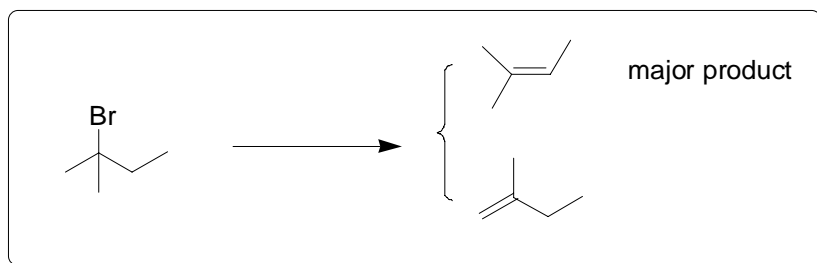


Chapter 7

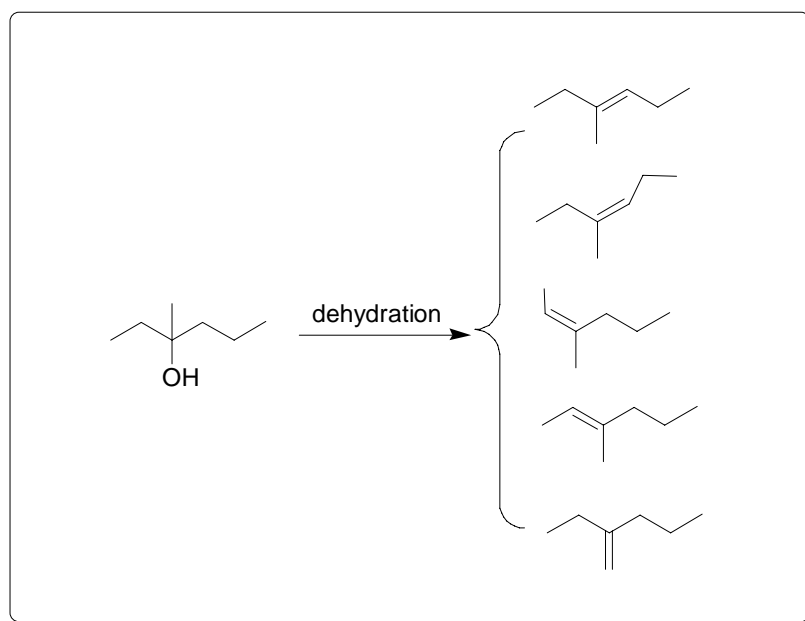
7.1 One problem with elimination reactions is that mixtures of products are often formed. For example, treatment of 2-bromo-2-methylbutane with KOH in ethanol yields a mixture of two alkene products. What are their likely structures?

Solution:



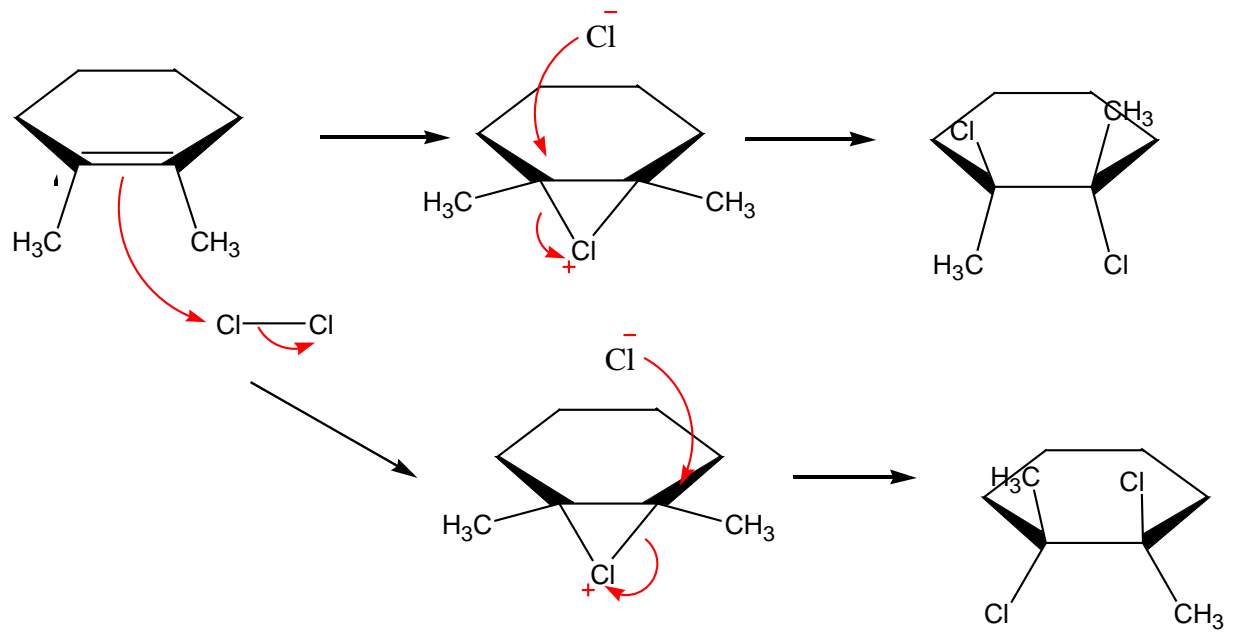
7.2 How many alkene products, including E,Z isomers, might be obtained by dehydration of 3-methyl-3-hexanol (3-methyl-3-hydroxyhexane) with aqueous sulfuric acid?

Solution:



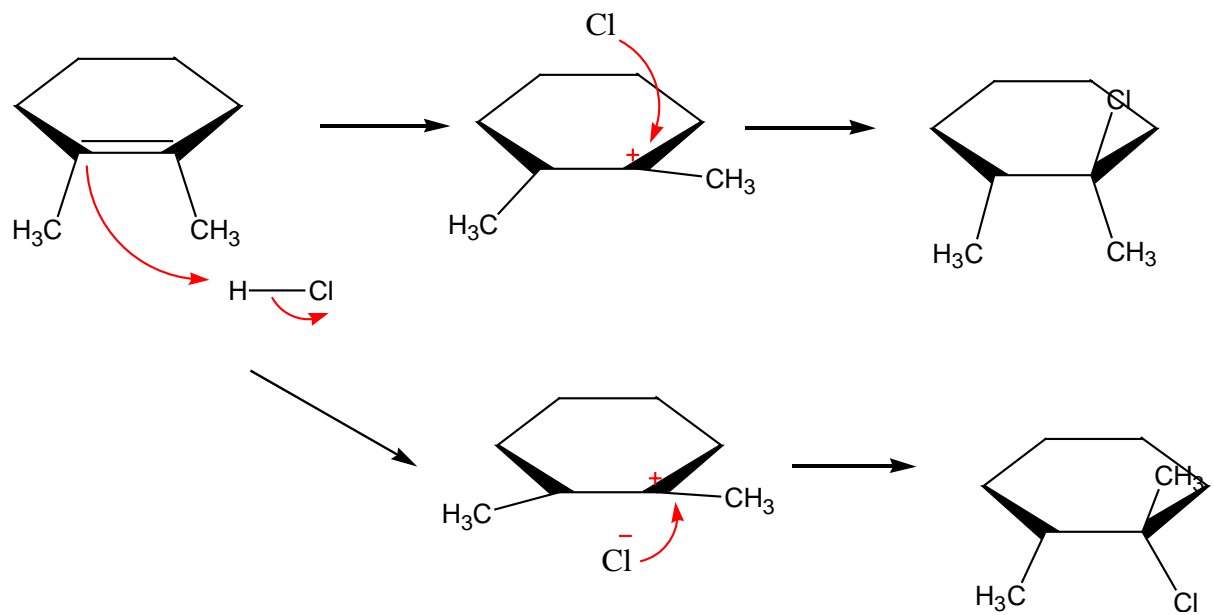
7.3 What product would you expect to obtain from addition of Cl_2 to 1,2-dimethylcyclohexene? Show the stereochemistry of the product.

Solution:



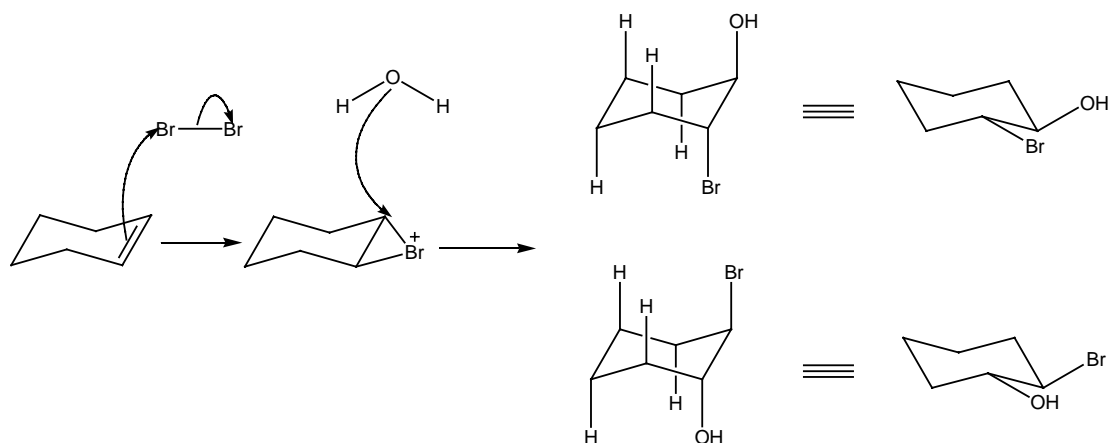
7.4 Addition of HCl to 1,2-dimethylcyclohexene yields a mixture of two products. Show the stereochemistry of each, and explain why a mixture is formed.

Solution:

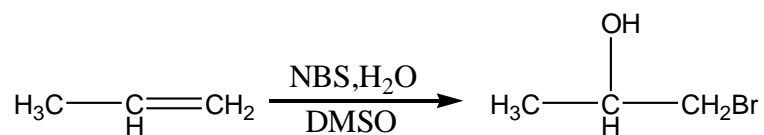


7.5 What product would you expect from the reaction of cyclopentene with NBS and water? Show the stereochemistry.

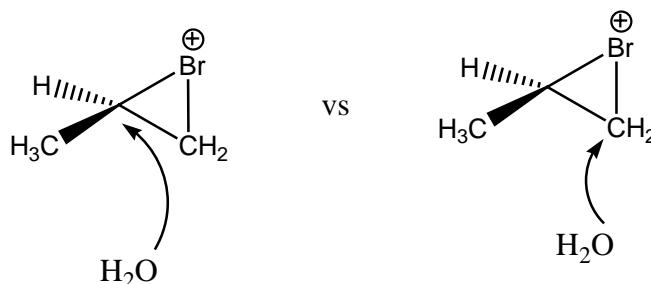
Solution:



7.6 When an unsymmetrical alkene such as propene is treated with NBS in aqueous DMSO, the major product has the bromine atom bonded to the less highly substituted carbon atom. Is this Markovnikov or non-Markovnikov orientation? Explain.



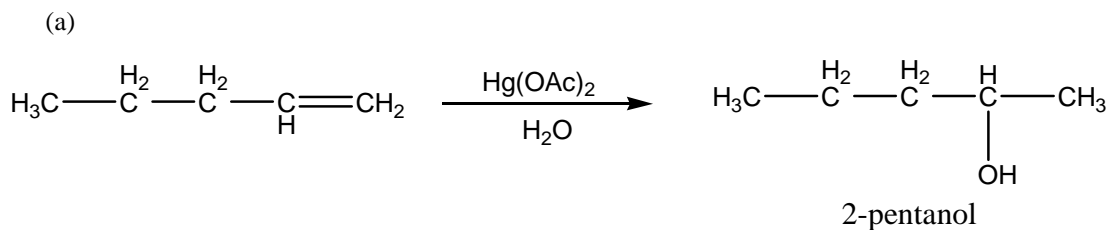
Solution:



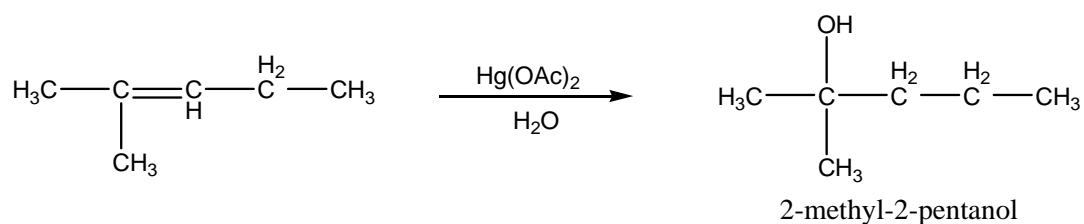
The product is Markovnikoff product.

7.7 What products would you expect from oxymercuration of the following alkenes?

Solution:



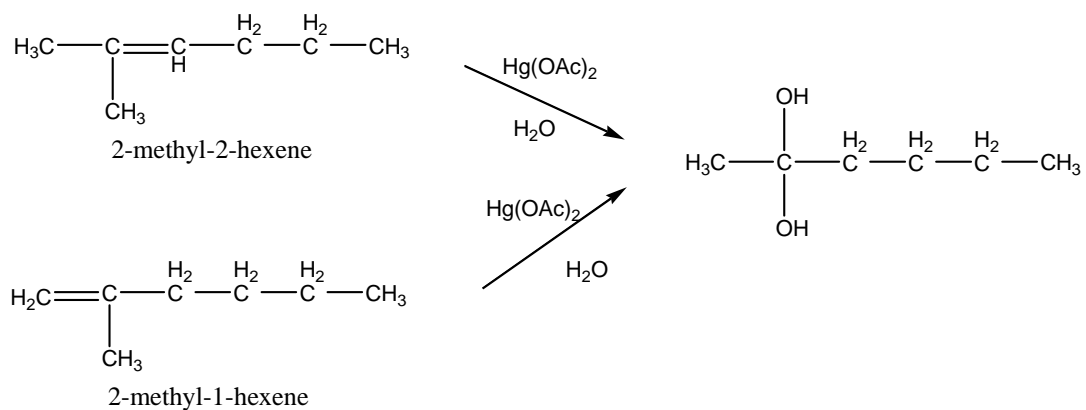
(b)



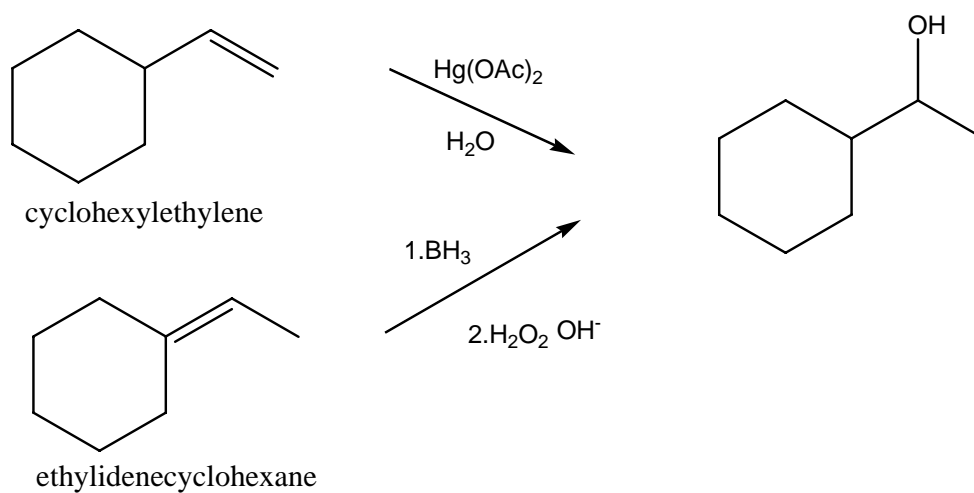
7.8 What alkanes might the following alcohols have been prepared from?

Solution:

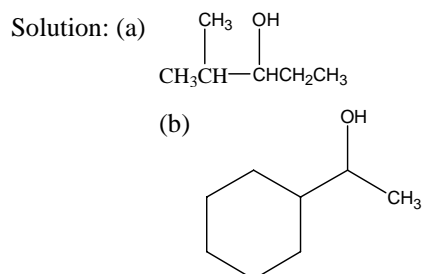
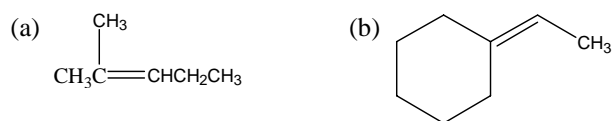
(a)



(b)

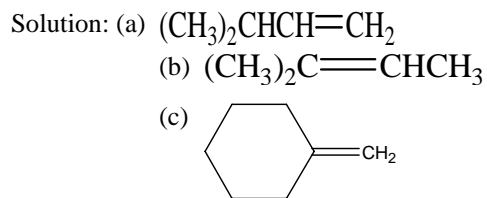
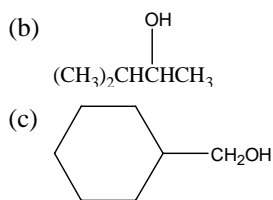


7.9 Show the structures of the products you would obtain by hydroboration/oxidation of the following alkenes:

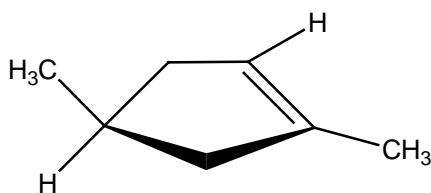


7.10 What alkenes might be used to prepare the following alcohols by hydroboration/oxidation?



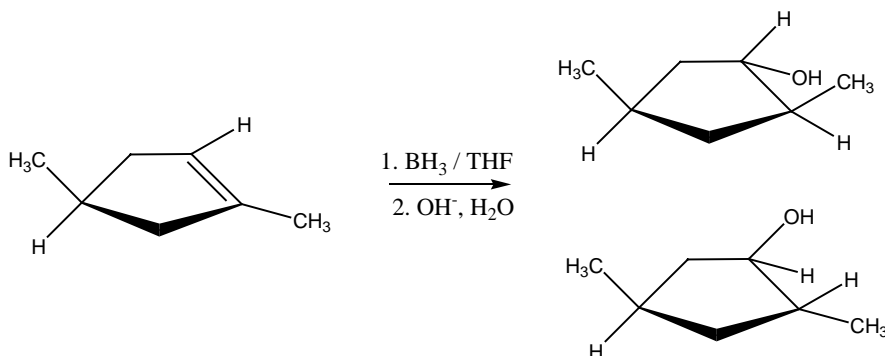


7.11 The following cycloalkene gives a mixture of two alcohols on hydroboration followed by oxidation, Draw the structures of both, and explain the result.

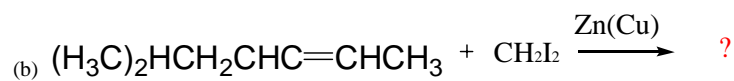
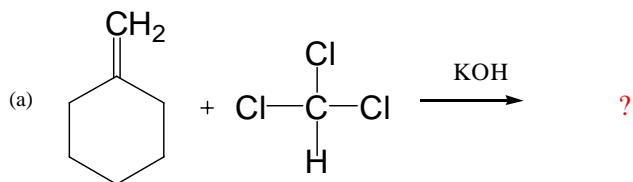


Solution:

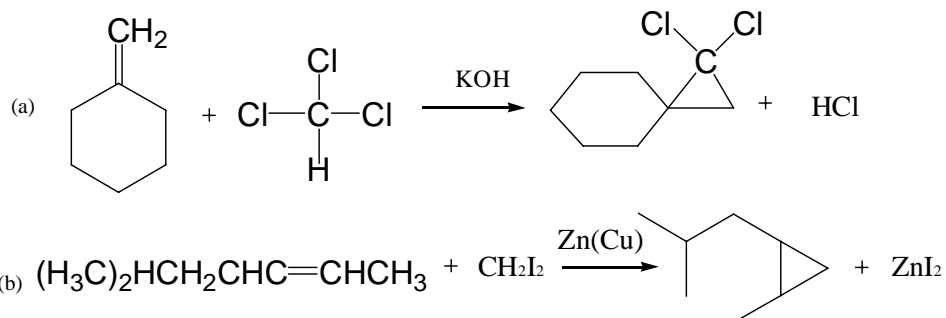
The structure of the two cycloalcohols:



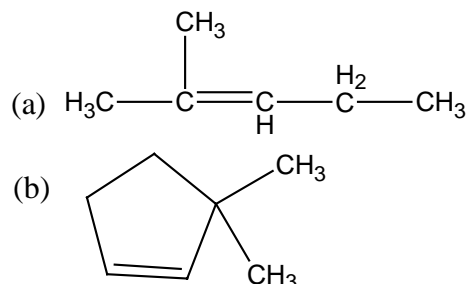
7.12 What products would you expect from the following reactions?



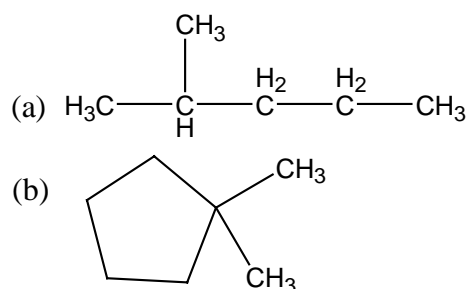
Solution:



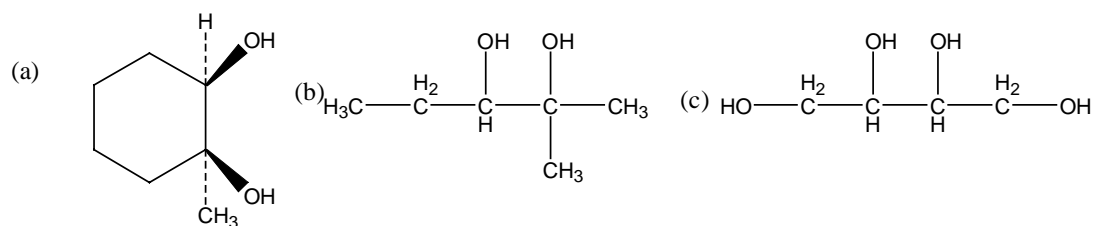
7.13 What product would you obtain from catalytic hydrogenation of the following alkenes?



Solution:

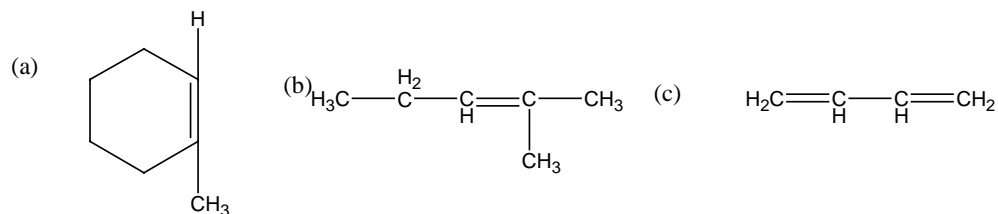


7.14 What alkene would you start with to prepare each of the following compounds?



S

olution:



7.15 What products would you expect?

Solution:



(b) O₃

Product CH₃COCH₂CH₂CH₂CH₂CHO

7.16 Propose structure for alkenes.

Solution:

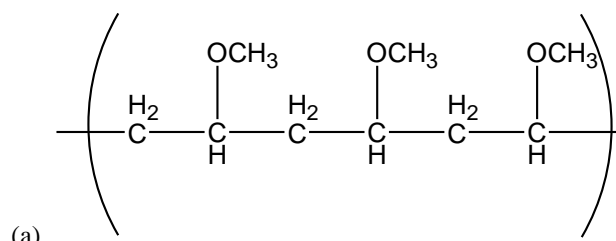
(a): (CH₃)₂C=O and H₂C=O

Structure (CH₃)₂C=CH₂

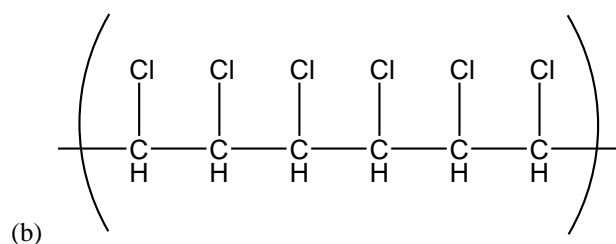
(b): 2 equiv CH₃CH₂CH=O

Structure CH₃CH₂CH=CHCH₂CH₃

7.17 Show the monomer units you would use to prepare the following polymers:

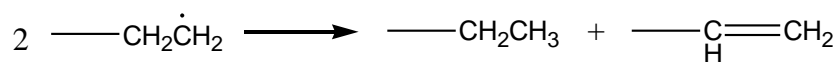


Solution: The monomer unit is $\text{H}_2\text{C}=\text{CH}-\text{OCH}_3$.



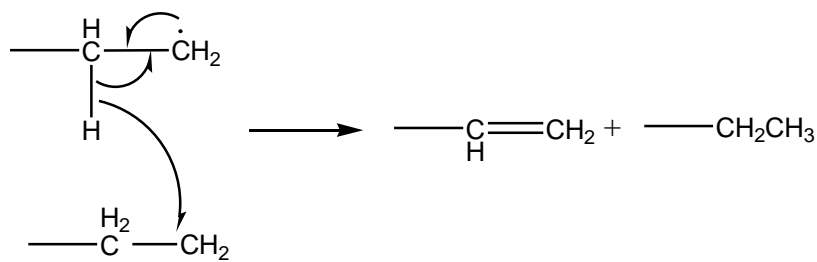
Solution: The monomer unit is ClHC=CHCl.

7.18 One of the chain-termination steps that sometimes occurs to interrupt polymerization is the following reaction between two radicals:



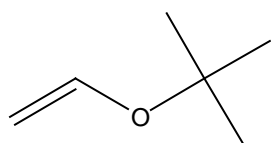
Propose a mechanism for this reaction, using fishhook arrows to indicate electron flow.

Solution:



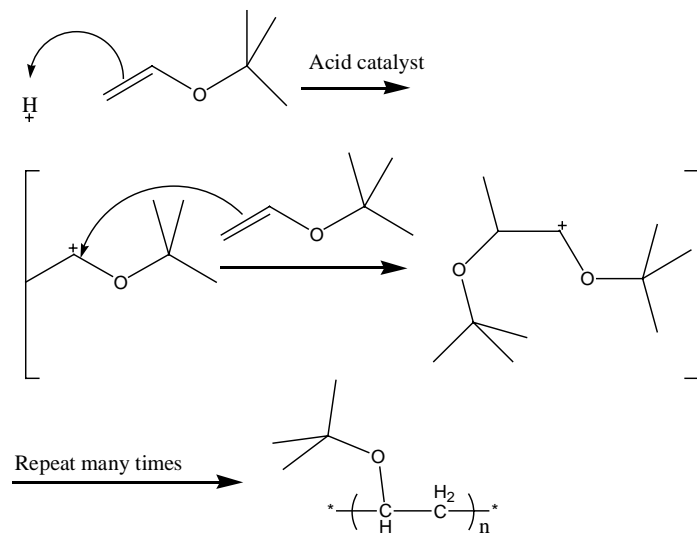
7.19 *tert*-Butyl vinyl ether is polymerized commercially for use in adhesives by a cationic process.

Draw a segment of poly(tert-butyl vinyl ether), and show the mechanism of the chain-carrying step.

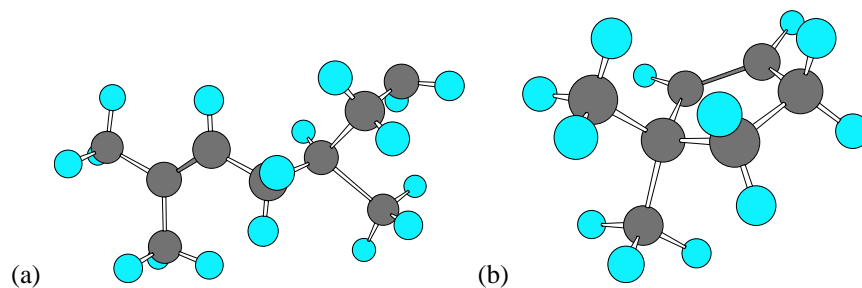


tert-butyl vinyl ether

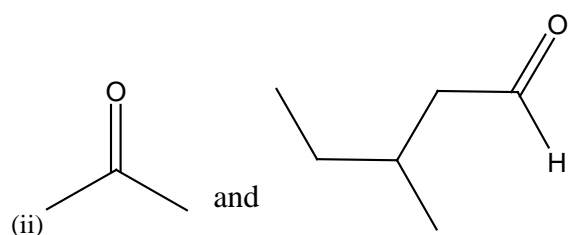
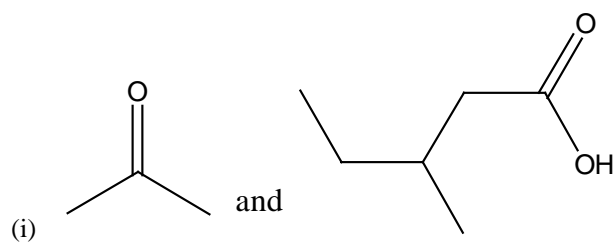
Solution:



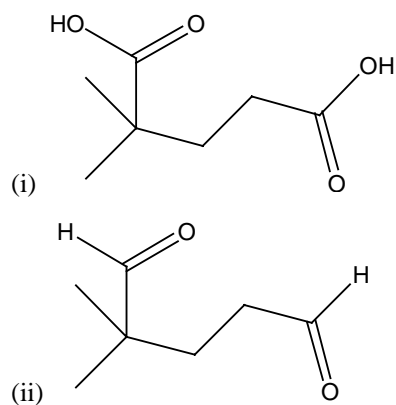
7.20 Name the following alkenes, and predict the products of their reaction with (i) KMnO_4 in aqueous acid and (ii) O_3 , following by Zn in acetic acid:



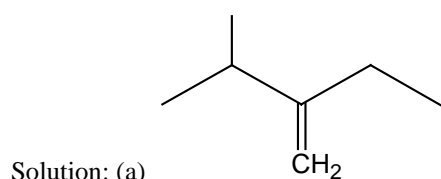
Solution: (a) 2,5-dimethyl-2-heptene



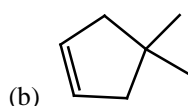
(b) 3,3-dimethylcyclopentene



7.21 Draw the structures of alkenes that would yield the following alcohols on hydration (red=O). Tell in each case whether you would use hydroboration/oxidation.



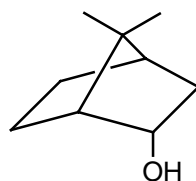
I would use oxymercuration in this case.



Both oxymercuration / demercuration and hydroboration / oxidation reactions could be used.

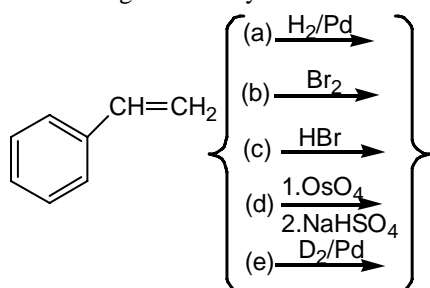
7.22 The following alkene undergoes hydroboration/oxidation to yield a single product rather than a mixture. Explain the result, and draw the product showing its stereochemistry.

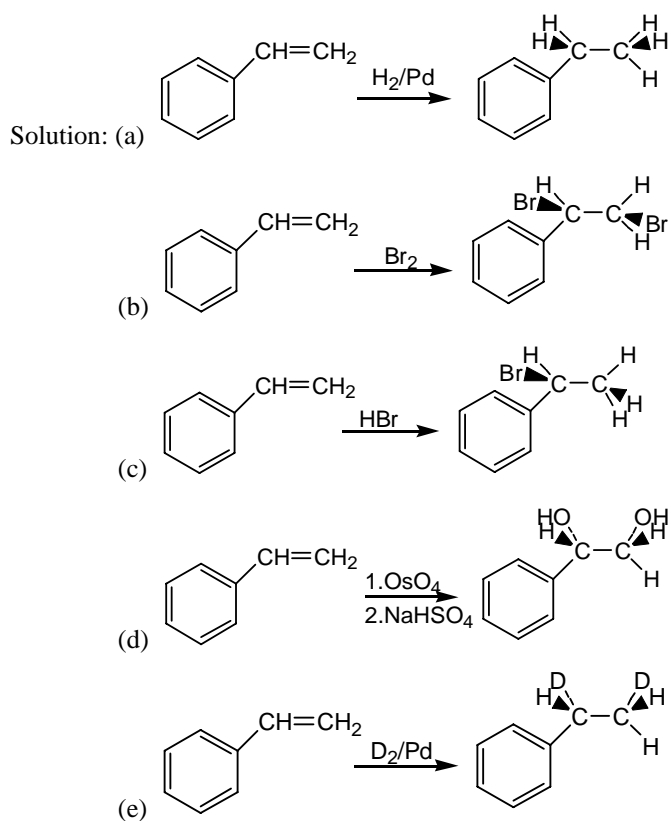
Solution: The reactant is symmetrical, so -OH adding to either of the carbon that is double bonded



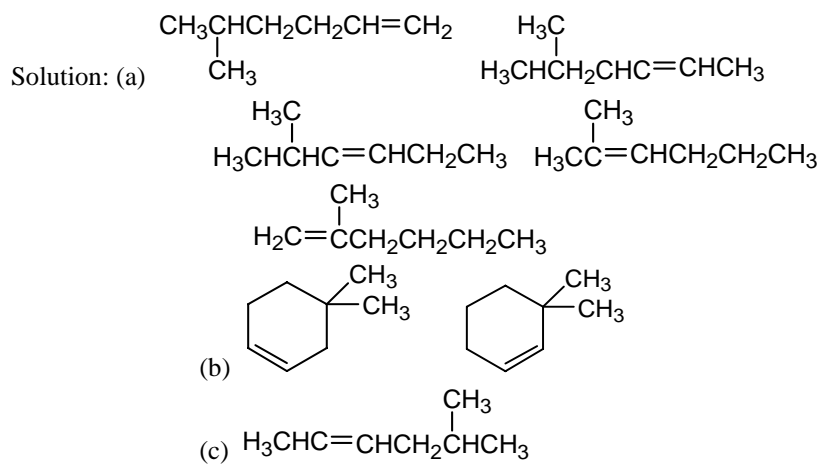
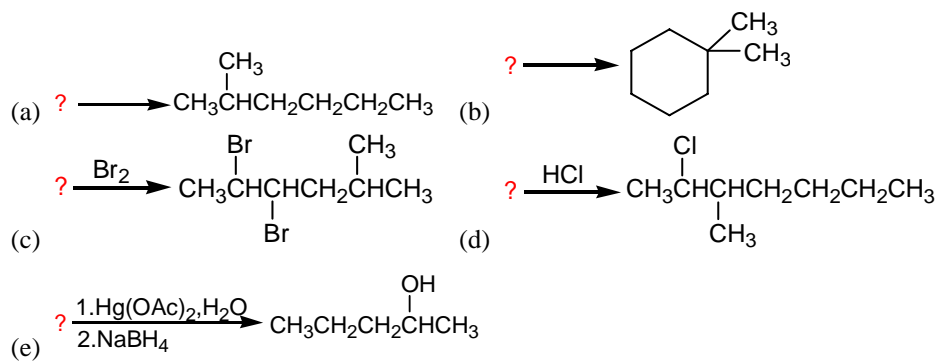
will yield the same product. The single product is:

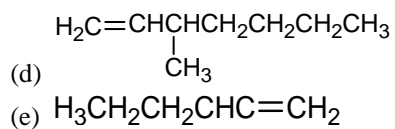
7.23 Predict the products of the following reactions (the aromatic ring is unreactive in all cases). Indicate regiochemistry when relevant.



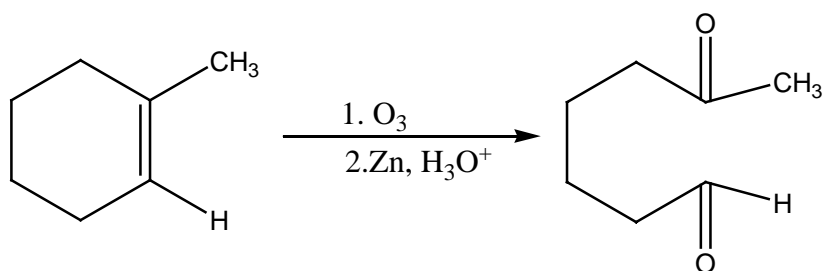
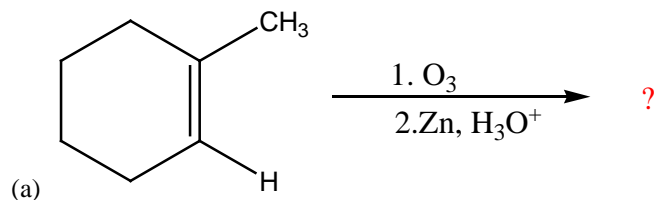


7.24 Suggest structures for alkenes that give the following reactions products. There may be more than one answer for some cases.

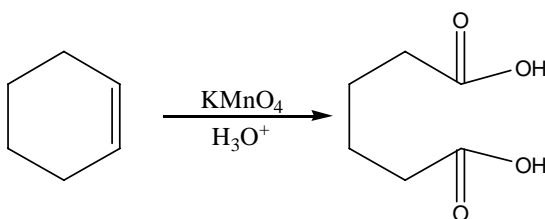
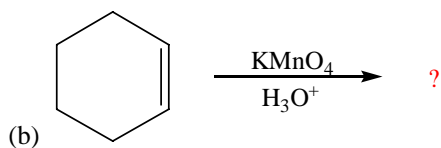




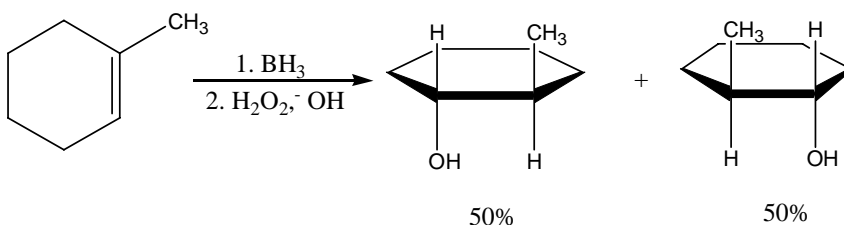
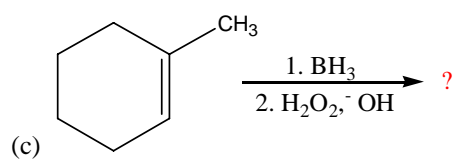
7.25 Predict the products of the following reactions, indicating both regiochemistry and stereochemistry when appropriate:



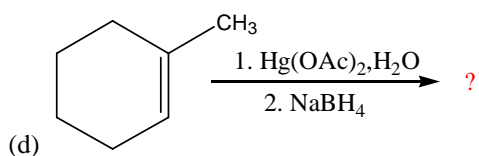
Solution:

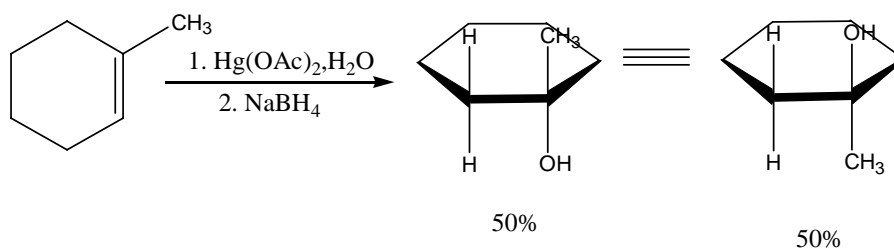


Solution:



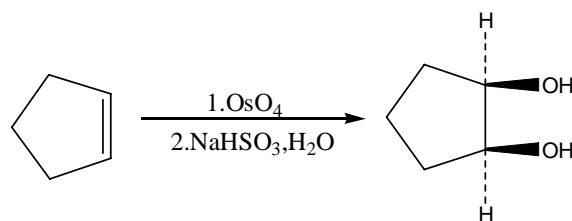
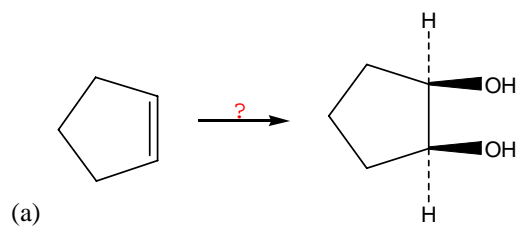
Solution:



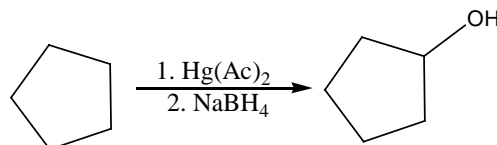
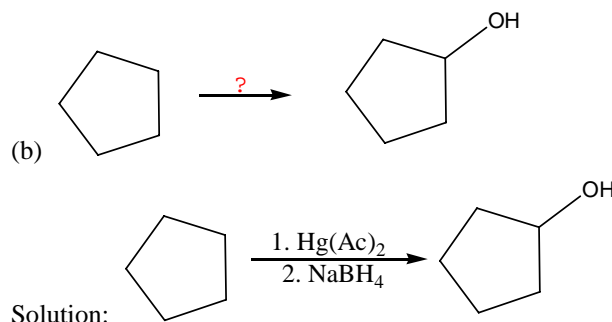


Solution:

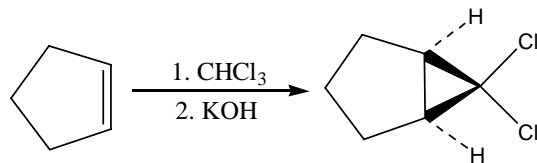
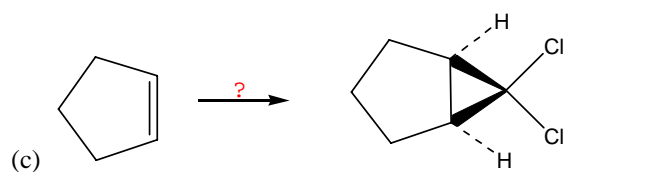
7.26 How would you carry out the following transformations? Indicate the reagents you would use in each case.



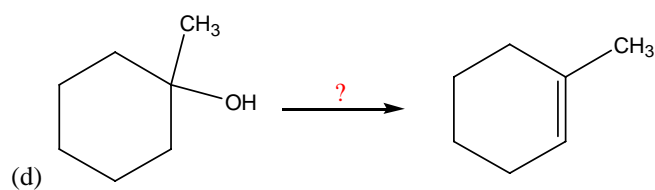
Solution:

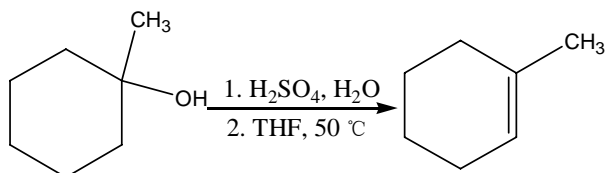


Solution:

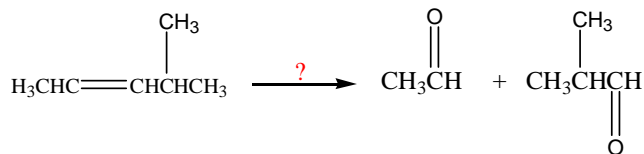


Solution:

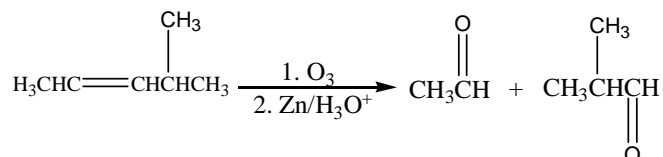




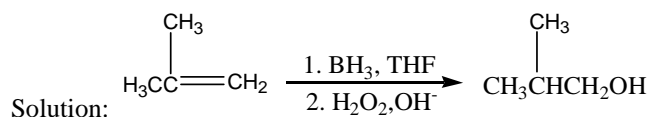
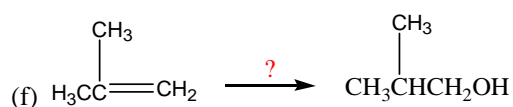
Solution:



(e)

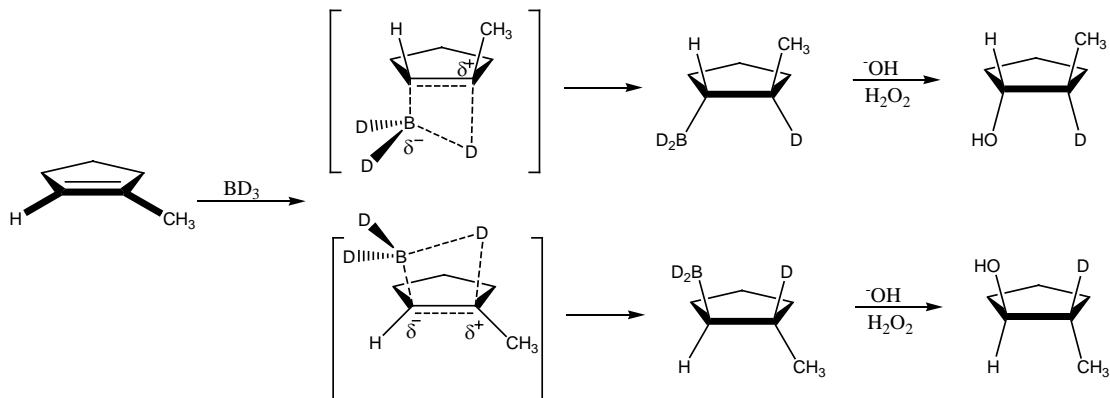


Solution:

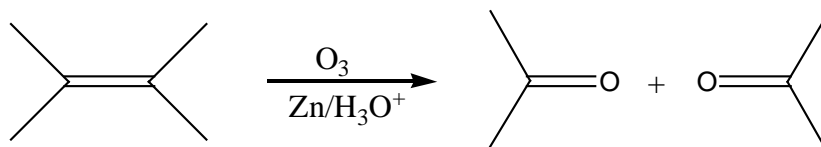


Solution:

7.27 What product will result from hydroboration/oxidation of 1-methylcyclopentene with deuterated borane, BD_3 ? Show both the stereochemistry (spatial arrangement) and the regiochemistry (orientation) of the product.



7.28 Draw the structure of an alkene that yield only acetone, $(\text{CH}_3)_2\text{C}=\text{O}$, on ozonolysis followed by treatment with Zn.



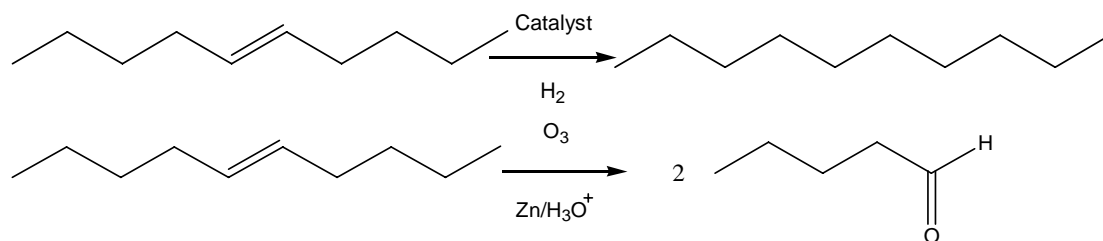
7.29 Draw the structure of a hydrocarbon that react with 1 molar equivalent of H_2 on catalytic hydrogenation and gives only pentanal, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$, on the ozonolysis followed by treatment with Zn. Write the reaction involved.

Solution:

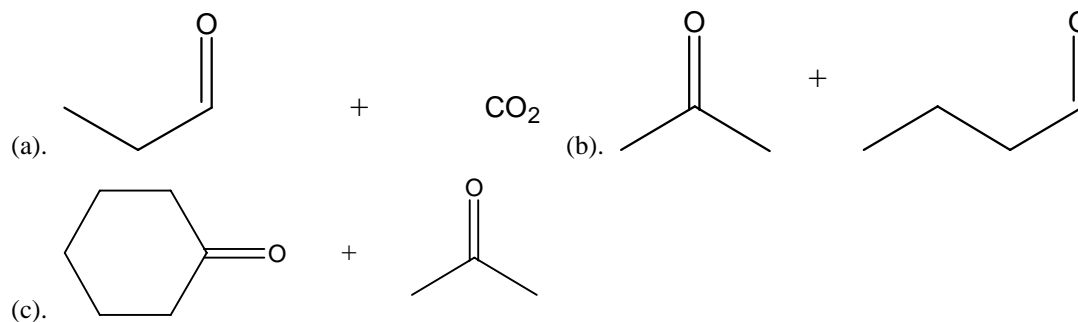
The structure of the hydrocarbon is showed in the following picture:



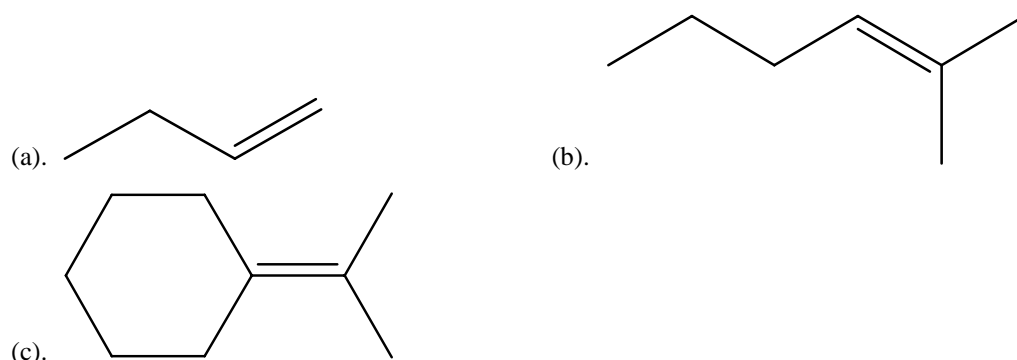
The reactions are showed as follow:



7.30 Draw the structure of alkenes that give the following products on oxidative cleavage with KMnO_4 in the acidic solution:



Solution:

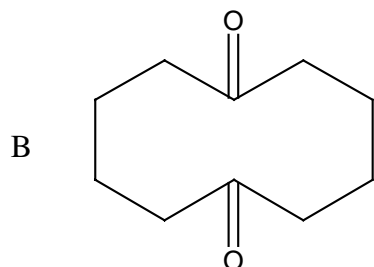
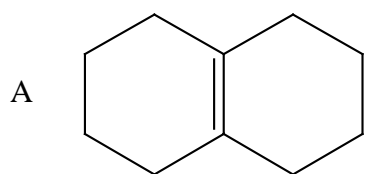


7.31 Compound A has the formula $\text{C}_{10}\text{H}_{16}$. On catalytic hydrogenation over palladium, it reacts with only 1 molar equivalent of H_2 . Compound A also undergoes reaction with ozone, followed by zinc treatment, to yield a symmetrical diketone, B ($\text{C}_{10}\text{H}_{16}\text{O}_2$).

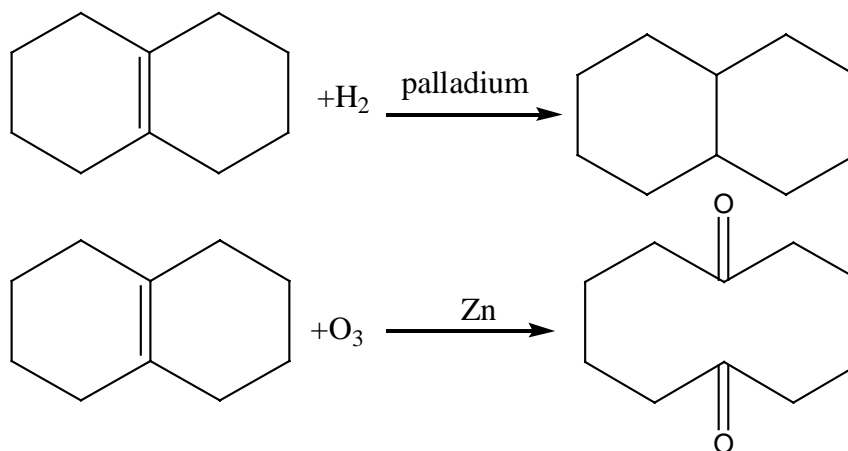
(a) How many rings does A have?

A have two rings.

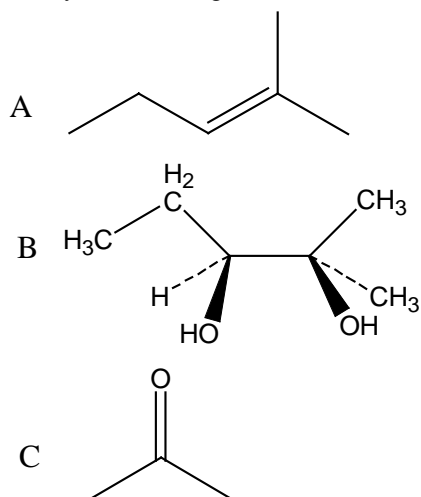
(b) What are the structures of A and B?

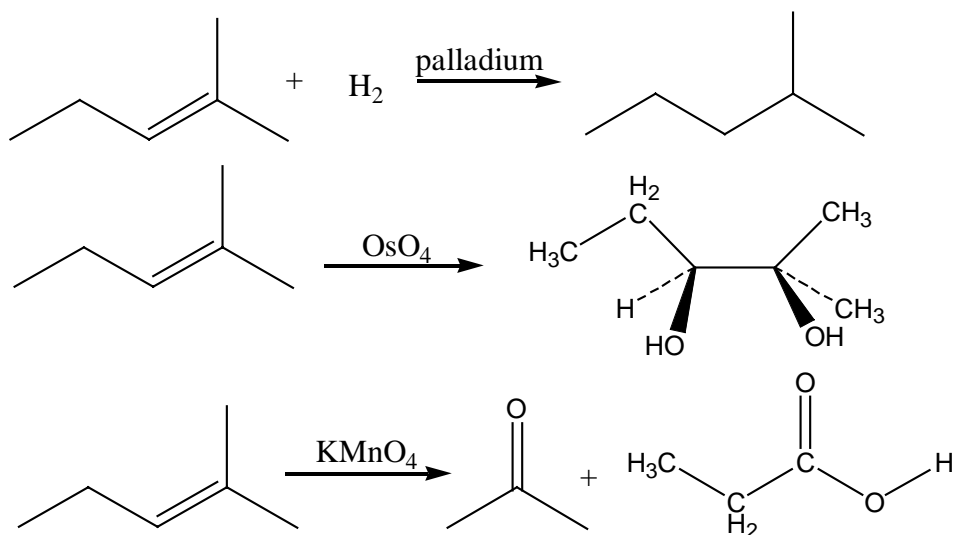


(c) Write the reactions.

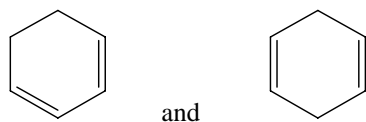


7.32 An unknown hydrocarbon A, with formula C_6H_{12} , reacts with 1 molar equivalent of H_2 over a palladium catalyst. Hydrocarbon A also reacts with OsO_4 to give a diol, B. When oxidized with $KMnO_4$ in acidic solution, A gives two fragments. One fragment is propanoic acid, $CH_3CH_2CO_2H$, and the other fragment is a ketone, C. What are the structures of A, B, and C? Write all reactions, and show your reasoning.





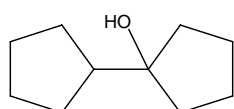
7.33 Using an oxidative cleavage reaction explain how you would distinguish between the following two isomeric dienes:



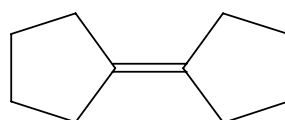
Solution: When they react with KMnO_4 in acid, the first one will yield two products and the second one will only yield one product.

7.34 Compound A, $\text{C}_{10}\text{H}_{18}\text{O}$, undergoes reaction with dilute H_2SO_4 at 250°C to yield a mixture of two alkenes, $\text{C}_{10}\text{H}_{16}$. The major alkene product, B, gives only cyclopentanone after ozone treatment followed by reduction with zinc in acetic acid. Identify A and B, and write the reaction.

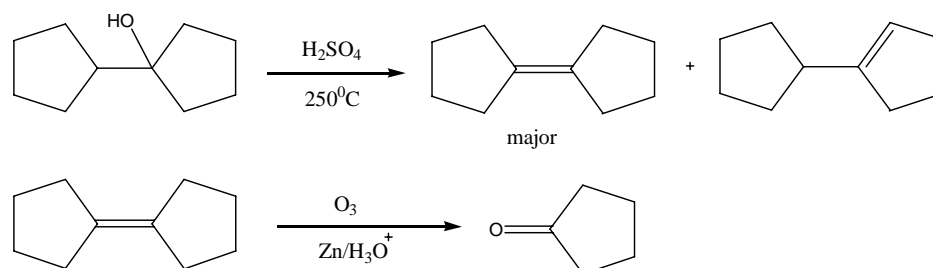
Solution: A:



B:



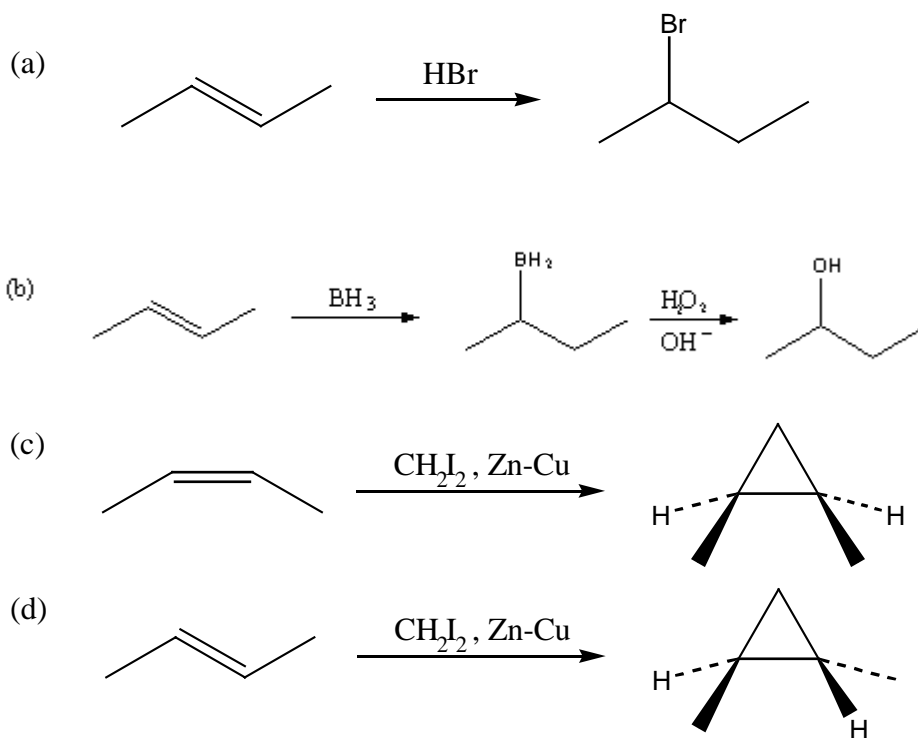
Reaction:



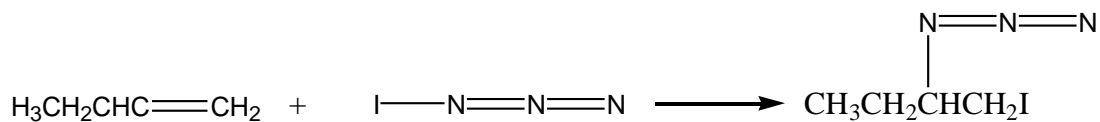
7.35 Which reaction would you expect to be faster, addition of HBr to cyclohexene or to 1-methylcyclohexene? Explain.

Solution: The intermediates of the two reactions are not equal in stability. Judge by Hammond postulate, the more stable intermediate forms faster, so addition of HBr to 1-methylcyclohexene may be faster.

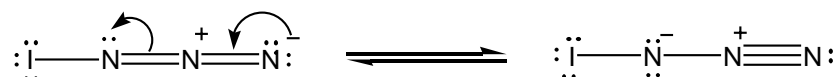
7.36 Predict the products of the following reactions, and indicate regiochemistry if relevant:



7.37 Iodine azide, IN_3 , adds to alkenes by an electrophilic mechanism similar to that of bromine. If a monosubstituted alkene such as 1-butene is used, only one product results:



(a) Add lone-pair electrons to the structure shown for IN_3 , and draw a second resonance form for the molecule.



(b) Calculate formal charges for the atoms in both resonance structures you drew for IN_3 in part

For the iodine:

| | |
|-----------------------------|---------------------|
| Iodine valence electrons | = 7 |
| Iodine bonding electrons | = 2 |
| Iodine nonbonding electrons | = 6 |
| Formal charge | $= 7 - 2/2 - 6 = 0$ |

For the left nitrogen:

| | |
|-------------------------------|---------------------|
| Nitrogen valence electrons | = 5 |
| Nitrogen bonding electrons | = 6 |
| Nitrogen nonbonding electrons | = 2 |
| Formal charge | $= 5 - 6/2 - 2 = 0$ |

For the middle nitrogen:

| | |
|----------------------------|-----|
| Nitrogen valence electrons | = 5 |
| Nitrogen bonding electrons | = 8 |

Nitrogen nonbonding electrons = 0

Formal charge = $5 - 8/2 - 0 = 1$

For the right nitrogen:

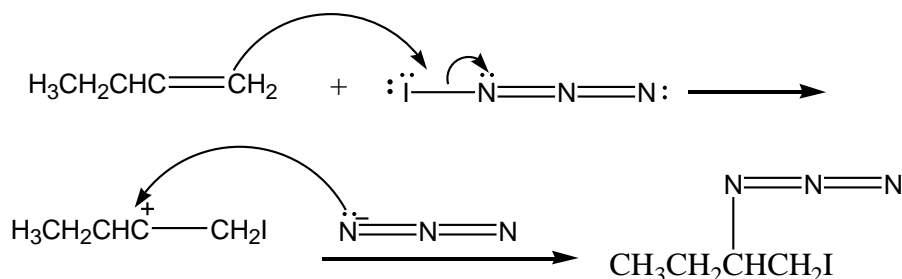
Nitrogen valence electrons = 5

Nitrogen bonding electrons = 4

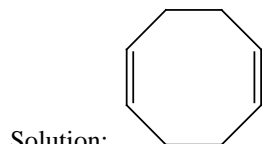
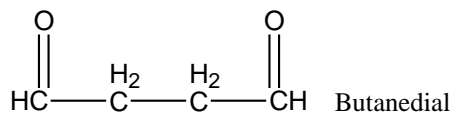
Nitrogen nonbonding electrons = 4

Formal charge = $5 - 4/2 - 4 = -1$

- (c) In light of the result observed when IN_3 adds to 1-butene, what is the polarity of the I-N bond? Propose a mechanism for the reaction using curved arrows to show the electron flow in each step.

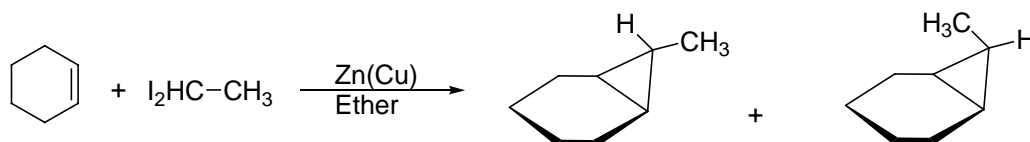


- 7.38 Draw the structure of a hydrocarbon that absorbs 2 molar equivalents of H_2 on catalytic hydrogenation and gives only butanedial on ozonolysis.



- 7.39 Simmons-Smith reaction of cyclohexene with diiodomethane gives a single cyclopropane product, but the analogous reaction of cyclohexene with 1,1-diiodoethane gives (in low yield) a mixture of two isomeric methylcyclopropane products. What are the two products, and how do they differ?

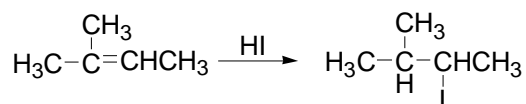
Solution: The reaction occurs as below:



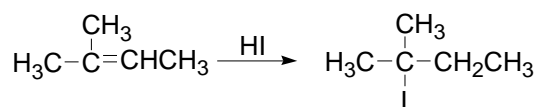
- 7.40 In planning the synthesis of one compound from another, it's just as important to know what not to do as to know what to do. The reactions all have serious drawbacks to them. Explain the potential problems of each.

Solution:

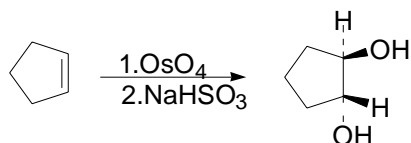
(a)



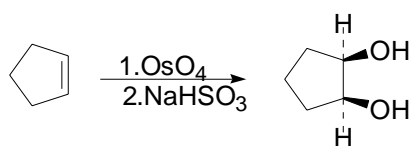
According to Markovnikov's rule the reaction should be:



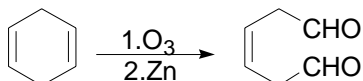
(b)



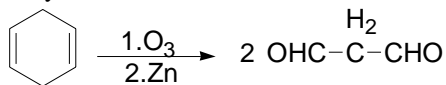
Actually it should be syn addition as below:



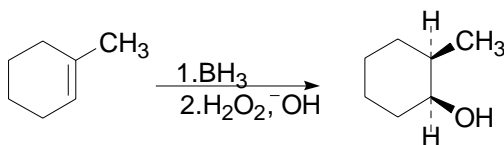
(c)



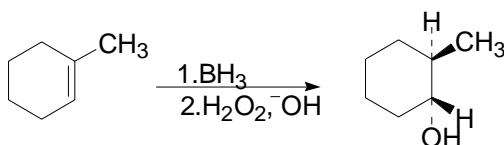
Actually the reaction should be:



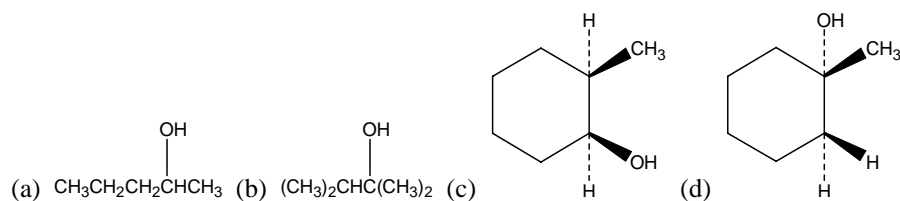
(d)



Actually the reaction should be:



7.41 Which of the following alcohols could be made selectively by hydroboration/oxidation of an alkene? Explain.



Solution:

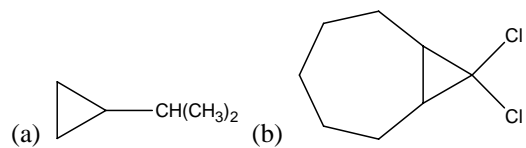
(a) No selectivity

(b) Selectively synthesized

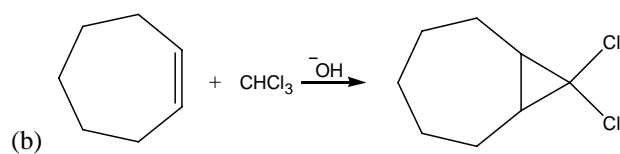
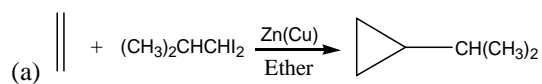
(c) Can't be formed

(d) Can't be formed

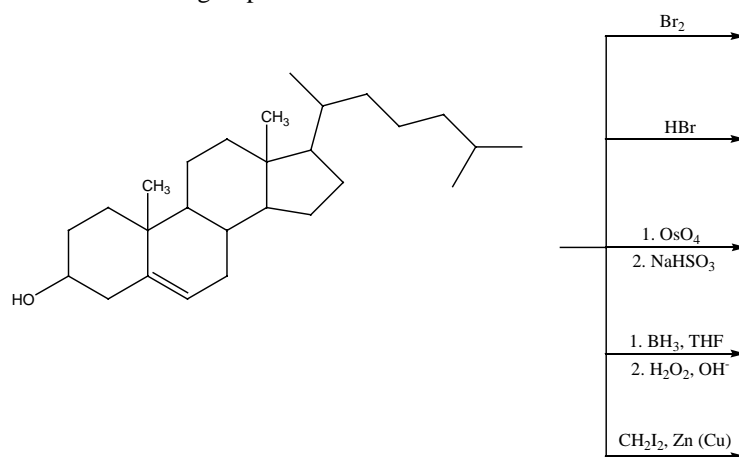
7.42 What alkenes might be used to prepare the following cyclopropane?



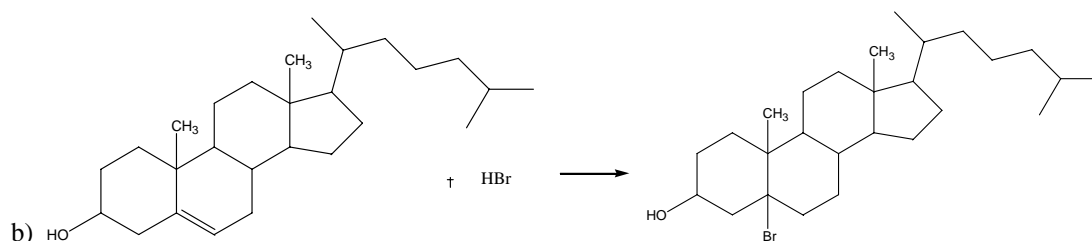
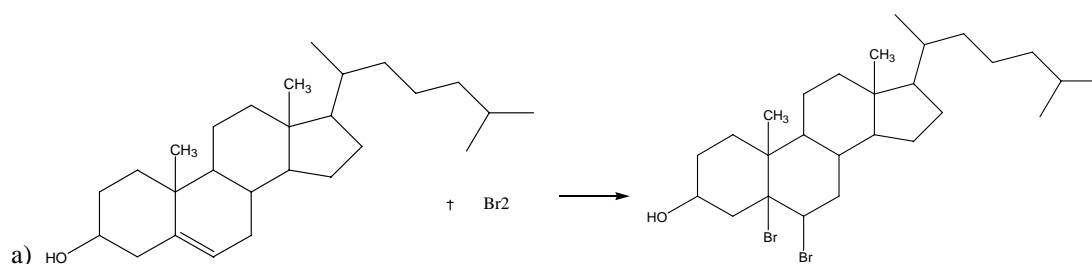
Solution:

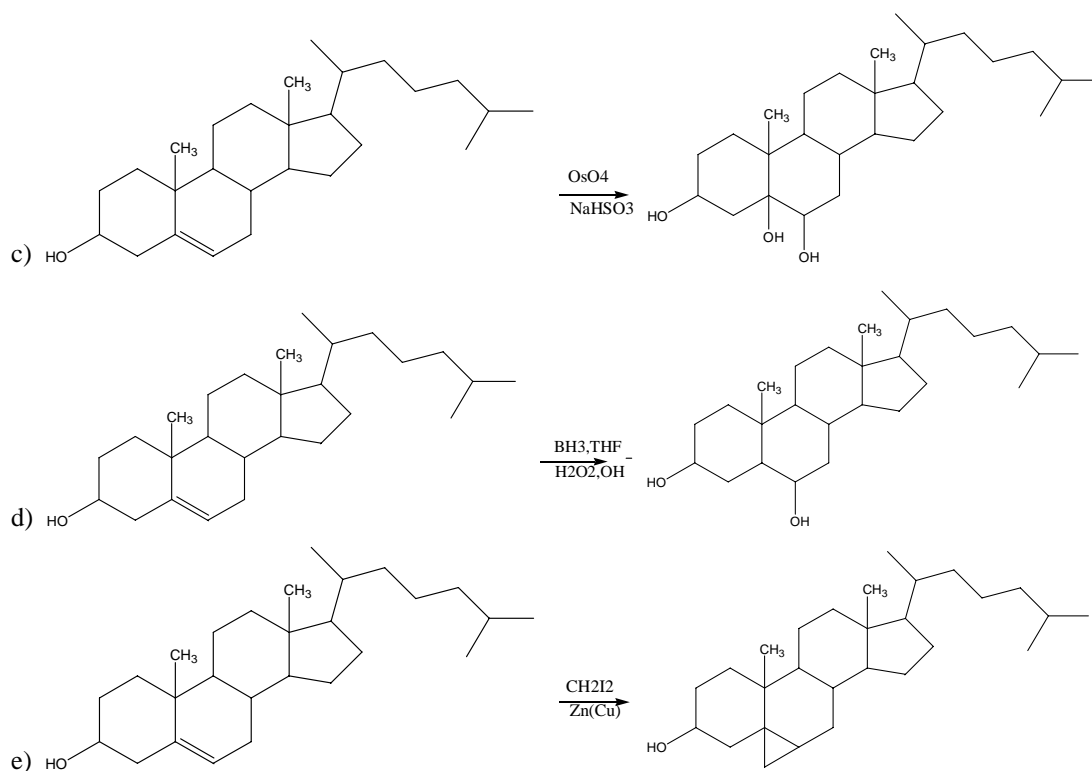


7.43 Predict the products of the following reactions. Don't worry about the size of the molecule; concentrate on the functional groups.



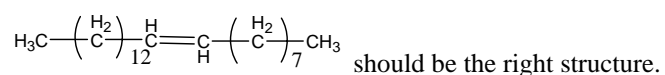
Solution:





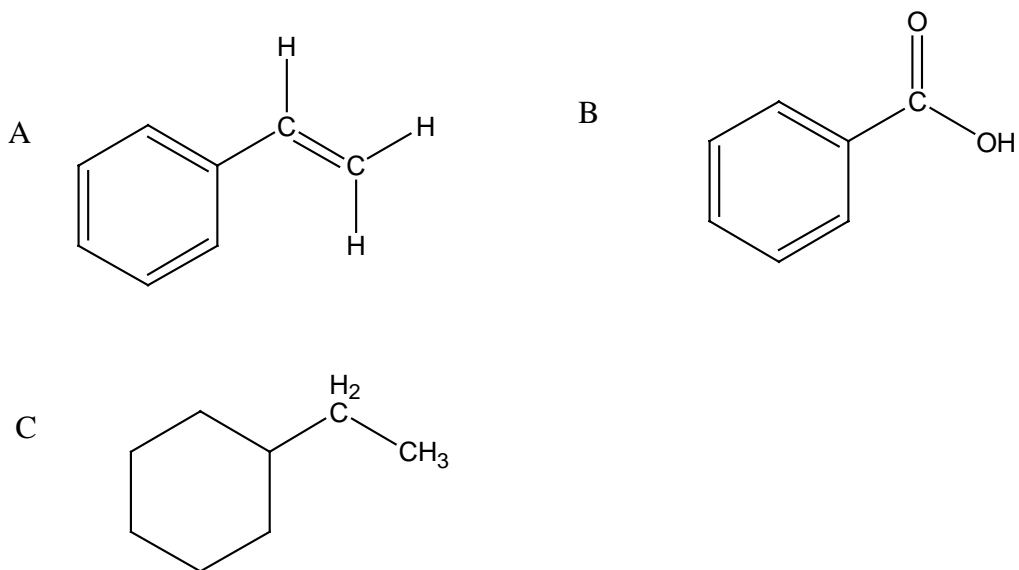
7.44 The sex attractant of the common housefly is a hydrocarbon with the formula $C_{23}H_{46}$. On treatment with aqueous acidic $KMnO_4$, two products are obtained, $CH_3(CH_2)_{12}CO_2H$ and $CH_3(CH_2)_7CO_2H$. Propose a structure.

Solution:

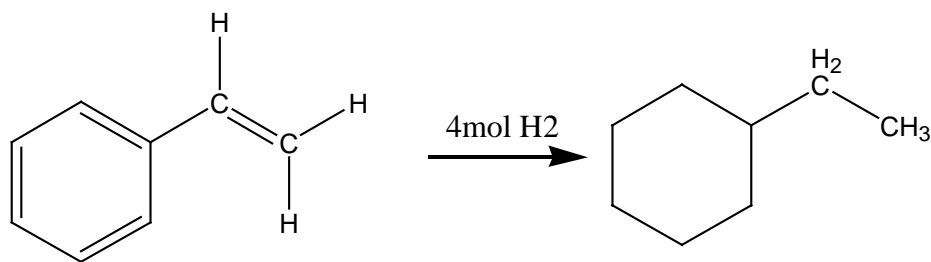
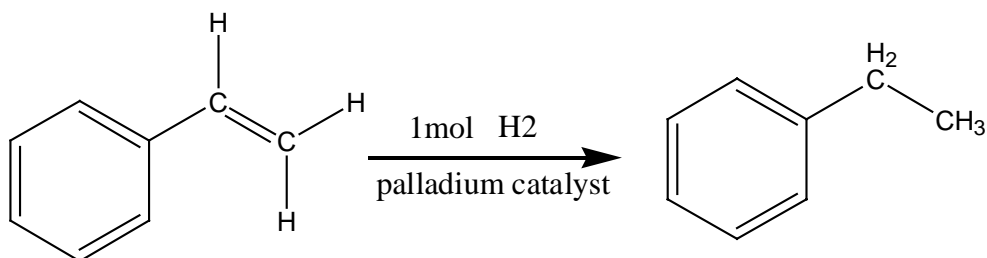
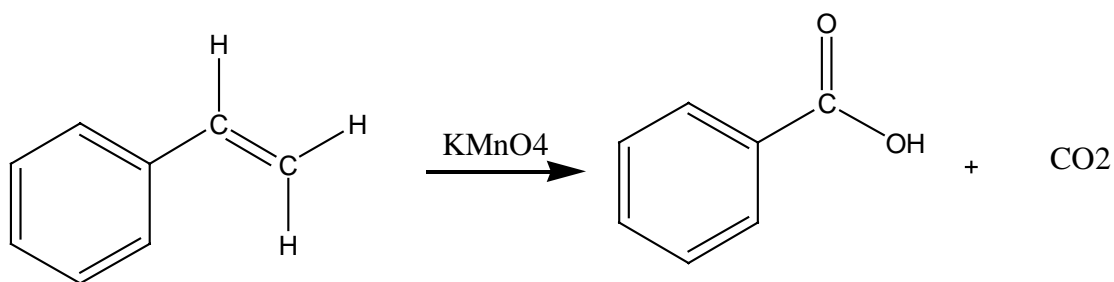


7.45 Compound A has the formula C_8H_8 . It reacts rapidly with $KMnO_4$ to give CO_2 and carboxylic acid, B ($C_7H_6O_2$), but reacts with only 1 molar equivalent of H_2 on catalytic hydrogenation over a palladium catalyst. On hydrogenation under conditions that reduce aromatic rings, 4 equivalents of H_2 are taken up and hydrocarbon C (C_8H_{16}) is produced. What are the structure of A, B, and C? Write the reactions.

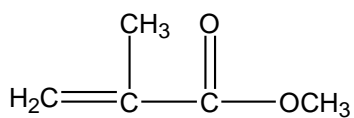
SOLUTION:



The reactions:



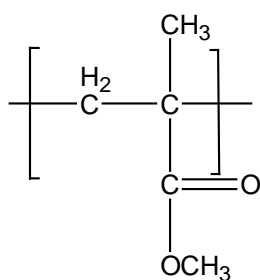
7.46. Plexiglas, a clear plastic used to make many molded articles, is made by polymerization of methyl methacrylate. Draw a representative segment of Plexiglas.



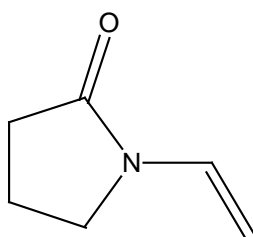
Methyl methacrylate

SOLUTION:

The segment of Plexiglas:

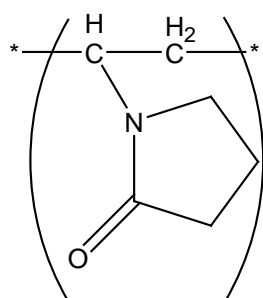


7.47 Poly (vinyl pyrrolidone), prepared from N-vinylpyrrolidone, is used both in cosmetics and as a synthetic blood substitute. Draw a representative segment of the polymer.



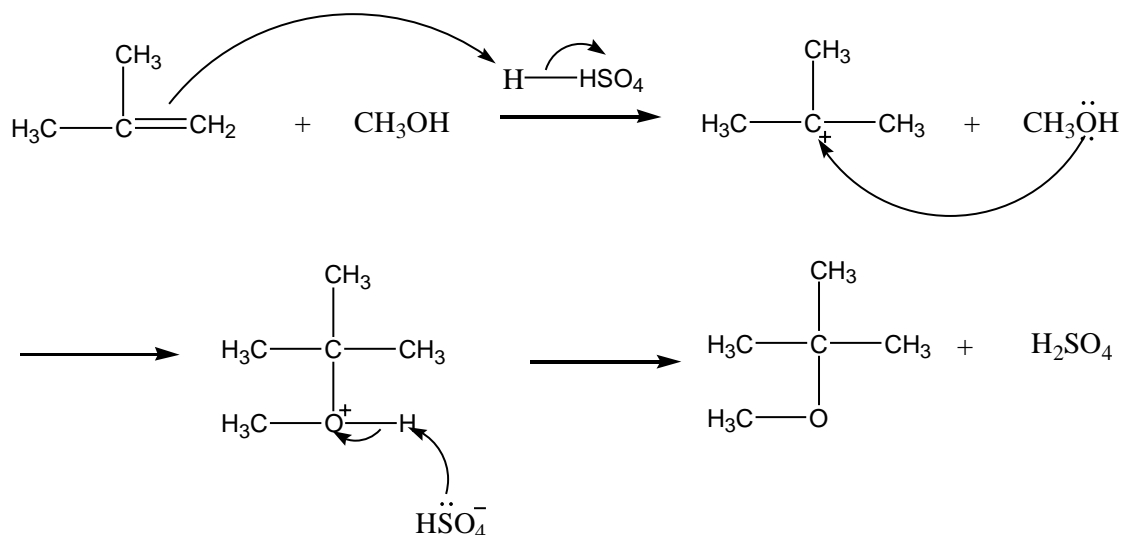
N-vinylpyrrolidone

Solution:



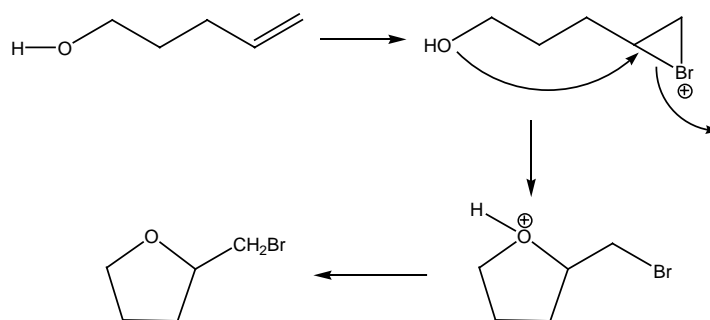
7.48 Reaction of 2-methylpropene with CH_3OH in the presence of H_2SO_4 catalyst yields methyl tert-butyl ether, $\text{CH}_3\text{OC}(\text{CH}_3)_3$, by a mechanism analogous to that of acid-catalyst alkene hydration. Write the mechanism, using curved arrows for each step.

Solution:



7.49 When 4-penten-1-ol is treated with aqueous Br_2 , a cyclic bromo ether is formed, rather than the expected bromohydrin. Propose a mechanism, using curved arrows to show electron movement.

Solution:

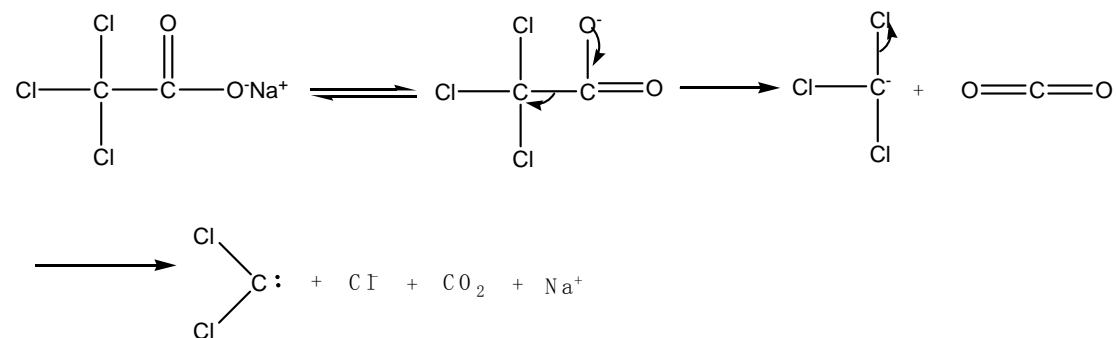


7.50 How would you distinguish between the following pairs of compounds using simple chemical tests? Tell what you would do and what you would see.

- (a) cyclopentene and cyclopentane
 (b) 2-hexene and benzene

Solution: Bromine in carbon tetrachloride solution is reddish-brown color. Using this one to identify the double bond by electrophilic addition reaction.

7.51

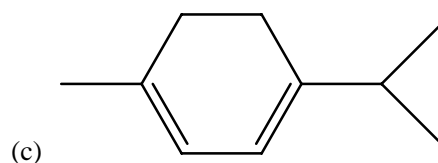


They have the same intermediate which is CCl_3^- .

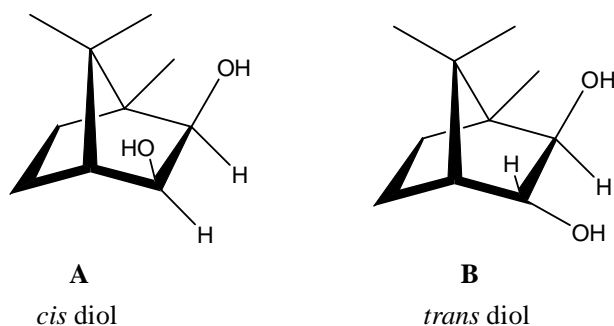
7.52

(a) 3

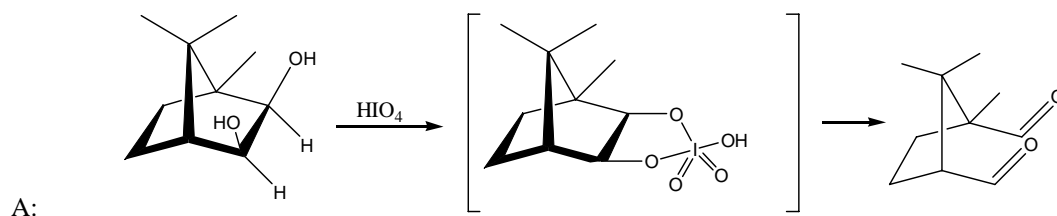
(b) double bonds:2



7.53 Evidence that cleavage of 1,2-diols by HIO_4 occurs through a five membered cyclic periodate intermediate is based on *kinetic* data – the measurement of reaction rates. When diols A and B were prepared and the rates of their reaction with HIO_4 were measured, it was found that diol A cleaved approximately 1 million times faster than diol B. Make molecular models of A and B and of potential cyclic periodate intermediates, and then explain the *kinetic* results.



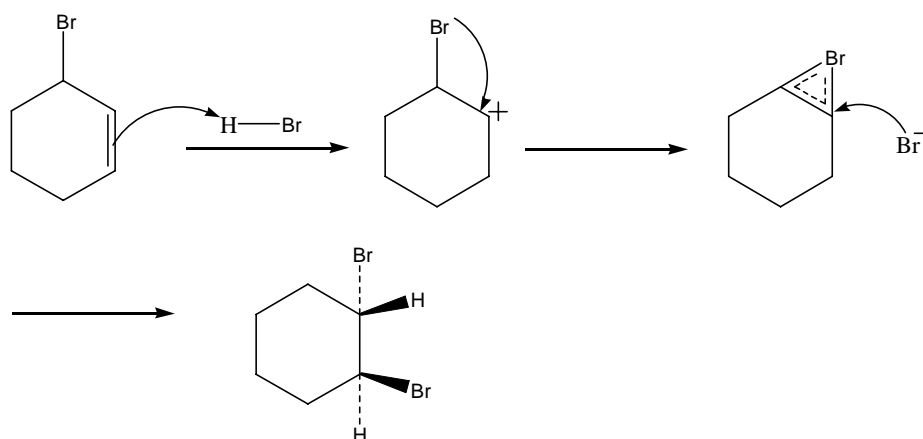
Solution:



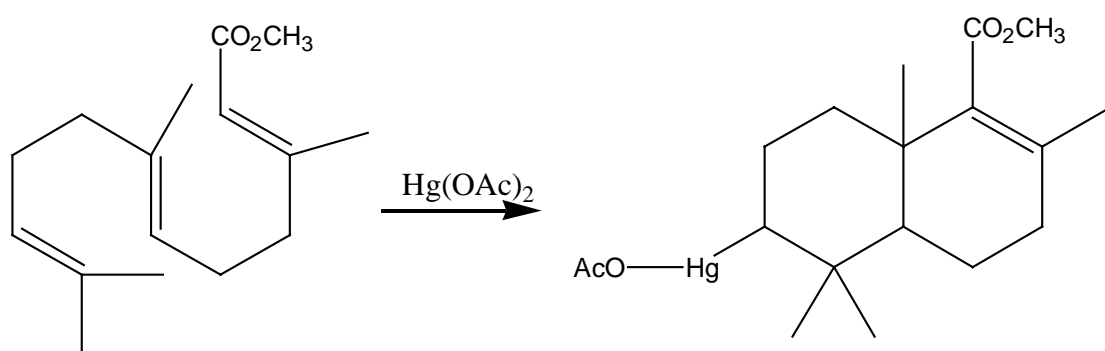
In *cis* diol, two $-\text{OH}$ are in one plane, so it is easier to form a cyclic periodate intermediate, while in *trans* diol, the two $-\text{OH}$ aren't in one plane, there is larger steric strain in the five membered cyclic periodate intermediate, it is less stable, so the rates of A is more faster.

7.54 Reaction of HBr with 3-methylcyclohexene yields a mixture of four products: *cis*- and *trans*-1-3-methylbromocyclohexane and *cis*- and *trans*-1-2-methylbromocyclohexane. The analogous reaction of HBr with 3-bromocyclohexene *trans*-1, 2-dibromocyclohexane as the sole product. Draw structures of the possible intermediates, and then Explain why only a single product is formed in the reaction of HBr with 3-bromocyclohexene.

Solution:

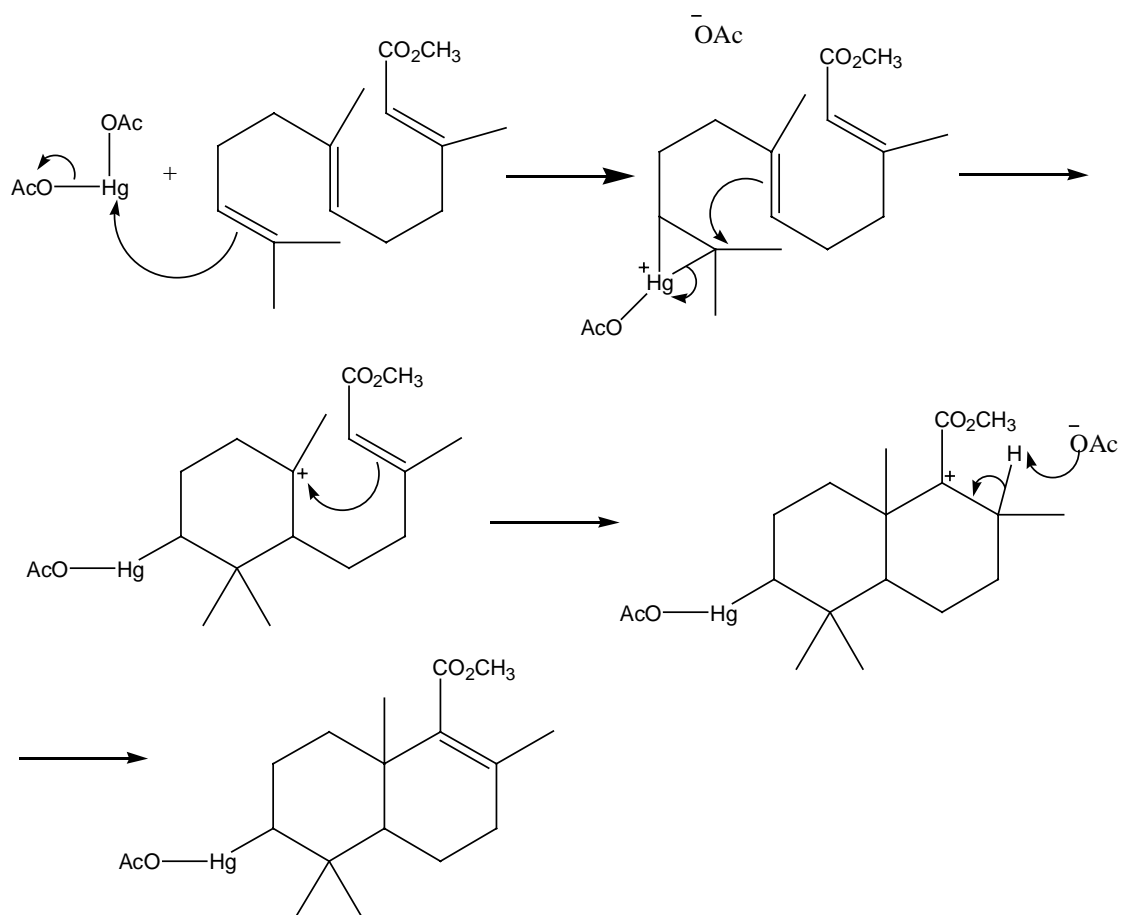


7.55 The following reaction takes place in high yield:

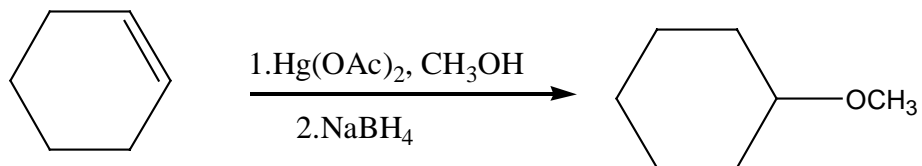


Use your general knowledge of alkene chemistry to propose a mechanism, even though you've never seen this reaction before.

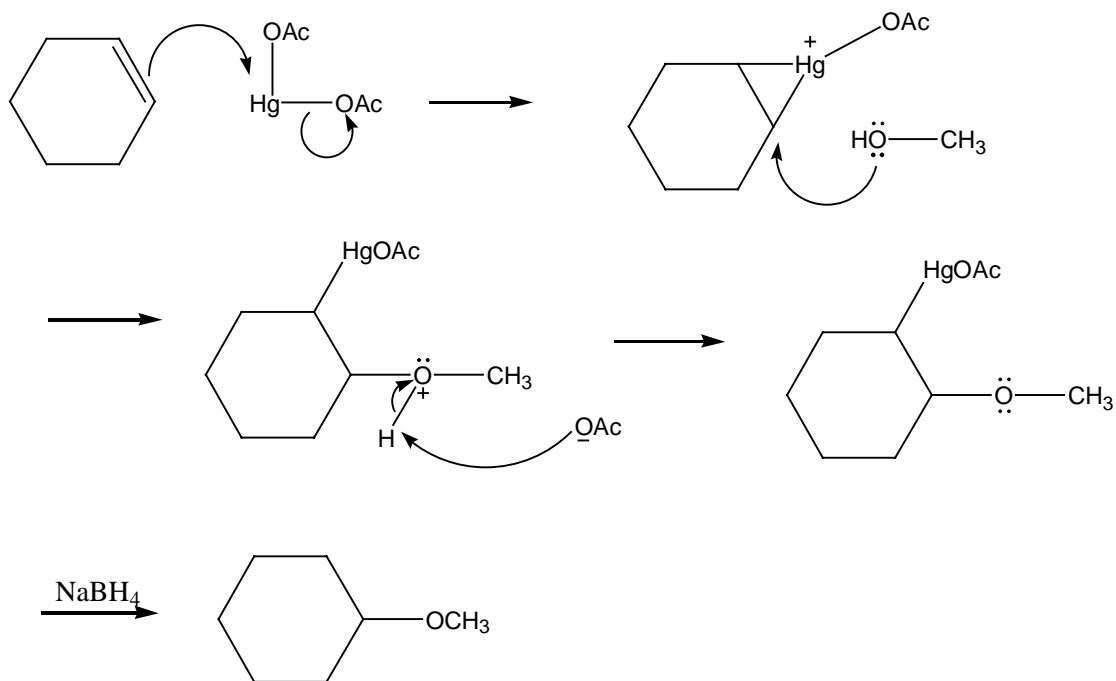
Solution:



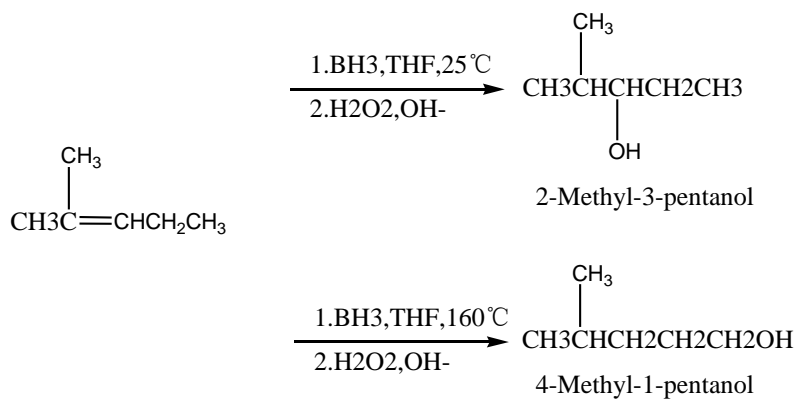
7.56 Reaction of cyclohexene with mercury(II) acetate in CH_3OH rather than H_2O , followed by treatment with NaBH_4 , yields cyclohexyl methyl ether rather than cyclohexanol. Suggest a mechanism.



Solution:

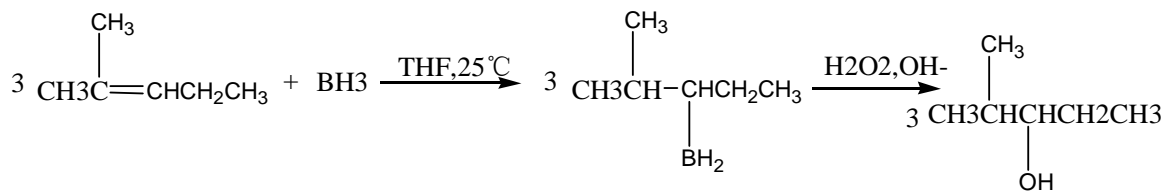


7.57 Hydroboration of 2-methyl-2-pentene at 25°C followed by oxidation with alkaline H₂O₂ yields 2-methyl-3-pentanol, but hydroboration at 160°C followed by oxidation yields 4-methyl-1-pentanol. Explain.

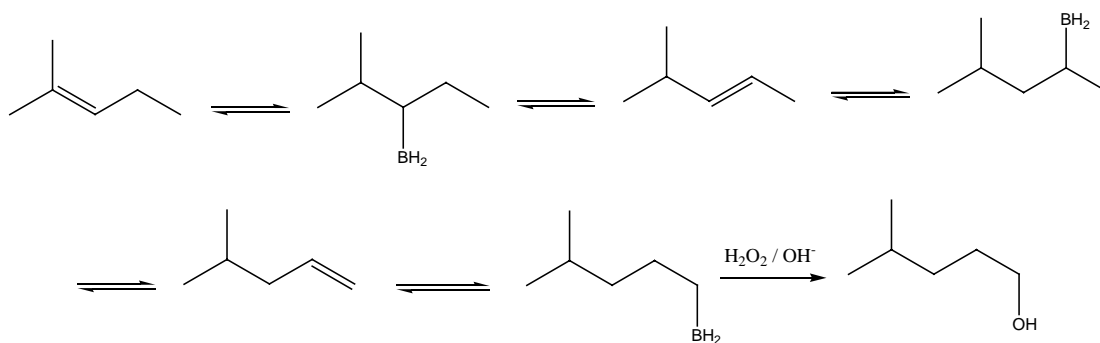


Solution:

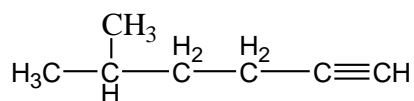
Case 1:



Case 2:



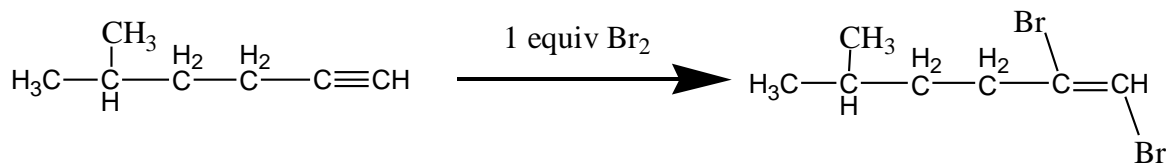
7.58 Alkynes undergo many of the same reactions that alkenes do. What products would you expect from each of the following reactions?



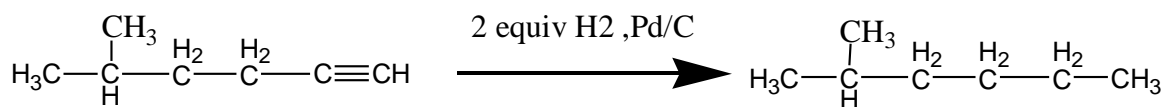
- (1) with 1 equiv Br_2 ;
- (2) with 2 equiv $\text{H}_2, \text{Pd/C}$
- (3) with 1 equiv HBr

Solutions:

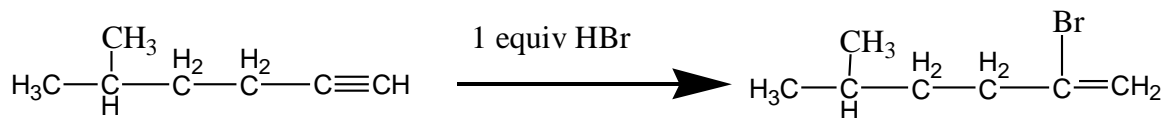
(1)



(2)



(3)



7.59 Explain the observation that hydroxylation of cis-2-butene with OsO_4 yields a different product than hydroxylation of trans-2-butene. First draw the structure and show the stereochemistry of each product, and then make molecular models.

Solution:

