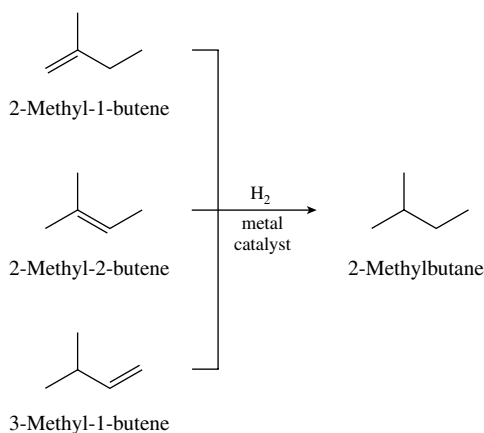


## CHAPTER 6

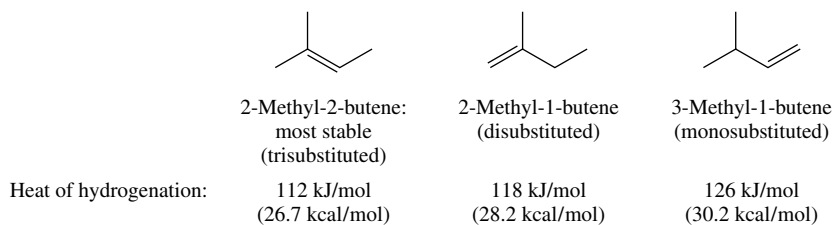
### REACTIONS OF ALKENES: ADDITION REACTIONS

#### SOLUTIONS TO TEXT PROBLEMS

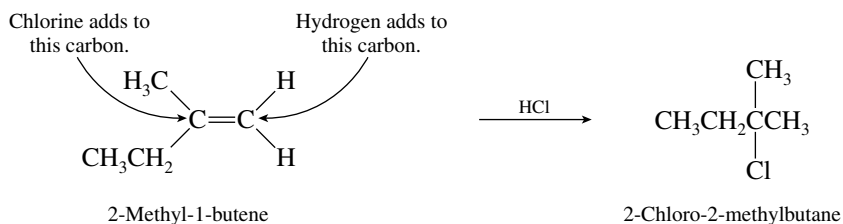
- 6.1 Catalytic hydrogenation converts an alkene to an alkane having the same carbon skeleton. Since 2-methylbutane is the product of hydrogenation, all three alkenes must have a four-carbon chain with a one-carbon branch. The three alkenes are therefore:



- 6.2 The most highly substituted double bond is the most stable and has the smallest heat of hydrogenation.

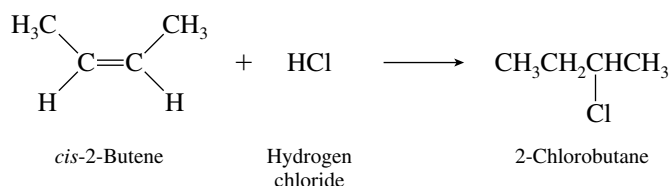


- 6.3 (b) Begin by writing out the structure of the starting alkene. Identify the doubly bonded carbon that has the greater number of attached hydrogens; this is the one to which the proton of hydrogen chloride adds. Chlorine adds to the carbon atom of the double bond that has the fewer attached hydrogens.

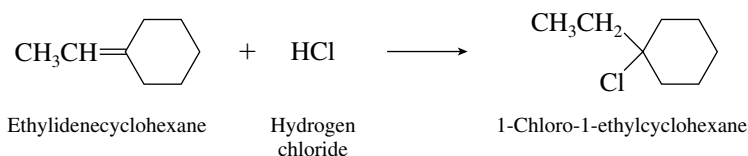


By applying Markovnikov's rule, we see that the major product is 2-chloro-2-methylbutane.

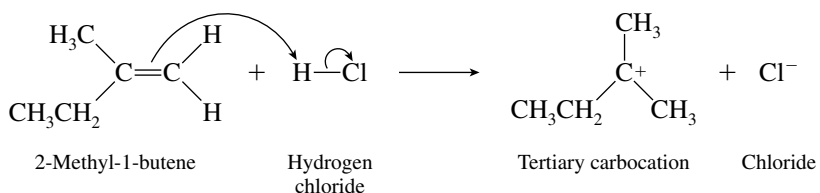
- (c) Regioselectivity of addition is not an issue here, because the two carbons of the double bond are equivalent in *cis*-2-butene. Hydrogen chloride adds to *cis*-2-butene to give 2-chlorobutane.



- (d) One end of the double bond has no attached hydrogens, but the other end has one. In accordance with Markovnikov's rule, the proton of hydrogen chloride adds to the carbon that already has one hydrogen. The product is 1-chloro-1-ethylcyclohexane.

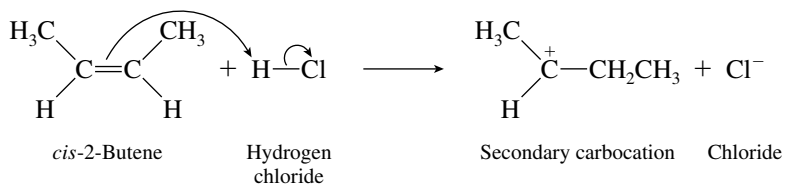


- 6.4 (b) A proton is transferred to the terminal carbon atom of 2-methyl-1-butene so as to produce a tertiary carbocation.



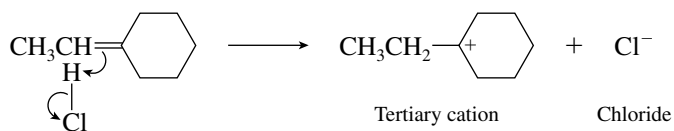
This is the carbocation that leads to the observed product, 2-chloro-2-methylbutane.

- (c) A secondary carbocation is an intermediate in the reaction of *cis*-2-butene with hydrogen chloride.



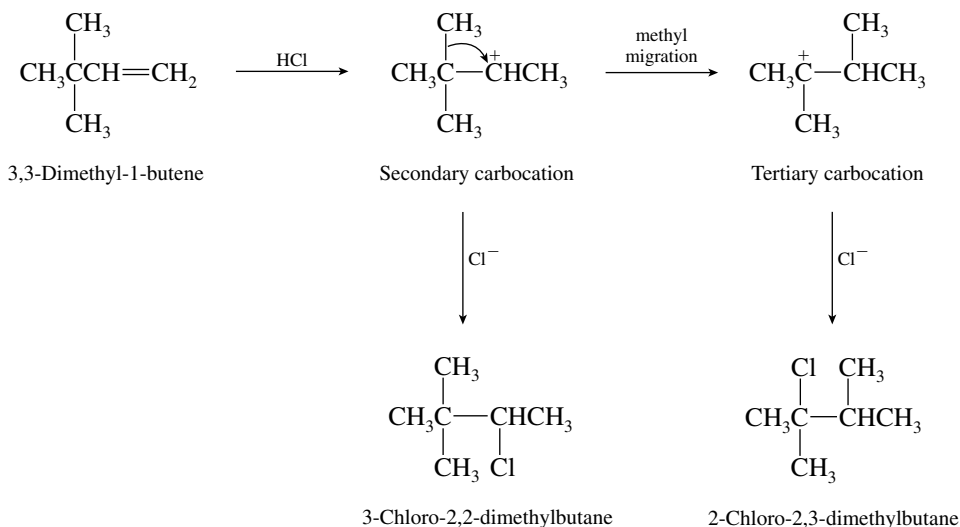
Capture of this carbocation by chloride gives 2-chlorobutane.

- (d) A tertiary carbocation is formed by protonation of the double bond.



This carbocation is captured by chloride to give the observed product, 1-chloro-1-ethylcyclohexane.

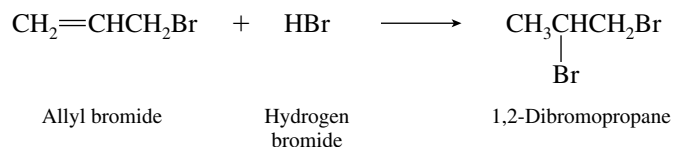
- 6.5 The carbocation formed by protonation of the double bond of 3,3-dimethyl-1-butene is secondary. Methyl migration can occur to give a more stable tertiary carbocation.



The two chlorides are 3-chloro-2,2-dimethylbutane and 2-chloro-2,3-dimethylbutane.

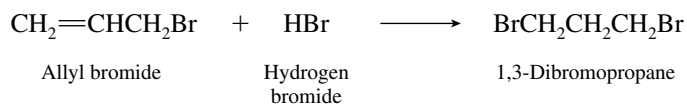
- 6.6 The structure of allyl bromide (3-bromo-1-propene) is  $\text{CH}_2=\text{CHCH}_2\text{Br}$ . Its reaction with hydrogen bromide in accordance with Markovnikov's rule proceeds by addition of a proton to the doubly bonded carbon that has the greater number of attached hydrogens.

**Addition according to Markovnikov's rule:**

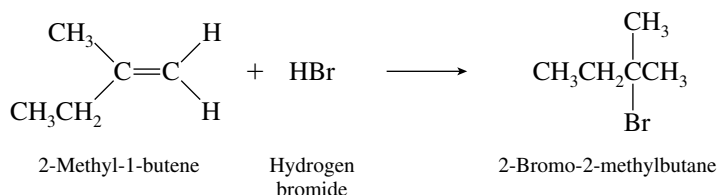


Addition of hydrogen bromide opposite to Markovnikov's rule leads to 1,3-dibromopropane.

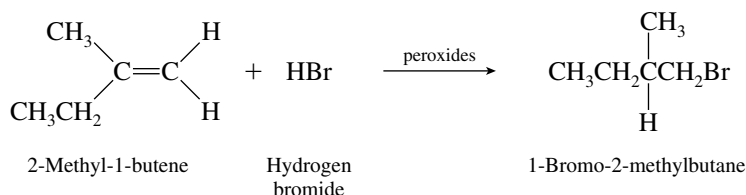
**Addition contrary to Markovnikov's rule:**



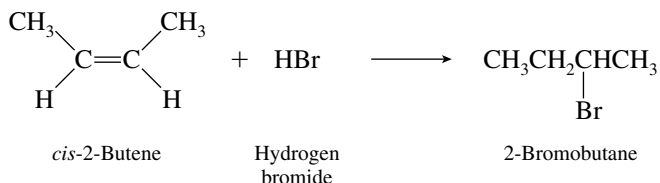
- 6.7 (b) Hydrogen bromide adds to 2-methyl-1-butene in accordance with Markovnikov's rule when peroxides are absent. The product is 2-bromo-2-methylbutane.



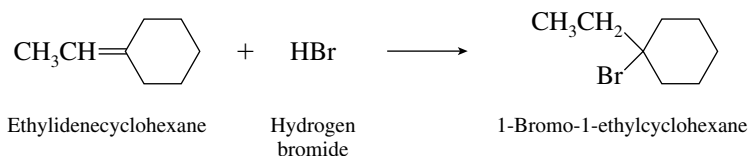
The opposite regioselectivity is observed when peroxides are present. The product is 1-bromo-2-methylbutane.



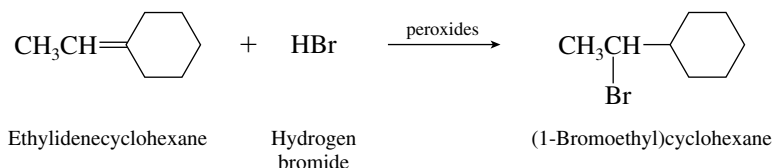
- (c) Both ends of the double bond in *cis*-2-butene are equivalently substituted, so that the same product (2-bromobutane) is formed by hydrogen bromide addition regardless of whether the reaction is carried out in the presence of peroxides or in their absence.



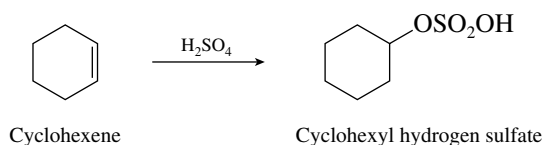
- (d) A tertiary bromide is formed on addition of hydrogen bromide to ethylidenecyclohexane in the absence of peroxides.



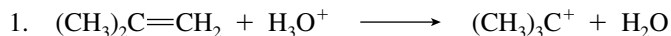
The regioselectivity of addition is reversed in the presence of peroxides, and the product is (1-bromoethyl)cyclohexane.



- 6.8 The first step is the addition of sulfuric acid to give cyclohexyl hydrogen sulfate.

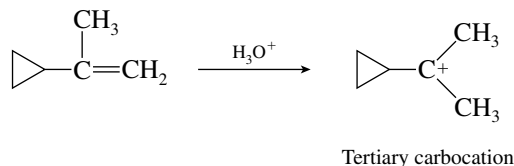


- 6.9 The presence of hydroxide ion in the second step is incompatible with the medium in which the reaction is carried out. The reaction as shown in step 1



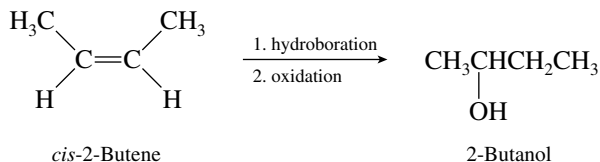
is performed in acidic solution. There are, for all practical purposes, no hydroxide ions in aqueous acid, the strongest base present being water itself. It is quite important to pay attention to the species that are actually present in the reaction medium whenever you formulate a reaction mechanism.

- 6.10 The more stable the carbocation, the faster it is formed. The more reactive alkene gives a tertiary carbocation in the rate-determining step.

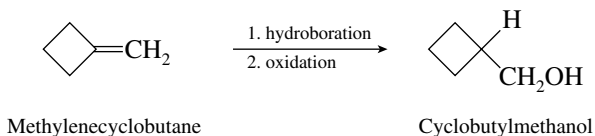


Protonation of  $\triangle-\text{CH}=\text{CHCH}_3$  gives a secondary carbocation.

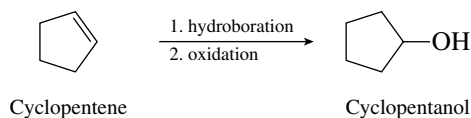
- 6.11 The mechanism of electrophilic addition of hydrogen chloride to 2-methylpropene as outlined in text Section 6.6 proceeds through a carbocation intermediate. This mechanism is the reverse of the E1 elimination. The E2 mechanism is concerted—it does not involve an intermediate.
- 6.12 (b) The carbon-carbon double bond is symmetrically substituted in *cis*-2-butene, and so the regioselectivity of hydroboration-oxidation is not an issue. Hydration of the double bond gives 2-butanol.



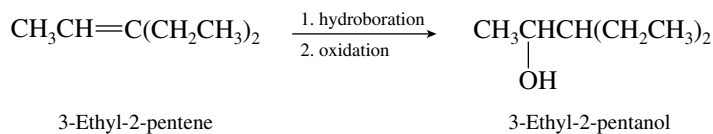
- (c) Hydroboration-oxidation of alkenes is a method that leads to hydration of the double bond with a regioselectivity opposite to Markovnikov's rule.



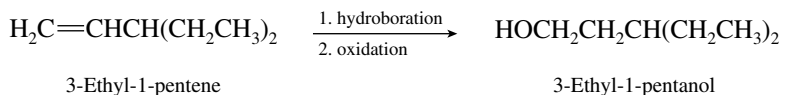
- (d) Hydroboration-oxidation of cyclopentene gives cyclopentanol.



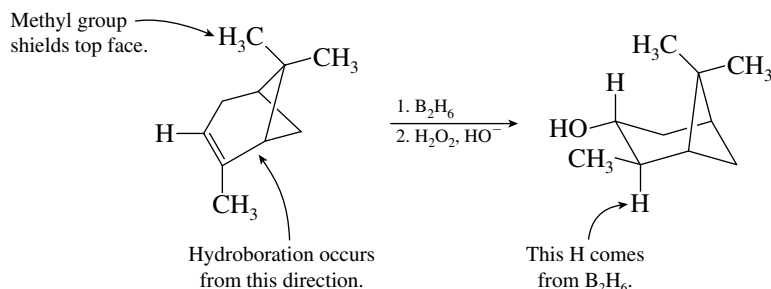
- (e) When alkenes are converted to alcohols by hydroboration-oxidation, the hydroxyl group is introduced at the less substituted carbon of the double bond.



- (f) The less substituted carbon of the double bond in 3-ethyl-1-pentene is at the end of the chain. It is this carbon that bears the hydroxyl group in the product of hydroboration–oxidation.

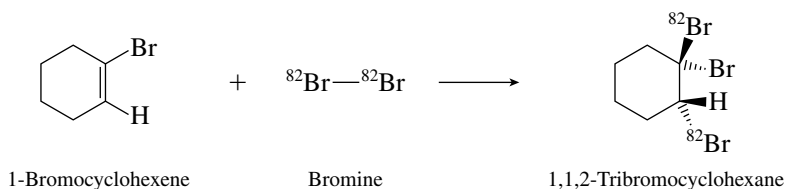


- 6.13** The bottom face of the double bond of  $\alpha$ -pinene is less hindered than the top face.

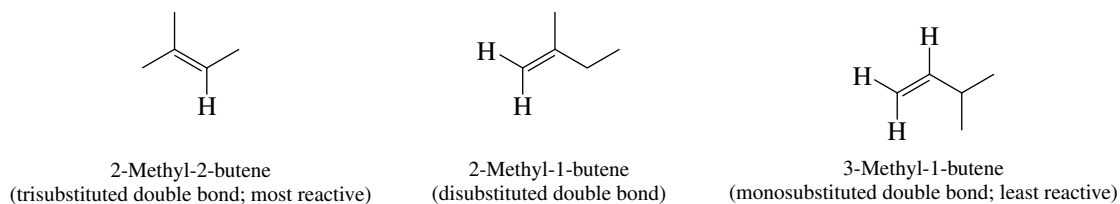


Syn addition of H and OH takes place and with a regioselectivity opposite to that of Markovnikov's rule.

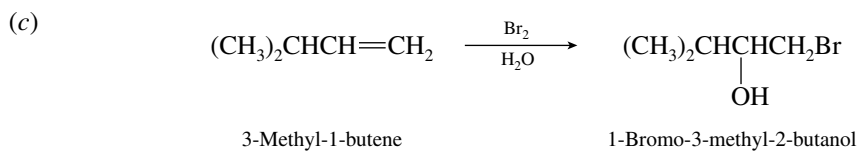
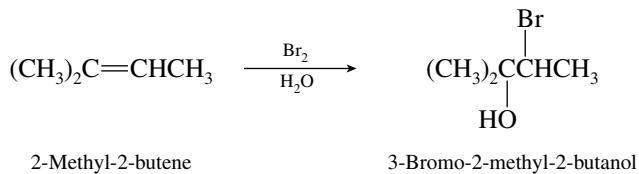
- 6.14** Bromine adds anti to the double bond of 1-bromocyclohexene to give 1,1,2-tribromocyclohexane. The radioactive bromines ( $^{82}\text{Br}$ ) are vicinal and trans to each other.



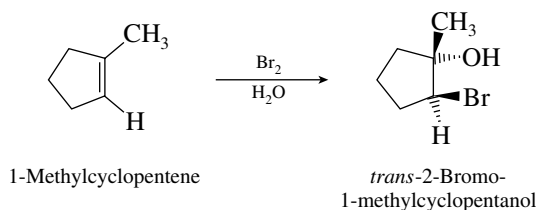
- 6.15** Alkyl substituents on the double bond increase the reactivity of the alkene toward addition of bromine.



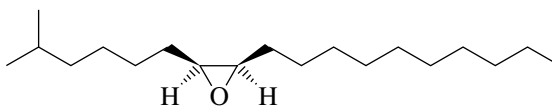
- 6.16** (b) Bromine becomes bonded to the less highly substituted carbon of the double bond, the hydroxyl group to the more highly substituted one.



(d) Anti addition occurs.

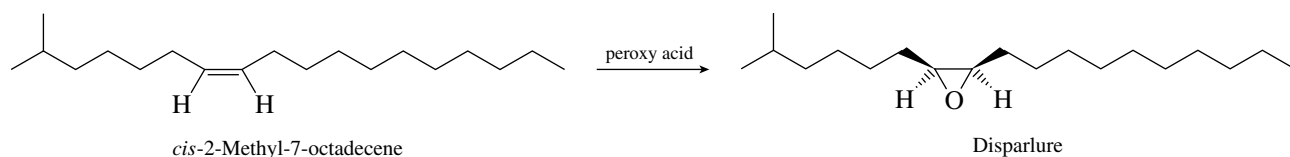


6.17 The structure of disparlure is as shown.

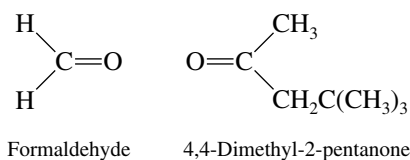


Its longest continuous chain contains 18 carbon atoms, and so it is named as an epoxy derivative of octadecane. Number the chain in the direction that gives the lowest number to the carbons that bear oxygen. Thus, disparlure is *cis*-2-methyl-7,8-epoxyoctadecane.

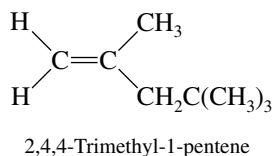
6.18 Disparlure can be prepared by epoxidation of the corresponding alkene. *Cis* alkenes yield *cis* epoxides upon epoxidation. *cis*-2-Methyl-7-octadecene is therefore the alkene chosen to prepare disparlure by epoxidation.



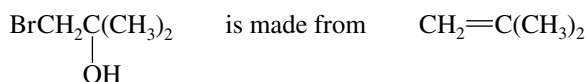
6.19 The products of ozonolysis are formaldehyde and 4,4-dimethyl-2-pentanone.



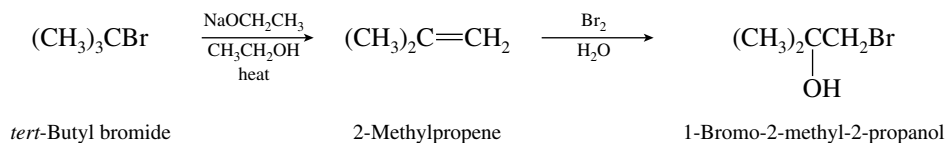
The two carbons that were doubly bonded to each other in the alkene become the carbons that are doubly bonded to oxygen in the products of ozonolysis. Therefore, mentally remove the oxygens and connect these two carbons by a double bond to reveal the structure of the starting alkene.



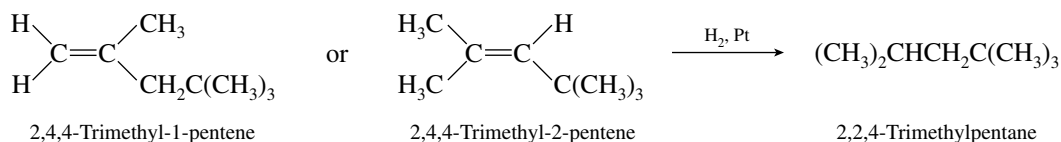
6.20 From the structural formula of the desired product, we see that it is a **vicinal bromohydrin**. Vicinal bromohydrins are made from alkenes by reaction with bromine in water.



Since the starting material given is *tert*-butyl bromide, a practical synthesis is:

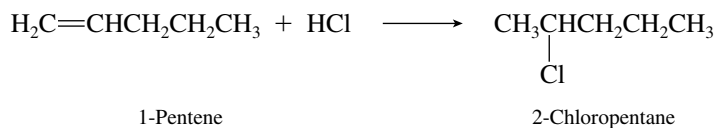


- 6.21** Catalytic hydrogenation of the double bond converts 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene to 2,2,4-trimethylpentane.

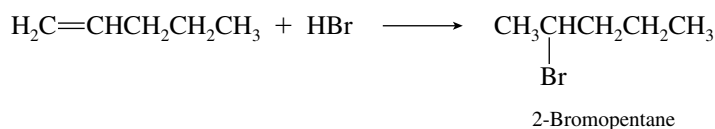


- 6.22** This problem illustrates the reactions of alkenes with various reagents and requires application of Markovnikov's rule to the addition of unsymmetrical electrophiles.

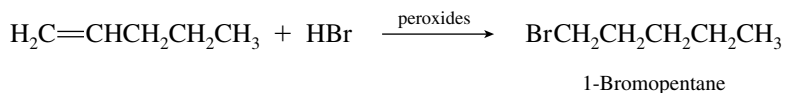
- (a) Addition of hydrogen chloride to 1-pentene will give 2-chloropentane.



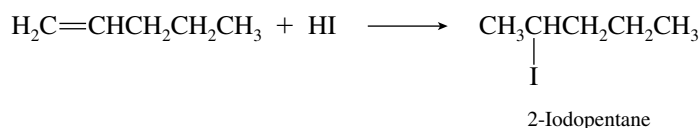
- (b) Electrophilic addition of hydrogen bromide will give 2-bromopentane.



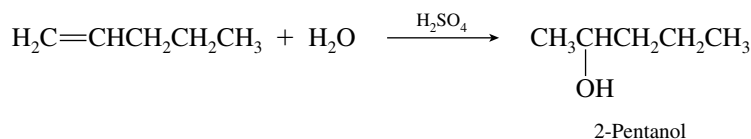
- (c) The presence of peroxides will cause free-radical addition of hydrogen bromide, and regioselective addition opposite to Markovnikov's rule will be observed.



- (d) Hydrogen iodide will add according to Markovnikov's rule.

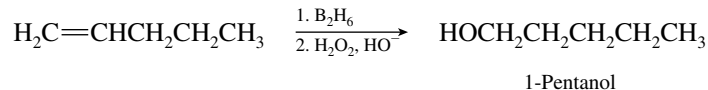


- (e) Dilute sulfuric acid will cause hydration of the double bond with regioselectivity in accord with Markovnikov's rule.

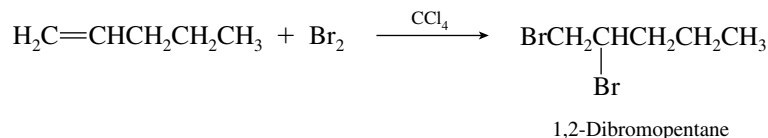




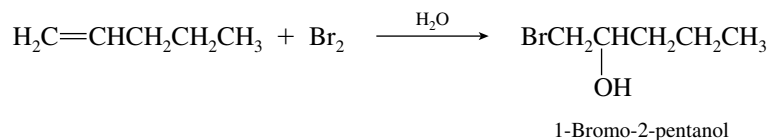
- (f) Hydroboration–oxidation of an alkene brings about hydration of the double bond opposite to Markovnikov’s rule; 1-pentanol will be the product.



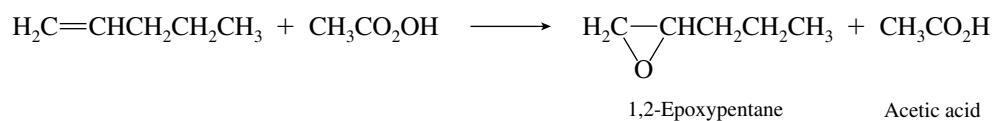
- (g) Bromine adds across the double bond to give a vicinal dibromide.



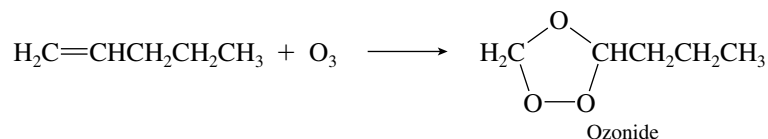
- (h) Vicinal bromohydrins are formed when bromine in water adds to alkenes. Br adds to the less substituted carbon, OH to the more substituted one.



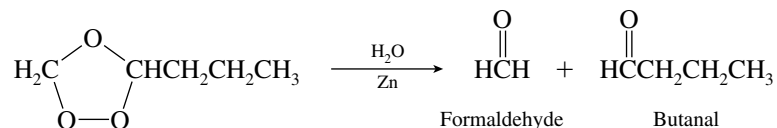
- (i) Epoxidation of the alkene occurs on treatment with peroxy acids.



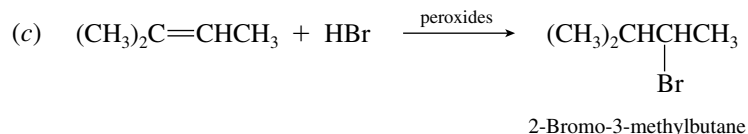
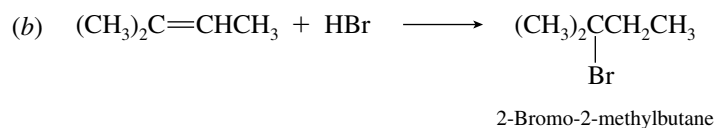
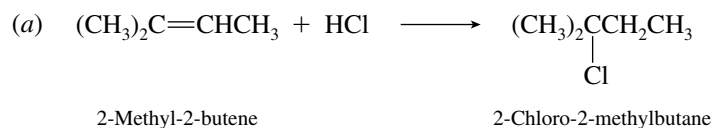
- (j) Ozone reacts with alkenes to give ozonides.

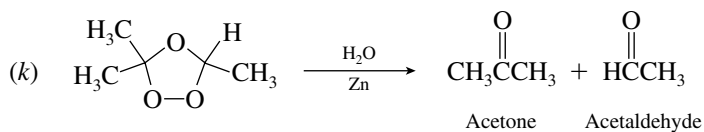
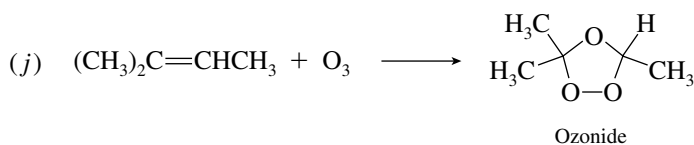
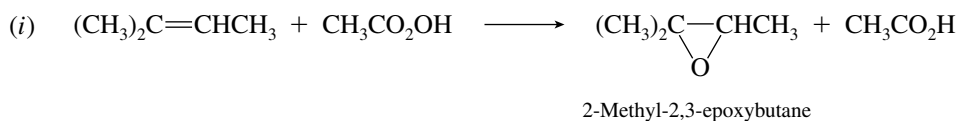
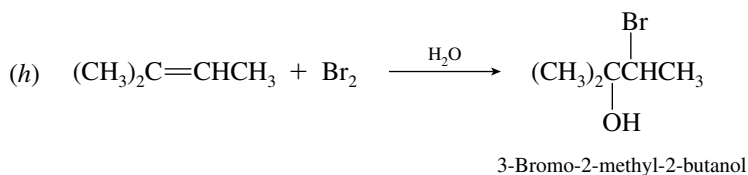
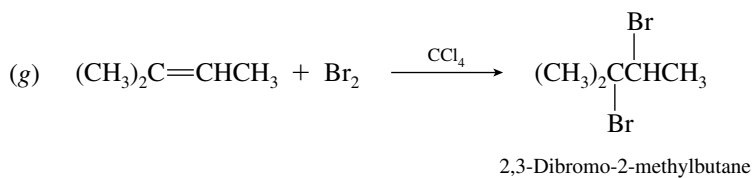
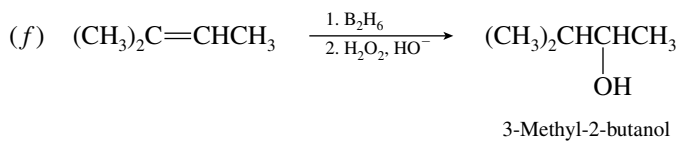
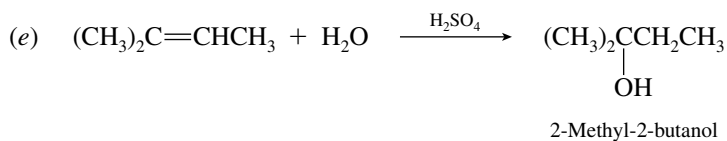
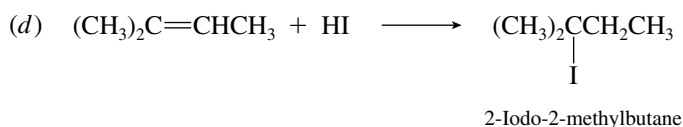


- (k) When the ozonide in part (j) is hydrolyzed in the presence of zinc, formaldehyde and butanal are formed.

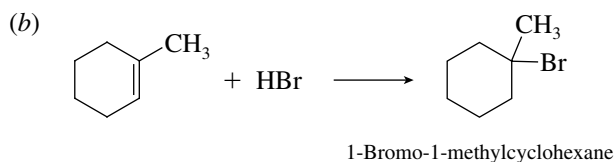
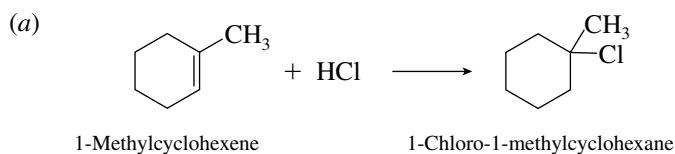


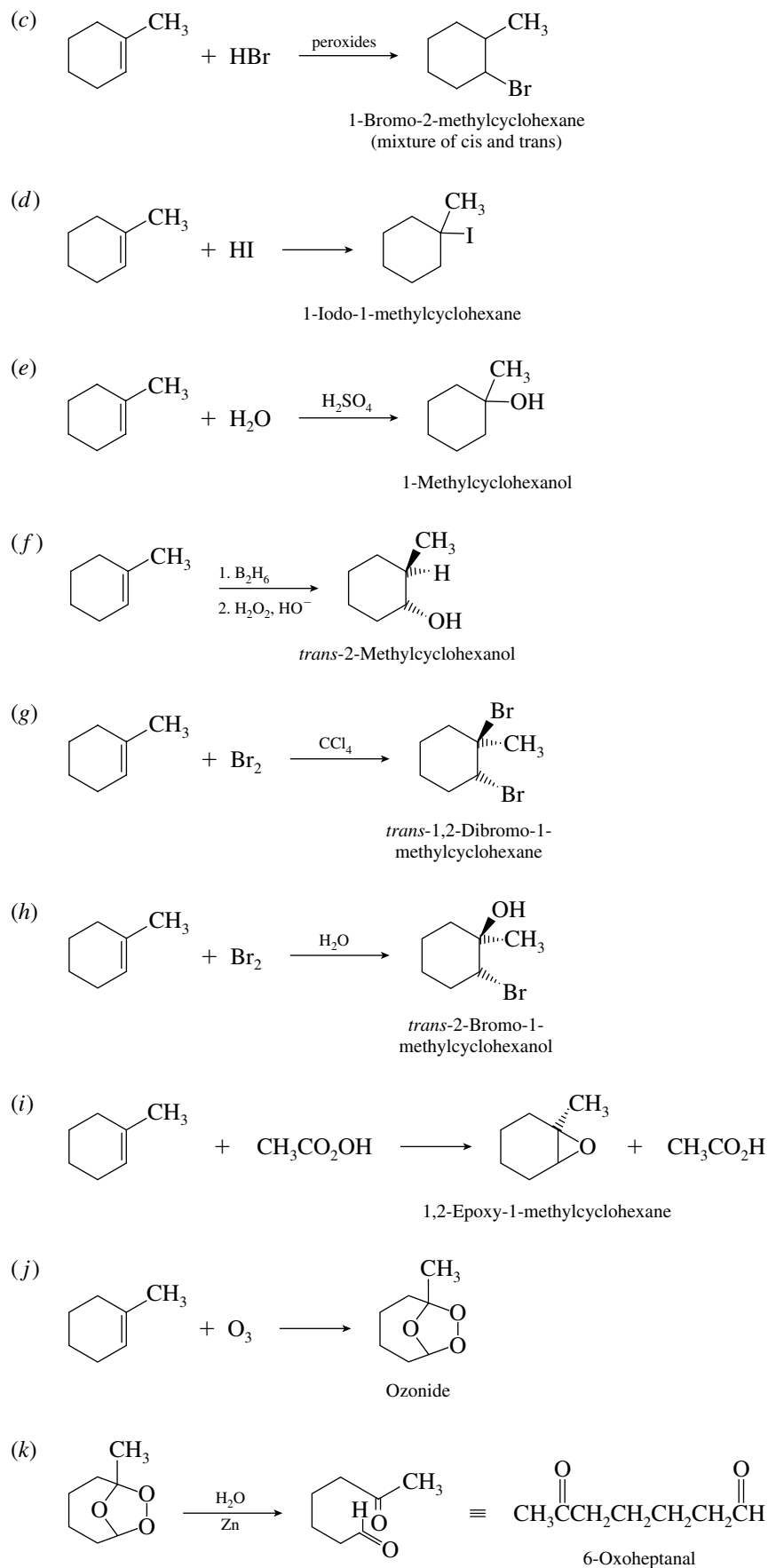
**6.23** When we compare the reactions of 2-methyl-2-butene with the analogous reactions of 1-pentene, we find that the reactions proceed in a similar manner.





**6.24** Cycloalkenes undergo the same kinds of reactions as do noncyclic alkenes.





**6.25** We need first to write out the structures in more detail to evaluate the substitution patterns at the double bonds.

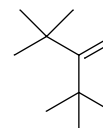
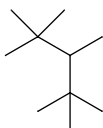
- |     |   |  |                                   |
|-----|---|--|-----------------------------------|
| (a) | 1-Pentene                                 |  | Monosubstituted                   |
| (b) | ( <i>E</i> )-4,4-Dimethyl-2-pentene       |  | trans-Disubstituted               |
| (c) | ( <i>Z</i> )-4-Methyl-2-pentene           |  | cis-Disubstituted                 |
| (d) | ( <i>Z</i> )-2,2,5,5-Tetramethyl-3-hexene |  | Two <i>tert</i> -butyl groups cis |
| (e) | 2,4-Dimethyl-2-pentene                    |  | Trisubstituted                    |

Compound *d*, having two *cis tert*-butyl groups, should have the least stable (highest energy) double bond. The remaining alkenes are arranged in order of increasing stability (decreasing heats of hydrogenation) according to the degree of substitution of the double bond: monosubstituted, *cis*-disubstituted, *trans*-disubstituted, trisubstituted. The heats of hydrogenation are therefore:

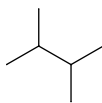
- |     |  |                            |
|-----|--|----------------------------|
| (d) |  | 151 kJ/mol (36.2 kcal/mol) |
| (a) |  | 122 kJ/mol (29.3 kcal/mol) |
| (c) |  | 114 kJ/mol (27.3 kcal/mol) |
| (b) |  | 111 kJ/mol (26.5 kcal/mol) |
| (e) |  | 105 kJ/mol (25.1 kcal/mol) |

**6.26** In all parts of this exercise we deduce the carbon skeleton on the basis of the alkane formed on hydrogenation of an alkene and then determine what carbon atoms may be connected by a double bond in that skeleton. Problems of this type are best done by using carbon skeleton formulas.

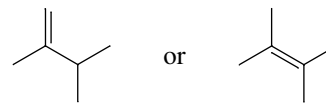
- (a) Product is 2,2,3,4,4-pentamethylpentane. The only possible alkene precursor is



- (b) Product is 2,3-dimethylbutane.



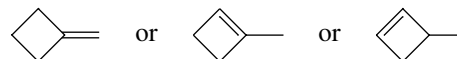
May be formed by hydrogenation of



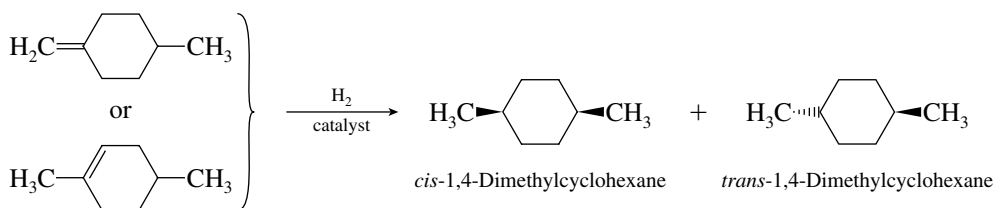
- (c) Product is methylcyclobutane.



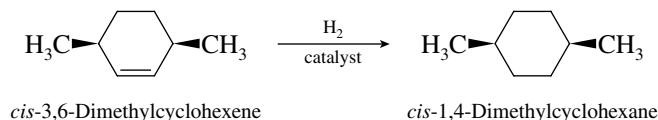
May be formed by hydrogenation of



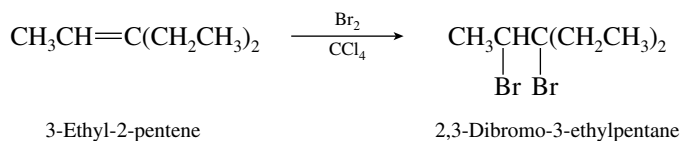
- 6.27 Hydrogenation of the alkenes shown will give a mixture of *cis*- and *trans*-1,4-dimethylcyclohexane.



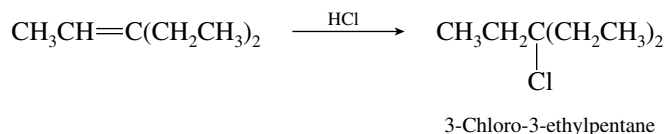
Only when the methyl groups are *cis* in the starting alkene will the *cis* stereoisomer be the sole product following hydrogenation. Hydrogenation of *cis*-3,6-dimethylcyclohexene will yield exclusively *cis*-1,4-dimethylcyclohexane.



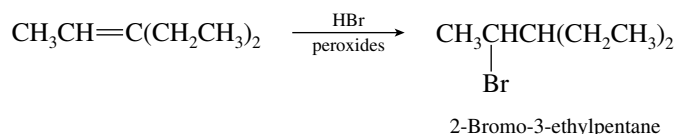
- 6.28 (a) The desired transformation is the conversion of an alkene to a vicinal dibromide.



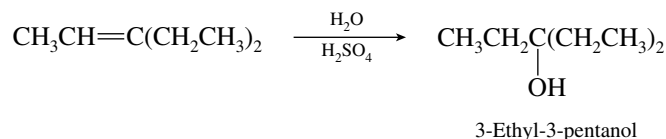
- (b) Markovnikov addition of hydrogen chloride is indicated.



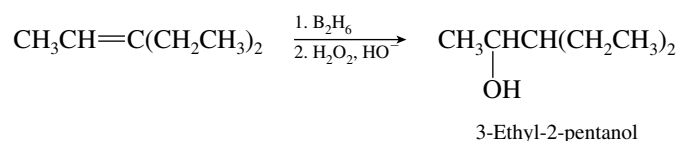
- (c) Free-radical addition of hydrogen bromide opposite to Markovnikov's rule will give the required regiochemistry.



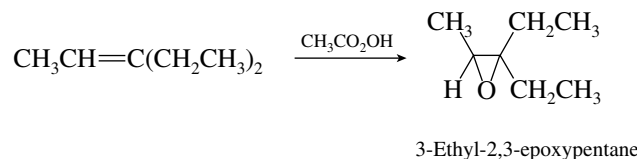
- (d) Acid-catalyzed hydration will occur in accordance with Markovnikov's rule to yield the desired tertiary alcohol.



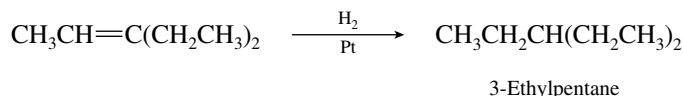
- (e) Hydroboration-oxidation results in hydration of alkenes with a regioselectivity opposite to that of Markovnikov's rule.



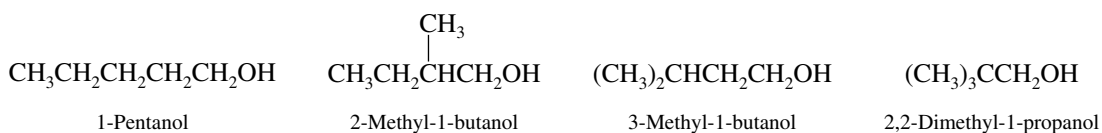
(f) A peroxy acid will convert an alkene to an epoxide.



(g) Hydrogenation of alkenes converts them to alkanes.

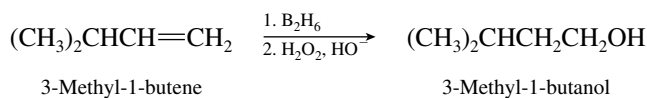
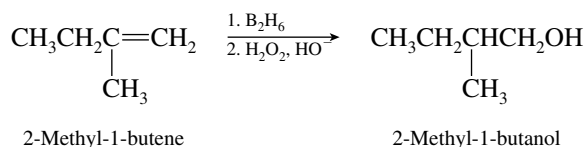
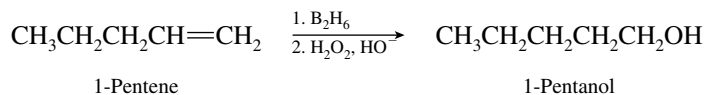


6.29 (a) Four primary alcohols have the molecular formula  $\text{C}_5\text{H}_{12}\text{O}$ :

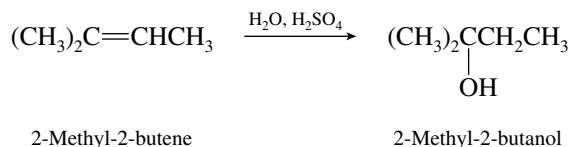
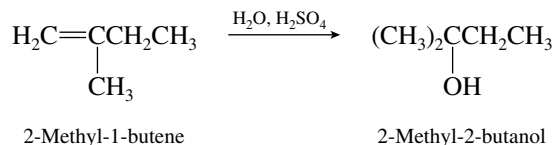


2,2-Dimethyl-1-propanol cannot be prepared by hydration of an alkene, because no alkene can have this carbon skeleton.

(b) Hydroboration–oxidation of alkenes is the method of choice for converting terminal alkenes to primary alcohols.

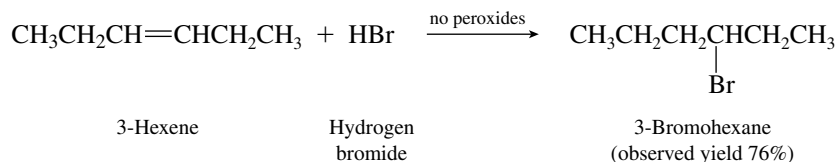


(c) The only tertiary alcohol is 2-methyl-2-butanol. It can be made by Markovnikov hydration of 2-methyl-1-butene or of 2-methyl-2-butene.

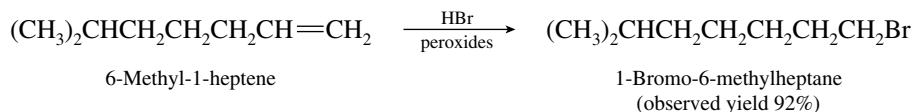


6.30 (a) Because the double bond is symmetrically substituted, the same addition product is formed under either ionic or free-radical conditions. Peroxides are absent, and so addition takes place

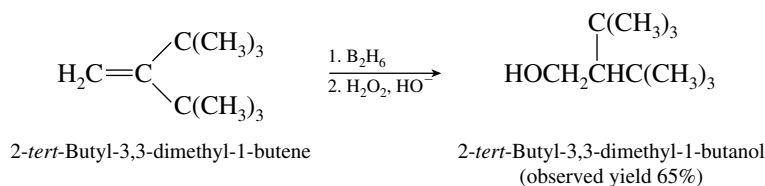
by an ionic mechanism to give 3-bromohexane. (It does not matter whether the starting material is *cis*- or *trans*-3-hexene; both give the same product.)



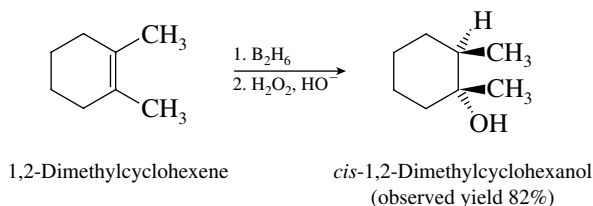
- (b) In the presence of peroxides, hydrogen bromide adds with a regioselectivity opposite to that predicted by Markovnikov's rule. The product is the corresponding primary bromide.



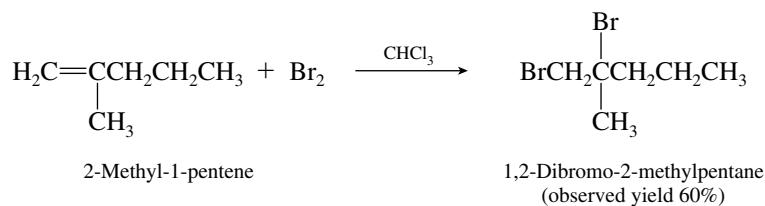
- (c) Hydroboration–oxidation of alkenes leads to hydration of the double bond with a regioselectivity contrary to Markovnikov's rule and without rearrangement of the carbon skeleton.



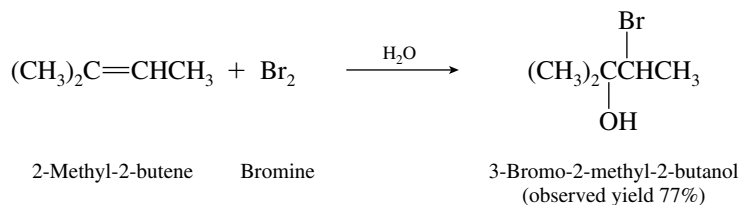
- (d) Hydroboration–oxidation of alkenes leads to *syn* hydration of double bonds.



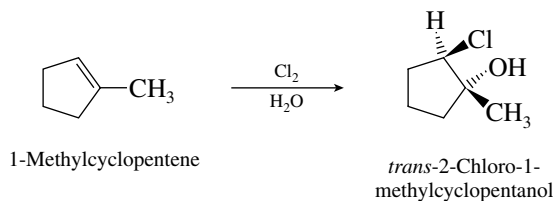
- (e) Bromine adds across the double bond of alkenes to give vicinal dibromides.



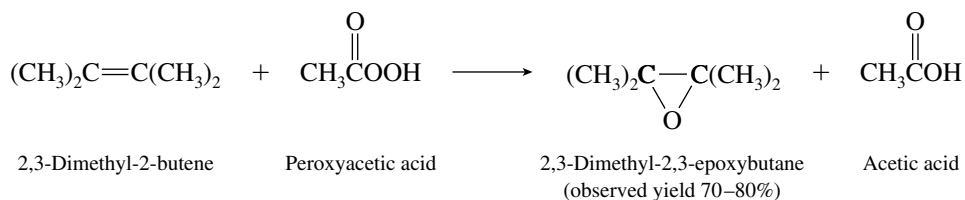
- (f) In aqueous solution bromine reacts with alkenes to give bromohydrins. Bromine is the electrophile in this reaction and adds to the carbon that has the greater number of attached hydrogens.



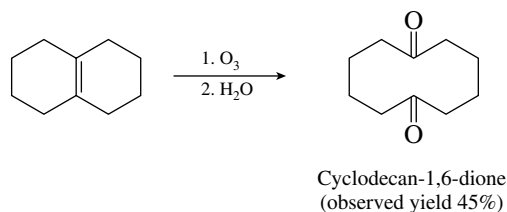
- (g) An aqueous solution of chlorine will react with 1-methylcyclopentene by an anti addition. Chlorine is the electrophile and adds to the less substituted end of the double bond.



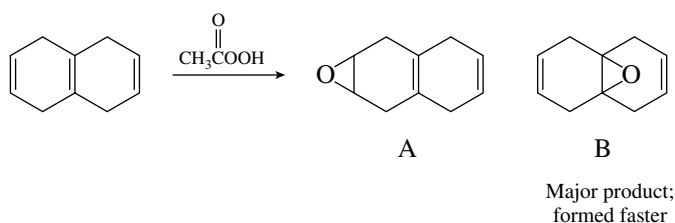
- (h) Compounds of the type  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OOH}$  are peroxy acids and react with alkenes to give epoxides.



- (i) The double bond is cleaved by ozonolysis. Each of the doubly bonded carbons becomes doubly bonded to oxygen in the product.

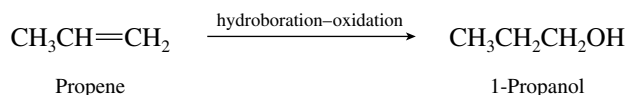


**6.31** The product is epoxide B.



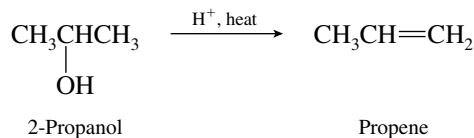
Epoxidation is an electrophilic addition; oxygen is transferred to the more electron-rich, more highly substituted double bond. A tetrasubstituted double bond reacts faster than a disubstituted one.

- 6.32** (a) There is no direct, one-step transformation that moves a hydroxyl group from one carbon to another, and so it is not possible to convert 2-propanol to 1-propanol in a single reaction. Analyze the problem by reasoning backward. 1-Propanol is a primary alcohol. What reactions do we have available for the preparation of primary alcohols? One way is by the hydroboration–oxidation of terminal alkenes.

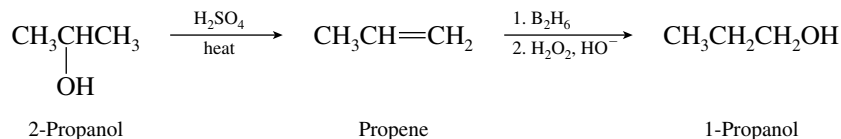




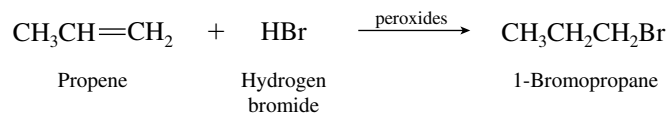
The problem now becomes the preparation of propene from 2-propanol. The simplest way is by acid-catalyzed dehydration.



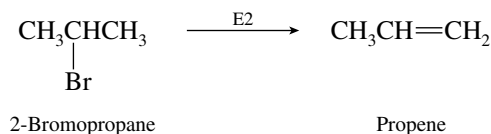
After analyzing the problem in terms of overall strategy, present the synthesis in detail showing the reagents required in each step. Thus, the answer is:



- (b) We analyze this synthetic exercise in a manner similar to the preceding one. There is no direct way to move a bromine from C-2 in 2-bromopropane to C-1 in 1-bromopropane. We can, however, prepare 1-bromopropane from propene by free-radical addition of hydrogen bromide in the presence of peroxides.

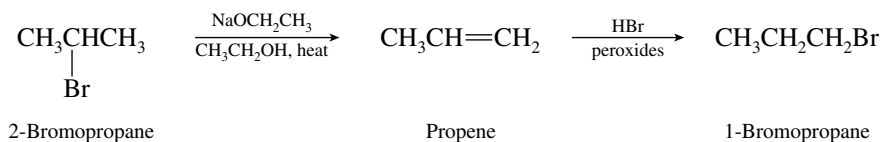


We prepare propene from 2-bromopropane by dehydrohalogenation.

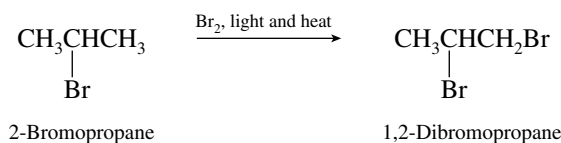


Sodium ethoxide in ethanol is a suitable base-solvent system for this conversion. Sodium methoxide in methanol or potassium *tert*-butoxide in *tert*-butyl alcohol could also be used, as could potassium hydroxide in ethanol.

Combining these two transformations gives the complete synthesis.

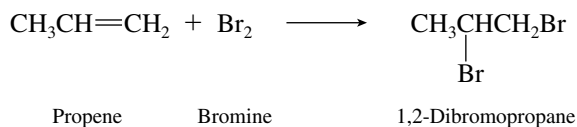


- (c) Planning your strategy in a forward direction can lead to problems when the conversion of 2-bromopropane to 1,2-dibromopropane is considered. There is a temptation to try to simply add the second bromine by free-radical halogenation.

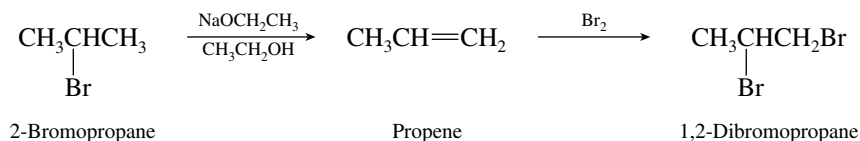


This is *incorrect!* There is no reason to believe that the second bromine will be introduced exclusively at C-1. In fact, the selectivity rules for bromination tell us that 2,2-dibromopropane is the expected major product.

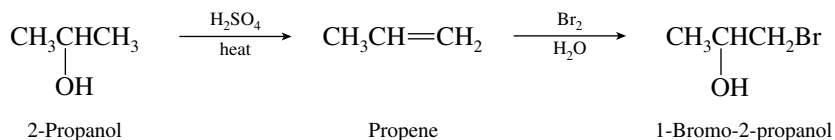
The best approach is to reason backward. 1,2-Dibromopropane is a vicinal dibromide, and we prepare vicinal dibromides by adding elemental bromine to alkenes.



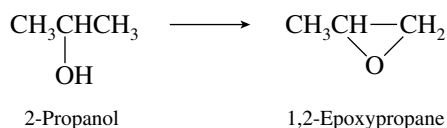
As described in part (b), we prepare propene from 2-bromopropane by E2 elimination. The correct synthesis is therefore



- (d) Do not attempt to reason forward and convert 2-propanol to 1-bromo-2-propanol by free-radical bromination. Reason backward! The desired compound is a vicinal bromohydrin, and vicinal bromohydrins are prepared by adding bromine to alkenes in aqueous solution. The correct solution is

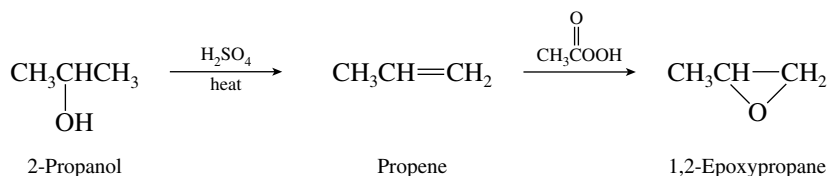


- (e) Here we have another problem where reasoning forward can lead to trouble. If we try to conserve the oxygen of 2-propanol so that it becomes the oxygen of 1,2-epoxypropane, we need a reaction in which this oxygen becomes bonded to C-1.



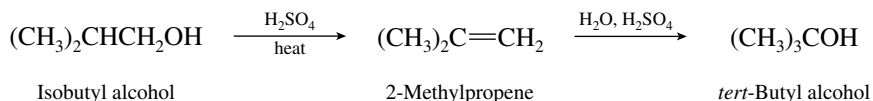
This will not work as no synthetic method for such a single-step transformation exists!

By reasoning backward, recalling that epoxides are made from alkenes by reaction with peroxy acids, we develop a proper synthesis.



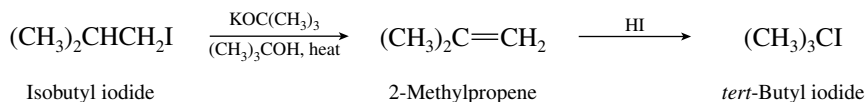
- (f) *tert*-Butyl alcohol and isobutyl alcohol have the same carbon skeleton; all that is required is to move the hydroxyl group from C-1 to C-2. As pointed out in part (a) of this problem, we

cannot do that directly but we can do it in two efficient steps through a synthesis that involves hydration of an alkene.

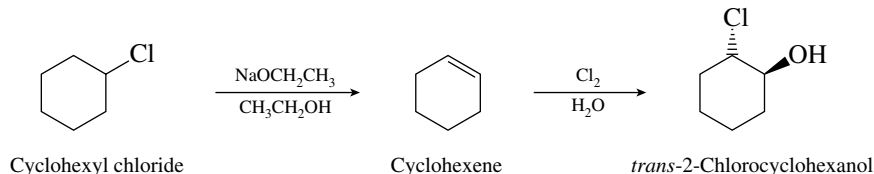


Acid-catalyzed hydration of the alkene gives the desired regioselectivity.

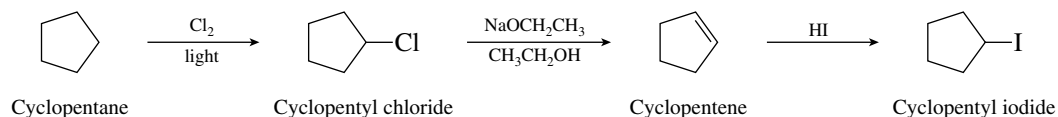
- (g) The strategy of this exercise is similar to that of the preceding one. Convert the starting material to an alkene by an elimination reaction, followed by electrophilic addition to the double bond.



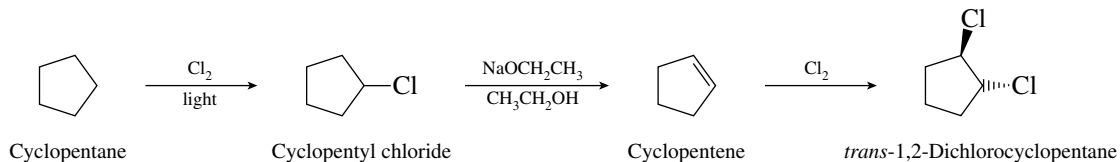
- (h) This problem is similar to the one in part (d) in that it requires the preparation of a halohydrin from an alkyl halide. The strategy is the same. Convert the alkyl halide to an alkene, and then form the halohydrin by treatment with the appropriate halogen in aqueous solution.



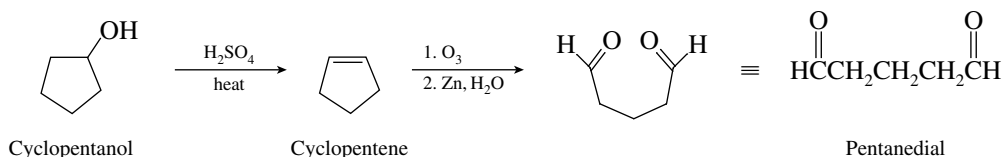
- (i) Halogenation of an alkane is required here. Iodination of alkanes, however, is not a feasible reaction. We can make alkyl iodides from alcohols or from alkenes by treatment with HI. A reasonable synthesis using reactions that have been presented to this point proceeds as shown:



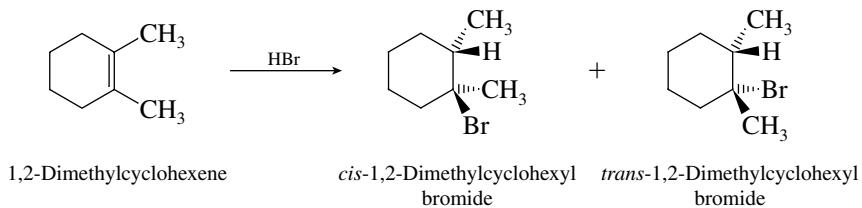
- (j) Dichlorination of cyclopentane under free-radical conditions is not a realistic approach to the introduction of two chlorines in a trans-1,2 relationship without contamination by isomeric dichlorides. Vicinal dichlorides are prepared by electrophilic addition of chlorine to alkenes. The stereochemistry of addition is anti.



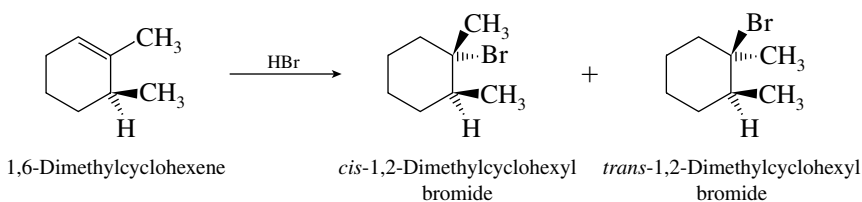
- (k) The desired compound contains all five carbon atoms of cyclopentane but is not cyclic. Two aldehyde functions are present. We know that cleavage of carbon-carbon double bonds by ozonolysis leads to two carbonyl groups, which suggests the synthesis shown in the following equation:



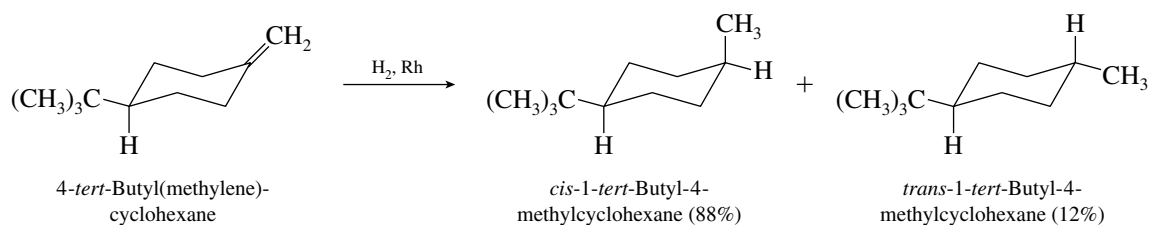
- 6.33 The two products formed by addition of hydrogen bromide to 1,2-dimethylcyclohexene cannot be regioisomers. Stereoisomers are possible, however.



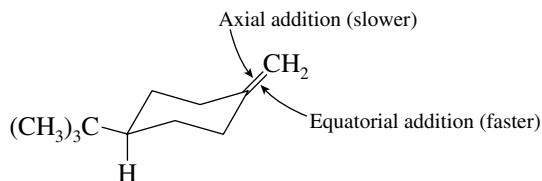
The same two products are formed from 1,6-dimethylcyclohexene because addition of hydrogen bromide follows Markovnikov's rule in the absence of peroxides.



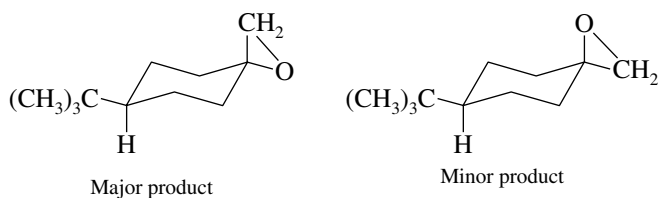
- 6.34 The problem presents the following experimental observation:



This observation tells us that the predominant mode of hydrogen addition to the double bond is from the equatorial direction. Equatorial addition is the less hindered approach and thus occurs faster.

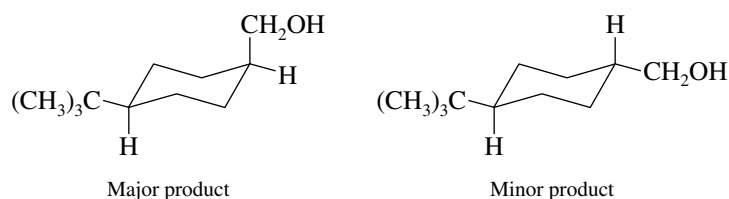


- (a) Epoxidation should therefore give the following products:

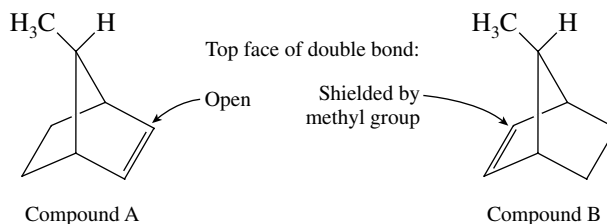


The major product is the stereoisomer that corresponds to transfer of oxygen from the equatorial direction.

(b) Hydroboration–oxidation occurs from the equatorial direction.

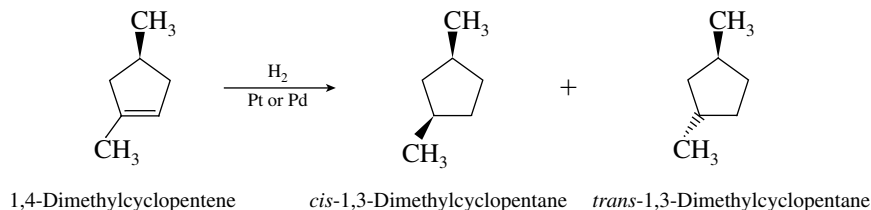


**6.35** The methyl group in compound B shields one face of the double bond from the catalyst surface, therefore hydrogen can be transferred only to the bottom face of the double bond. The methyl group in compound A does not interfere with hydrogen transfer to the double bond.



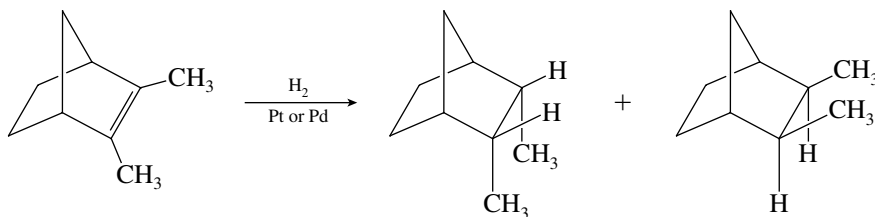
Thus, hydrogenation of A is faster than that of B because B contains a more sterically hindered double bond.

**6.36** Hydrogen can add to the double bond of 1,4-dimethylcyclopentene either from the same side as the C-4 methyl group or from the opposite side. The two possible products are *cis*- and *trans*-1,3-dimethylcyclopentane.

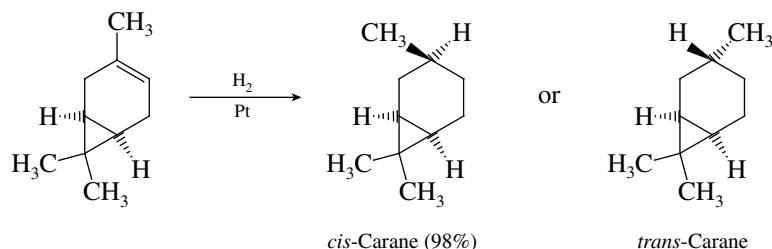


Hydrogen transfer occurs to the less hindered face of the double bond, that is, *trans* to the C-4 methyl group. Thus, the major product is *cis*-1,3-dimethylcyclopentane.

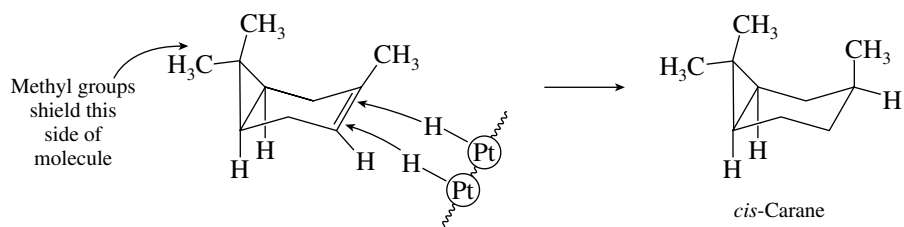
**6.37** Hydrogen can add to either the top face or the bottom face of the double bond. Syn addition to the double bond requires that the methyl groups in the product be *cis*.



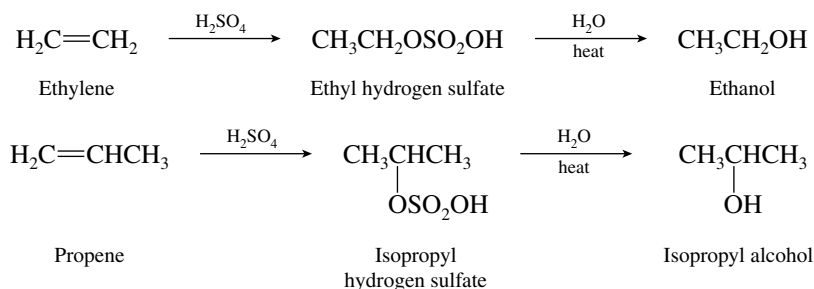
**6.38** 3-Carene can in theory undergo hydrogenation to give either *cis*-carane or *trans*-carane.



The exclusive product is *cis*-carane, since it corresponds to transfer of hydrogen from the less hindered side.

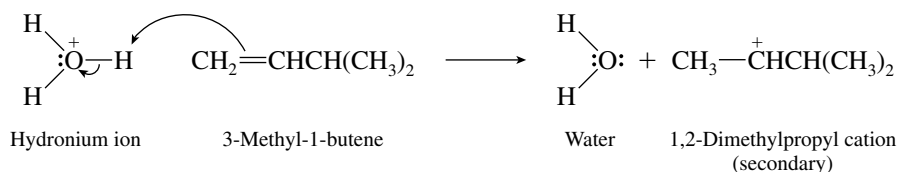


- 6.39** Ethylene and propene react with concentrated sulfuric acid to form alkyl hydrogen sulfates. Addition of water hydrolyzes the alkyl hydrogen sulfates to the corresponding alcohols.

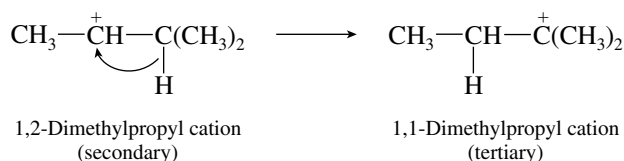


Recall that alkyl substituents on the double bond increase the reactivity of alkenes toward electrophilic addition. Propene therefore reacts faster than ethylene with sulfuric acid, and the mixture of alkyl hydrogen sulfates is mainly isopropyl hydrogen sulfate, and the alcohol obtained on hydrolysis is isopropyl alcohol.

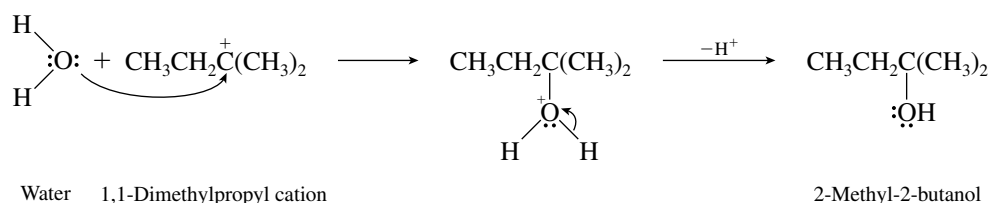
- 6.40** The first step in the mechanism of acid-catalyzed hydration of alkenes is protonation of the double bond to give a carbocation intermediate.



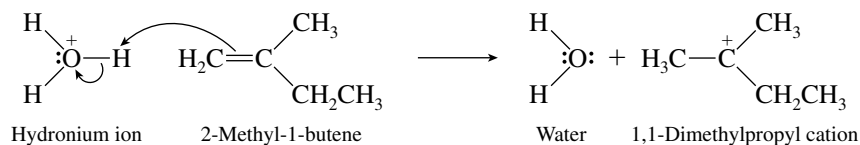
The carbocation formed in this step is secondary and capable of rearranging to a more stable tertiary carbocation by a hydride shift.



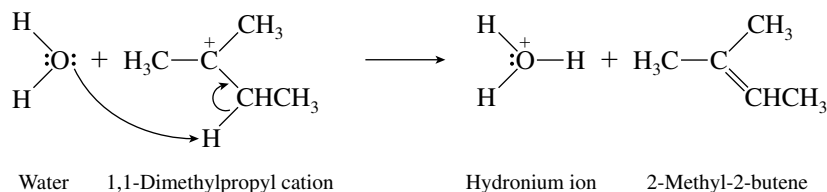
The alcohol that is formed when water reacts with the tertiary carbocation is 2-methyl-2-butanol, not 3-methyl-2-butanol.



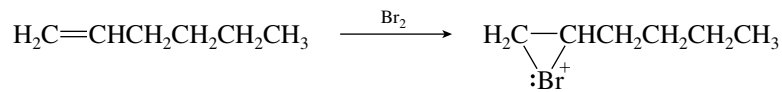
- 6.41** In the presence of sulfuric acid, the carbon–carbon double bond of 2-methyl-1-butene is protonated and a carbocation is formed.



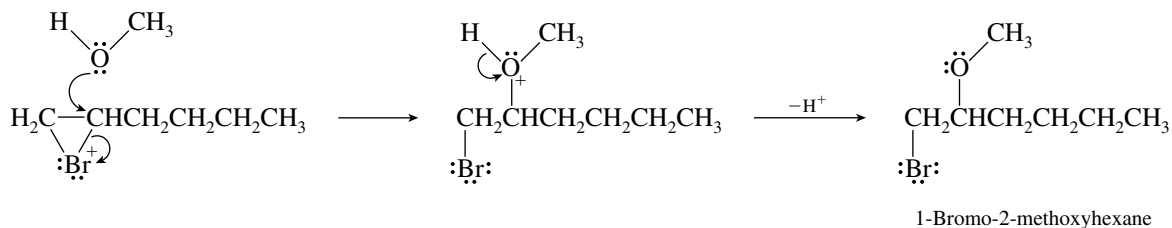
This carbocation can then lose a proton from its CH<sub>2</sub> group to form 2-methyl-2-butene.



- 6.42** The first step in the reaction of an alkene with bromine is the formation of a bromonium ion.

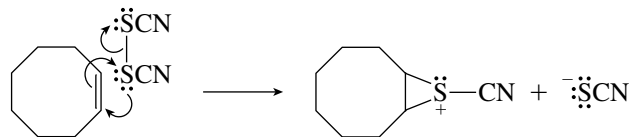


This bromonium ion can react with Br<sup>−</sup> to form 1,2-dibromohexane, or it can be attacked by methanol.

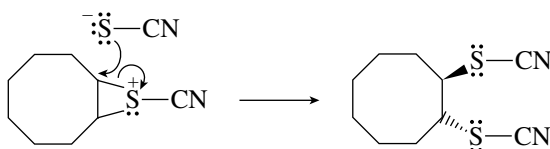


Attack on the bromonium ion by methanol is analogous to the attack by water in the mechanism of bromohydrin formation.

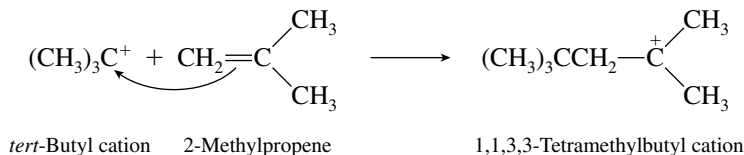
- 6.43** The problem stipulates that a bridged sulfonium ion is an intermediate. Therefore, use the  $\pi$  electrons of the double bond to attack one of the sulfur atoms of thiocyanogen and cleave the S—S bond in a manner analogous to cleavage of a Br—Br bond in the reaction of bromine with an alkene.



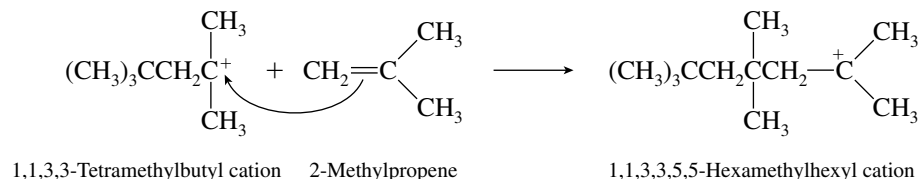
The sulfonium ion is then attacked by thiocyanate (NCS<sup>−</sup>) to give the observed product, which has the trans stereochemistry.



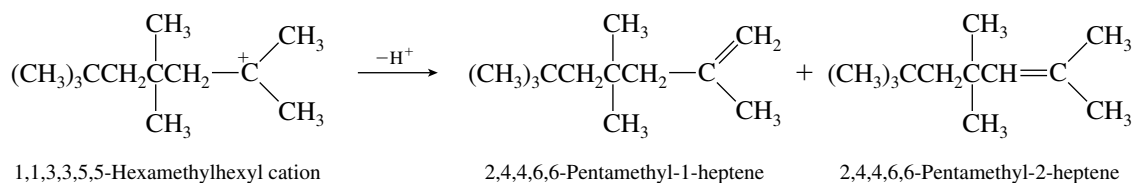
- 6.44** Alkenes of molecular formula  $C_{12}H_{24}$  are **trimers** of 2-methylpropene. The first molecule of 2-methylpropene is protonated to form *tert*-butyl cation, which reacts with a second molecule of 2-methylpropene to give a tertiary carbocation having eight carbons.



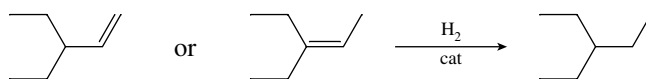
This carbocation reacts with a third molecule of 2-methylpropene to give a 12-carbon tertiary carbocation.



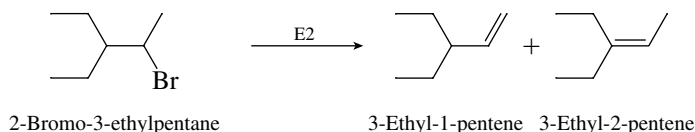
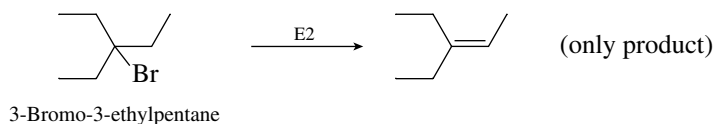
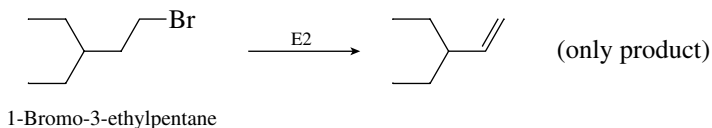
The 12-carbon carbocation can lose a proton in either of two directions to give the alkenes shown.



- 6.45** The carbon skeleton is revealed by the hydrogenation experiment. Compounds B and C must have the same carbon skeleton as 3-ethylpentane.



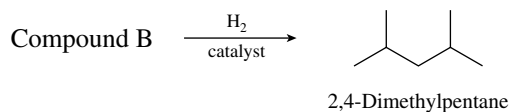
Three alkyl bromides have this carbon skeleton, namely, 1-bromo-3-ethylpentane, 2-bromo-3-ethylpentane, and 3-bromo-3-ethylpentane. Of these three only 2-bromo-3-ethylpentane will give two alkenes on dehydrobromination.



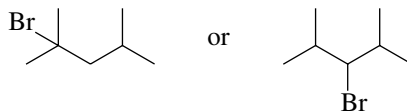
Compound A must therefore be 2-bromo-3-ethylpentane. Dehydrobromination of A will follow Zaitsev's rule, so that the major alkene (compound B) is 3-ethyl-2-pentene and the minor alkene (compound C) is 3-ethyl-1-pentene.



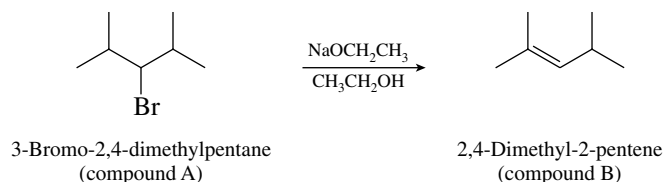
- 6.46 The information that compound B gives 2,4-dimethylpentane on catalytic hydrogenation establishes its carbon skeleton.



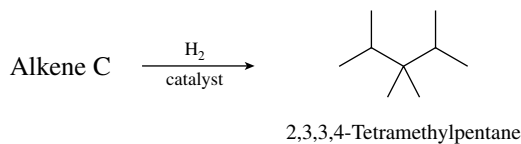
Compound B is an alkene derived from compound A—an alkyl bromide of molecular formula  $\text{C}_7\text{H}_{15}\text{Br}$ . We are told that compound A is not a primary alkyl bromide. Compound A can therefore be only:



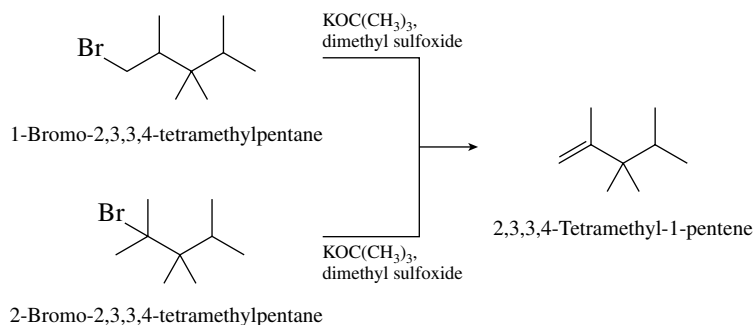
Since compound A gives a single alkene on being treated with sodium ethoxide in ethanol, it can only be 3-bromo-2,4-dimethylpentane, and compound B must be 2,4-dimethyl-2-pentene.



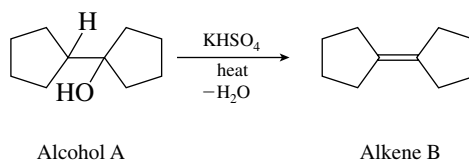
- 6.47 Alkene C must have the same carbon skeleton as its hydrogenation product, 2,3,3,4-tetramethylpentane.



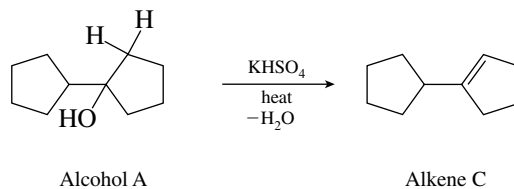
Alkene C can only therefore be 2,3,3,4-tetramethyl-1-pentene. The two alkyl bromides, compounds A and B, that give this alkene on dehydrobromination have their bromine substituents at C-1 and C-2, respectively.



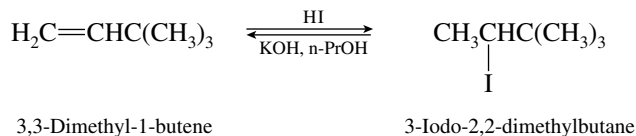
- 6.48 The only alcohol (compound A) that can undergo acid-catalyzed dehydration to alkene B without rearrangement is the one shown in the equation.



Dehydration of alcohol A also yields an isomeric alkene under these conditions.

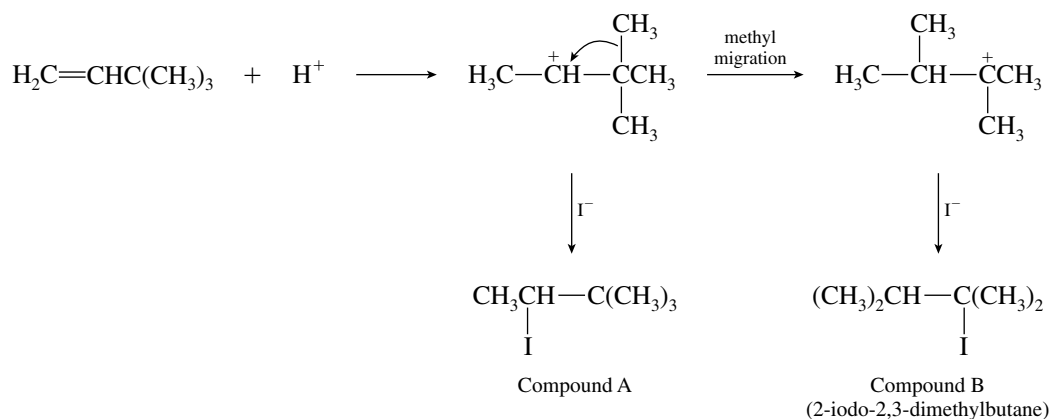


**6.49** Electrophilic addition of hydrogen iodide should occur in accordance with Markovnikov's rule.

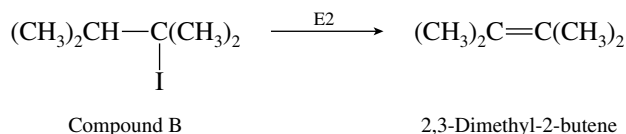


Treatment of 3-iodo-2,2-dimethylbutane with alcoholic potassium hydroxide should bring about E2 elimination to regenerate the starting alkene. Hence, compound A is 3-iodo-2,2-dimethylbutane.

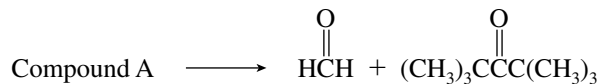
The carbocation intermediate formed in the addition of hydrogen iodide to the alkene is one which can rearrange by a methyl group migration.



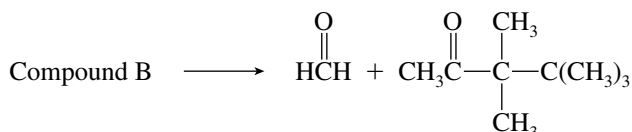
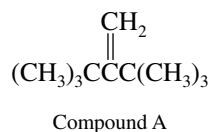
A likely candidate for compound B is therefore the one with a rearranged carbon skeleton, 2-iodo-2,3-dimethylbutane. This is confirmed by the fact that compound B undergoes elimination to give 2,3-dimethyl-2-butene.



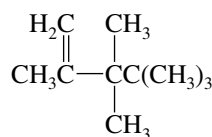
**6.50** The ozonolysis data are useful in quickly identifying alkenes A and B.



Compound A is therefore 2-*tert*-butyl-3,3-dimethyl-1-butene.

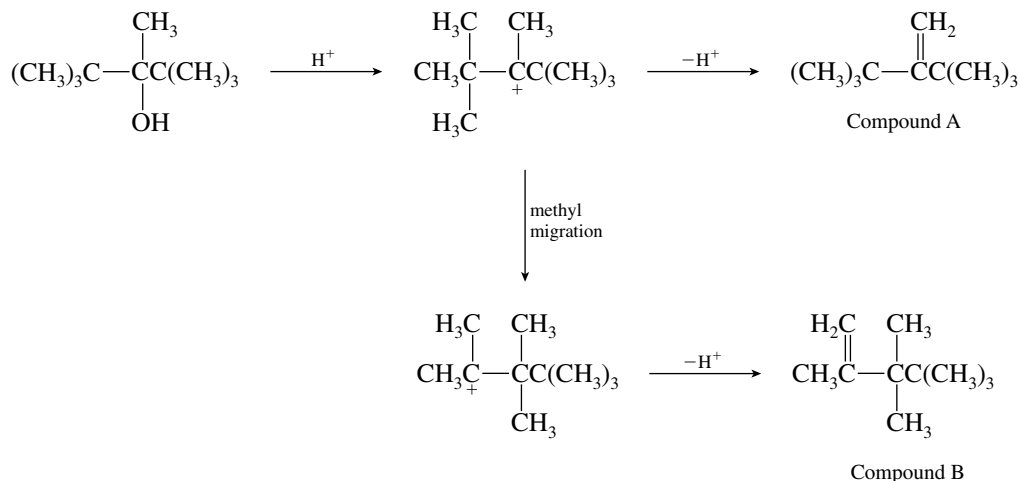


Compound B is therefore 2,3,3,4-pentamethyl-1-pentene.

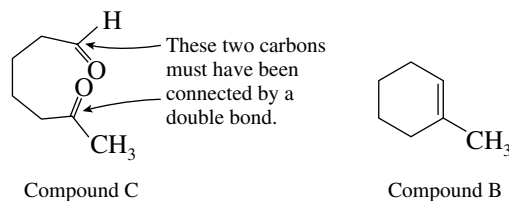


Compound B

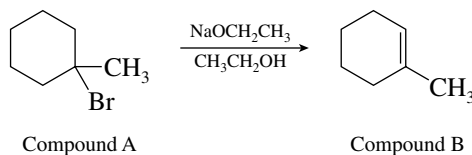
Compound B has a carbon skeleton different from the alcohol that produced it by dehydration. We are therefore led to consider a carbocation rearrangement.



- 6.51** The important clue to deducing the structures of A and B is the ozonolysis product C. Remembering that the two carbonyl carbons of C must have been joined by a double bond in the precursor B, we write

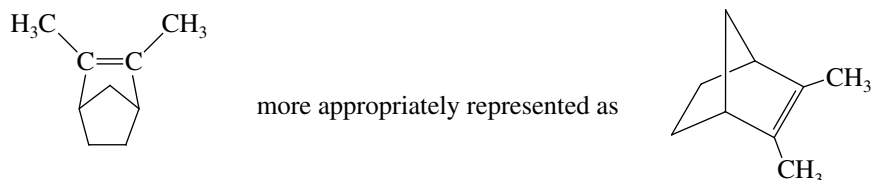


The tertiary bromide that gives compound B on dehydrobromination is 1-methylcyclohexyl bromide.

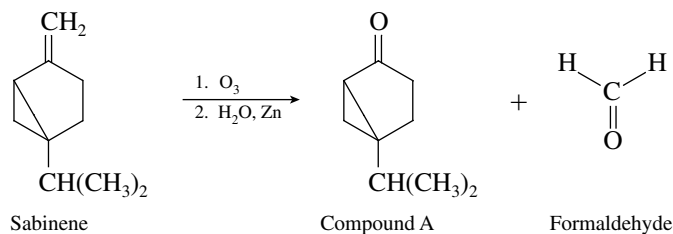


When tertiary halides are treated with base, they undergo E2 elimination. The regioselectivity of elimination of tertiary halides follows the Zaitsev rule.

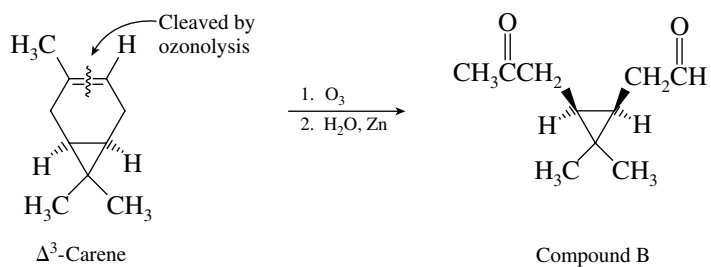
- 6.52** Since santene and 1,3-diacetylcyclopentane (compound A) contain the same number of carbon atoms, the two carbonyl carbons of the diketone must have been connected by a double bond in santene. The structure of santene must therefore be



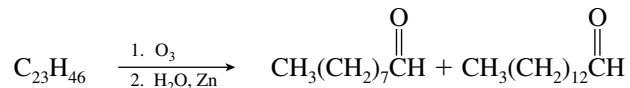
- 6.53 (a) Compound A contains nine of the ten carbons and 14 of the 16 hydrogens of sabinene. Ozonolysis has led to the separation of one carbon and two hydrogens from the rest of the molecule. The carbon and the two hydrogens must have been lost as formaldehyde,  $\text{H}_2\text{C}=\text{O}$ . This  $\text{H}_2\text{C}$  unit was originally doubly bonded to the carbonyl carbon of compound A. Sabinene must therefore have the structure shown in the equation representing its ozonolysis:



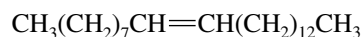
- (b) Compound B contains all ten of the carbons and all 16 of the hydrogens of  $\Delta^3$ -carene. The two carbonyl carbons of compound B must have been linked by a double bond in  $\Delta^3$ -carene.



- 6.54 The sex attractant of the female housefly consumes one mole of hydrogen on catalytic hydrogenation (the molecular formula changes from  $\text{C}_{23}\text{H}_{46}$  to  $\text{C}_{23}\text{H}_{48}$ ). Thus, the molecule has one double bond. The position of the double bond is revealed by the ozonolysis data.



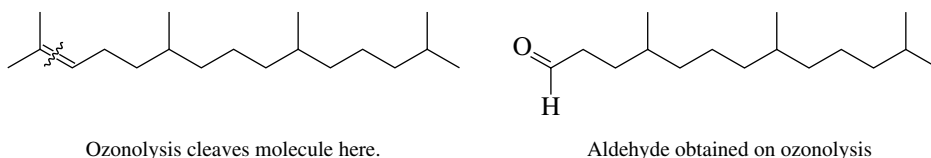
An unbranched 9-carbon unit and an unbranched 14-carbon unit make up the carbon skeleton, and these two units must be connected by a double bond. The housefly sex attractant therefore has the constitution:




9-Tricosene

The data cited in the problem do not permit the stereochemistry of this natural product to be determined.

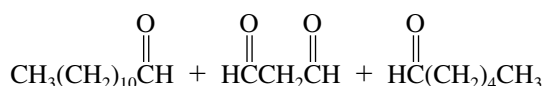
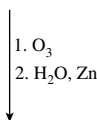
- 6.55 The hydrogenation data tell us that  $\text{C}_{19}\text{H}_{38}$  contains one double bond and has the same carbon skeleton as 2,6,10,14-tetramethylpentadecane. We locate the double bond at C-2 on the basis of the fact that acetone,  $(\text{CH}_3)_2\text{C}=\text{O}$ , is obtained on ozonolysis. The structures of the natural product and the aldehyde produced on its ozonolysis are as follows:



- 6.56  Since  $\text{HCCH}_2\text{CH}$  is one of the products of its ozonolysis, the sex attractant of the arctiid moth must contain the unit  $=\text{CHCH}_2\text{CH}=\text{}$ . This unit must be bonded to an unbranched 12-carbon unit at one end and an unbranched 6-carbon unit at the other in order to give  $\text{CH}_3(\text{CH}_2)_{10}\text{CH}=\text{O}$  and  $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{O}$  on ozonolysis.



Sex attractant of arctiid moth  
(wavy lines show positions of cleavage on ozonolysis)



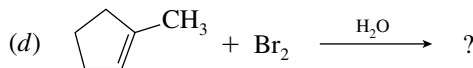
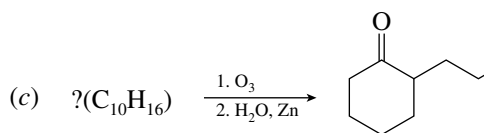
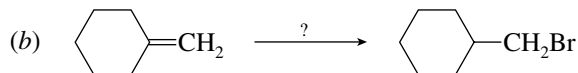
The stereochemistry of the double bonds cannot be determined on the basis of the available information.

- 6.57–6.59 Solutions to molecular modeling exercises are not provided in this *Study Guide and Solutions Manual*. You should use *Learning By Modeling* for these exercises.

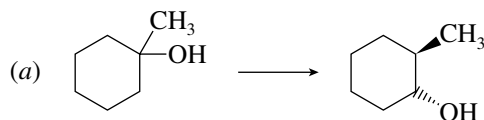
## SELF-TEST

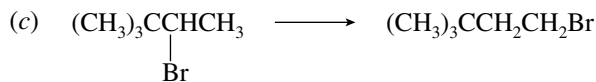
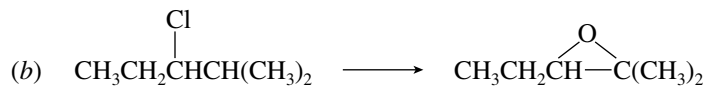
### PART A

- A-1. How many different alkenes will yield 2,3-dimethylpentane on catalytic hydrogenation? Draw their structures, and name them.
- A-2. Write structural formulas for the reactant, reagents, or product omitted from each of the following:

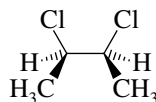


- A-3. Provide a sequence of reactions to carry out the following conversions. More than one synthetic step is necessary for each. Write the structure of the product of each synthetic step.

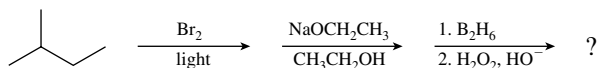




- A-4.** Provide a detailed mechanism describing the elementary steps in the reaction of 1-butene with HBr in the presence of peroxides.
- A-5.** Chlorine reacts with an alkene to give the 2,3-dichlorobutane isomer whose structure is shown. What are the structure and name of the alkene? Outline a mechanism for the reaction.



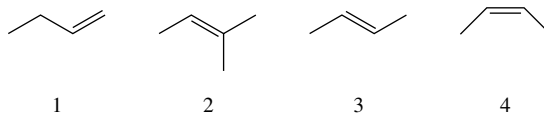
- A-6.** Write a structural formula, including stereochemistry, for the compound formed from *cis*-3-hexene on treatment with peroxyacetic acid.
- A-7.** Give a mechanism describing the elementary steps in the reaction of 2-methyl-1-butene with hydrogen chloride. Use curved arrows to show the flow of electrons.
- A-8.** What two alkenes give 2-chloro-2-methylbutane on reaction with hydrogen chloride?
- A-9.** Give the major organic product formed from the following sequence of reactions.



- A-10.** The reaction of 3-methyl-1-butene with hydrogen chloride gives two alkyl halide products; one is a secondary alkyl chloride and the other is tertiary. Write the structures of the products, and provide a mechanism explaining their formation.
- A-11.** A hydrocarbon A ( $\text{C}_6\text{H}_{12}$ ) undergoes reaction with HBr to yield compound B ( $\text{C}_6\text{H}_{13}\text{Br}$ ). Treatment of B with sodium ethoxide in ethanol yields C, an isomer of A. Reaction of C with ozone followed by treatment with water and zinc gives acetone,  $(\text{CH}_3)_2\text{C}=\text{O}$ , as the only organic product. Provide structures for A, B, and C, and outline the reaction pathway.

## PART B

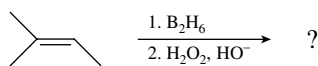
- B-1.** Rank the following alkenes in order of decreasing heats of hydrogenation (largest first)





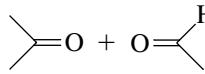


- (a)  $2 > 3 > 4 > 1$                       (d)  $2 > 4 > 3 > 1$   
 (b)  $1 > 3 > 4 > 2$                       (e)  $1 > 2 > 3 > 4$   
 (c)  $1 > 4 > 3 > 2$

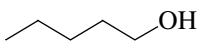
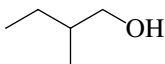
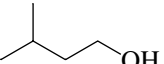

- B-2.** The product from the reaction of 1-pentene with  $\text{Cl}_2$  in  $\text{H}_2\text{O}$  is named:
- (a) 1-Chloro-2-pentanol                      (c) 1-Chloro-1-pentanol  
 (b) 2-Chloro-2-pentanol                      (d) 2-Chloro-1-pentanol
- B-3.** In the reaction of hydrogen bromide with an alkene (in the absence of peroxides), the first step of the reaction is the \_\_\_\_\_ to the alkene.
- (a) Fast addition of an electrophile                      (c) Slow addition of an electrophile  
 (b) Fast addition of a nucleophile                      (d) Slow addition of a nucleophile

**B-4.** The major product of the following reaction sequence is

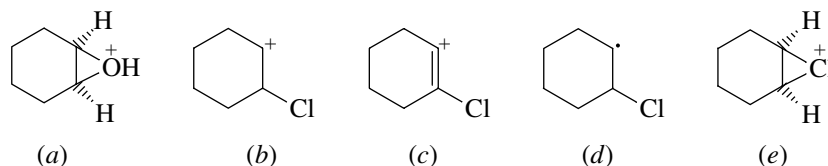


- (a)  (b)  (c)  (d)  (e) 

**B-5.** Which, if any, of the following alcohols *cannot* be prepared from an alkene?

- (a)  (b)  (c)  (d)   
(e) None of these—all of the alcohols shown can be prepared from an alkene

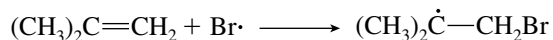
**B-6.** Which of the species shown is the most stable form of the intermediate in the electrophilic addition of  $\text{Cl}_2$  in water to cyclohexene to form a halohydrin? Electron pairs have been omitted for convenience, and their absence should not be considered as part of the problem.



**B-7.** Treatment of 2-methyl-2-butene with HBr in the presence of a peroxide yields

- (a) A primary alkyl bromide  
(b) A secondary alkyl bromide  
(c) A tertiary alkyl bromide  
(d) A vicinal dibromide

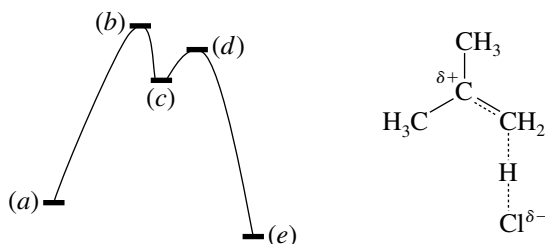
**B-8.** The reaction



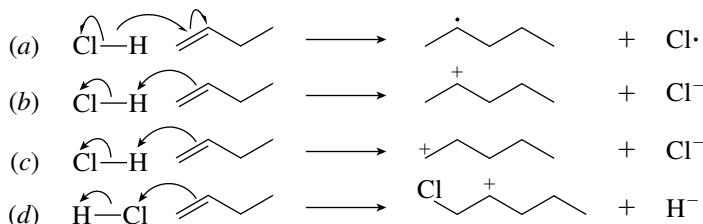
is an example of a(n) \_\_\_\_\_ step in a radical chain reaction.

- (a) Initiation (b) Propagation (c) Termination (d) Heterolytic cleavage

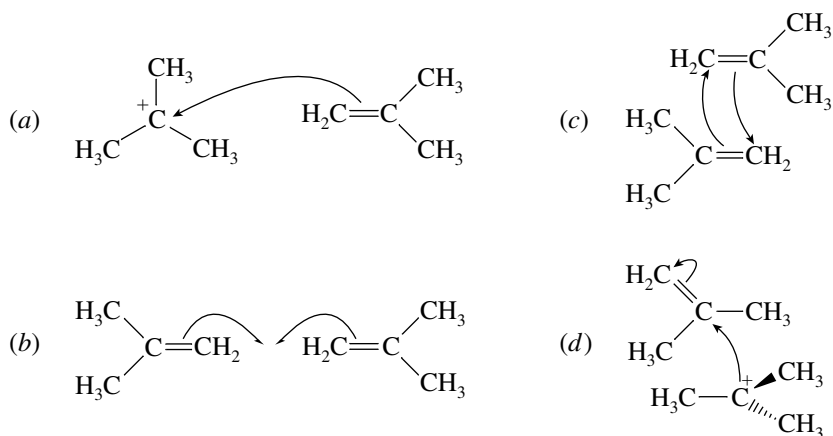
**B-9.** To which point on the potential energy diagram for the reaction of 2-methylpropene with hydrogen chloride does the figure shown at the right correspond?



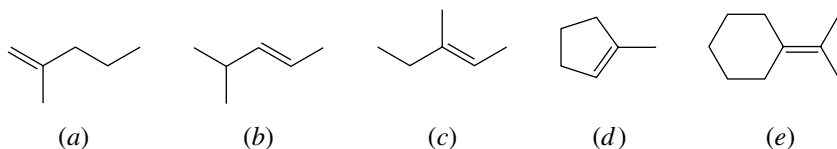
**B-10.** Which of the following most accurately describes the first step in the reaction of hydrogen chloride with 1-butene?



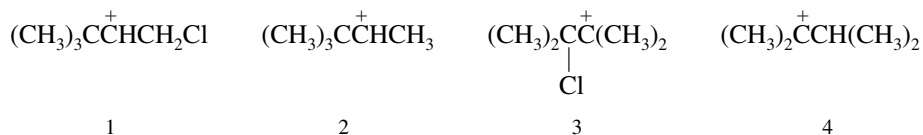
**B-11.** Which of the following best describes the flow of electrons in the acid-catalyzed dimerization of  $(\text{CH}_3)_2\text{C}=\text{CH}_2$ ?



**B-12.** Which one of the following compounds gives acetone  $(\text{CH}_3)_2\text{C}=\text{O}$  as one of the products of its ozonolysis?



**B-13.** Addition of HCl to 3,3-dimethyl-1-butene yields two products, one of which has a rearranged carbon skeleton. Which of the following cations are intermediates in that reaction?



- (a) 1, 2      (b) 1, 3      (c) 1, 4      (d) 2, 3      (e) 2, 4