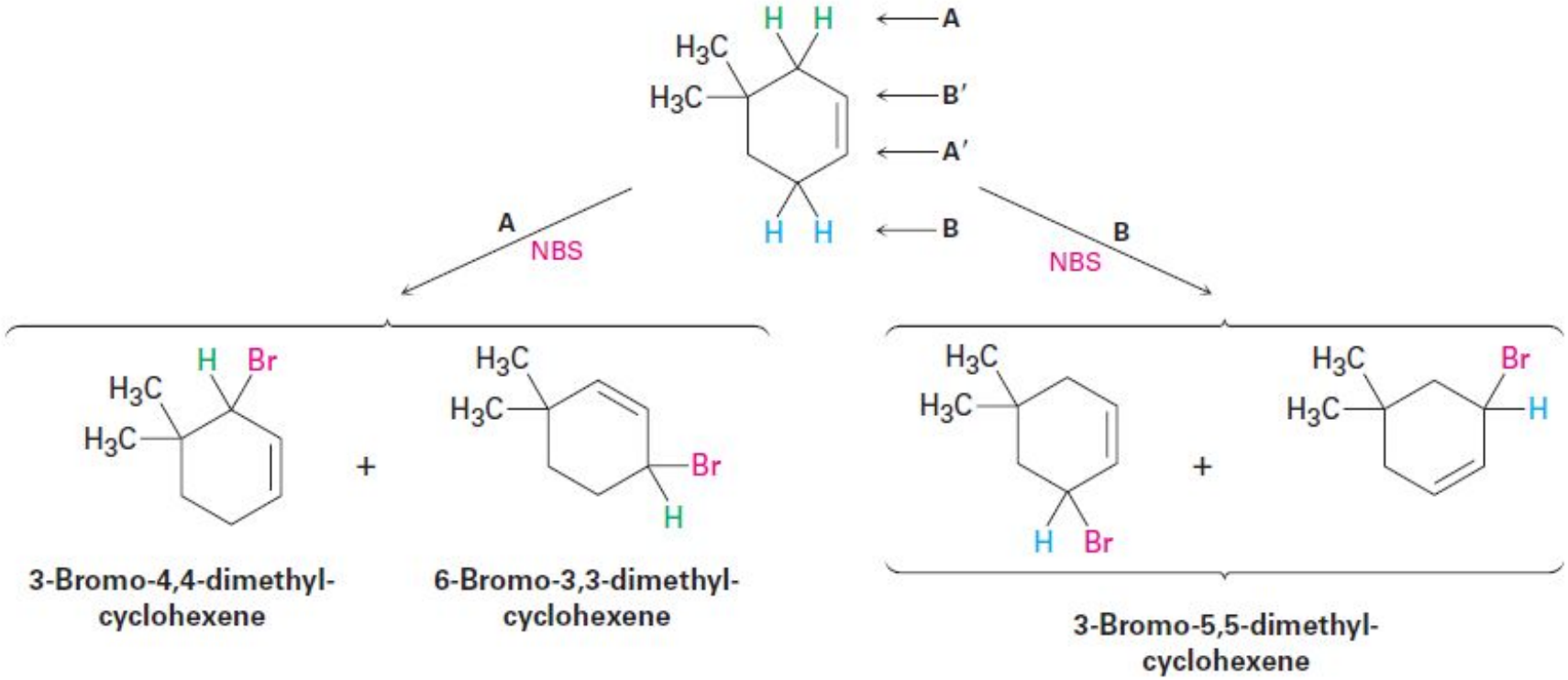
$$\left[CH_3CH_2CH_2CH_2CH_2\dot{C}HCH{=}CH_2 \longleftrightarrow CH_3CH_2CH_2CH_2CH_2CH{=}CH\dot{C}H_2\right]$$

$\downarrow$

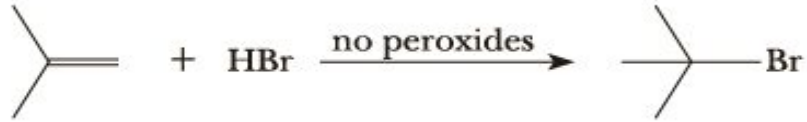
$$CH_3CH_2CH_2CH_2CH_2\overset{Br}{\overset{|}{C}}HCH{=}CH_2 \quad + \quad CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_2Br$$

3-Bromo-1-octene (17%) | **1-Bromo-2-octene (83%) (53 : 47 trans : cis)**

Solution


H H
H3C
H3C
A
B′
A′
B
H H
A
NBS
B
NBS
H Br
H3C
H3C
+
H3C
H3C
Br
H
H3C
H3C
H Br
+
H3C
H3C
Br
H
3-Bromo-4,4-dimethyl-cyclohexene
6-Bromo-3,3-dimethyl-cyclohexene
3-Bromo-5,5-dimethyl-cyclohexene

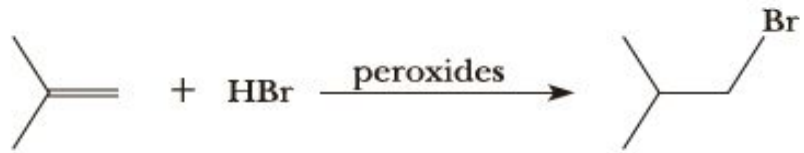
Markovnikov addition



2-Methylpropene

2-Bromo-2-methylpropane

Non-Markovnikov addition



2-Methylpropene

1-Bromo-2-methylpropane

Step 1:

A dialkyl peroxide

Two alkoxy radicals

Step 2:

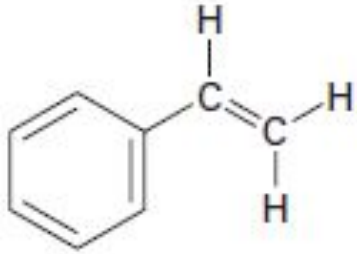
Bromine radical

Step 3:

A 3° radical

Step 4:

1-Bromo-2-methylpropane



(a) $\xrightarrow{H_2/Pd}$?

(b) $\xrightarrow{Br_2}$?

(c) $\xrightarrow[NMO]{OsO_4}$?

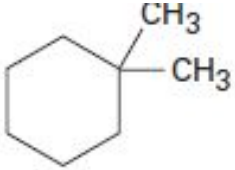
(d) $\xrightarrow{Cl_2,\ H_2O}$?

(e) $\xrightarrow{CH_2I_2,\ Zn/Cu}$?

(f) $\xrightarrow{\textit{meta}\text{-Chloroperoxy-benzoic acid}}$?

(a) ? $\xrightarrow{H_2/Pd}$ $CH_3CH(CH_3)CH_2CH_2CH_2CH_3$

(b) ? $\xrightarrow{H_2/Pd}$

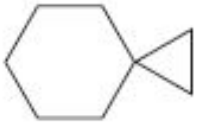


(c) ? $\xrightarrow{Br_2}$ $CH_3CH(Br)CH(Br)CH_2CH(CH_3)CH_3$

(d) ? $\xrightarrow{HCl}$ $CH_3CH(Cl)CH(CH_3)CH_2CH_2CH_2CH_3$

(e) ? $\xrightarrow[2.\ NaBH_4]{1.\ Hg(OAc)_2,\ H_2O}$ $CH_3CH_2CH_2CH(OH)CH_3$

(f) ? $\xrightarrow{CH_2I_2,\ Zn/Cu}$

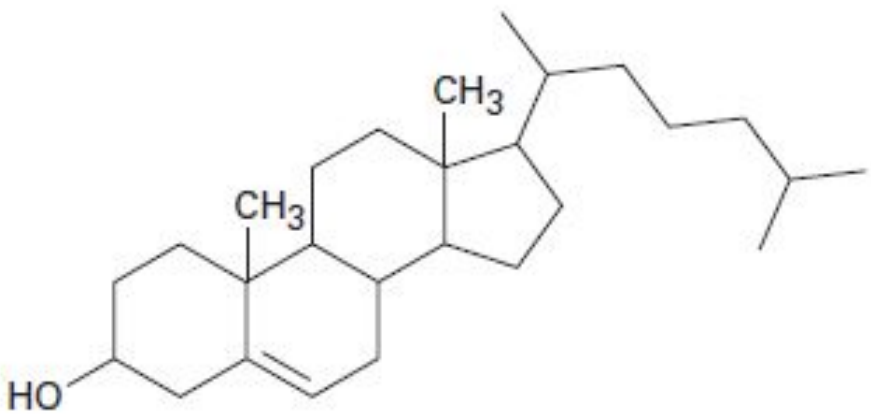


The cis and trans isomers of 2-butene give different cyclopropane products in the Simmons–Smith reaction. Show the structures of both, and explain the difference.

$$\textit{cis}\text{-}CH_3CH{=}CHCH_3 \xrightarrow{CH_2I_2,\ Zn(Cu)} ?$$

$$\textit{trans}\text{-}CH_3CH{=}CHCH_3 \xrightarrow{CH_2I_2,\ Zn(Cu)} ?$$

Predict the products of the following reactions. Don't worry about the size of the molecule; concentrate on the functional groups.



Cholesterol

$$\xrightarrow{Br_2} \text{A?}$$

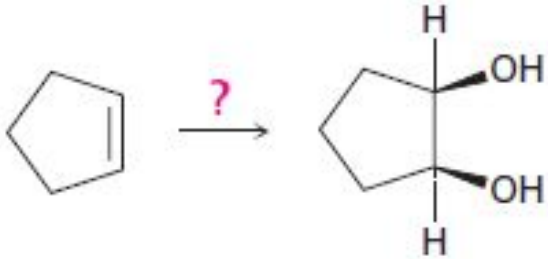
$$\xrightarrow{HBr} \text{B?}$$

$$\xrightarrow[2.\ NaHSO_3]{1.\ OsO_4} \text{C?}$$

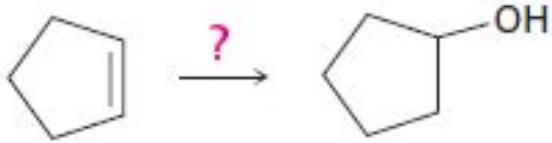
$$\xrightarrow[2.\ H_2O_2,\ {}^{-}OH]{1.\ BH_3,\ THF} \text{D?}$$

$$\xrightarrow{CH_2I_2,\ Zn(Cu)} \text{E?}$$

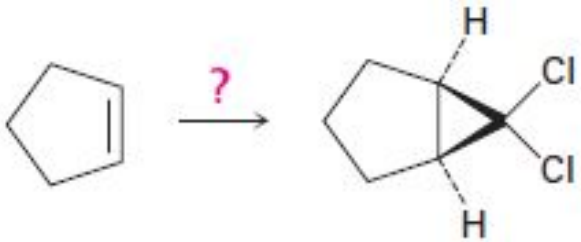
(a)



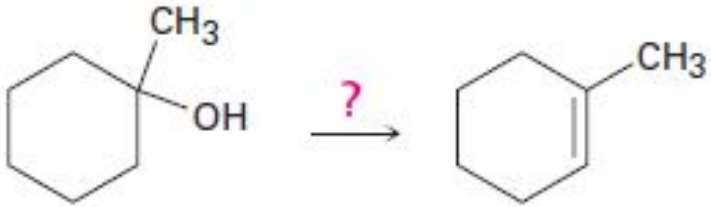
(b)



(c)



(d)



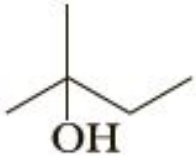
(e)

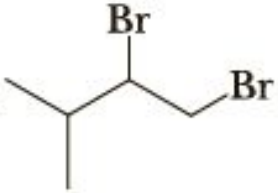
$$CH_3CH{=}CHCH(CH_3)CH_3 \xrightarrow{?} CH_3C(=O)H + CH_3CH(CH_3)C(=O)H$$

(f)

$$CH_3C(CH_3){=}CH_2 \xrightarrow{?} CH_3CH(CH_3)CH_2OH$$

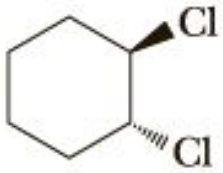
Draw a structural formula for an alkene with the indicated molecular formula that gives the compound shown as the major product (more than one alkene may give the same compound as the major product).

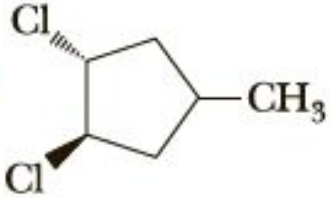
(a) $C_5H_{10} + H_2O \xrightarrow{H_2SO_4}$ 

(b) $C_5H_{10} + Br_2 \longrightarrow$ 

(c) $C_7H_{12} + HCl \longrightarrow$

Draw a structural formula for the cycloalkene with the molecular formula C_6H_{10} that reacts with Cl_2 to give each compound.

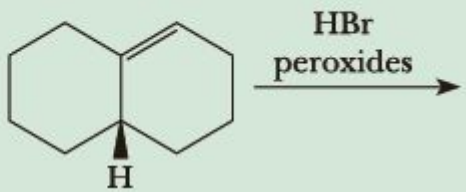
(a) 

(b) 

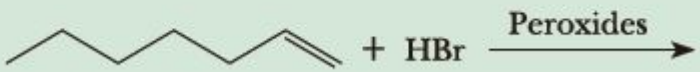
(c)

(d)

Predict the product of the following reaction:

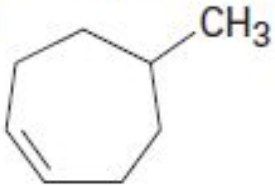
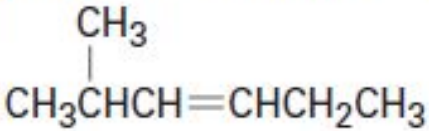


Predict the major product of the following reaction:



What products would you expect from reaction of the following alkenes with NBS? If more than one product is formed, show the structures of all.

(a)



(b)