

## CHAPTER 7—STRUCTURE AND SYNTHESIS OF ALKENES; ELIMINATION

7-1 The number of elements of unsaturation in a hydrocarbon formula is given by:

$$\frac{2(\#C) + 2 - (\#H)}{2}$$

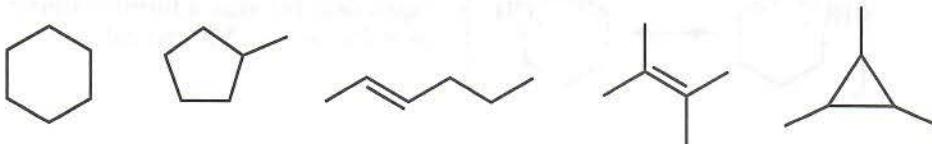
(a) Solve this equation for #H. Three double bonds plus one ring make 4 elements of unsaturation.

$$4 = \frac{2(9) + 2 - (\#H)}{2} \Rightarrow \boxed{\#H = 12}$$

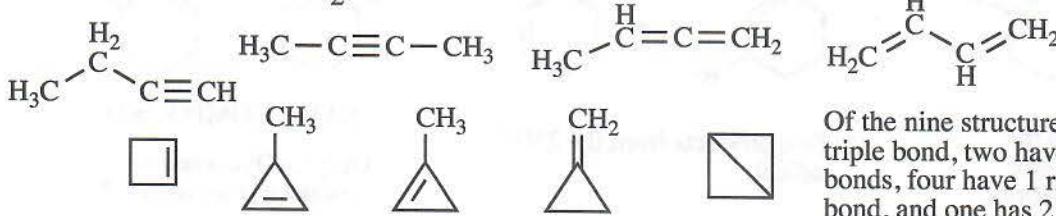
$C_9H_{12}$  has 4 elements of unsaturation.

(b)  $C_6H_{12} \Rightarrow \frac{2(6) + 2 - (12)}{2} = 1$  element of unsaturation

(c) Many examples are possible. Yours may not match these structures, but all possible answers must have either one double bond or one ring, that is, one element of unsaturation.

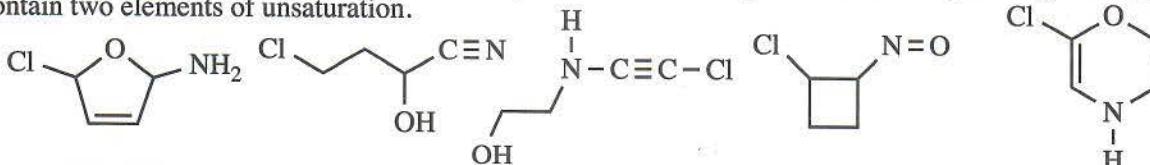


7-2  $C_4H_6 \Rightarrow \frac{2(4) + 2 - (6)}{2} = 2$  elements of unsaturation



Of the nine structures, two have 1 triple bond, two have 2 double bonds, four have 1 ring plus 1 double bond, and one has 2 rings.

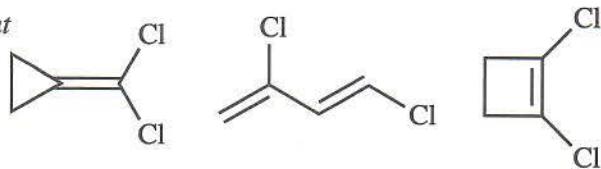
7-3 Hundreds of examples of  $C_4H_6NOCl$  are possible. Yours may not match these, although all must contain two elements of unsaturation.



7-4 Many examples (sometimes thousands) of these formulas are possible. Yours may not match these, but correct answers must have the same number of elements of unsaturation. *Check your answers in your study group.*

(a)  $C_4H_4Cl_2 \Rightarrow C_4H_6 = \text{hydrocarbon equivalent}$   
 $C_4H_{10} = \text{saturated formula}$

a 4H deficiency =  
2 elements of unsaturation



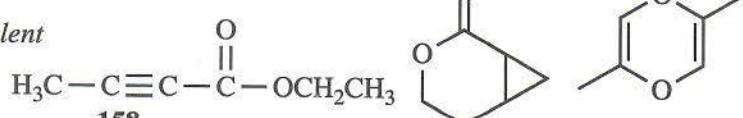
(b)  $C_4H_8O \Rightarrow C_4H_8 = \text{hydrocarbon equivalent}$   
 $C_4H_{10} = \text{saturated formula}$

a 2H deficiency =  
1 element of unsaturation



(c)  $C_6H_8O_2 \Rightarrow C_6H_8 = \text{hydrocarbon equivalent}$   
 $C_6H_{14} = \text{saturated formula}$

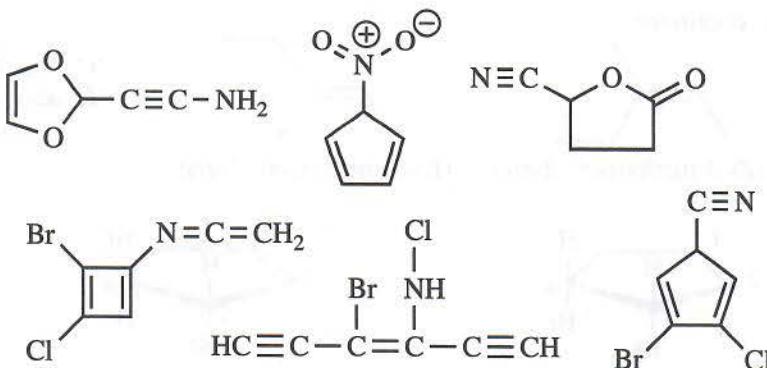
a 6H deficiency =  
3 elements of unsaturation



7-4 continued

(d)  $\text{C}_5\text{H}_5\text{NO}_2$  —using the formula:

$$\frac{2(5) + 2 + (1) - (5)}{2} = 4$$



(e)  $\text{C}_6\text{H}_3\text{NClBr}$  —using the formula:

$$\frac{2(6) + 2 + (1) - (3 + 2)}{2} = 5$$

Note to the student: The IUPAC system of nomenclature is undergoing many changes, most notably in the placement of position numbers. The new system places the position number close to the functional group designation, which is what this Solutions Manual will attempt to follow; however, you should be able to use and recognize names in either the old or the new style. Ask your instructor which system to use.

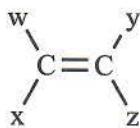
7-5 The *E/Z* system is unambiguous and is generally preferred for designating stereochemistry around a double bond. However, *cis* and *trans* are still used for geometric isomers from substituents on a ring.

- |  |   |
|--|---|
| (a) 4-methylpent-1-ene                   | (b) 2-ethylhex-1-ene (Number the longest chain <i>containing the double bond</i> .) |
| (c) penta-1,4-diene                      | (d) penta-1,2,4-triene  |
| (e) 2,5-dimethylcyclopenta-1,3-diene     | (f) 3-methylene-4-vinylcyclohex-1-ene ("1" is optional)                             |
| (g) 3-phenylprop-1-ene ("1" is optional) |   |

For comparison, these are the old IUPAC names for problem 7-5. The old names will not be used in this Solutions Manual.

- |  |   |
|--|---|
| (a) 4-methyl-1-pentene                   | (b) 2-ethyl-1-hexene                                    |
| (c) 1,4-pentadiene                       | (d) 1,2,4-pentatriene                                   |
| (e) 2,5-dimethyl-1,3-cyclopentadiene     | (f) 3-methylene-4-vinyl-1-cyclohexene ("1" is optional) |
| (g) 3-phenyl-1-propene ("1" is optional) |   |

Note to the student: How to tell whether a double bond has geometric isomers? Look at the four groups bonded to the two carbons of the double bond: w, x, y, and z.

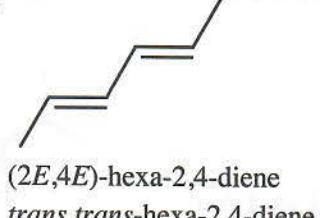
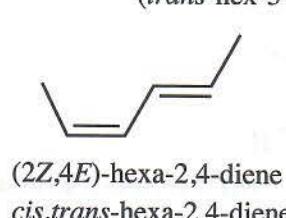
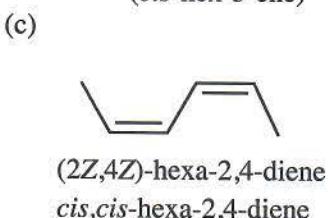
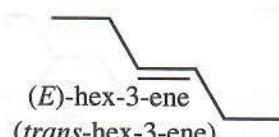
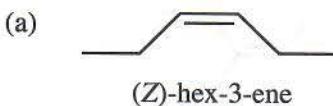


If  $w \neq x$  AND  $y \neq z$ , it will have geometric isomers.

If  $w = y$  (or  $x = z$ ), it is the *cis* isomer.

If  $w = z$  (or  $x = y$ ), it is the *trans* isomer.

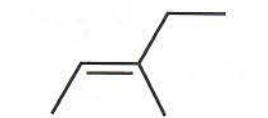
7-6 Parts (b) and (e) do not show *cis,trans* isomerism.



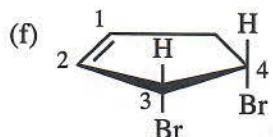
7-6 continued



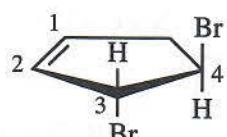
(Z)-3-methylpent-2-ene



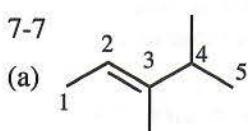
"*Cis*" and "*trans*" are not clear for this example;  
"*E*" and "*Z*" are unambiguous.



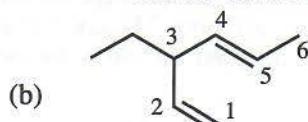
*cis*-3,4-dibromocyclopent-1-ene  
(Both Br atoms could also be up, the enantiomer.)



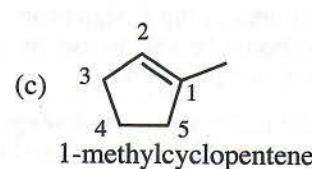
*trans*-3,4-dibromocyclopent-1-ene  
(Both Br atoms could also be inverted, the enantiomer.)



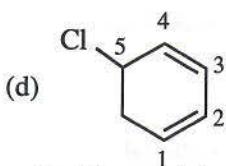
*cis*-3,4-dimethylpent-2-ene  
(The only positions to attach two methyl groups to make the double bond *cis* are at C-3 and C-4.)



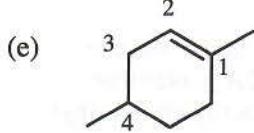
*trans*-3-ethylhexa-1,4-diene  
(Whether *cis* or *trans* is not specified in the problem; the vinyl group is part of the main chain.  
This could also be named as the *E* isomer. The *cis* (*Z*) isomer is equally good.)



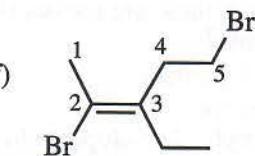
1-methylcyclopentene



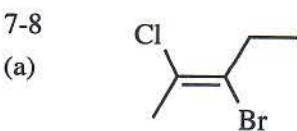
5-chlorocyclohexa-1,3-diene  
(Positions of double bonds need to be specified.)



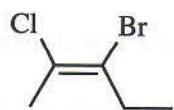
1,4-dimethylcyclohexene



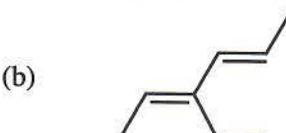
(*E*)-2,5-dibromo-3-ethylpent-2-ene  
(The *cis* designation does not apply—four different groups on the double bond.)



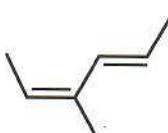
(*E*)-3-bromo-2-chloropent-2-ene



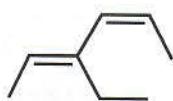
(*Z*)-3-bromo-2-chloropent-2-ene



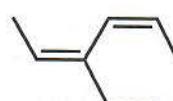
(2*E*,4*E*)-3-ethylhexa-2,4-diene



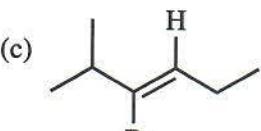
(2*Z*,4*E*)-



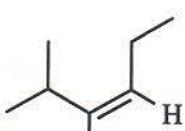
(2*E*,4*Z*)-



(2*Z*,4*Z*)-

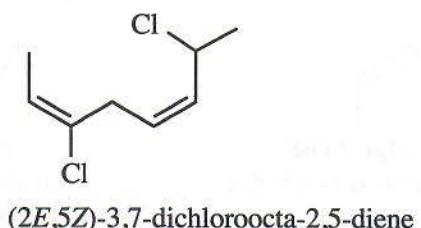
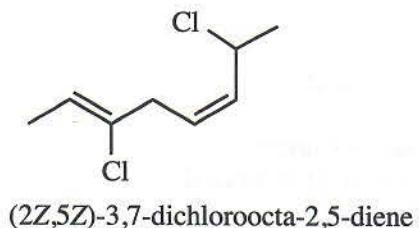
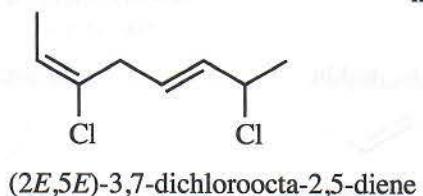
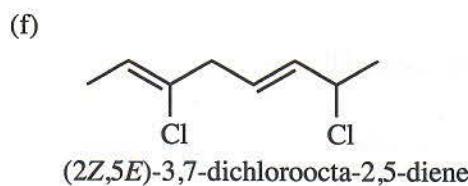
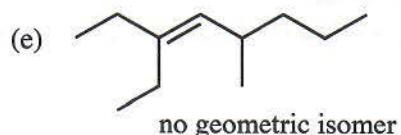
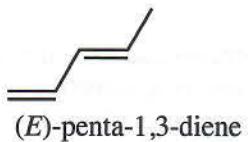
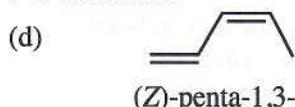


(*Z*)-3-bromo-2-methylhex-3-ene

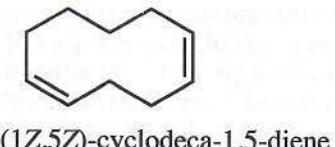
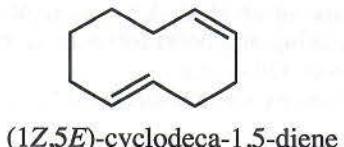
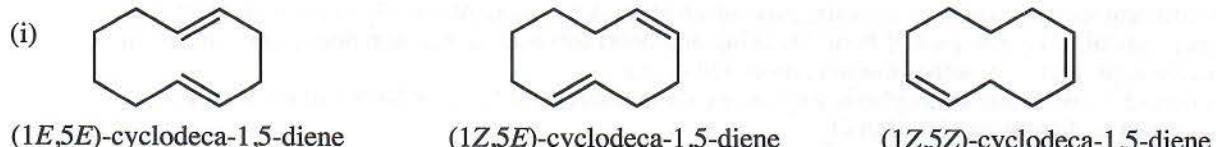
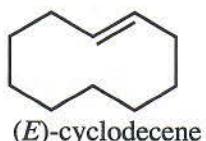
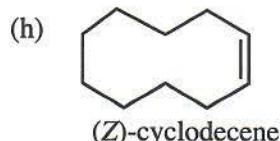


(*E*)-3-bromo-2-methylhex-3-ene

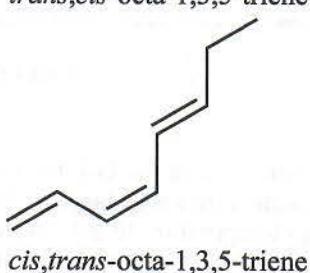
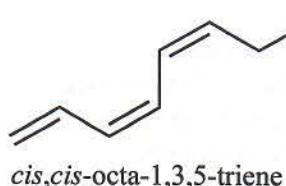
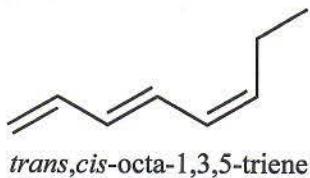
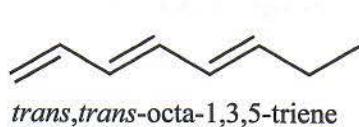
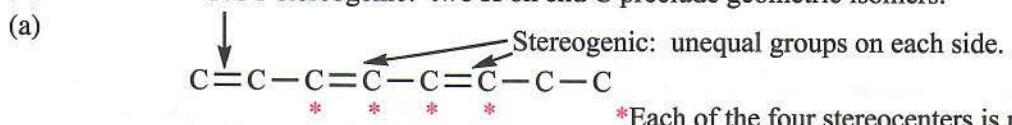
7-8 continued



(g) no geometric isomers (An *E* double bond would be too highly strained.)



7-9 NOT stereogenic: two H on end C preclude geometric isomers.



7-9 continued

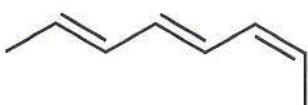


Whereas octa-2,4,6-triene has three stereogenic double bonds, because of symmetry, the middle one has two equal and indistinguishable ends, reducing the total number of stereoisomers very much like a meso form with chiral stereocenters.

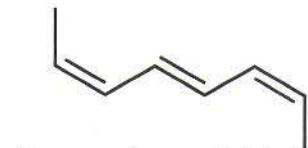
isomers with trans in the middle



*trans,trans,trans-octa-2,4,6-triene*



*trans,trans,cis-octa-2,4,6-triene*  
(same as *cis,trans,trans-* if numbered in the reverse direction)

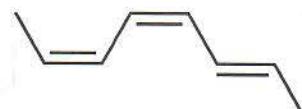


*cis,trans,cis-octa-2,4,6-triene*

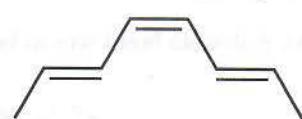
isomers with cis in the middle



*cis,cis,cis-octa-2,4,6-triene*



*cis,cis,trans-octa-2,4,6-triene*  
(same as *trans,cis,cis-* if numbered in the reverse direction)



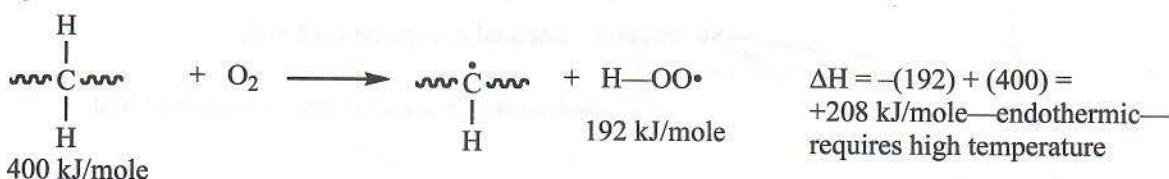
*trans,cis,trans-octa-2,4,6-triene*

7-10

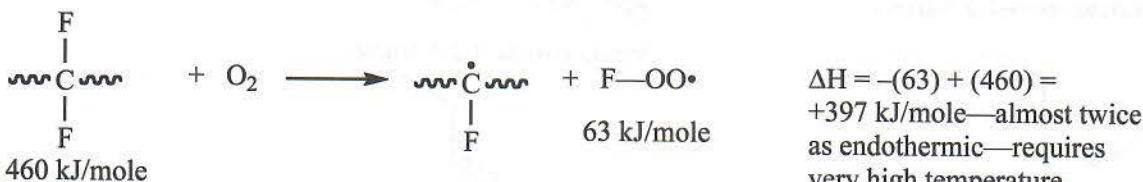
The rate-limiting step in oxidation is abstraction of an atom A by atmospheric  $\text{O}_2$  to form  $\text{A}-\text{OO}\cdot$  and a carbon free radical. The energies of bond breaking and bond forming in this step determine whether it will be successful, that is, whether the oxidation will occur.

It is important to note that atmospheric oxygen exists in a diradical form ( $\cdot\text{O}-\text{O}\cdot$ ), so there is no energy required to disrupt any bond in  $\text{O}_2$ .

polyethylene



Teflon

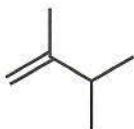


Because the C-F bond is particularly strong, and the O-F bond is particularly weak, the energy required for  $\text{O}_2$  to abstract an F atom is huge, almost twice as large as the energy required for  $\text{O}_2$  to abstract an H from polyethylene. Both require high temperature to get over the energy barrier, but Teflon will decompose at a much higher temperature because the rate-limiting step has a higher energy barrier.

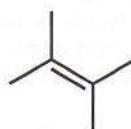
7-11

- (a) The dibromo compound should boil at a higher temperature because of its much larger molecular weight.  
 (b) The *cis* should boil at a higher temperature than the *trans* as the *trans* has a zero dipole moment and therefore no dipole-dipole interactions.  
 (c) 1,2-Dichlorocyclohexene should boil at a higher temperature because of its much larger molecular weight and larger dipole moment than cyclohexene.

7-12 From Table 7-2, approximate heats of hydrogenation can be determined for similarly substituted alkenes. The energy difference is approximately 6 kJ/mole (1.4 kcal/mole), the more substituted alkene being more stable.



*gem*-disubstituted  
116.3 kJ/mole  
(27.8 kcal/mole)

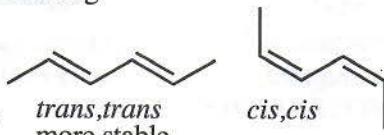


tetrasubstituted  
110.4 kJ/mole  
(26.4 kcal/mole)

7-13 Use the values in Table 7-2. Alternatively, the relative values in Figure 7-8 could be used to reach the same conclusions. Minor discrepancies between kcal and kJ are due to rounding.

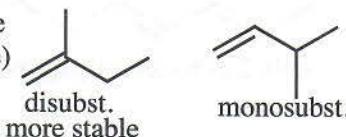
(a)  $2 \times (\text{cis-disubstituted} - \text{trans-disubstituted}) =$

$$\begin{aligned} 2 \times (118.5 - 114.6) &= 7.8 \text{ kJ/mole more stable for } \text{trans, trans} \\ (2 \times (28.3 - 27.4)) &= 1.8 \text{ kcal/mole} \end{aligned}$$



(b) monosubstituted - *gem*-disubstituted =  $126.3 - 118.2 = 8.1 \text{ kJ/mole}$

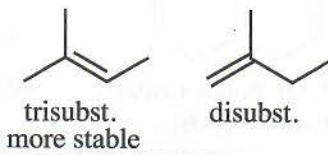
2-methylbut-1-ene is more stable



(c) *gem*-disubstituted - trisubstituted =  $118.2 - 111.6 = 6.6 \text{ kJ/mole}$

$$(28.3 - 26.7 = 1.6 \text{ kcal/mole})$$

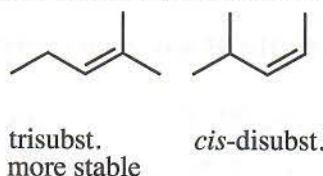
2-methylbut-2-ene is more stable



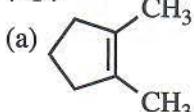
(d) *cis*-disubstituted - trisubstituted =  $117.7 - 111.6 = 6.1 \text{ kJ/mole}$

$$(28.1 - 26.7 = 1.4 \text{ kcal/mole})$$

2-methylpent-2-ene is more stable

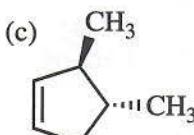


7-14



(a) Slightly strained but stable with C=C in a 5-membered ring.

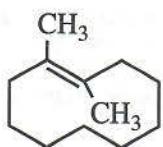
(b) Could not exist as the ring size must be 8 atoms or greater to include *trans* double bond—see answer to part (e).



The *trans* refers to the two methyls since this compound can exist, rather than the *trans* referring to the alkene, a molecule that could not exist because the ring would have too much strain. A ring must have 8 or more atoms before a *trans* double bond can exist in the ring.

7-14 continued

(d)



stable—*trans* in 10-membered ring

(e) Unstable at room temperature—it cannot have *trans* alkene in 7-membered ring (possibly isolable at very low temperature—this type of experiment is one of the challenges chemists attack with gusto).

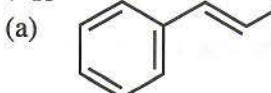
(f) Stable—the alkene is not at a bridgehead.

(g) Unstable—violates Bredt's Rule (alkene at bridgehead in 6-membered ring).

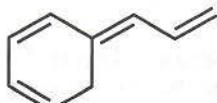
(h) Stable—alkene is at bridgehead in 8-membered ring.

(i) Unstable—violates Bredt's Rule (alkene at bridgehead in 7-membered ring).

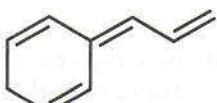
7-15



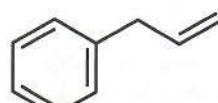
aromatic and  
conjugated;  
MOST STABLE



not aromatic,  
fully conjugated

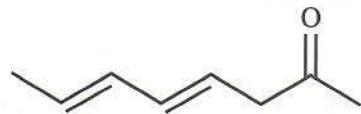


not aromatic,  
partially conjugated;  
LEAST STABLE

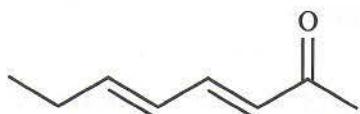


aromatic but  
not conjugated

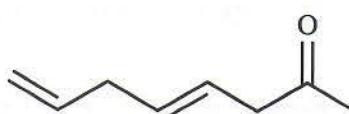
(b)



only 2 pi bonds conjugated

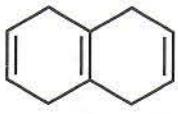


all 3 pi bonds conjugated;  
MOST STABLE

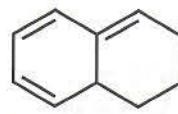


all 3 pi bonds isolated;  
LEAST STABLE

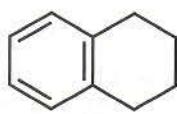
(c)



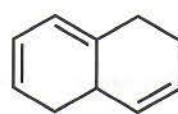
all 3 pi bonds isolated;  
LEAST STABLE



all 3 pi bonds conjugated



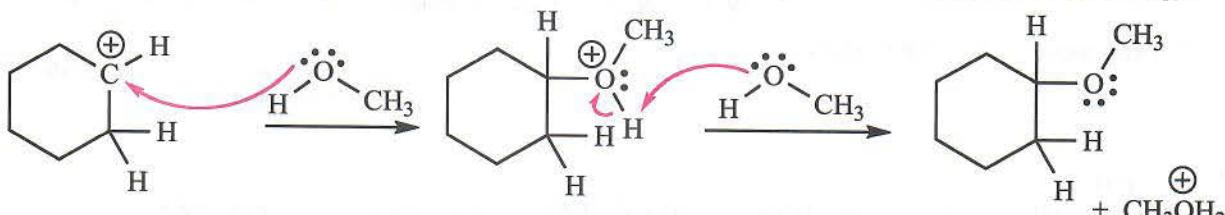
aromatic;  
MOST STABLE



only 2 pi bonds  
conjugated

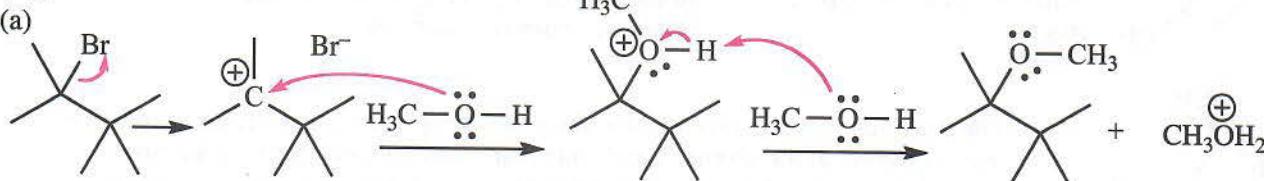
7-16

If the CH<sub>3</sub>OH acts as a nucleophile, the product will be a substitution; the overall mechanism will be S<sub>N</sub>1.



7-17

(a)

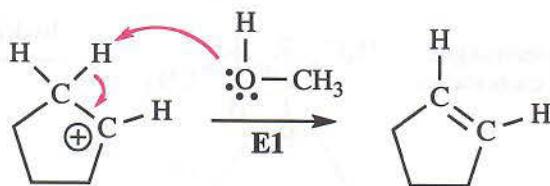
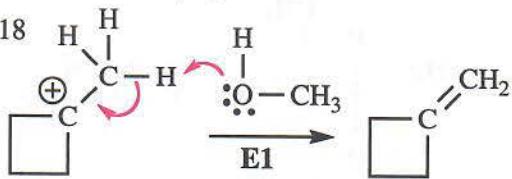


The S<sub>N</sub>1 mechanism begins with ionization to form a carbocation, attack of a nucleophile, and in the case of ROH nucleophiles, removal of a proton by a base to form a neutral product.

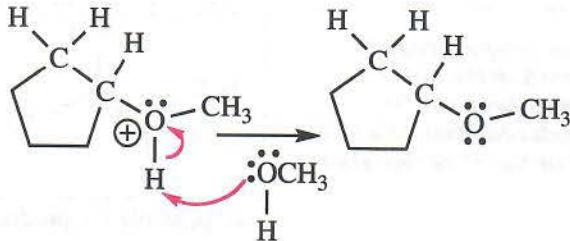
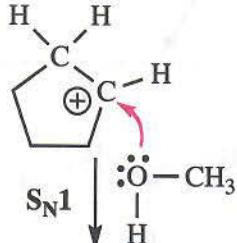
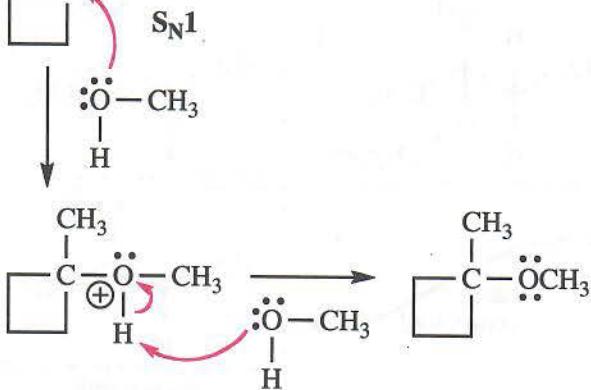
7-17 continued

(b) In the E1 reaction, the solvent (methanol, in this case) serves two functions: it aids the ionization process by solvating both the leaving group (bromide) and the carbocation; and second, it serves as a base to remove the proton from a carbon adjacent to the carbocation in order to form the carbon–carbon double bond. The S<sub>N</sub>1 mechanism adds a third function to the solvent: the first step is the same as in E1, ionization to form the carbocation; the second step has the solvent acting as a nucleophile—this step is different from E1; third, the solvent acts like a base and removes a proton, although from an oxygen (S<sub>N</sub>1) and not a carbon (E1). Solvents are versatile!

7-18

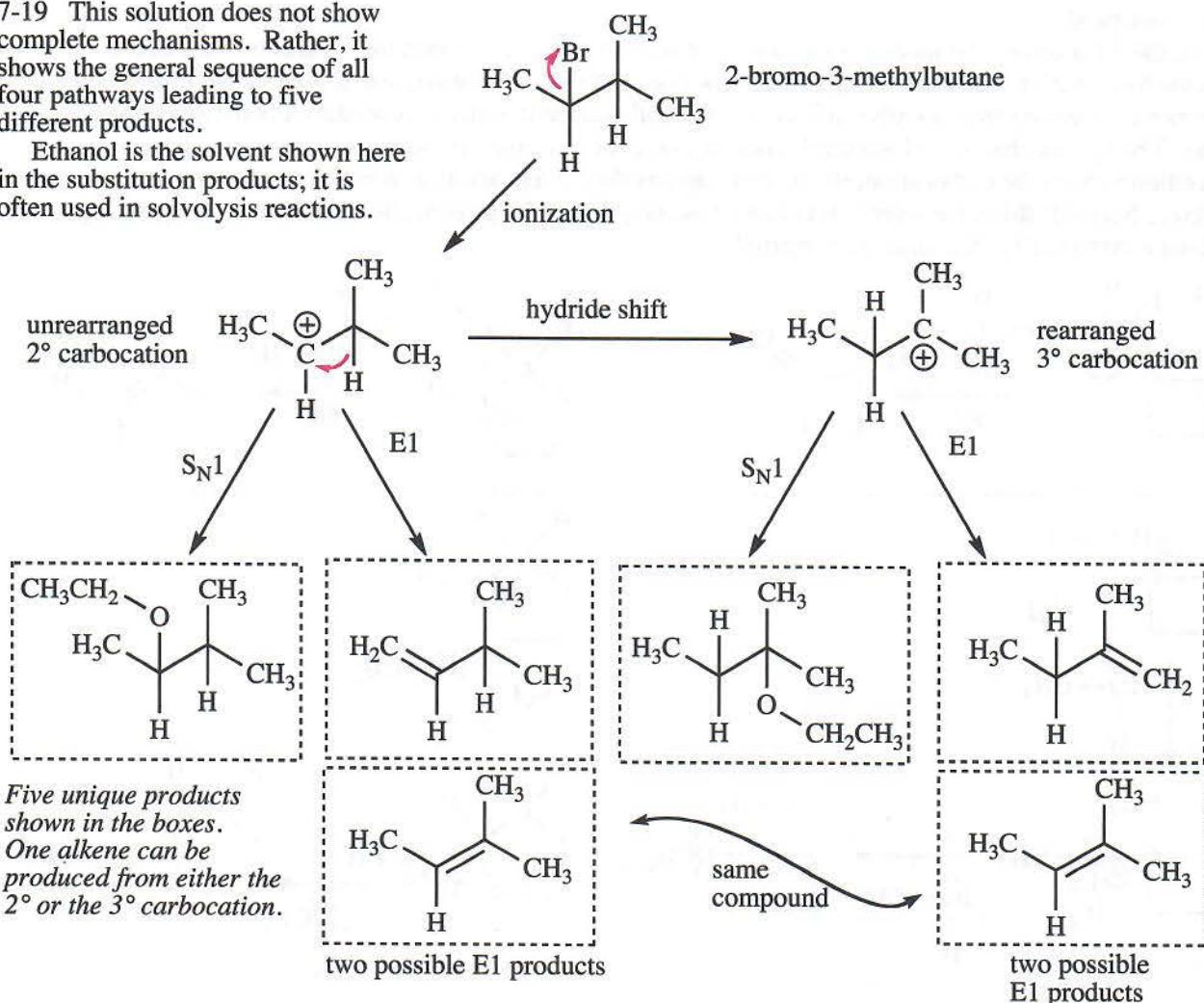


S<sub>N</sub>1

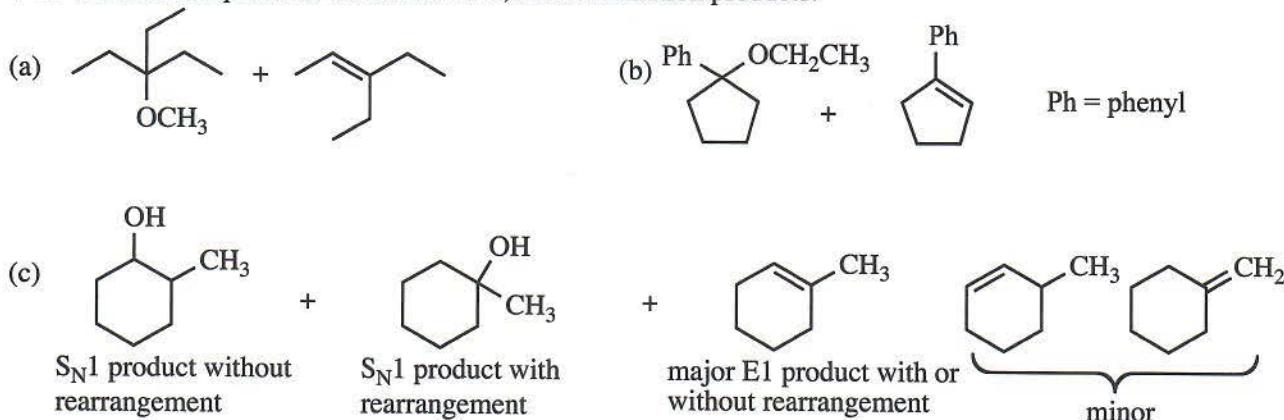


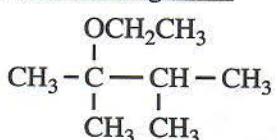
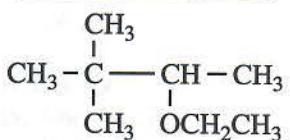
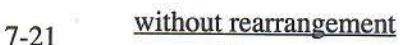
7-19 This solution does not show complete mechanisms. Rather, it shows the general sequence of all four pathways leading to five different products.

Ethanol is the solvent shown here in the substitution products; it is often used in solvolysis reactions.

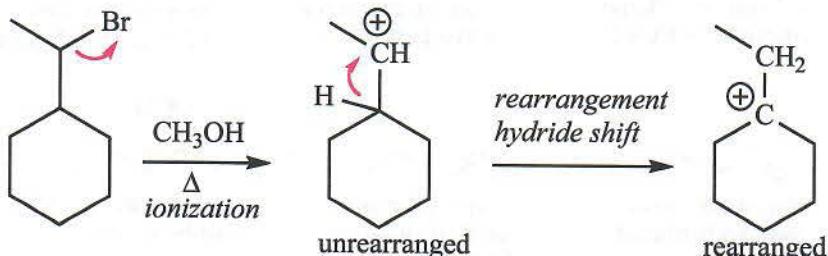


7-20 Substitution products are shown first, then elimination products.



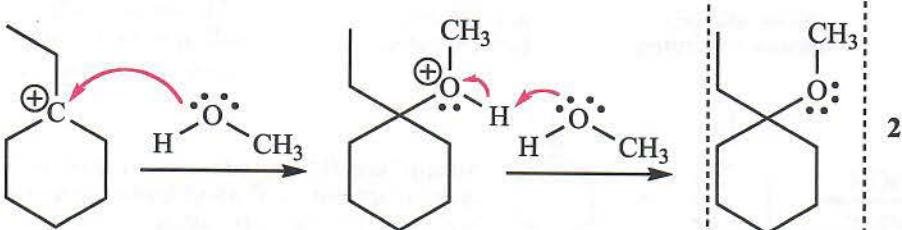
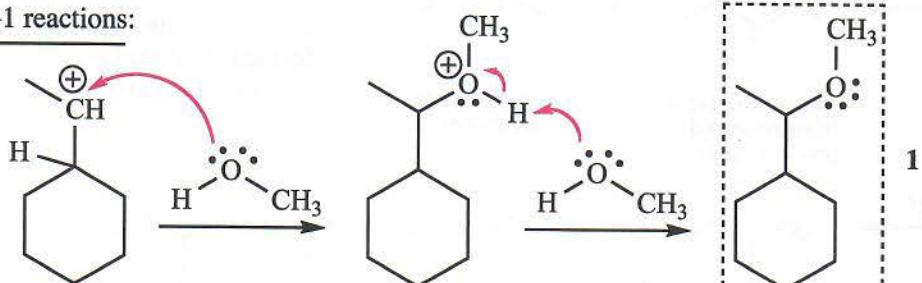


7-22

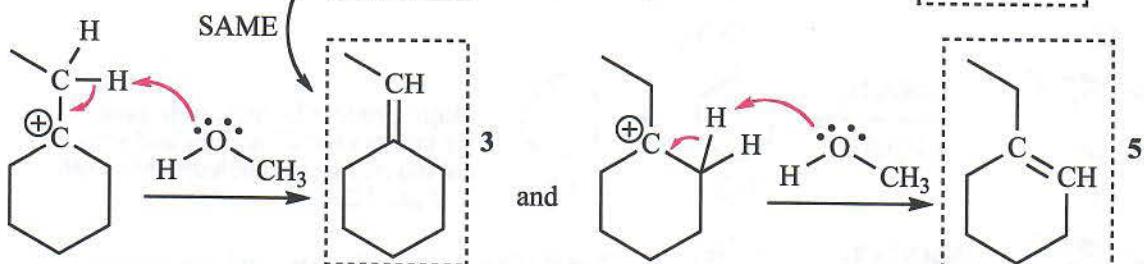
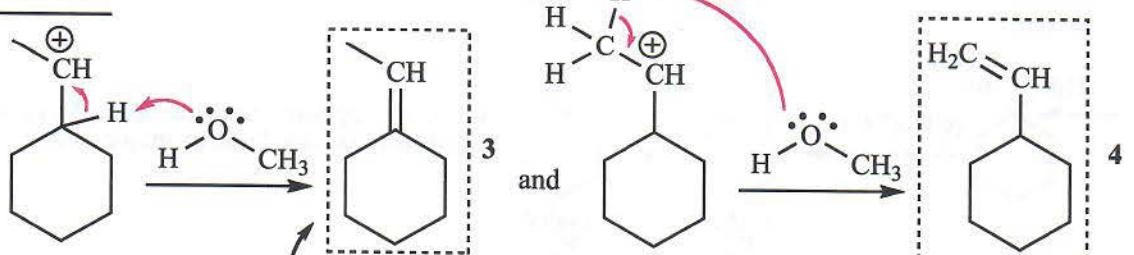


Rearrangement by ring expansion is theoretically possible but very unlikely because the ring size is already at the optimum six-membered.

### **S<sub>N</sub>1 reactions:**

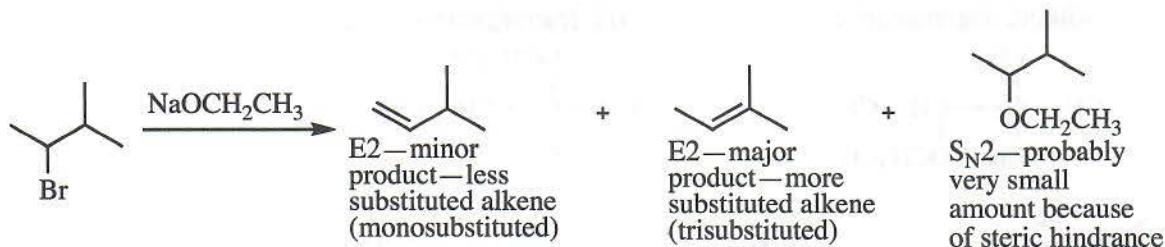


E1 reactions:

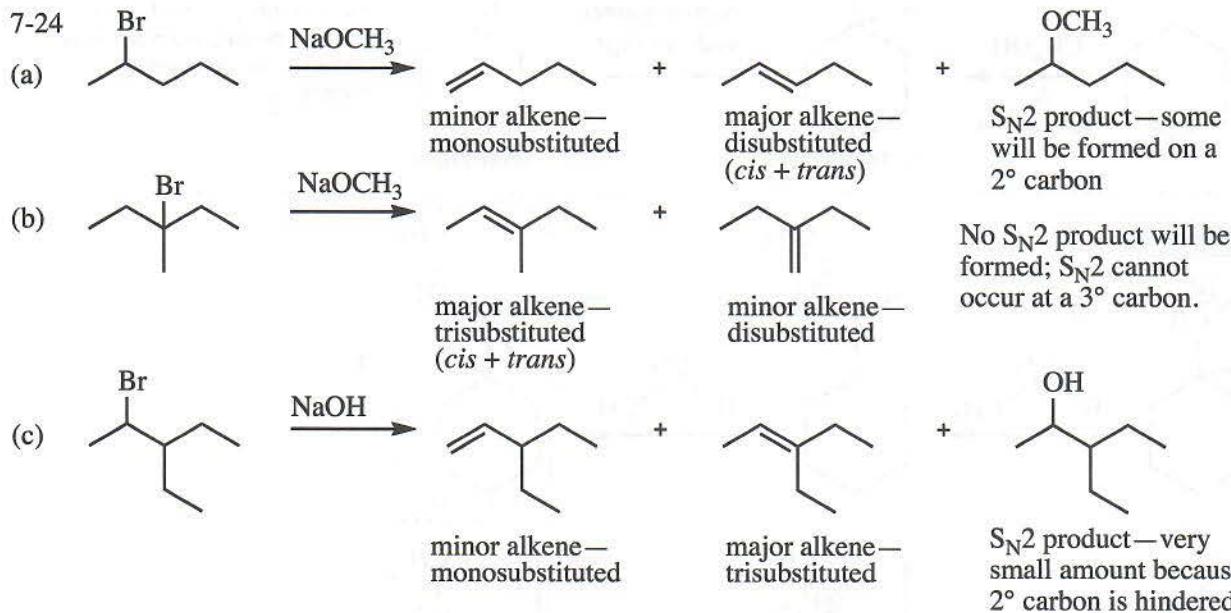


5 is the major elimination product: trisubstituted and endocyclic (in the ring), the more stable position.  
3 is trisubstituted but is exocyclic, a less stable position.

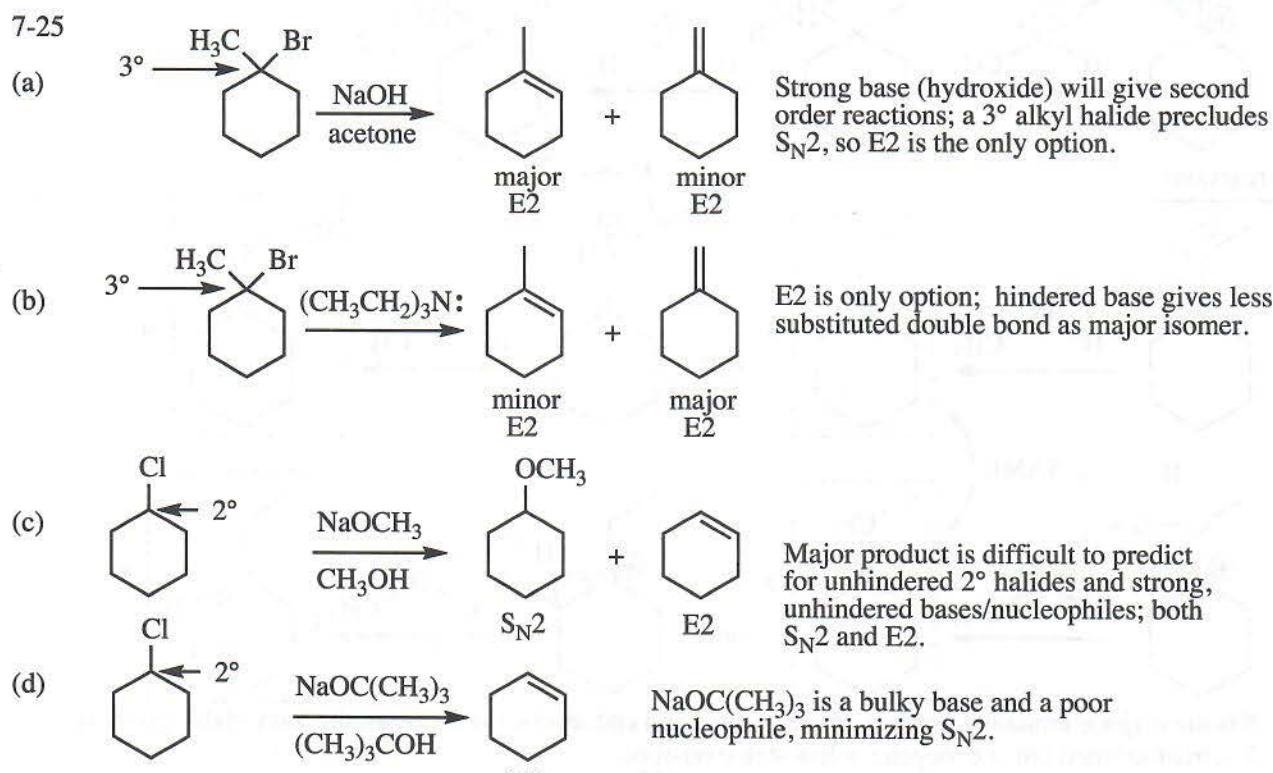
7-23



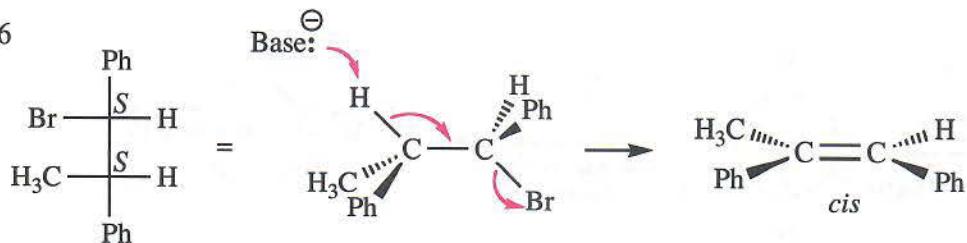
7-24



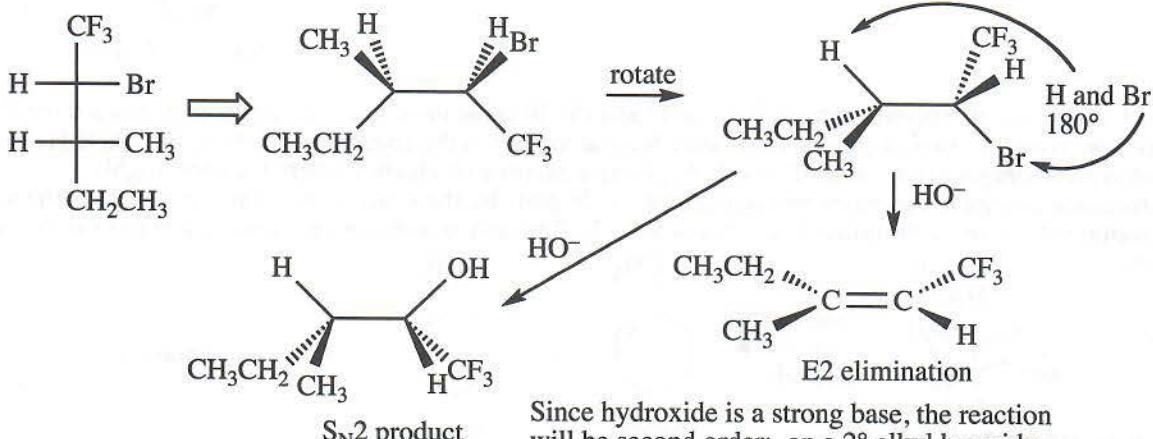
7-25



7-26

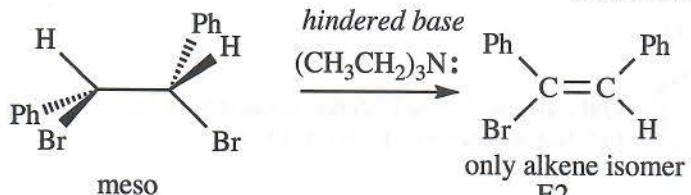


7-27(a)



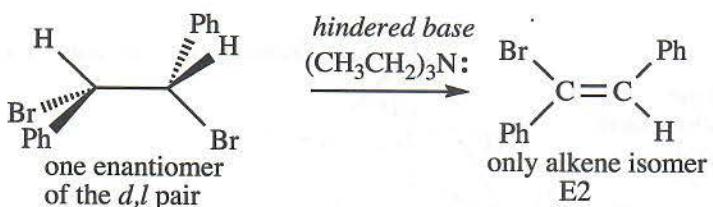
Since hydroxide is a strong base, the reaction will be second order: on a  $2^\circ$  alkyl bromide, both substitution and elimination will occur.

(b)

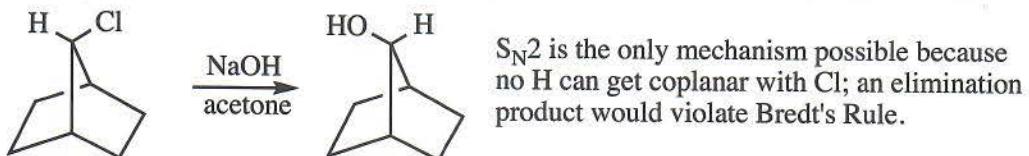


Note that these products are geometric isomers. If a reaction starts with stereoisomers and produces stereoisomers, that is the definition of a *stereospecific* reaction.

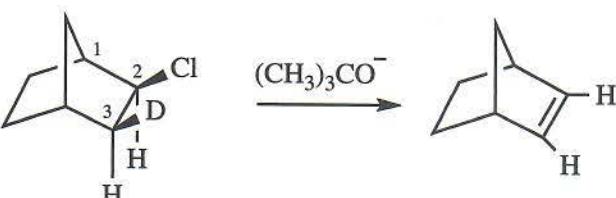
(c)



(d)

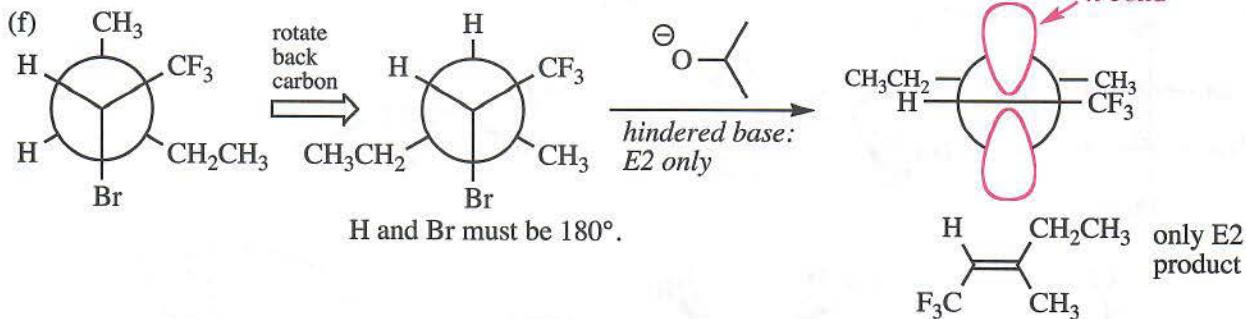


(e)

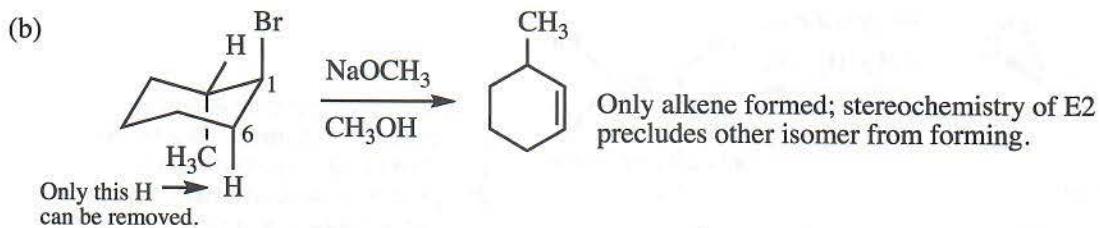
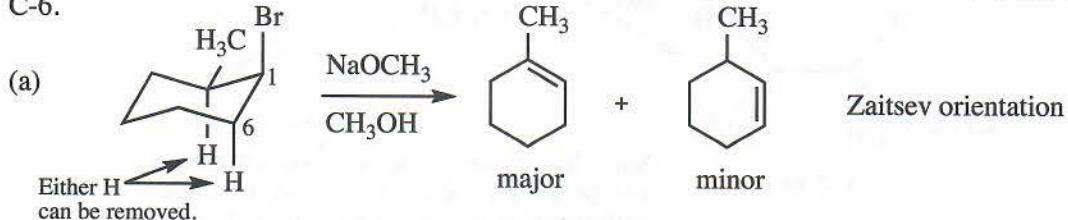


Models show that the H on C-3 cannot be anti-coplanar with the Cl on C-2. Thus, this E2 elimination must occur with a *syn*-coplanar orientation: the D must be removed as the Cl leaves.

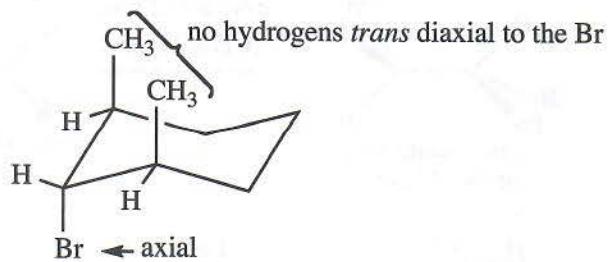
7-27 continued



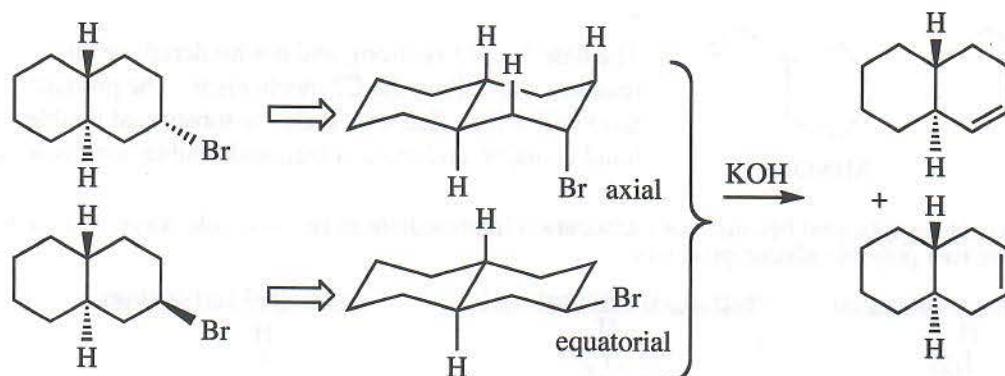
7-28 As shown in Solved Problem 7-5, the H and the Br must have *trans*-dialixial orientation for the E2 reaction to occur. In part (a), the *cis* isomer has the methyl in the equatorial position, the  $\text{NaOCH}_3$  can remove a hydrogen from either C-2 or C-6, giving a mixture of alkenes where the most highly substituted isomer is the major product (Zaitsev). In part (b), the *trans* isomer has the methyl in the axial position at C-2, so no elimination can occur at C-2. The only possible elimination orientation is toward C-6.



7-29 E2 elimination requires that the H and the leaving group be anti-coplanar; in a chair cyclohexane, this requires that the two groups be *trans* dialixial. However, when the bromine atom is in an axial position, there are no hydrogens in axial positions on adjacent carbons, so no elimination can occur.

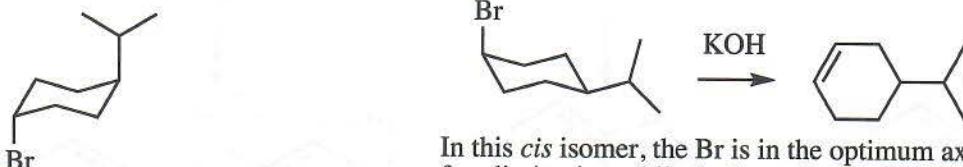


7-30



Showing the chair form of the decalins makes the answer clear. The top isomer locks the H and the Br that eliminate into a *trans*-dixial conformation—optimum for E2 elimination. The bottom isomer has Br equatorial where it is exceedingly slow to eliminate.

(b)

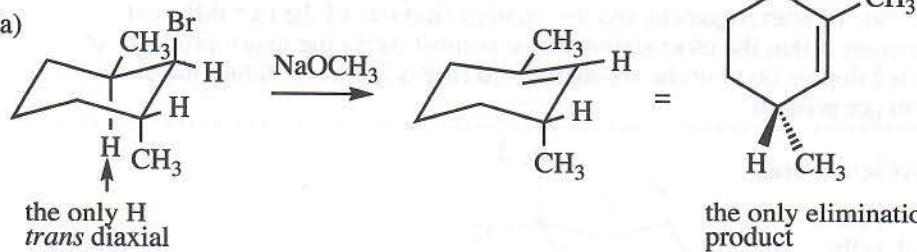


Br must be axial to eliminate by E2, forcing the large isopropyl group axial, a very unstable conformer; this *trans* isomer will be exceedingly slow to react as the preferred conformer will be diequatorial.

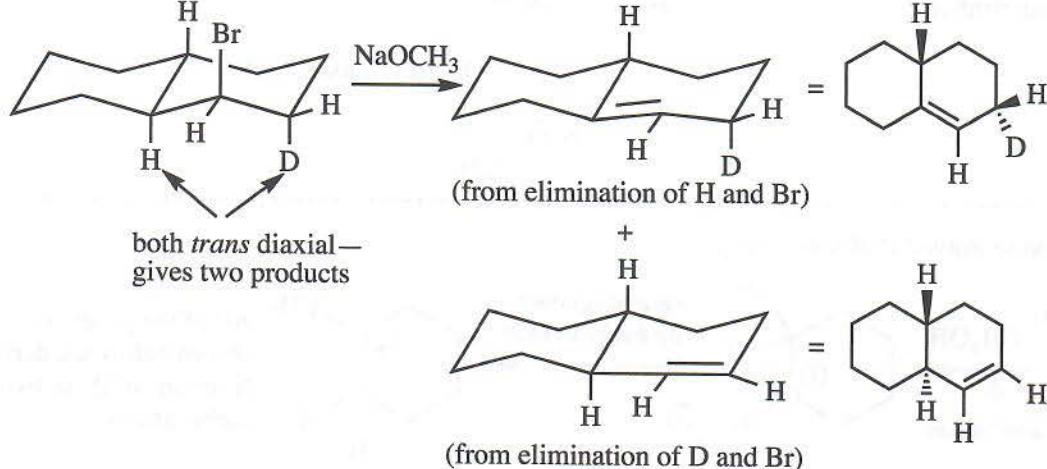
In this *cis* isomer, the Br is in the optimum axial position for elimination while the large isopropyl group is in the energetically preferred equatorial position; this will be the reactive conformer.

7-31 Models are a big help for this problem.

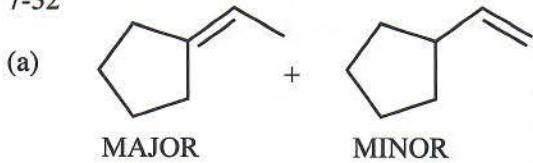
(a)



(b)

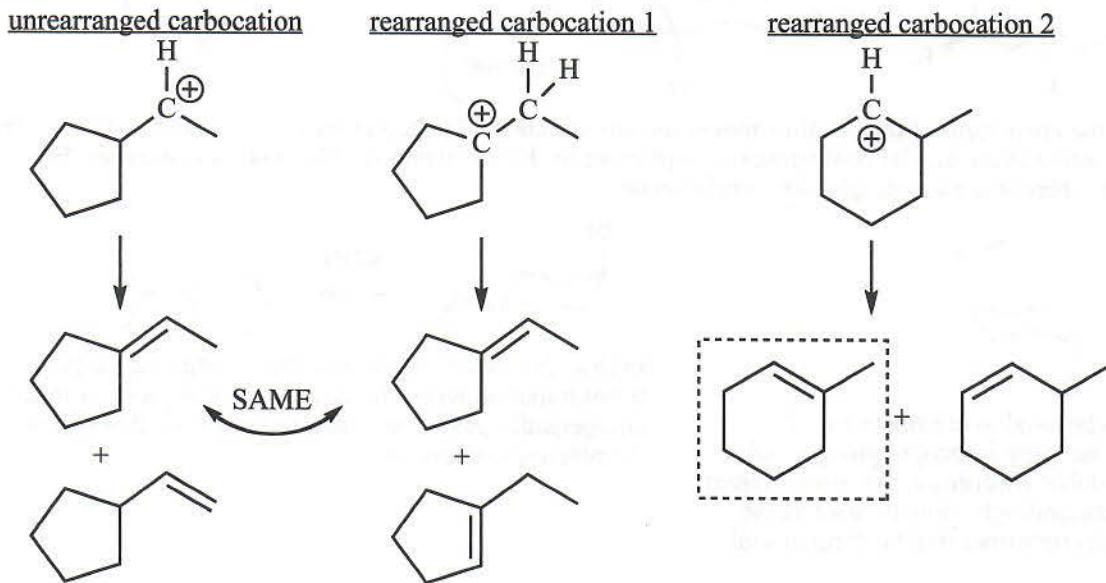


7-32



The base NaOEt is strong and not hindered, so this reaction will follow the E2 mechanism. The product ratio will follow Zaitsev's Rule: trisubstituted double bond is major, and monosubstituted double bond is minor.

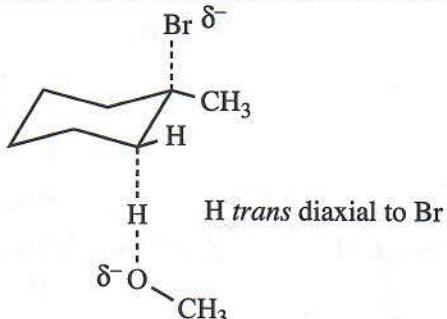
(b) This E1 reaction is complicated because the carbocation intermediate in two possible ways, and each carbocation can give two possible alkene products.



Five different alkene products are possible in this E1 reaction. The ratio of products is difficult to predict because it depends on the rate of rearrangement and the relative amounts of the two different rearrangements. The safest prediction is that the most stable alkene is most likely the major product: of these five alkenes, the trisubstituted double bond in the six-membered ring is the most stable (the one in the box), so it is likely to be the major product.

Follow-up question to Solved Problem 7-6(a):

In the E2 transition state, the C—H bond and the C—Br bond are stretched as the O—H bond is being formed.

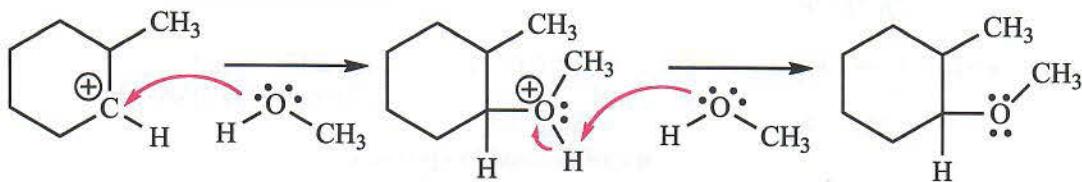


Follow-up question to Solved Problem 7-6(b):

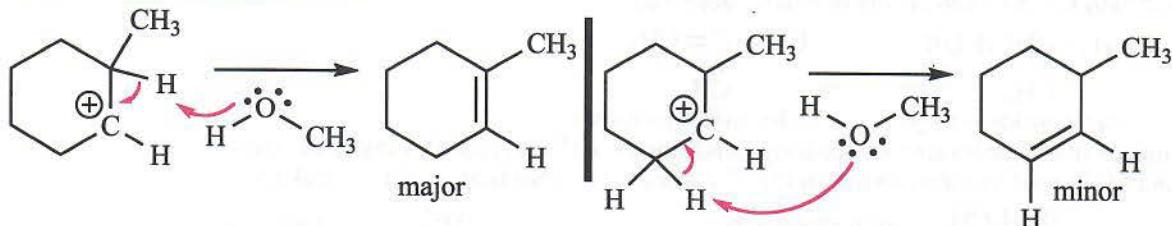


Follow-up question to Solved Problem 7-6(b), continued

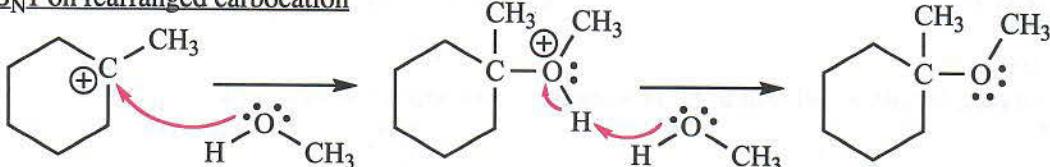
$S_N1$  on un rearranged carbocation



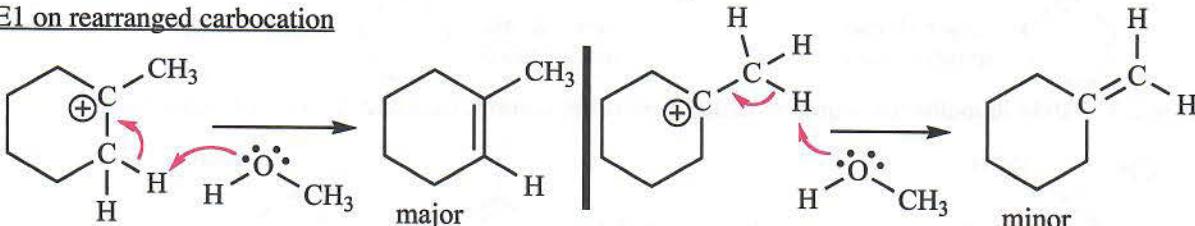
E1 on un rearranged carbocation



$S_N1$  on rearranged carbocation



E1 on rearranged carbocation

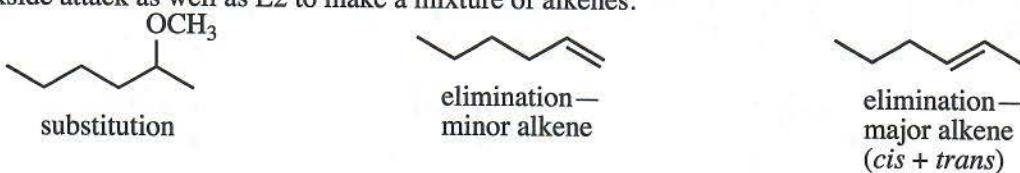


7-33

- (a) Ethoxide is a strong base/nucleophile—second-order conditions. The  $1^\circ$  bromide favors substitution over elimination, so  $S_N2$  will predominate over E2.



- (b) Methoxide is a strong base/nucleophile—second-order conditions. The  $2^\circ$  chloride will undergo  $S_N2$  by backside attack as well as E2 to make a mixture of alkenes.

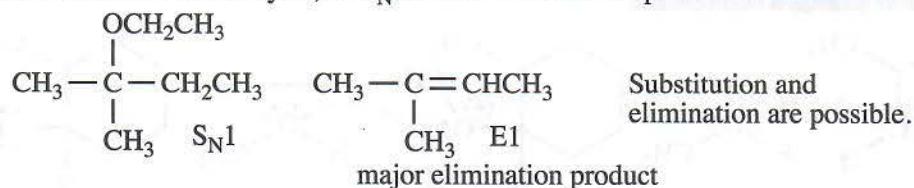


- (c) Ethoxide is a strong base/nucleophile—second-order conditions. The  $3^\circ$  chloride is hindered and cannot undergo  $S_N2$  by backside attack. E2 is the only route possible.

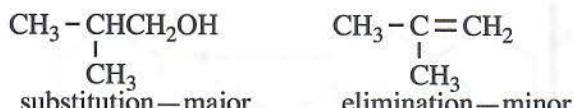


7-33 continued

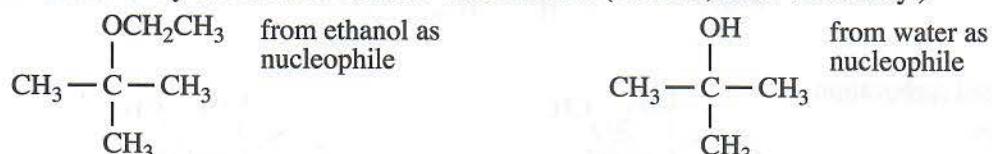
(d) Heating in ethanol are conditions for solvolysis, an  $S_N1$  reaction. Heat also promotes elimination.



(e) Hydroxide is a strong base/nucleophile—second-order conditions. The 1° iodide is more likely to undergo S<sub>N</sub>2 than E2, but both products will be observed.



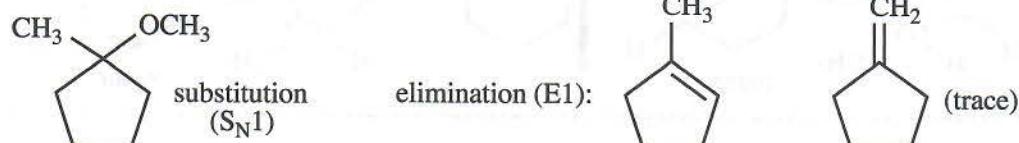
(f) Silver nitrate in ethanol/water are ionizing conditions for  $1^\circ$  alkyl halides that will lead to rearrangement followed by substitution on the  $3^\circ$  carbocation. (No heat, so E1 is unlikely.)



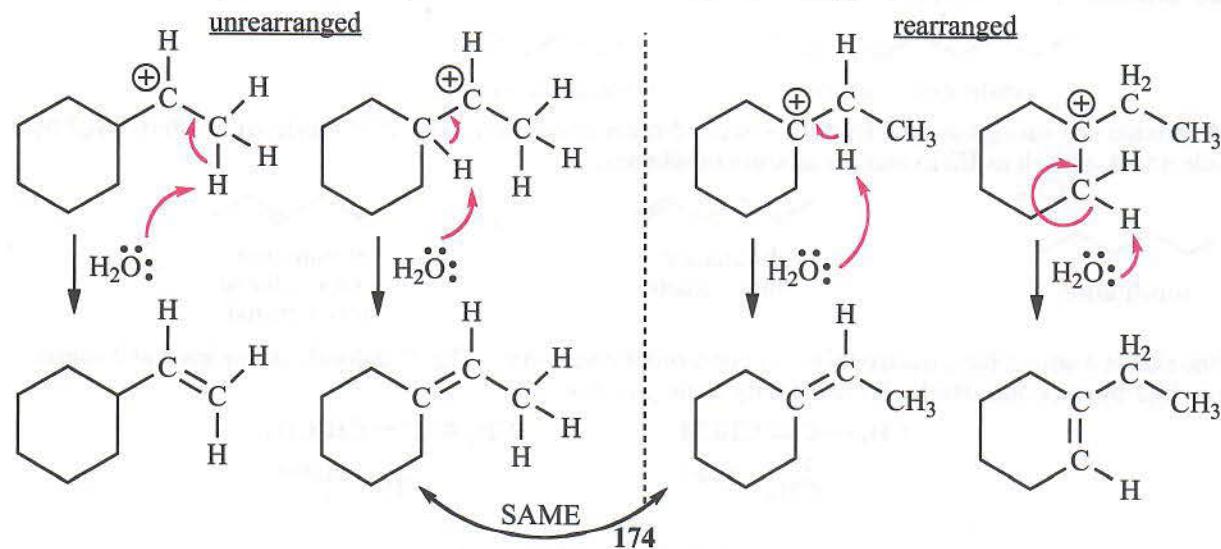
(g) Ethoxide in ethanol on a 3° halide will lead to E2 elimination; there will be no substitution.



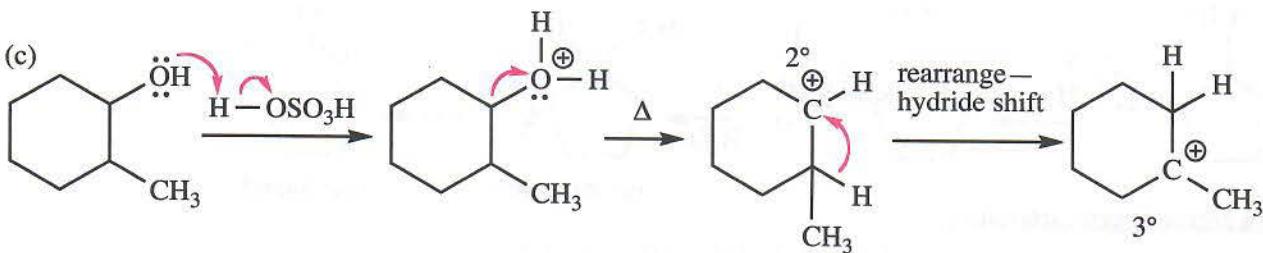
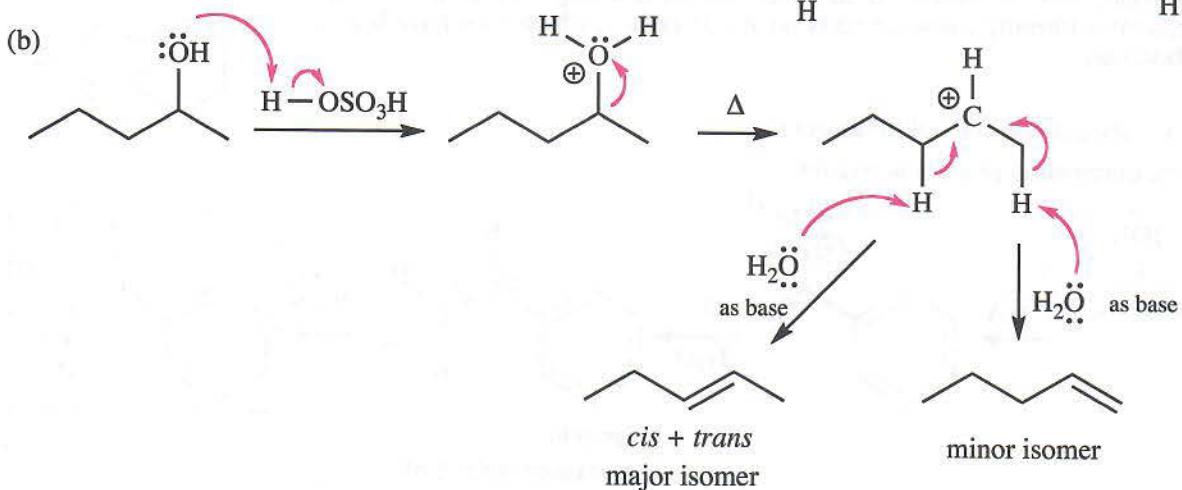
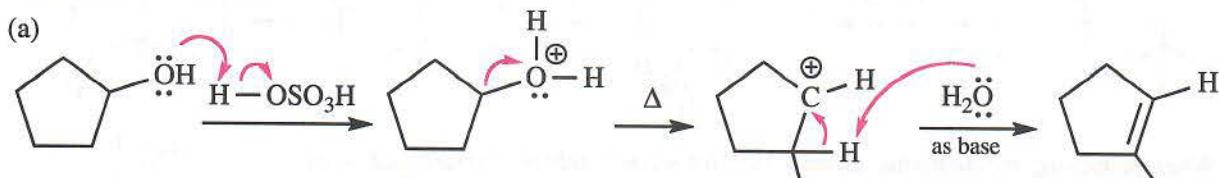
(h) Heating a 3° halide in methanol is quintessential first-order conditions, either E1 or S<sub>N</sub>1 (solvolytic).



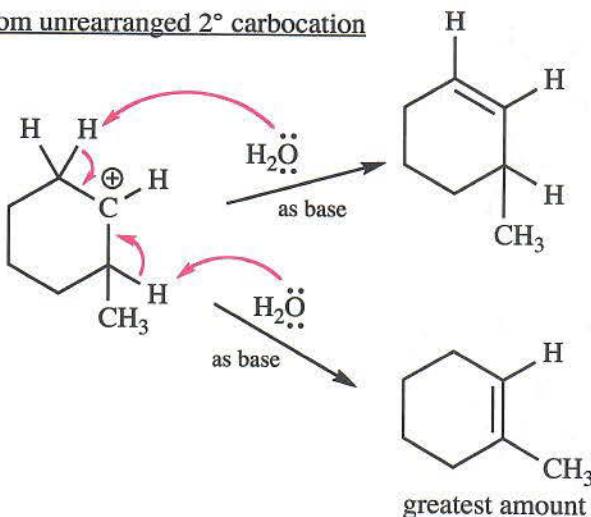
Solved Problem 7-7(b): removal of protons from carbocation intermediates:



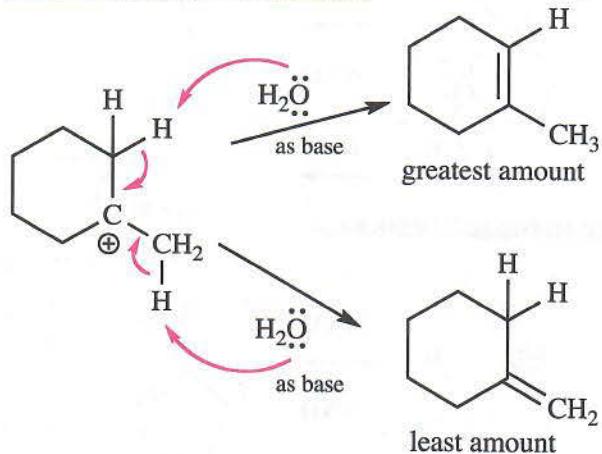
7-34 In these mechanisms, the base removing the final proton is shown as water. Other alcohols are just as likely to serve as the base.



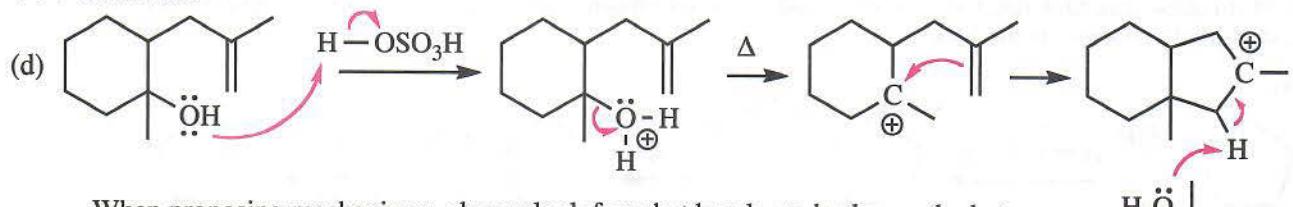
from unrearranged 2° carbocation



from rearranged 3° carbocation



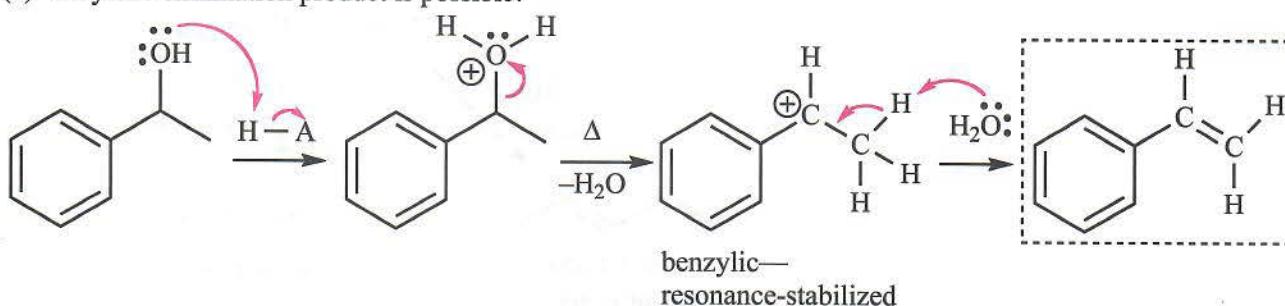
### 7-34 continued



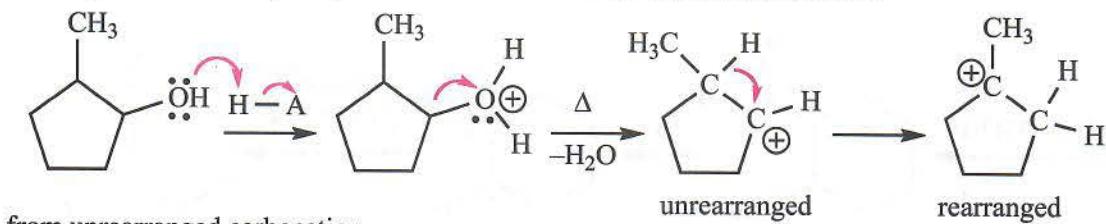
When proposing mechanisms, always look for what bonds are broken and what new bonds must be formed. In this problem, the new ring must come from the pi electrons forming a new sigma bond at a 3° carbon, which must have been a carbocation.

7-35 H—A is the generic symbol for an acid.

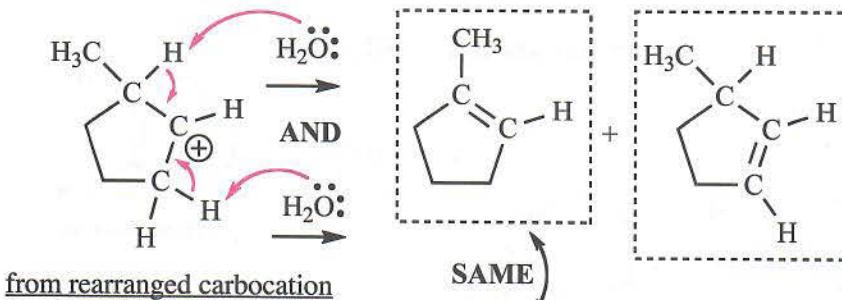
(a) Only one elimination product is possible.



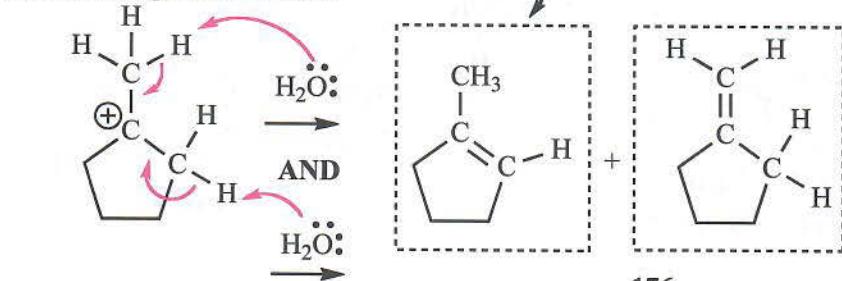
(b) Three elimination products are possible: two from an unrearranged carbocation, and two from a rearranged carbocation, one product of which is the same to both pathways.



### from unrearanged carbocation

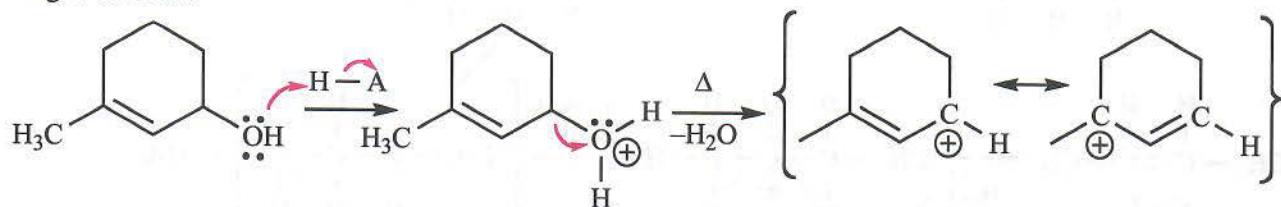


from rearranged carbocation

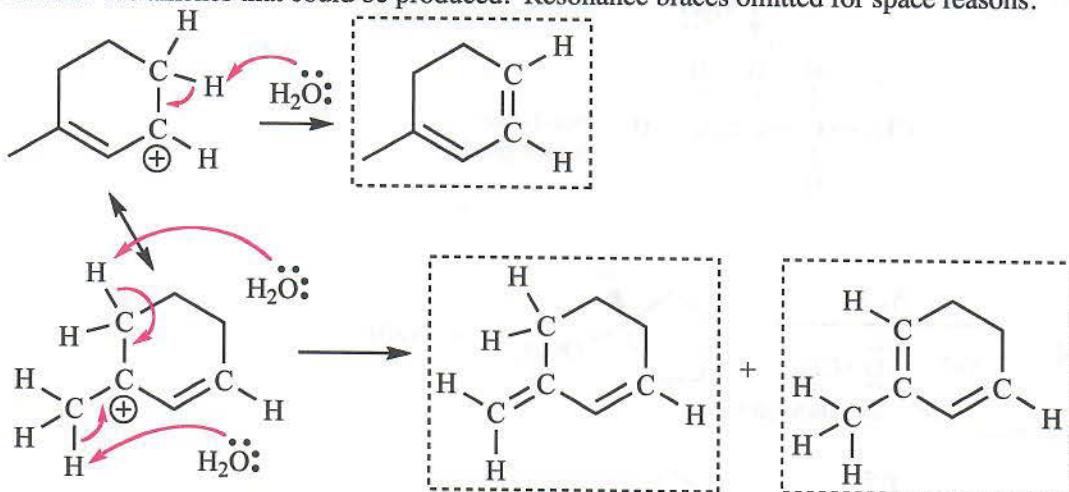


7-35 continued

(c) Three elimination products are possible: the intermediate carbocation is allylic, with positive charge shared by two different carbons. An H can be removed from any of three carbons adjacent to positively-charged carbons.



Although the two resonance forms do not represent real structures, each can be treated separately to determine the alkenes that could be produced. Resonance braces omitted for space reasons.



7-36

$$(a) \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= +116,000 \text{ J/mol} - 298 \text{ }^\circ\text{K} (117 \text{ J}/\text{K}\cdot\text{mol}) = +116,000 \text{ J/mol} - 34,866 \text{ J/mol}$$

$$= +81,134 \text{ J/mol} = +81.1 \text{ kJ/mol (+19.3 kcal/mole)}$$

$\Delta G^\circ$  is positive, the reaction is **disfavored** at 25°C.

$$(b) \Delta G_{1000} = +116,000 \text{ J/mol} - 1273 \text{ }^\circ\text{K} (117 \text{ J}/\text{K}\cdot\text{mol}) = +116,000 \text{ J/mol} - 148,941 \text{ J/mol}$$

$$= -32,941 \text{ J/mol} = -32.9 \text{ kJ/mol (-8.0 kcal/mole)}$$

$\Delta G$  is negative, the reaction is **favored** at 1000°C.

7-37

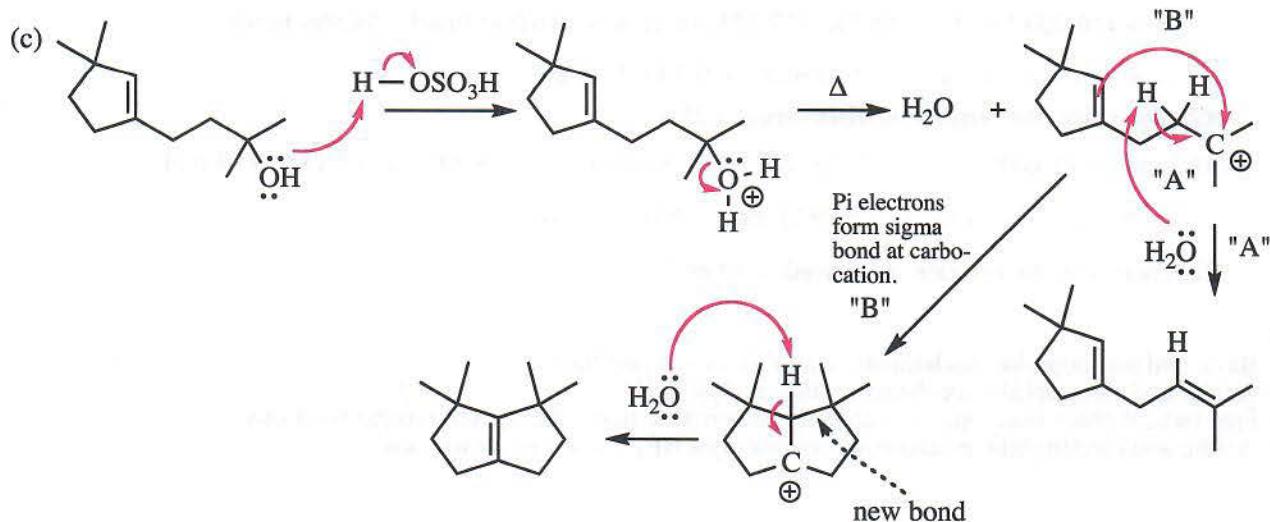
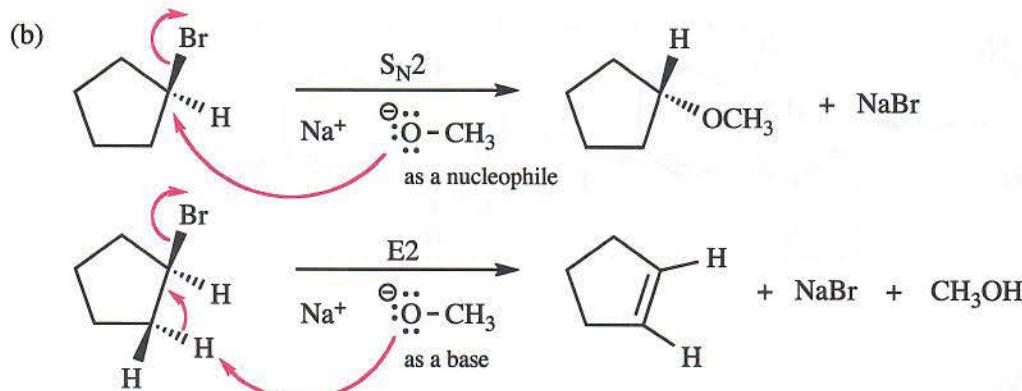
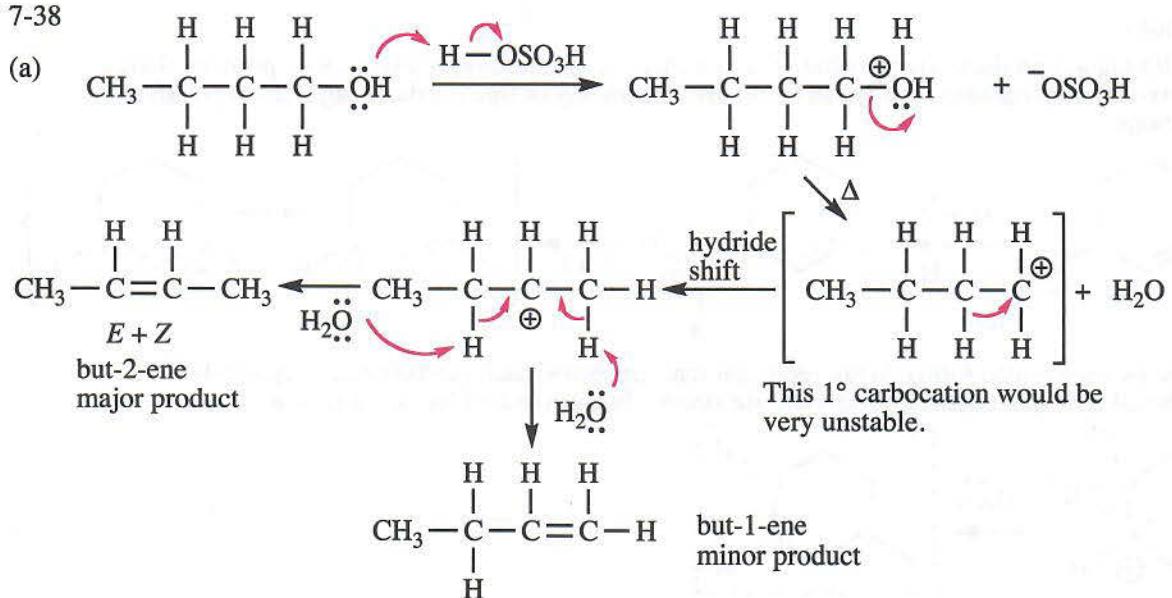
(a) Basic and nucleophilic mechanism:  $\text{Ba}(\text{OH})_2$  is a strong base.

(b) Acidic and electrophilic mechanism: the catalyst is  $\text{H}^+$ .

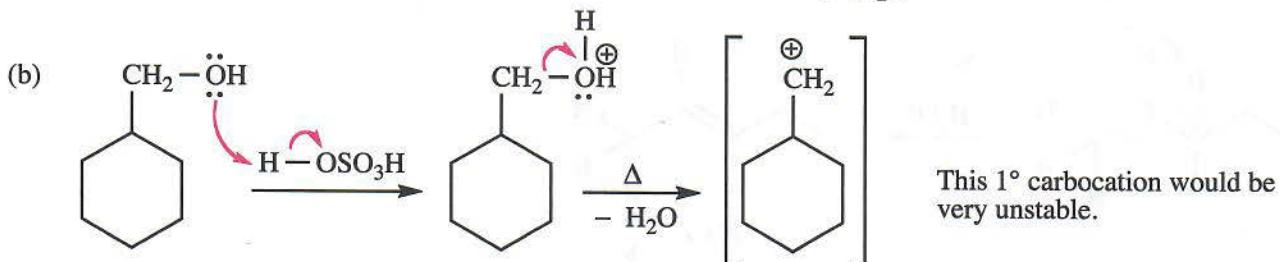
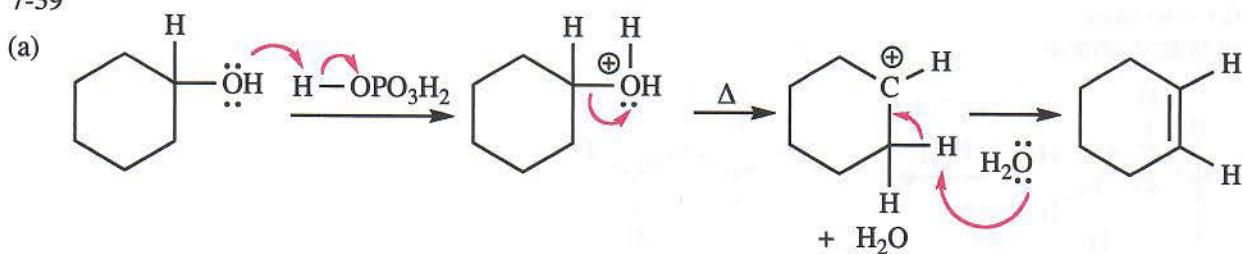
(c) Free radical chain reaction: the catalyst is a peroxide that initiates free radical reactions.

(d) Acidic and electrophilic mechanism: the catalyst  $\text{BF}_3$  is a strong Lewis acid.

7-38

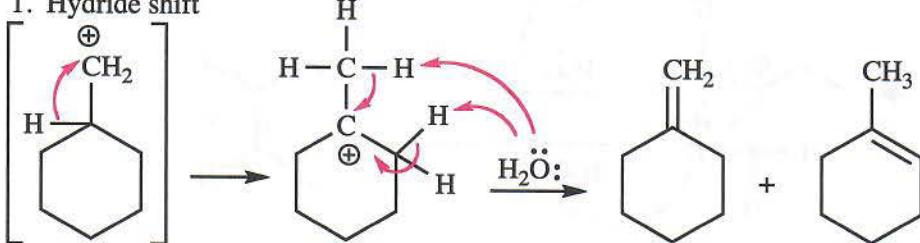


7-39

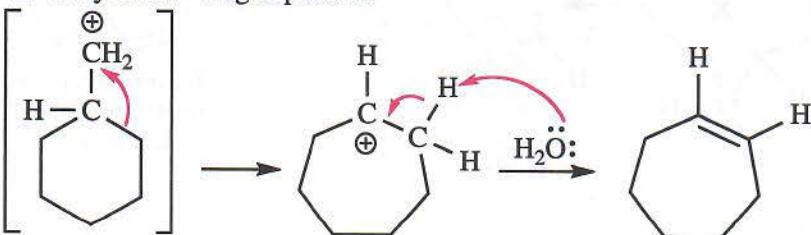


Two possible rearrangements

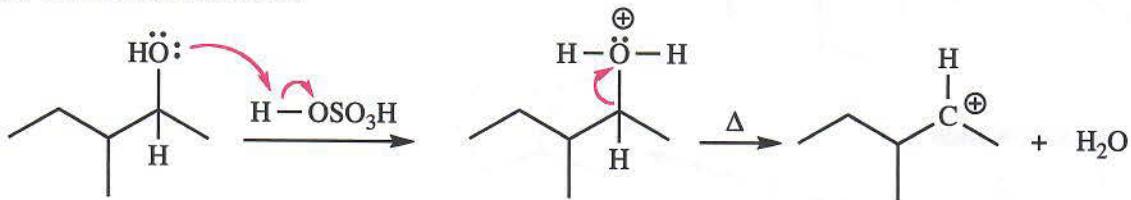
1. Hydride shift



2. Alkyl shift—ring expansion

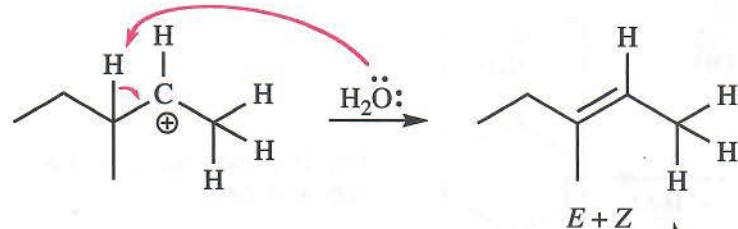
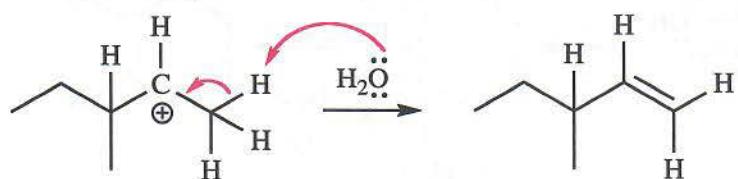


(c) carbocation formation

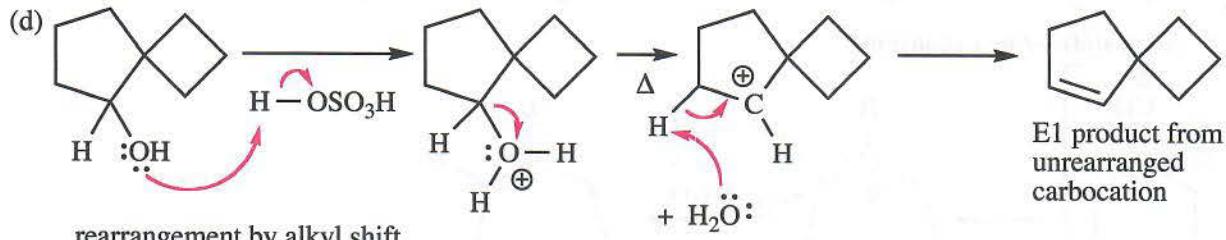
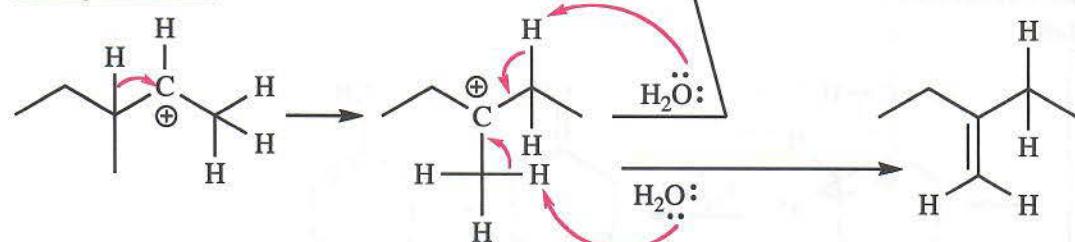


continued on next page

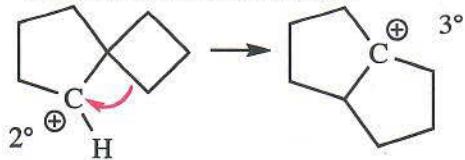
7-39 (c) continued  
without rearrangement



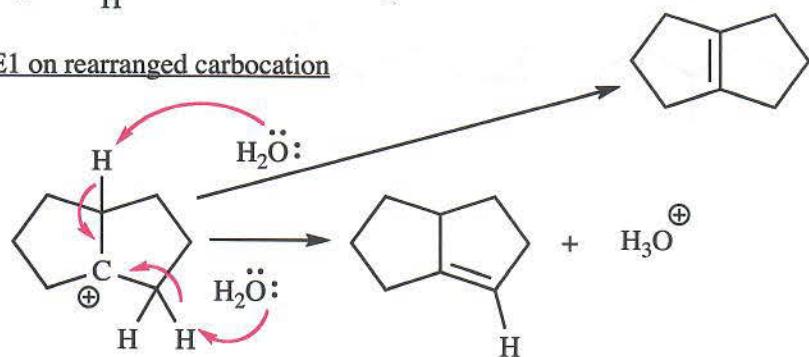
with hydride shift



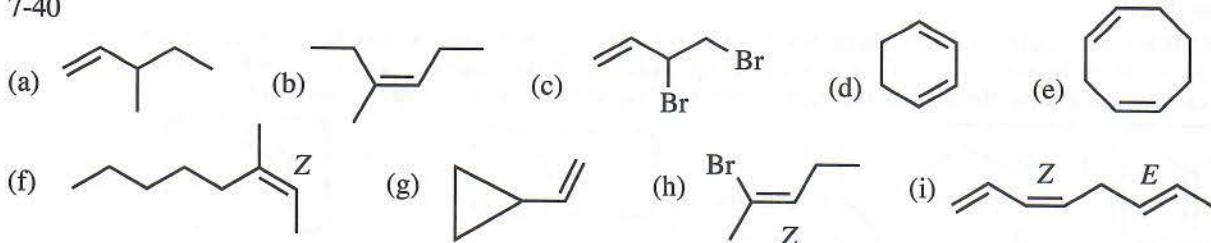
rearrangement by alkyl shift



E1 on rearranged carbocation

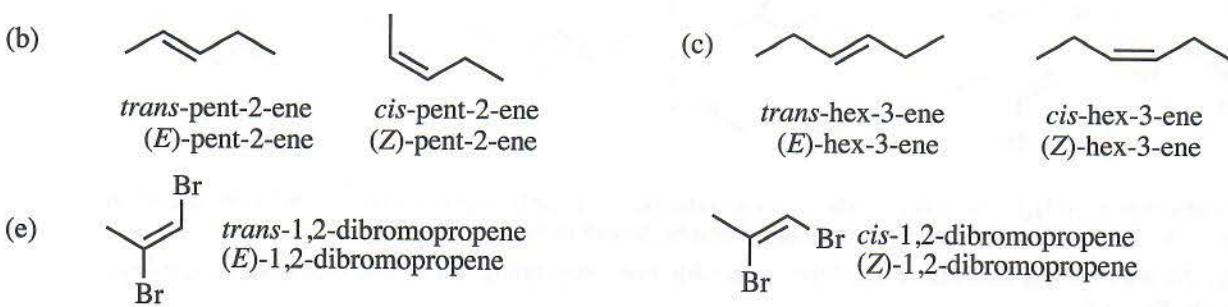


7-40

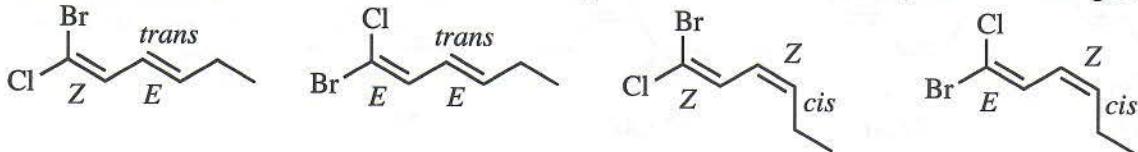


7-41 (a) *E* (b) neither—two methyl groups on one carbon (c) *Z* (d) *Z*

7-42 Parts (a) and (d) have no geometric isomers.



(f) *Cis* and *trans* do not apply to the C=C at C-1, only the one at C-3. The *E/Z* system is unambiguous.



7-43 These names follow the modern IUPAC system of placement of position numbers.

(a) 2-ethylpent-1-ene (Number the longest chain *containing the double bond*.)

(b) 3-ethylpent-2-ene

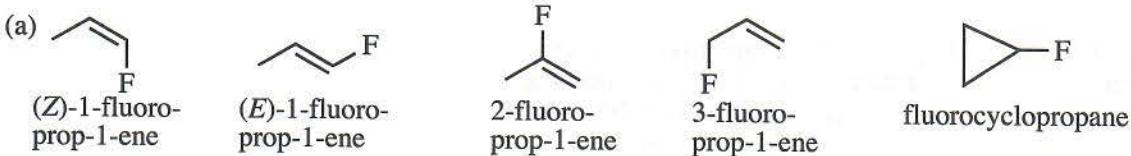
(c) (*3E,5E*)-2,6-dimethylocta-1,3,5-triene

(d) (*E*)-4-ethylhept-3-ene

(e) 1-cyclohexylcyclohexa-1,3-diene

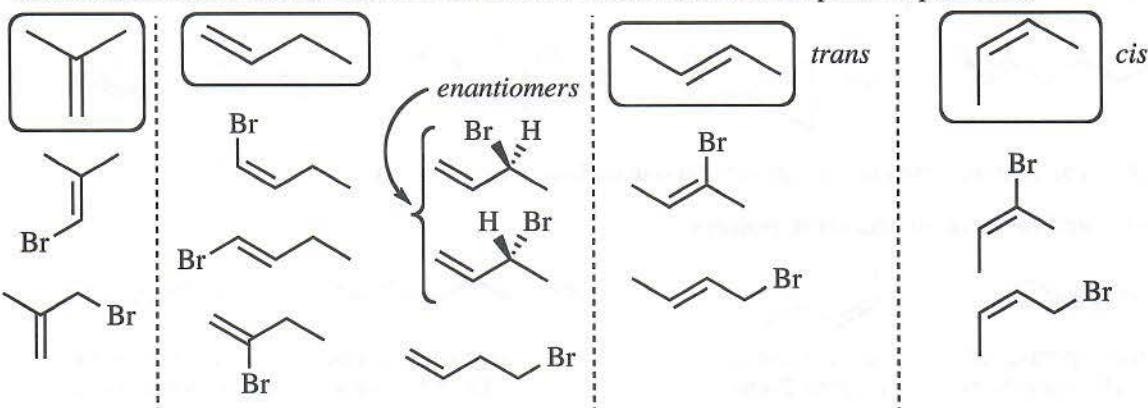
(f) (*3Z,5Z*)-6-chloro-3-(chloromethyl)octa-1,3,5-triene

7-44



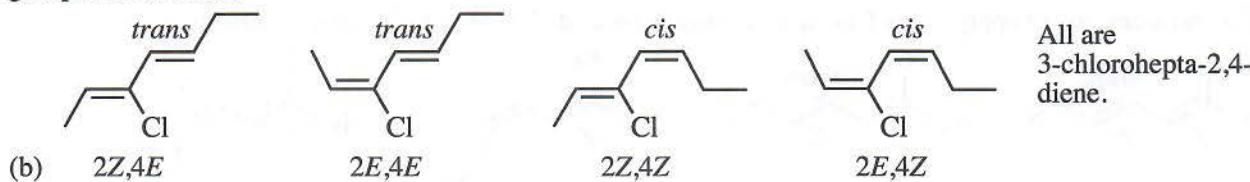
7-44 continued

(b)  $C_4H_7Br$  has one element of unsaturation, but no rings are permitted in the problem, so all the isomers must have one double bond. Only four isomers are possible with four carbons and one double bond, so the 12 answers must have these four skeletons with a Br substituted in all possible positions.

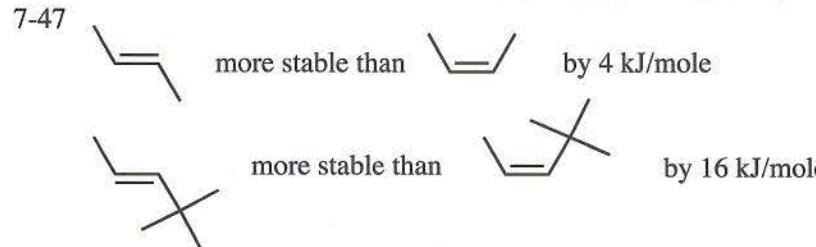
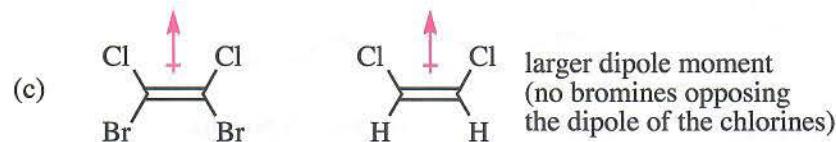
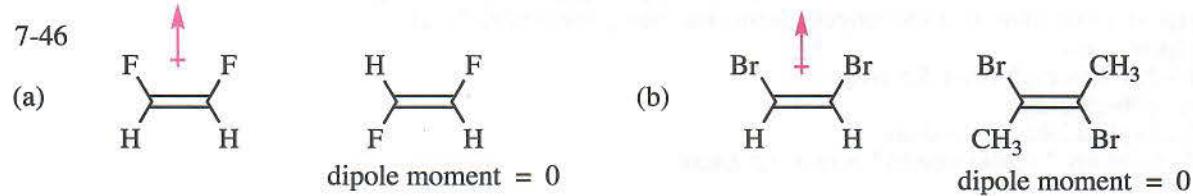


(c) Cholesterol,  $C_{27}H_{46}O$ , has five elements of unsaturation. If only one of those is a pi bond, the other four must be rings. (The structure of cholesterol can be found in text section 25-6.)

7-45 (a) Neither *cis* nor *trans* is defined for the double bond beginning at C-2 because none of the four groups are the same.

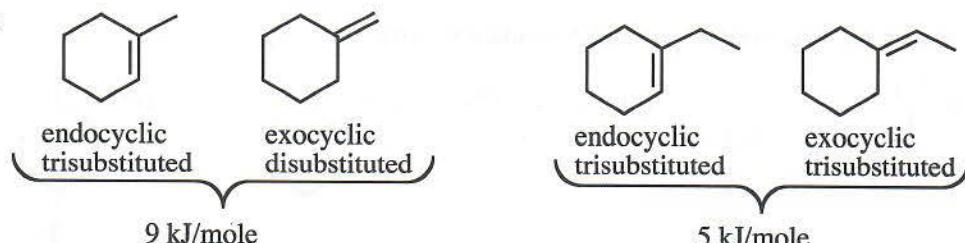


The *E/Z* nomenclature is unambiguous and is preferred for all four of these isomers.



Steric crowding by the *tert*-butyl group is responsible for the energy difference. In *cis*-but-2-ene, the two methyl groups have only slight interaction. However, in the 4,4-dimethylpent-2-enes, the larger size of the *tert*-butyl group crowds the methyl group in the *cis* isomer, increasing its strain and therefore its energy.

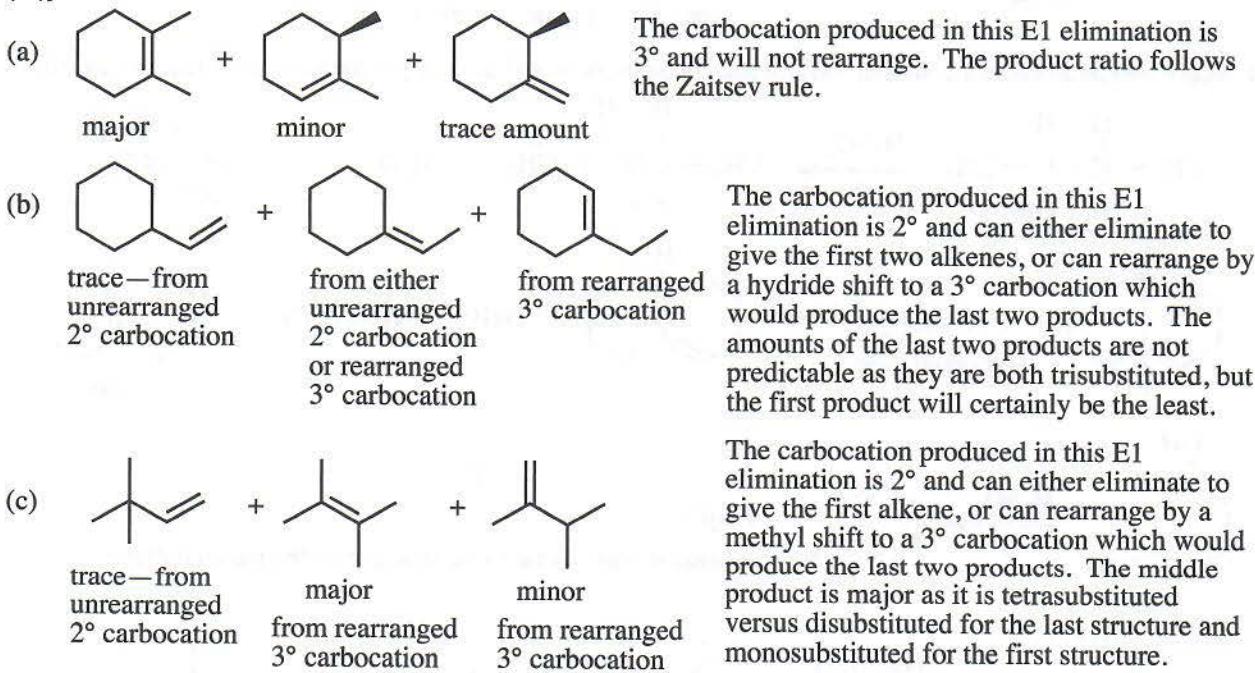
7-48



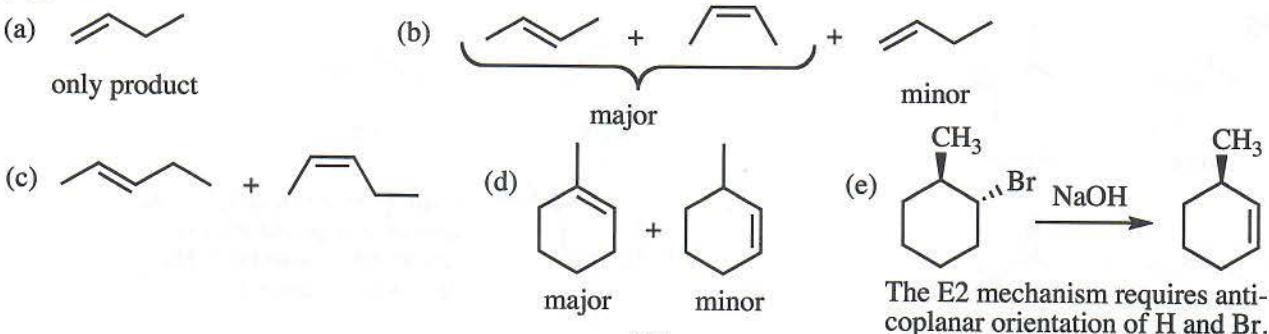
A standard principle of science is to compare experiments that differ by only one variable. Changing more than one variable clouds the interpretation, possibly to the point of invalidating the experiment.

The first set of structures compares endo and exocyclic double bonds, but the degree of substitution on the alkene is also different, so this comparison is not valid—we are not isolating simply the exo or endocyclic effect. The second pair is a much better measure of endo versus exocyclic stability because both alkenes are trisubstituted, so the degree of substitution plays no part in the energy values. Thus, 5 kJ/mole is a better value.

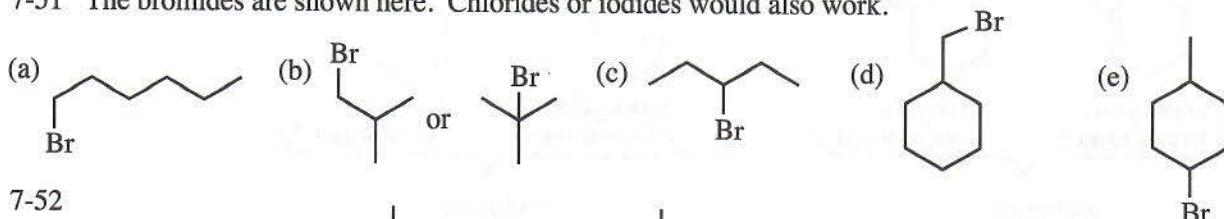
7-49



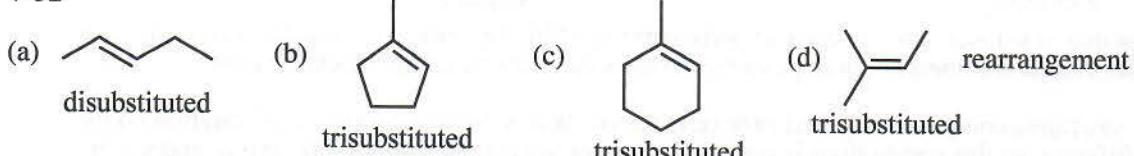
7-50



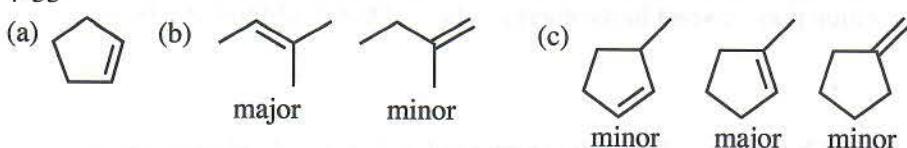
7-51 The bromides are shown here. Chlorides or iodides would also work.



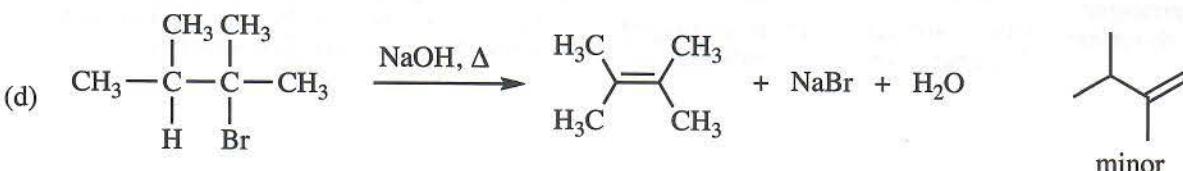
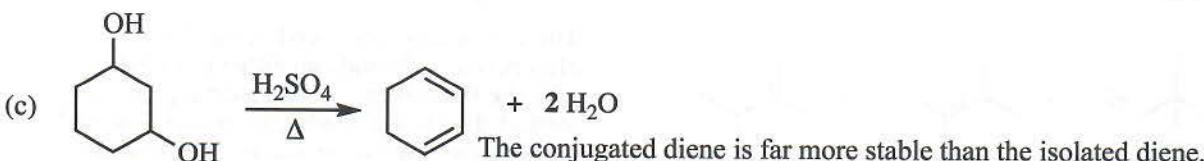
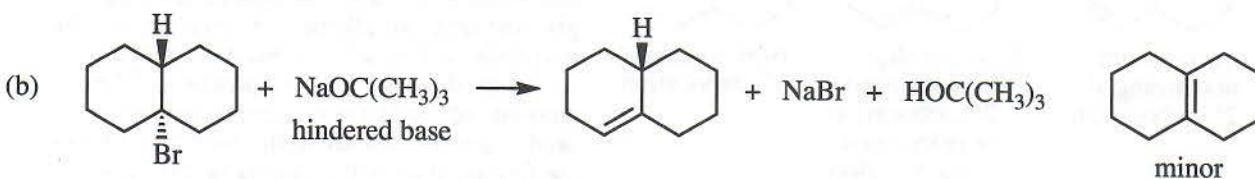
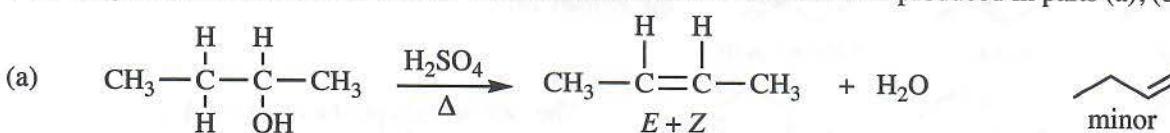
7-52



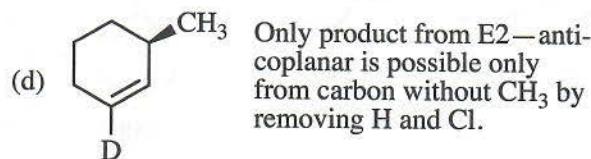
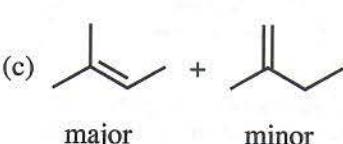
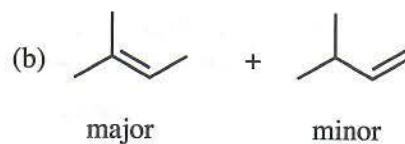
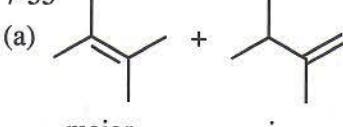
7-53



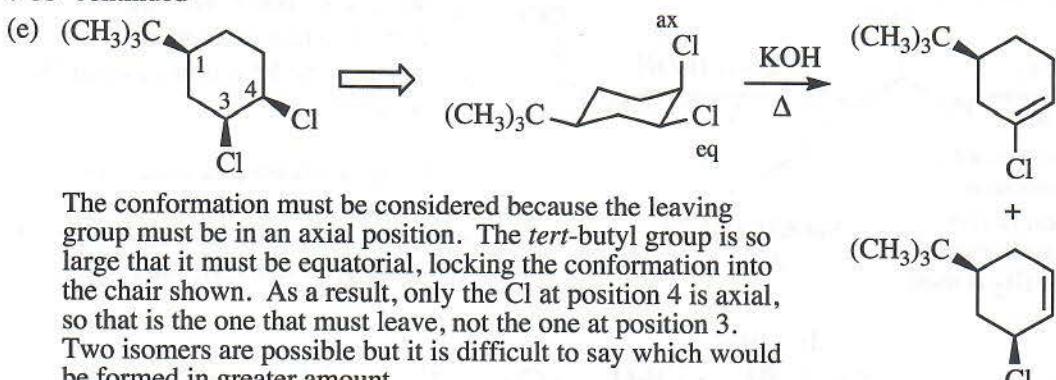
7-54 Major alkene isomers are shown. Minor alkene isomers would also be produced in parts (a), (b) and (d).



7-55

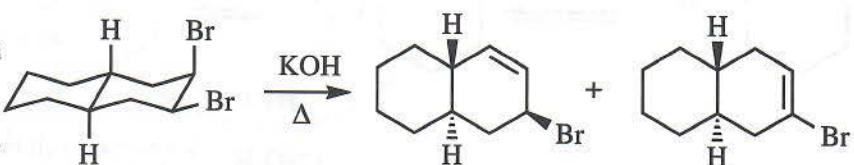


7-55 continued

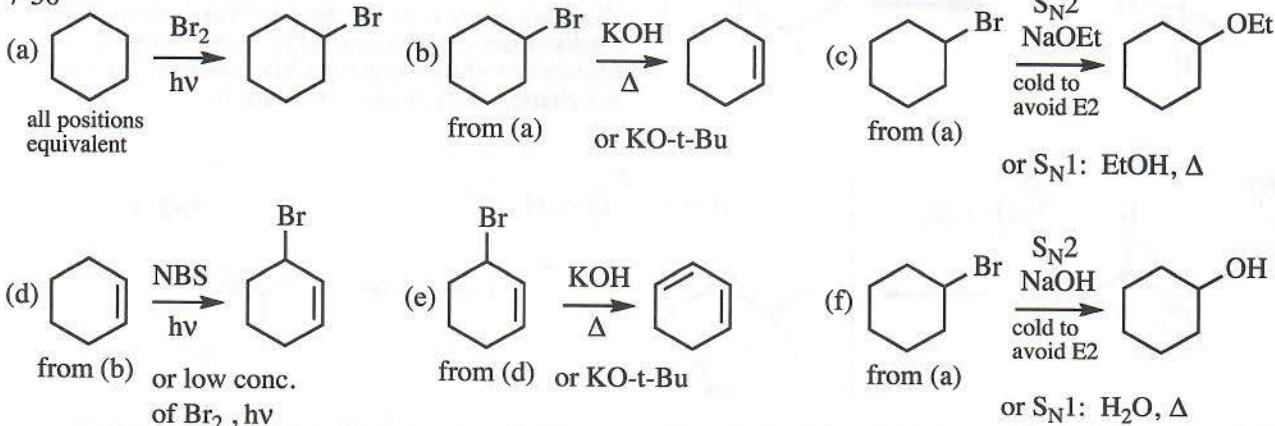


(f)

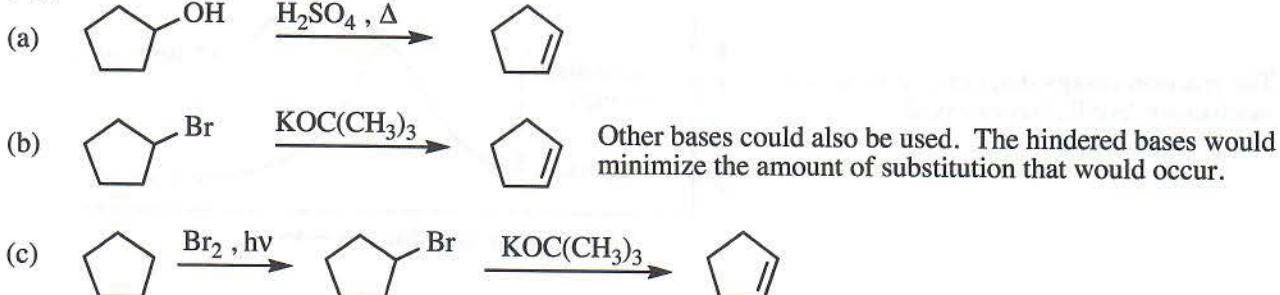
Only one of the two Br atoms is in the required axial position for E2 elimination. There are axial H atoms at the two adjacent carbons, so two alkene products can be formed. Predicting major and minor would be difficult.



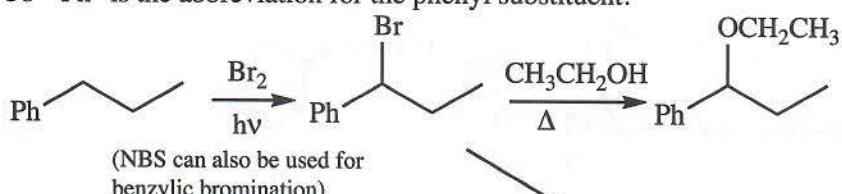
7-56



7-57



7-58 "Ph" is the abbreviation for the phenyl substituent.

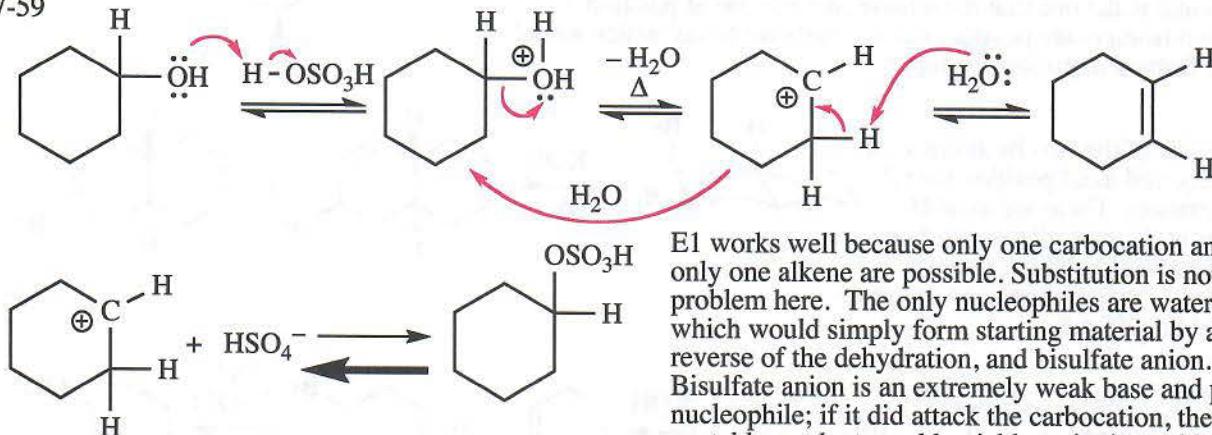


Benzylic bromination is very selective; dibromination might occur if an excess of  $\text{Br}_2$  is used.

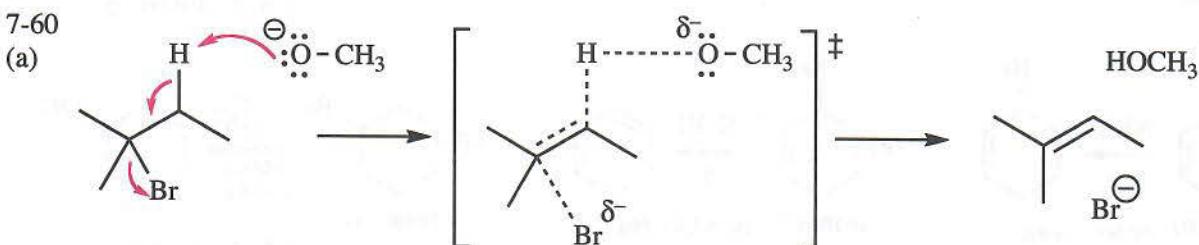
solvolytic conditions— $S_N1$   
If the reaction mixture got too warm, some E1 elimination might occur.

Using a hindered base like *tert*-butoxide will give exclusively the E2 product, with no competing  $S_N2$  as KOH or  $\text{NaOCH}_3$  might give.

7-59

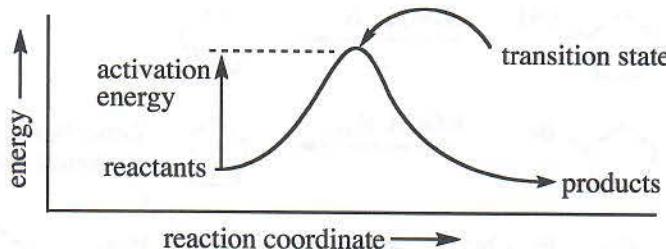


7-60

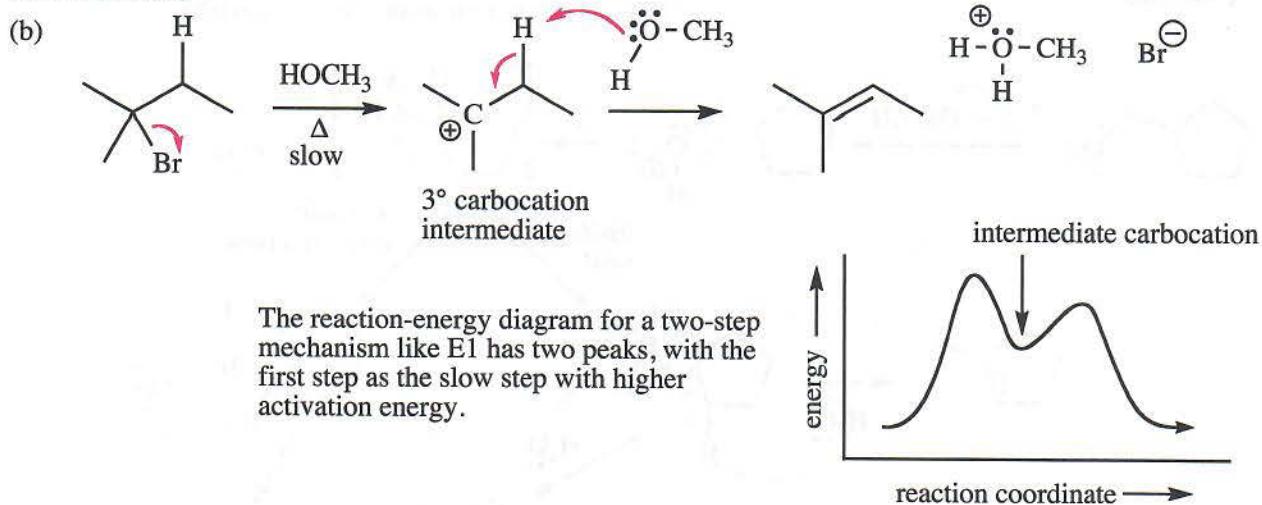


Methoxide is a strong base and nucleophile so the reaction is second order. The Br is on a  $3^\circ$  carbon so  $S_N2$  is not possible, only E2. The transition state shows bond-forming and bond-breaking with dashed bonds.

The reaction-energy diagram for a one-step mechanism like E2 has one peak.

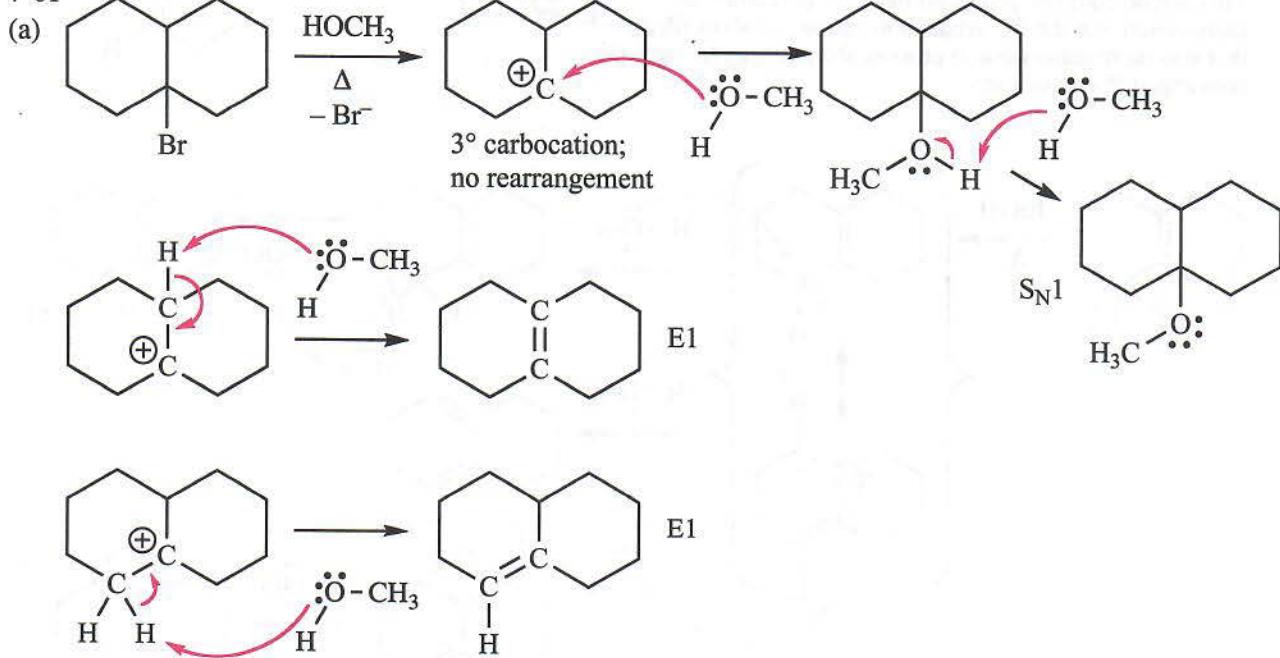


7-60 continued



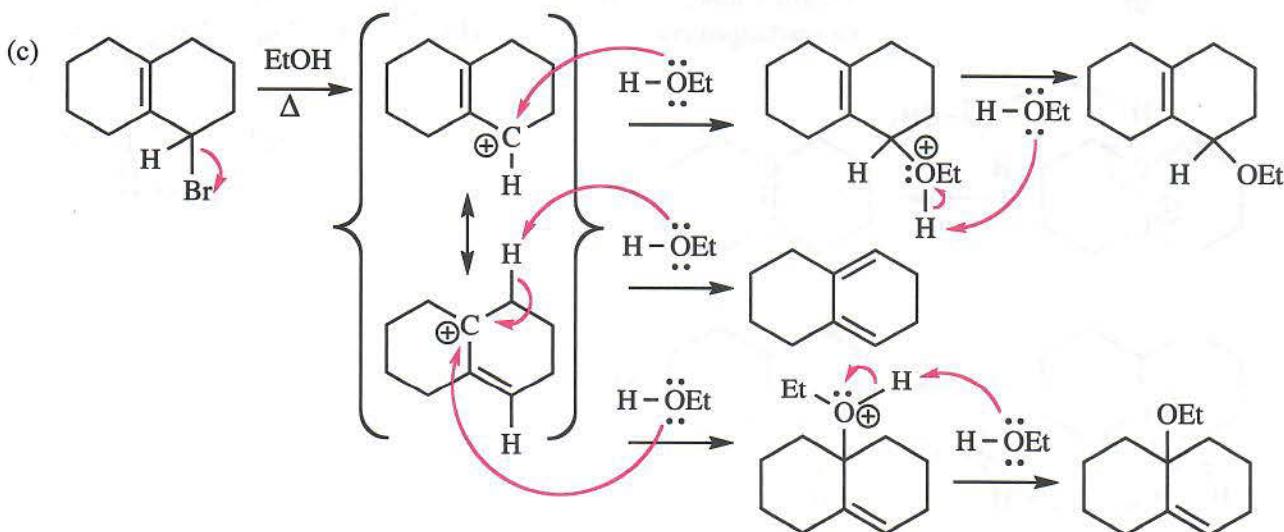
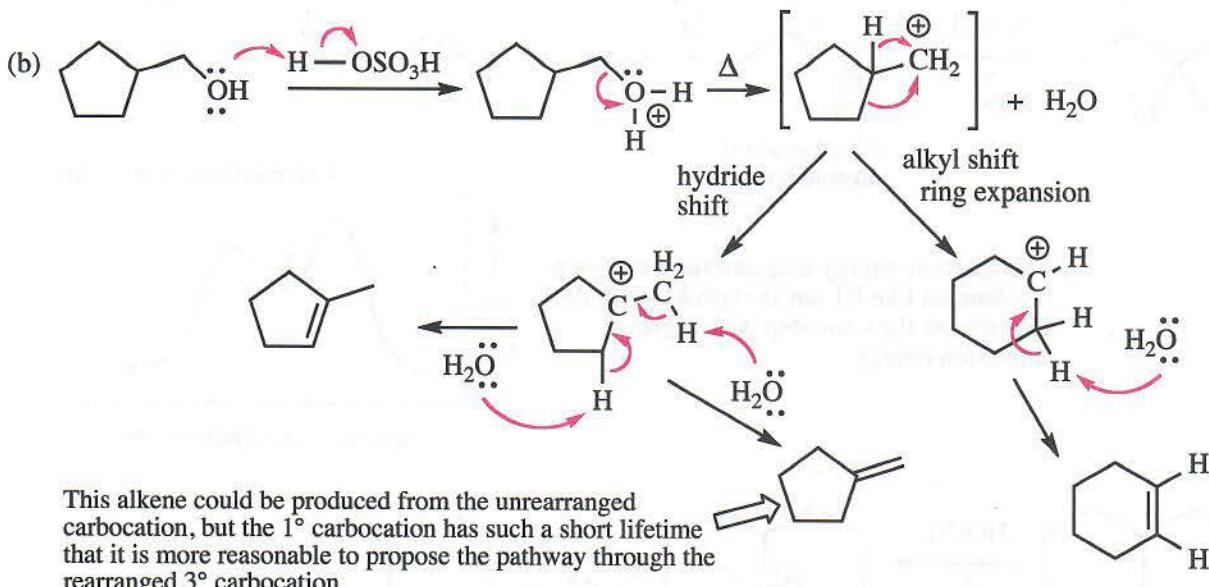
The reaction-energy diagram for a two-step mechanism like E1 has two peaks, with the first step as the slow step with higher activation energy.

7-61



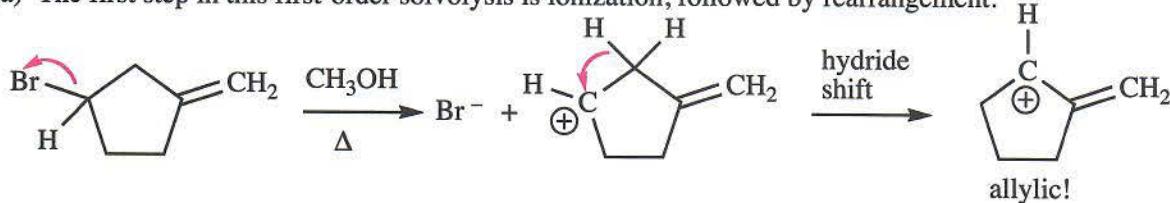
7-61 continued

This 1° carbocation would be very unstable.



7-62

(a) The first step in this first-order solvolysis is ionization, followed by rearrangement.



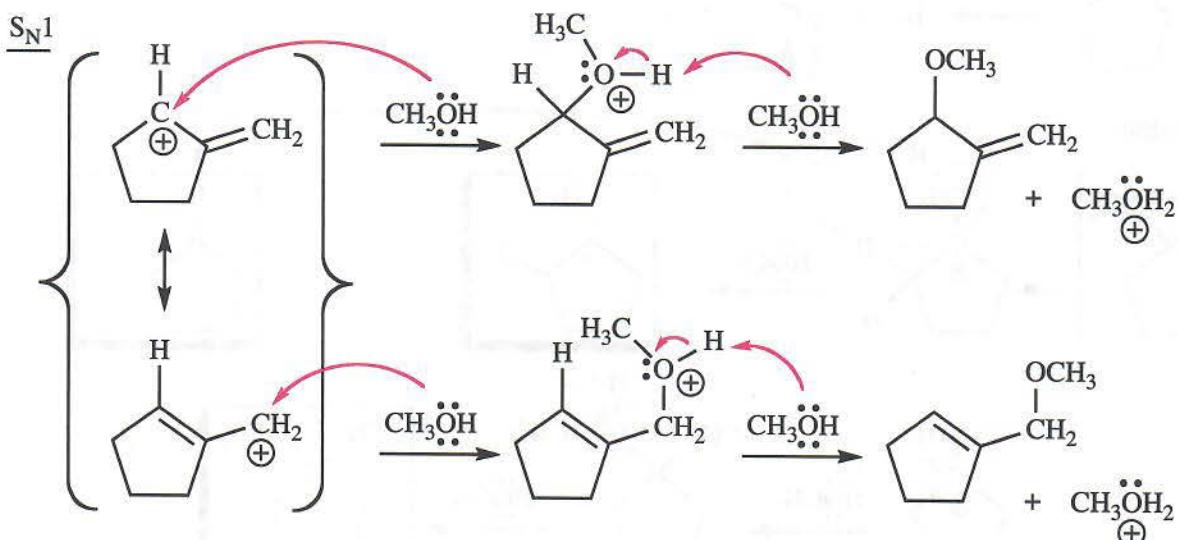
*continued on next page*

7-62(a) continued

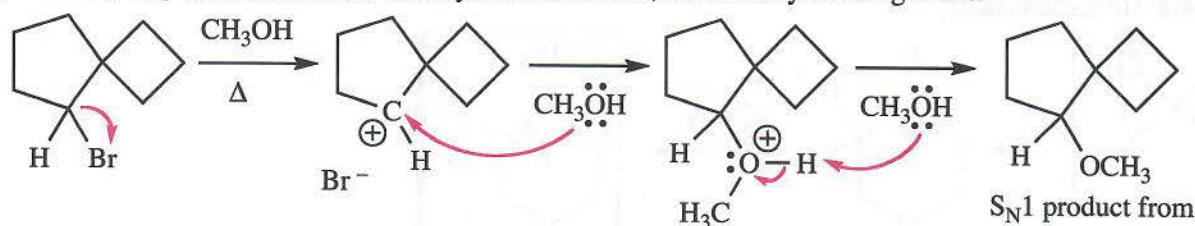
E1



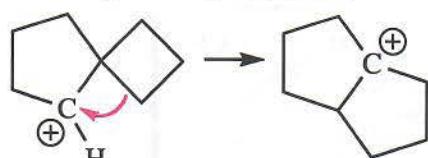
S<sub>N</sub>1



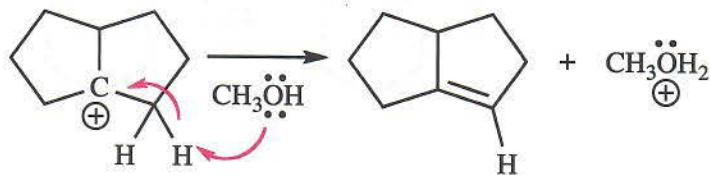
(b) The first step in this first-order solvolysis is ionization, followed by rearrangement.



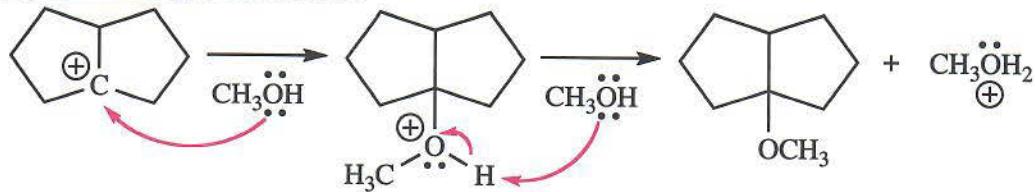
rearrangement by alkyl shift



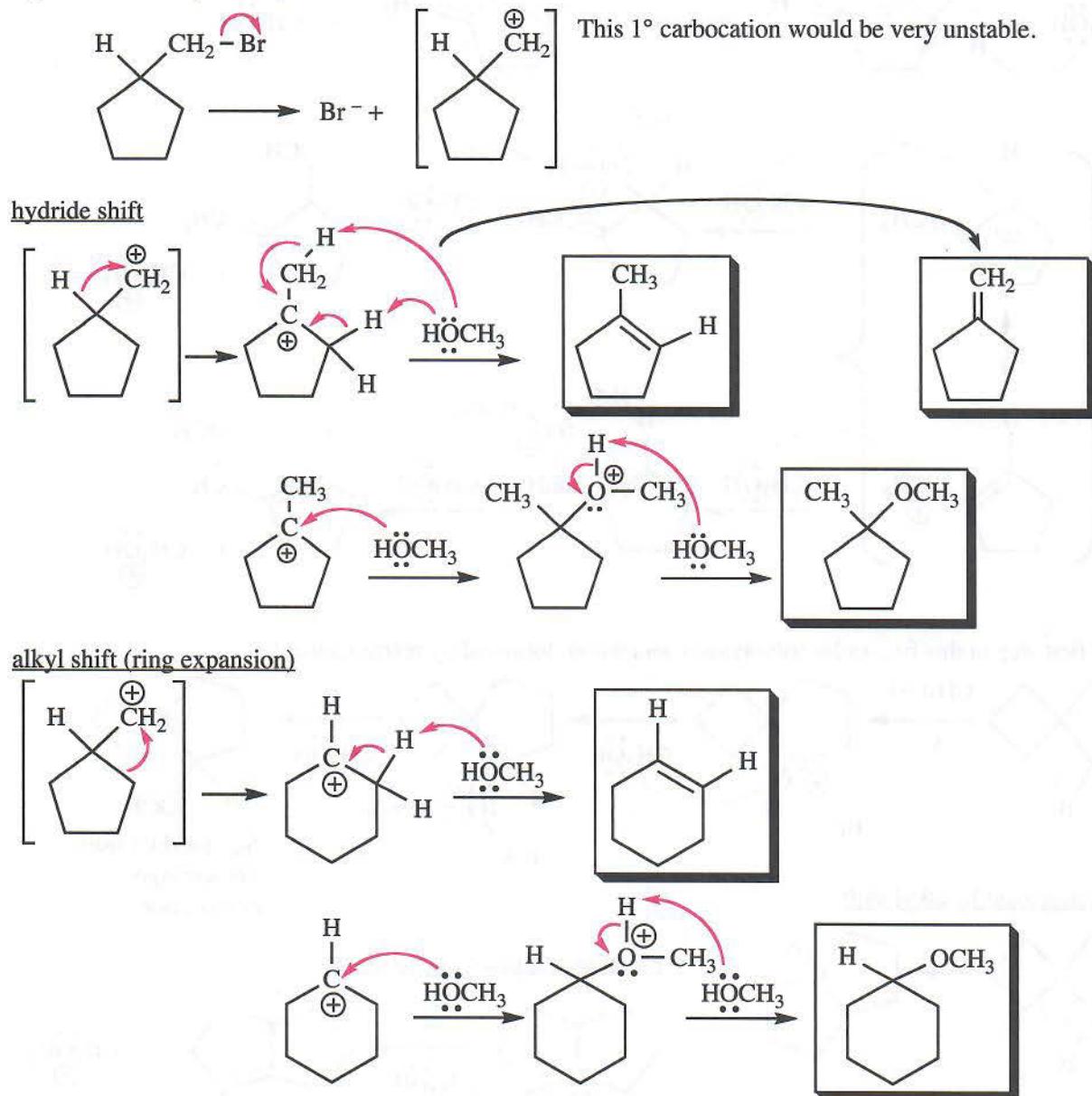
E1 on rearranged carbocation



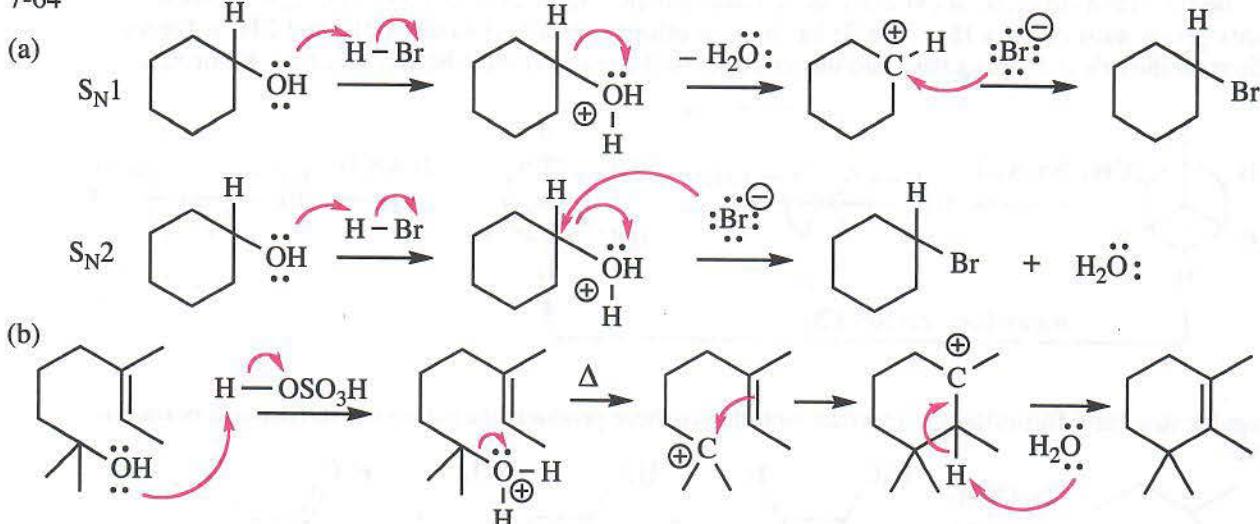
S<sub>N</sub>1 on rearranged carbocation



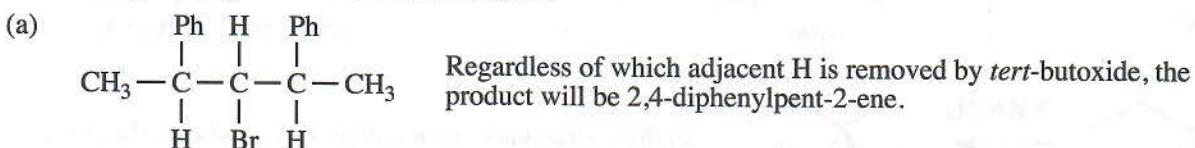
7-63 All five products (boxed) come from rearranged carbocations. Rearrangement, which may occur simultaneously with ionization, can occur by hydride shift to the  $3^\circ$  methylcyclopentyl cation, or by ring expansion to the cyclohexyl cation.



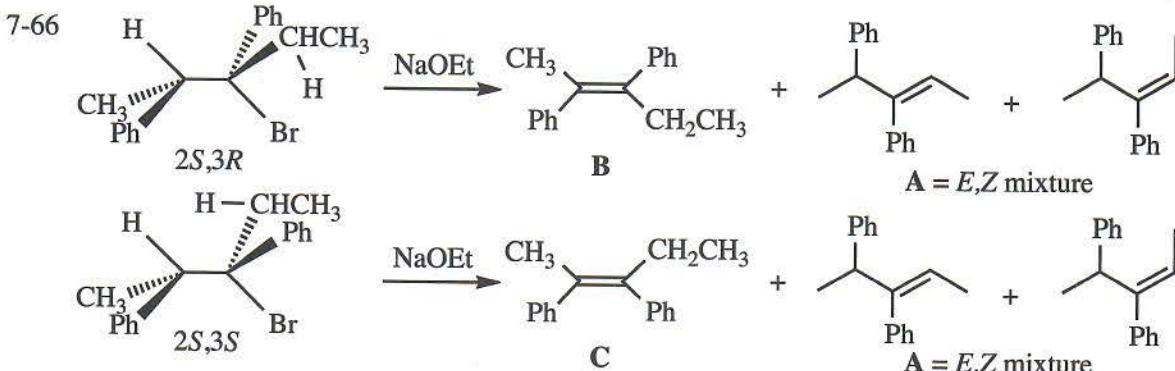
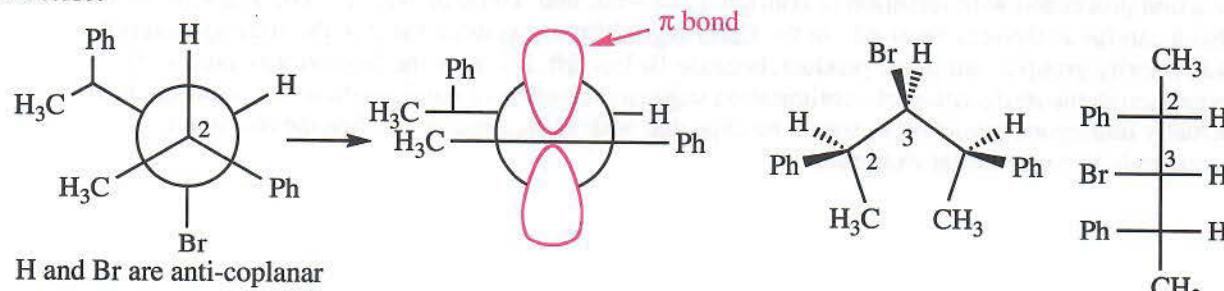
7-64



7-65 The symmetry of this molecule is crucial.

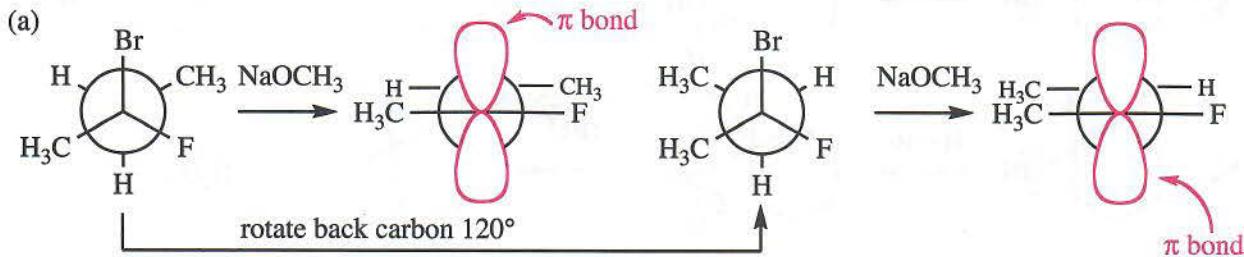


(b) Here are a Newman projection, a three-dimensional representation, and a Fischer projection of the required diastereomer. On both carbons 2 and 4, the H has to be anti-coplanar with the bromine while leaving the other groups to give the same product. Not coincidentally, the correct diastereomer is a meso structure.

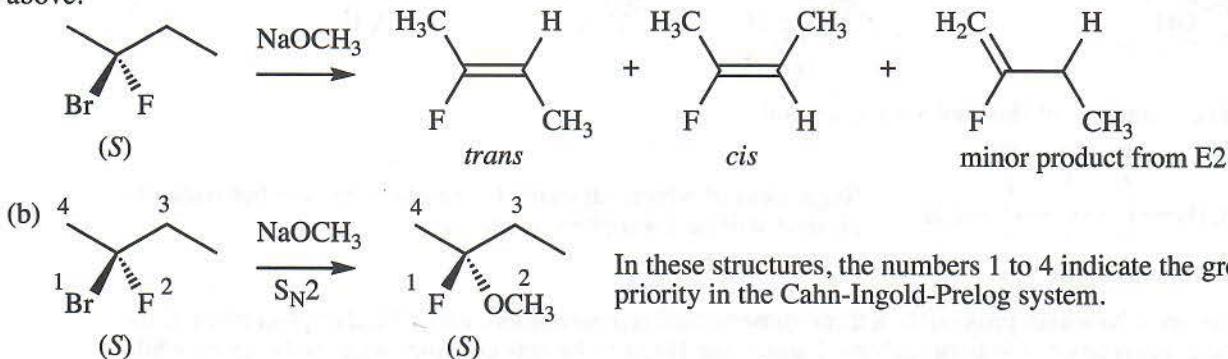


E2 dehydrohalogenation requires anti-coplanar arrangement of H and Br, so specific *cis-trans* isomers (B or C) are generated depending on the stereochemistry of the starting material. Removing a hydrogen from C-4 (achiral) will give about the same mixture of *E* and *Z* (A) from either diastereomer.

7-67 Begin with a structure of (*S*)-2-bromo-2-fluorobutane. Since there is no H on C-2, the lowest priority group must be the CH<sub>3</sub>. The Br has highest priority, then F, then CH<sub>2</sub>CH<sub>3</sub>, and CH<sub>3</sub> is fourth. Sodium methoxide is a strong base and nucleophile, so the reaction must be second order, E2 or S<sub>N</sub>2.

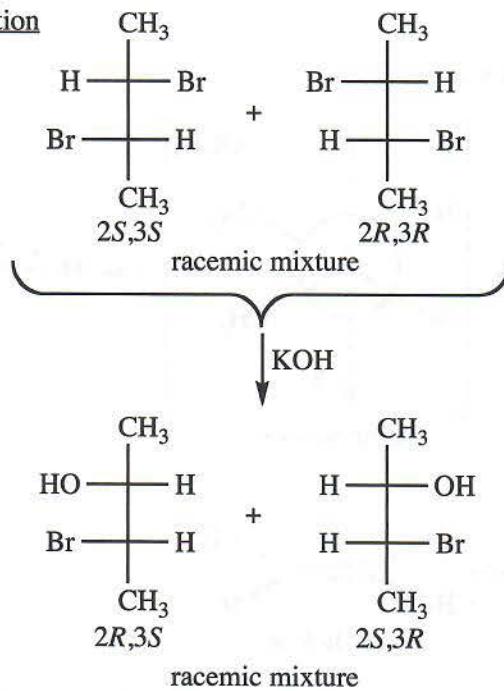


In regular structural formulas, the reaction would give three products including the stereoisomers shown above.



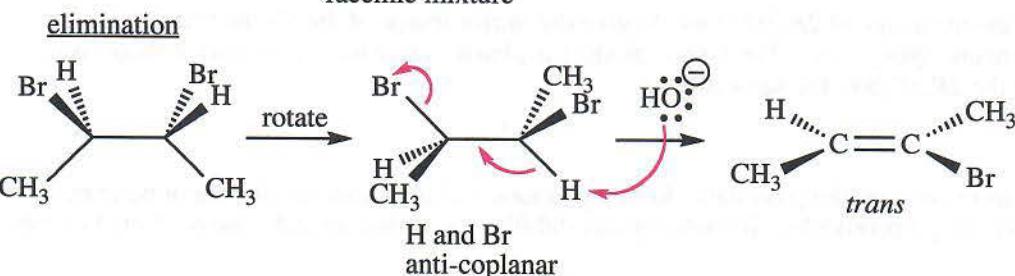
A cursory analysis of the *designation* of configuration would suggest to the uncritical mind that this reaction proceeded with retention of configuration—but that would be wrong! You know by now that a careful analysis is required. In the Cahn-Ingold-Prelog system, the F in the starting material was priority group 2, but in the product, because Br has left, F is now the first priority group. So even though the *designation* of configuration suggests retention of configuration, the molecule has actually undergone inversion as would be expected with an S<sub>N</sub>2 reaction. (See the solution to problem 6-21 for a similar example.)

7-68 substitution



Regardless of which bromine is substituted on each molecule, the same mixture of products results.

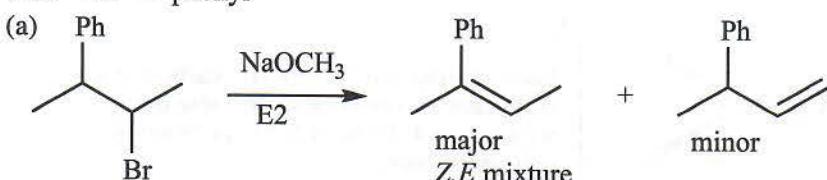
Each of the substitution products has one chiral center inverted from the starting material. The mechanism that accounts for inversion is  $S_N2$ . If an  $S_N1$  process were occurring, the product mixture would also contain  $2R,3R$  and  $2S,3S$  diastereomers. Their absence argues against an  $S_N1$  process occurring here.



The other enantiomer gives the same product (you should prove this to yourself).

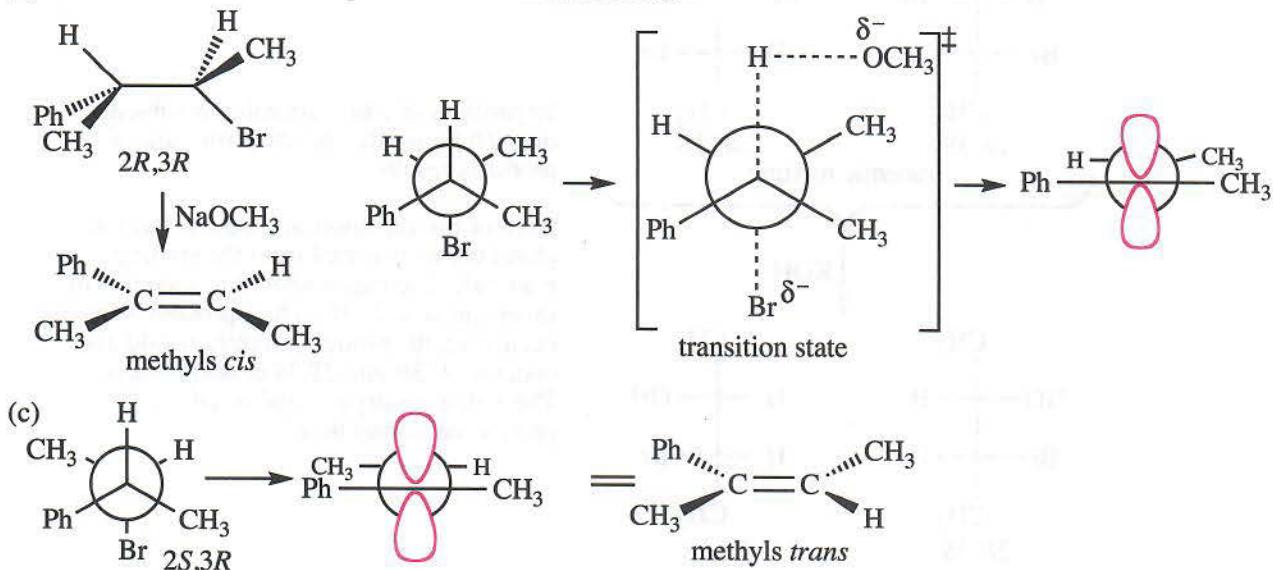
The absence of *cis* product is evidence that only the E2 elimination is occurring in one step through an anti-coplanar transition state with no chance of rotation. If E1 had been occurring, rotation around the carbocation intermediate would have been possible, leading to both the *cis* and *trans* products.

7-69 "Ph" = phenyl



7-69 continued

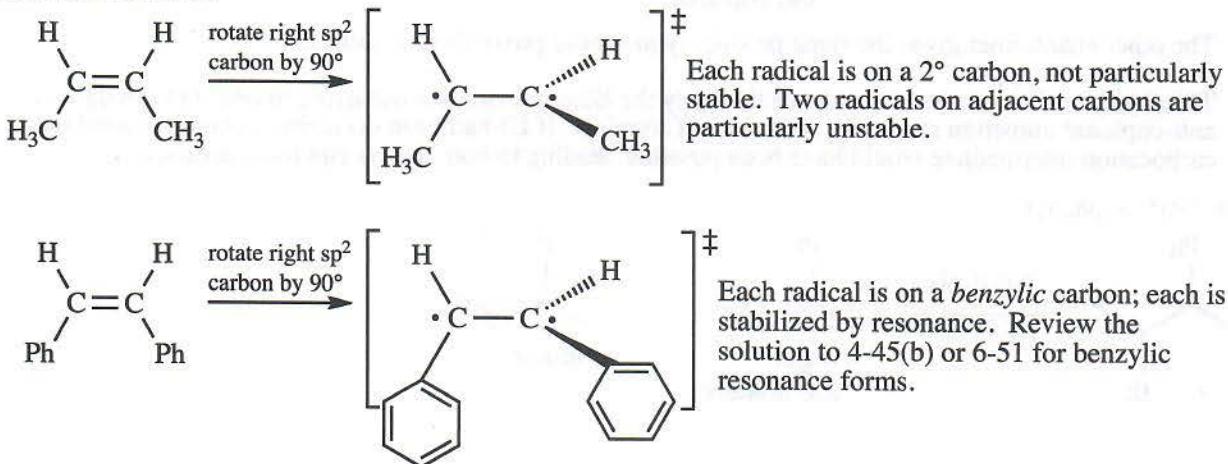
(b) H and Br must be anti-coplanar in the transition state.



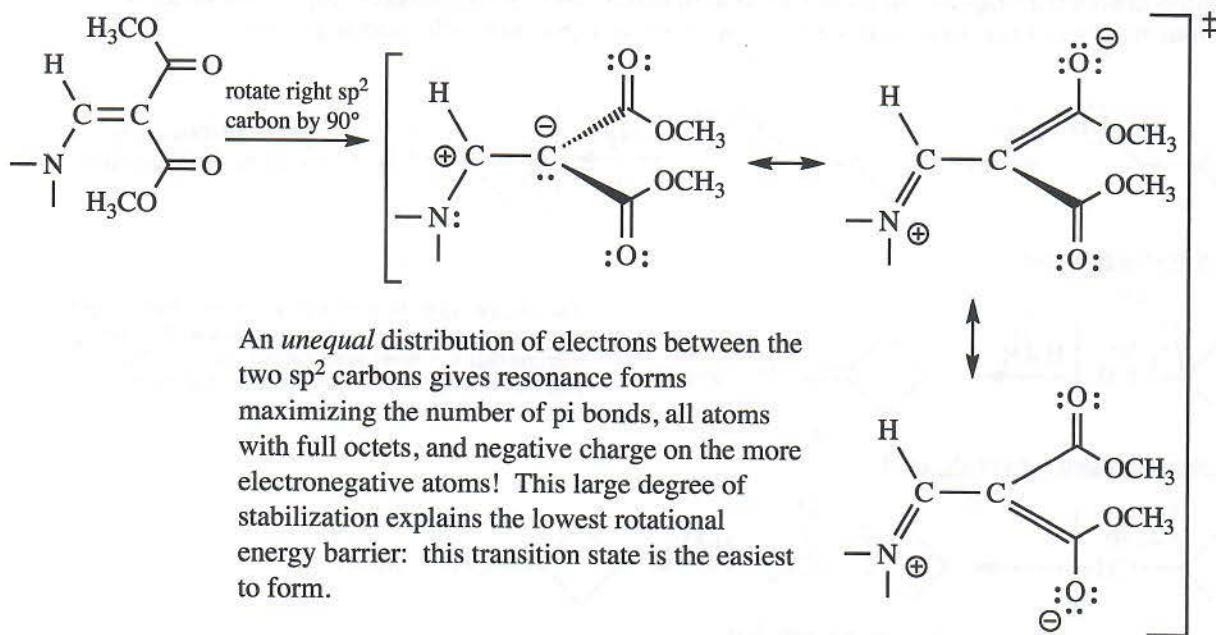
(d) The  $2S,3S$  is the mirror image of  $2R,3R$ ; it would give the mirror image of the alkene that  $2R,3R$  produced (with two methyl groups *cis*). The alkene product is planar, not chiral, so its mirror image is the same: the  $2S,3S$  and the  $2R,3R$  give the same alkene.

7-70

A pi bond is formed from two parallel p orbitals. Rotating around a double bond breaks the pi bond by forcing the p orbitals to be perpendicular. If anything can stabilize the transition state, the rotational energy barrier will be lower.

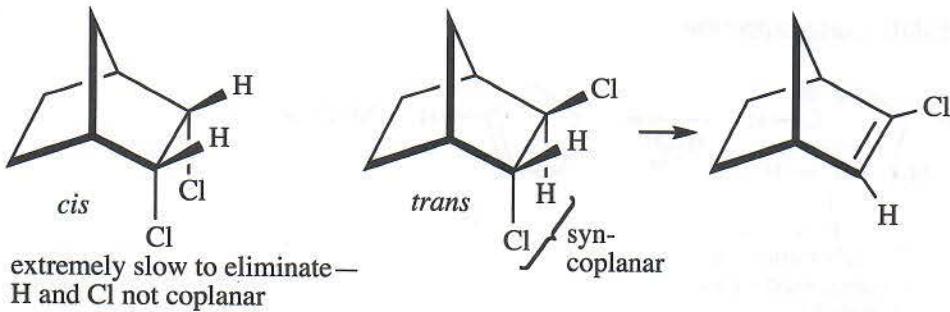


7-70 continued

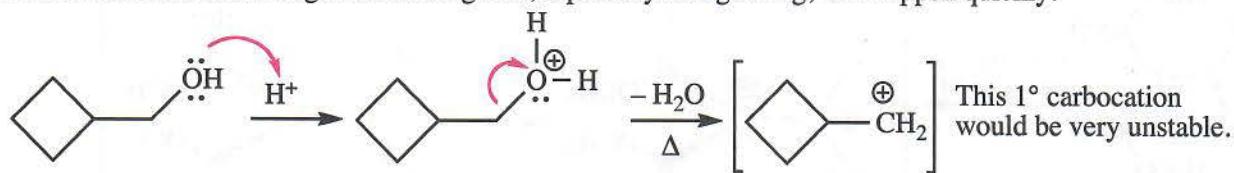


7-71 In E2, the two groups to be eliminated must be coplanar. In conformationally mobile systems like acyclic molecules, or in cyclohexanes, anti-coplanar is the preferred orientation where the H and leaving group are  $180^\circ$  apart. In rigid systems like norbornanes, however, SYN-coplanar (angle  $0^\circ$ ) is the only possible orientation and E2 will occur, although at a slower rate than anti-coplanar.

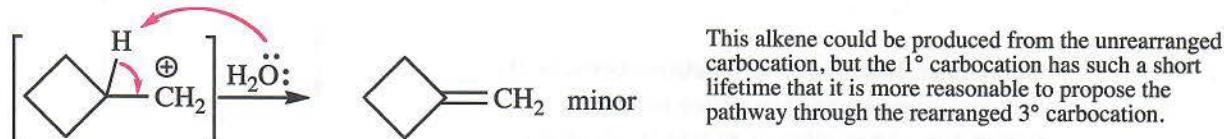
The structure having the H and the Cl *syn*-coplanar is the *trans*, which undergoes the E2 elimination. (It is possible that the *other* H and Cl eliminate from the *trans* isomer; the results from this reaction cannot distinguish between these two possibilities.)



7-72 It is interesting to note that even though three-membered rings are more strained than four-membered rings, three-membered rings are far more common in nature than four-membered rings. Rearrangement from a four-membered ring to something else, especially a larger ring, will happen quickly.

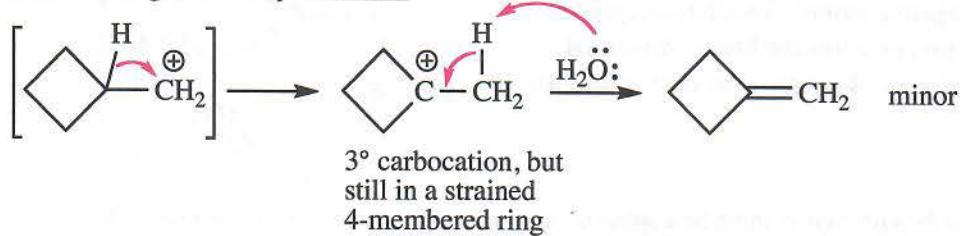


without rearrangement

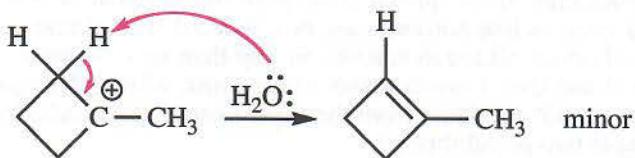


This alkene could be produced from the unrearranged carbocation, but the 1° carbocation has such a short lifetime that it is more reasonable to propose the pathway through the rearranged 3° carbocation.

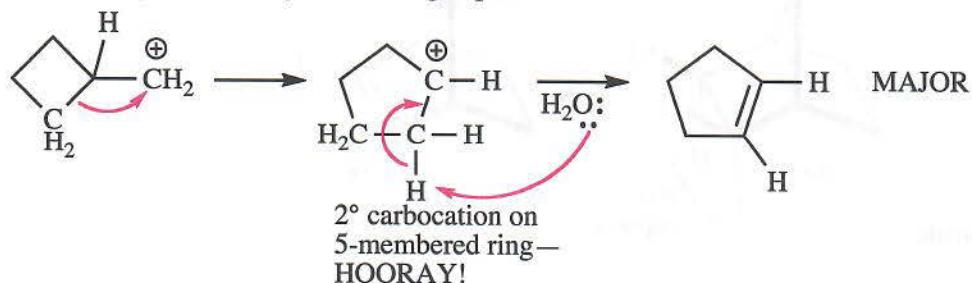
with rearrangement—hydride shift



3° carbocation, but  
still in a strained  
4-membered ring

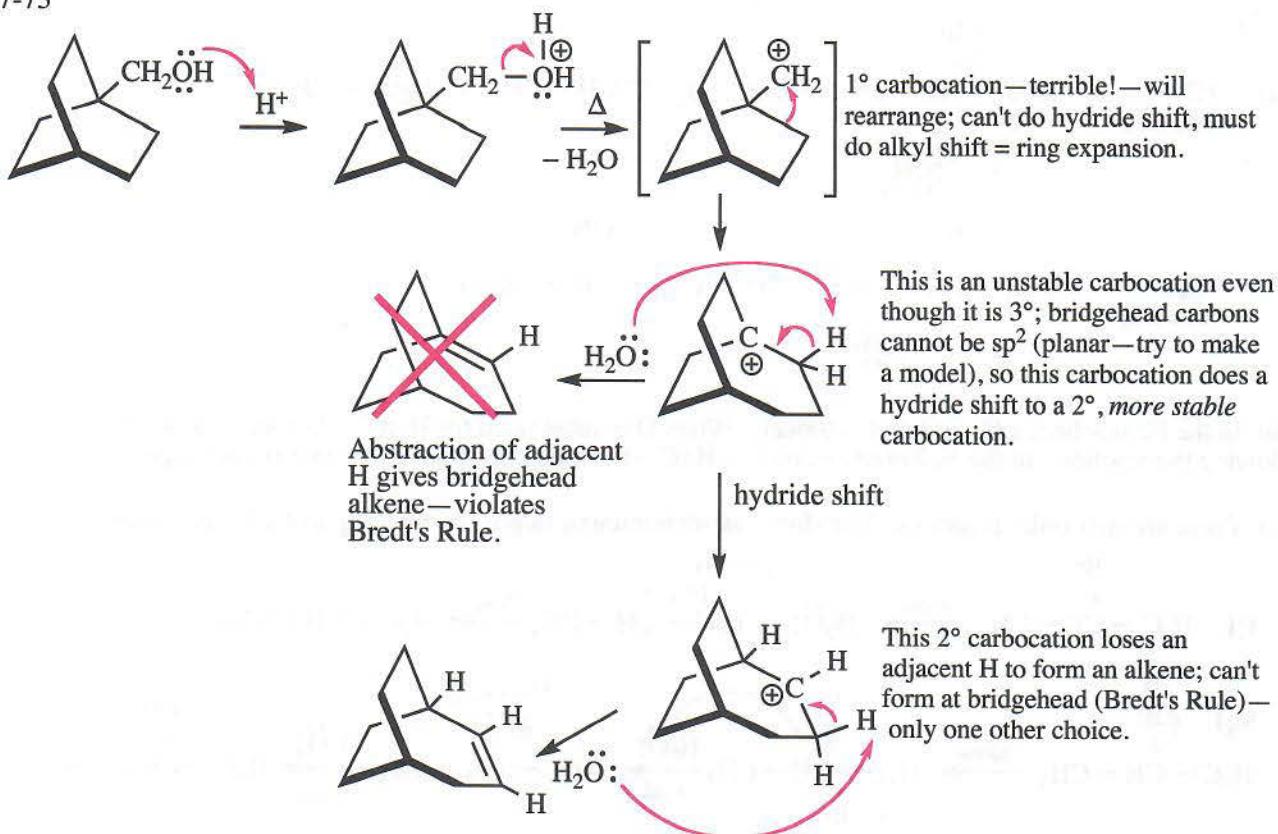


with rearrangement—alkyl shift—ring expansion

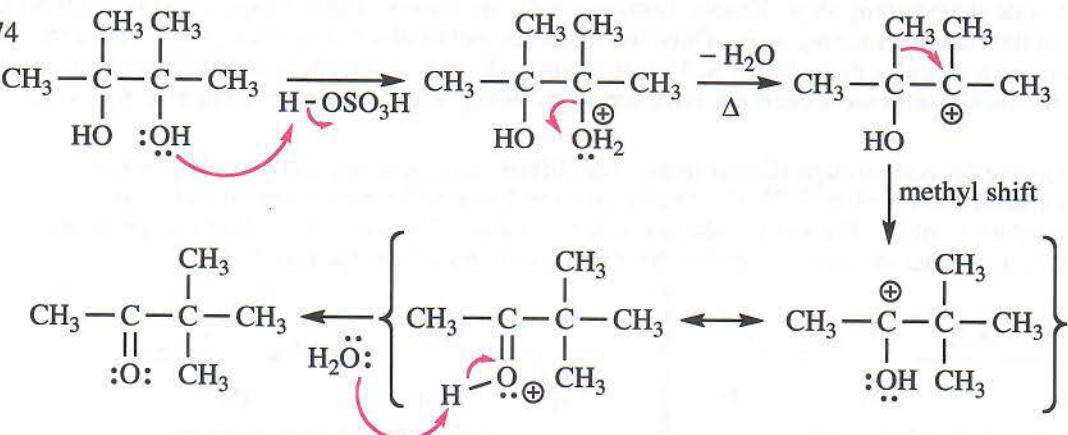


2° carbocation on  
5-membered ring—  
HOORAY!

7-73

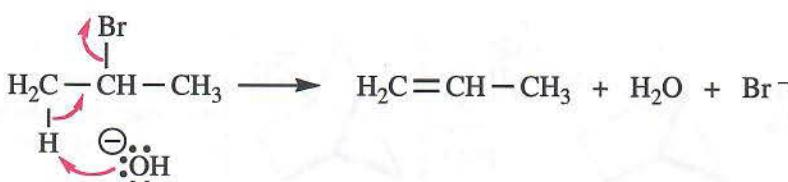
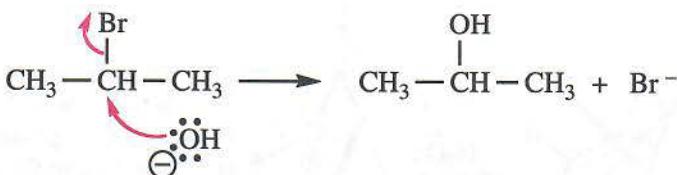


7-74



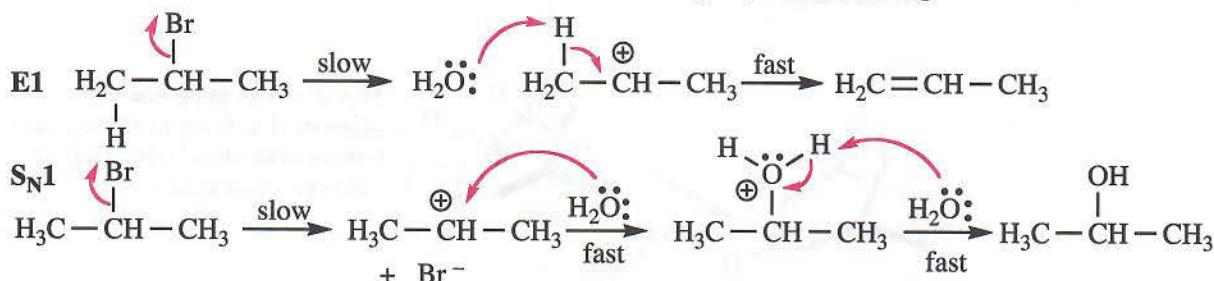
The driving force for this rearrangement is the great stability of the resonance-stabilized, protonated carbonyl group.

7-75

(a) E2—  
one step $\text{S}_{\text{N}}2$ —  
one step

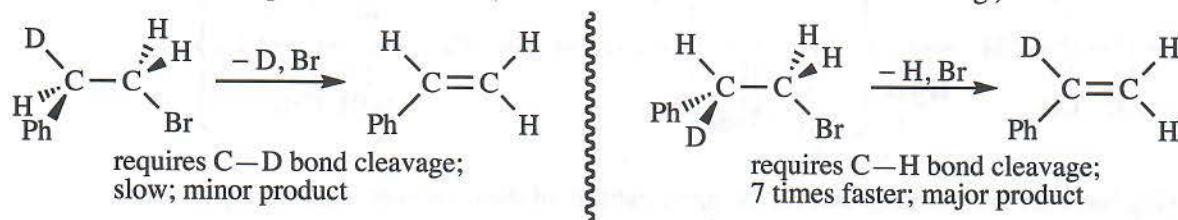
(b) In the E2 reaction, a C—H bond is broken. When D is substituted for H, a C—D bond is broken, slowing the reaction. In the  $\text{S}_{\text{N}}2$  reaction, no C—H (C—D) bond is broken, so the rate is unchanged.

(c) These are first-order reactions. The slow, rate-determining step is the first step in each mechanism.



The only mechanism of these two involving C—H bond cleavage is the E1, but the C—H cleavage does NOT occur in the slow, rate-determining step. Kinetic isotope effects are observed only when C—H (C—D) bond cleavage occurs in the rate-determining step. Thus, we would expect to observe *no change in rate* for the deuterium-substituted molecules in the E1 or  $\text{S}_{\text{N}}1$  mechanisms. (In fact, this technique of measuring isotope effects is one of the most useful tools chemists have for determining what mechanism a reaction follows.)

7-76 Both products are formed through E2 reactions. The difference is whether a D or an H is removed by the base. As explained in Problem 7-75, C—D cleavage can be up to 7 times slower than C—H cleavage, so the product from C—H cleavage should be formed about 7 times as fast. This rate preference is reflected in the 7 : 1 product mixture. ("Ph" is the abbreviation for a benzene ring.)

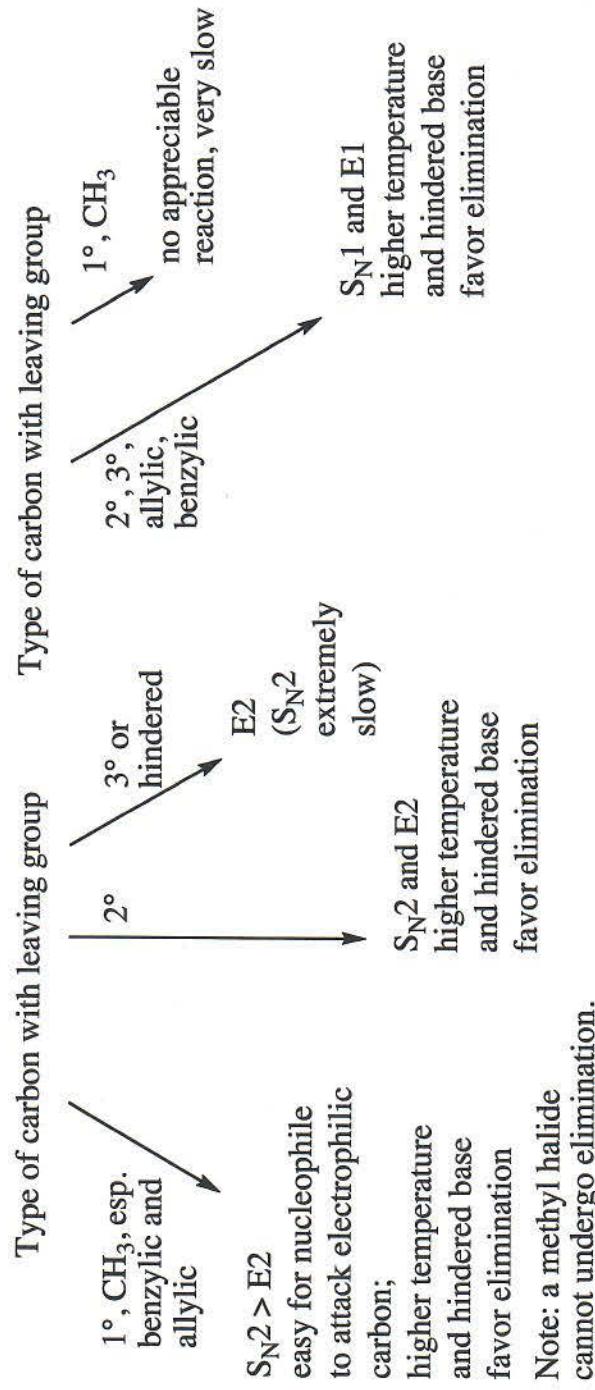


Note to the student: The most common question from students studying Chapter 7 material is: How do I know whether a reaction will follow an S<sub>N</sub>1, S<sub>N</sub>2, E1, or E2 mechanism? The answer is not always simple even for experienced chemists, and mixtures of substitution and elimination products are typical. Here are some generalizations that can provide guidelines about how to make reasonable predictions. Most instructors have their own version of this "concept map"; this one was modified from one of my colleagues, Dr. Hima Joshi, who has permitted its use here.

## HOW TO PREDICT S<sub>N</sub> VS. E MECHANISMS

Is the base/nucleophile strong or weak?

(like HO<sup>-</sup> or RO<sup>-</sup>)    STRONG  
Second order: S<sub>N</sub>2, E2



**Students:** use this space for notes or to solve problems.

## WORD PROBLEMS

Some problems require more than one step.

1. A school has 100 students. If each student needs 2 pencils, how many pencils does the school need?

2. A school has 100 students. If each student needs 2 pencils, how many pencils does the school need?

3. A school has 100 students. If each student needs 2 pencils, how many pencils does the school need?

4. A school has 100 students. If each student needs 2 pencils, how many pencils does the school need?

5. A school has 100 students. If each student needs 2 pencils, how many pencils does the school need?

6. A school has 100 students. If each student needs 2 pencils, how many pencils does the school need?

7. A school has 100 students. If each student needs 2 pencils, how many pencils does the school need?

8. A school has 100 students. If each student needs 2 pencils, how many pencils does the school need?

9. A school has 100 students. If each student needs 2 pencils, how many pencils does the school need?

10. A school has 100 students. If each student needs 2 pencils, how many pencils does the school need?

11. A school has 100 students. If each student needs 2 pencils, how many pencils does the school need?

12. A school has 100 students. If each student needs 2 pencils, how many pencils does the school need?

13. A school has 100 students. If each student needs 2 pencils, how many pencils does the school need?

14. A school has 100 students. If each student needs 2 pencils, how many pencils does the school need?

15. A school has 100 students. If each student needs 2 pencils, how many pencils does the school need?

16. A school has 100 students. If each student needs 2 pencils, how many pencils does the school need?

17. A school has 100 students. If each student needs 2 pencils, how many pencils does the school need?

18. A school has 100 students. If each student needs 2 pencils, how many pencils does the school need?