

CHAPTER 9

Substitution and Elimination Reactions of Alkyl Halides

Important Terms

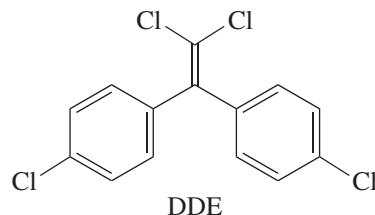
β-elimination reaction or 1,2-elimination reaction	an elimination reaction where the groups being eliminated are bonded to adjacent carbons.
anti elimination	an elimination reaction in which the substituents being eliminated are removed from opposite sides of the molecule.
anti-periplanar	substituents are attached to parallel bonds on opposite sides of a molecule.
aprotic solvent	a solvent that does not have a hydrogen bonded to an oxygen or to a nitrogen; some aprotic solvents are polar; others are nonpolar.
back-side attack	nucleophilic attack on the side of the carbon opposite the side bonded to the leaving group.
base	a substance that gains a proton.
basicity	the tendency of a compound to share its electrons with a proton.
bifunctional molecule	a molecule with two functional groups.
bimolecular reaction	a reaction in which two molecules are involved in the transition state of the rate-determining step.
complete racemization	formation of a pair of enantiomers in equal amounts.
dehydrohalogenation	elimination of a proton and a halide ion.
E1 reaction	a unimolecular elimination reaction.
E2 reaction	a bimolecular elimination reaction.
elimination reaction	a reaction that removes atoms or groups from the reactant to form a π bond.
first-order reaction	a reaction whose rate is proportional to the concentration of one reactant.
intermolecular reaction	a reaction that takes place between two molecules.
intimate ion pair	an ion pair that results when the covalent bond that joined the cation and anion has broken but the cation and anion are still next to each other.
intramolecular reaction	a reaction that takes place within a molecule.

inversion of configuration	turning the carbon inside out like an umbrella so that the resulting product has a configuration opposite that of the reactant.
ion-dipole interaction	the interaction between an ion and the dipole of a molecule.
kinetics	the field of chemistry that deals with the rates of chemical reactions.
leaving group	the group that is displaced in a substitution reaction.
nucleophile	an electron-rich atom or molecule.
nucleophilicity	a measure of how readily an atom or a molecule with a lone pair attacks another atom.
nucleophilic substitution reaction	a reaction in which a nucleophile substitutes for an atom or a group.
partial racemization	formation of a pair of enantiomers in unequal amounts.
protic solvent	a solvent that has a hydrogen bonded to an oxygen or to a nitrogen.
rate constant	the constant of proportionality in the rate law for a reaction; it describes how difficult it is to overcome the energy barrier of a reaction.
rate law	the equation that shows the relationship between the rate of a reaction and the concentration of the reactants.
regioselectivity	the preferential formation of a constitutional isomer.
sawhorse projection	a way to represent the three-dimensional spatial relationships of atoms by looking at the carbon–carbon bond from an oblique angle.
second-order reaction	a reaction whose rate is dependent on the concentration of two reactants.
S_N1 reaction	a unimolecular nucleophilic substitution reaction.
S_N2 reaction	a bimolecular nucleophilic substitution reaction.
solvent-separated ion pair	an ion pair that results when the cation and anion are separated by one or more solvent molecules.
solvolytic reaction	reaction with a solvent.
steric effects	effects due to the fact that groups occupy a certain volume of space.
steric hindrance	caused by bulky groups at the site of a reaction that make it difficult for the reactants to approach each other.
substitution reaction	a reaction that exchanges one substituent of a reactant for another.

syn elimination	an elimination reaction in which substituents being eliminated are removed from the same side of the molecule.
syn-periplanar	substituents are attached to parallel bonds on the same side of a molecule.
target molecule	the desired product of a synthesis.
unimolecular reaction	a reaction in which only one molecule is involved in the transition state of the rate-determining step.
Williamson ether synthesis	formation of an ether from the reaction of an alkoxide ion with an alkyl halide.
Zaitsev's rule	the rule that states that the more stable alkene product of an elimination reaction is obtained by removing a proton from the β -carbon that is bonded to the fewest hydrogens.

Solutions to Problems

1. DEE is formed when HCl is eliminated from DDT. (See the box on page 392.)



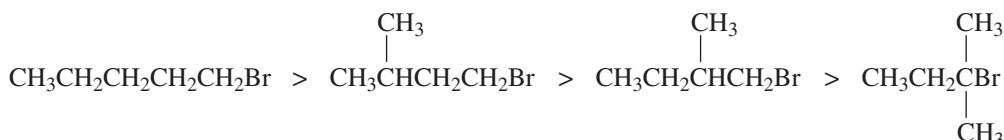
- 2.** Methoxychlor has methoxy groups in place of the chlorines on the benzene rings of DDT. The oxygen of the methoxy groups can form hydrogen bonds with water, making methoxychlor more soluble in water and, therefore, less soluble in fatty tissues.

$$\text{rate} = k [\text{alkyl halide}] [\text{nucleophile}]$$

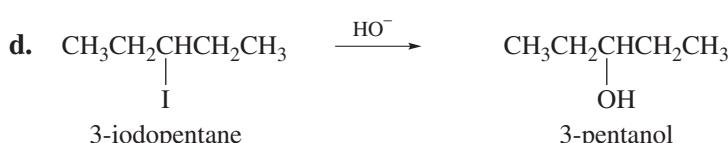
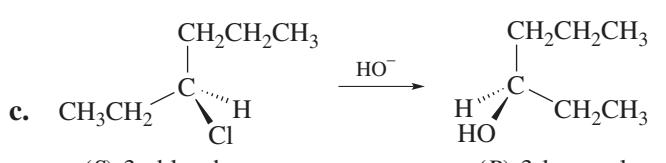
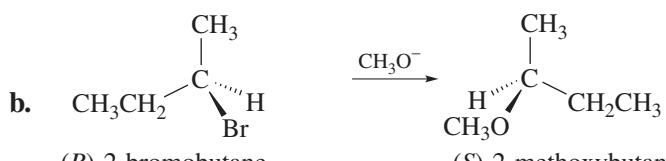
original: rate = $k[1.0][1.0]$

- a. rate = $k [1.0][3.0] = 3.0$ The rate is tripled.
 - b. rate = $k [0.50][1.0] = 0.50$ The rate is cut in half.
 - c. rate = $k [0.5][2.0] = 1.0$ The rate is not changed.

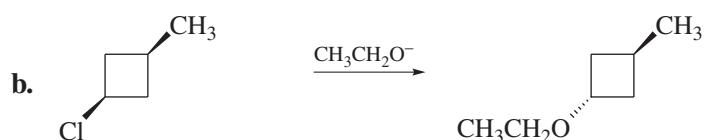
4. Increasing the height of the energy barrier decreases the magnitude of the rate constant; this causes the reaction to be slower.
 5. The closer the methyl group is to the site of nucleophilic attack, the greater the steric hindrance to nucleophilic attack and the slower the rate of the reaction.

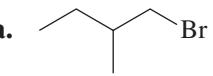


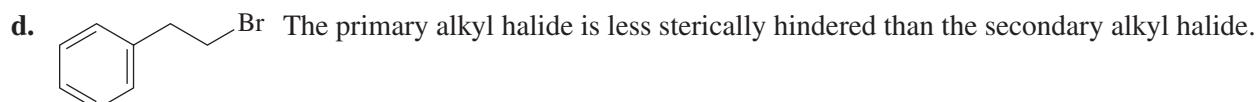
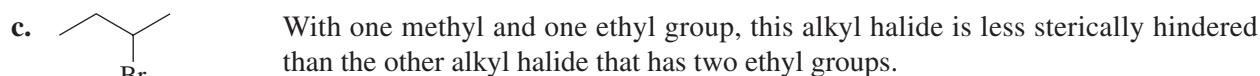
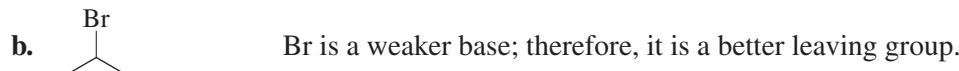
- 6.** a. Solved in the text.



7. Solved in the text.



9. a.  The primary alkyl halide is less sterically hindered than the secondary alkyl halide (the CH_3 group is farther away from the back side of the carbon attached to the Br).



10. A protic solvent has a hydrogen bonded to an oxygen or to a nitrogen, whereas an aprotic solvent does not have a hydrogen bonded to an oxygen or to a nitrogen.

a. aprotic b. aprotic c. protic d. aprotic

11. a. RO^- , because ROH is a weaker acid than RSH since the hydrogen is attached to a smaller atom.

b. RS^- , because it is less well solvated by water and sulfur is more polarizable than oxygen.

c. RO^- , because, although they differ in size, they are in an aprotic solvent. Remember that the stronger base is always the better nucleophile in an aprotic solvent.

12. Remember that the stronger base is always the better nucleophile unless they differ in size *and* they are in a protic solvent.

a. They differ in size, and because they are in a protic solvent, the larger one (Br^-) is the better nucleophile.

b. They differ in size, and because they are in an aprotic solvent, the stronger base (Cl^-) is the better nucleophile.

c. Because the oxygen is negatively charged, CH_3O^- is the better nucleophile.

d. Because the oxygen is negatively charged, CH_3O^- is the better nucleophile.

e. Because H_2O is a stronger acid than NH_3 , NH_2^- is the stronger base and the better nucleophile.

f. Because H_2O is a stronger acid than NH_3 , NH_2^- is the stronger base and the better nucleophile.

g. They differ in size and, because they are in a protic solvent, the larger one (I^-) is the better nucleophile.

h. They differ in size and, because they are in an aprotic solvent, the stronger base (Br^-) is the better nucleophile.

13. Solved in the text.

14. a. $\text{CH}_3\text{CH}_2\text{Br} + \text{HO}^-$ HO^- is a better nucleophile than H_2O .
 b. $\text{CH}_3\underset{\text{CH}_3}{\text{CH}}\text{CH}_2\text{Br} + \text{HO}^-$ This alkyl halide has less steric hindrance toward nucleophilic attack.
 c. $\text{CH}_3\text{CH}_2\text{Cl} + \text{CH}_3\text{S}^-$ CH_3S^- is a better nucleophile than CH_3O^- in a protic solvent (a solvent that can form hydrogen bonds).
 d. $\text{CH}_3\text{CH}_2\text{Br} + \text{I}^-$ Br^- is a weaker base than Cl^- , so Br^- is a better leaving group.

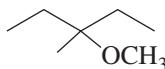
15. These are all $\text{S}_{\text{N}}2$ reactions.

- a. $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$
 b. $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CCH}_3$
 c. $\text{CH}_3\text{CH}_2\overset{+}{\text{N}}(\text{CH}_3)_3 \text{ Br}^-$
 d. $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$

16. Solved in the text.

17. a. Reaction of an alkyl halide with ammonia gives a low yield of primary amine, because as soon as the primary amine is formed, it can react with another molecule of alkyl halide to form a secondary amine; the secondary amine can react with the alkyl halide to form a tertiary amine, which can then react with an alkyl halide to form a quaternary ammonium salt. (See Problem 16 on page 404.)
 b. The alkyl azide is not treated with hydrogen until after all the alkyl halide has reacted with azide ion. Therefore, when the primary amine is formed, there is no alkyl halide for it to react with to form a secondary amine.

18. a.



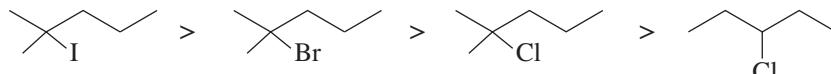
one product because the leaving group is not attached to an asymmetric center

b.

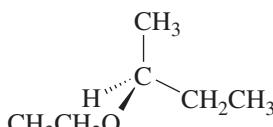


R and S because the leaving group is attached to an asymmetric center

19.

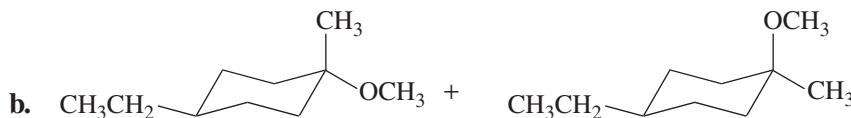


20. a.



The product has the inverted configuration compared to that of the reactant.

b.

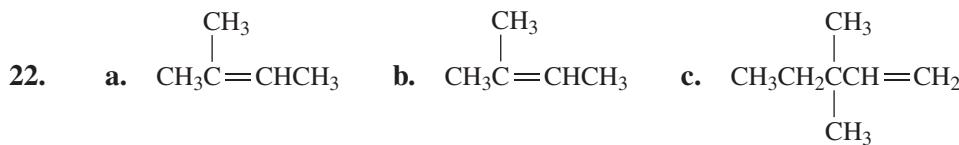


Once the tertiary carbocation forms, methanol can attack the sp^2 carbon from the top or bottom of the planar carbocation.

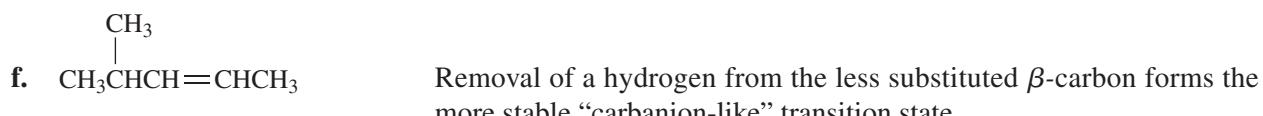
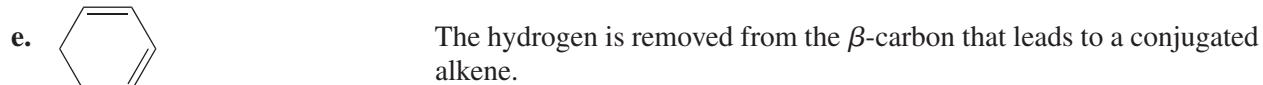
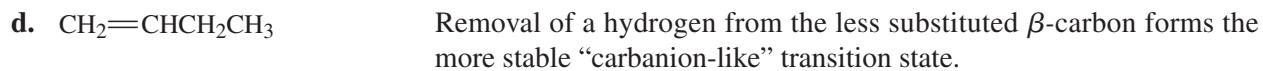
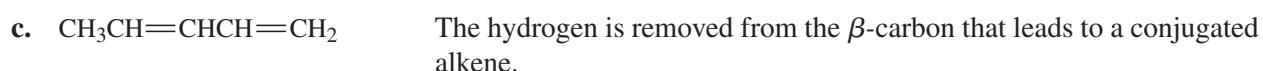
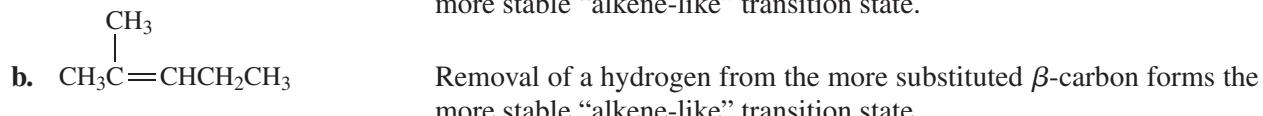
21. The rate of an S_N1 reaction is not affected by increasing the concentration of the nucleophile, whereas the rate of an S_N2 reaction is increased when the concentration of the nucleophile is increased. Therefore, we first have to determine whether the reactions are S_N1 or S_N2 reactions.

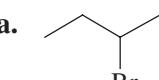
- A is an S_N2 reaction because the reactant is a secondary alkyl halide (and the configuration of the product is inverted compared to that of the reactant).
- B is an S_N2 reaction because the reactant is a primary alkyl halide.
- C is an S_N1 reaction because the reactant is a tertiary alkyl halide.

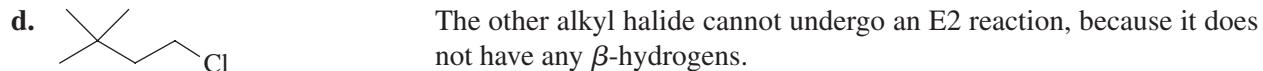
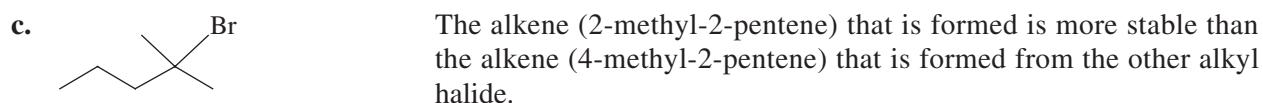
Because they are S_N2 reactions, the rate of A and B increases if the concentration of the nucleophile is increased. Because it is an S_N1 reaction, the rate of C does not change if the concentration of the nucleophile is increased.

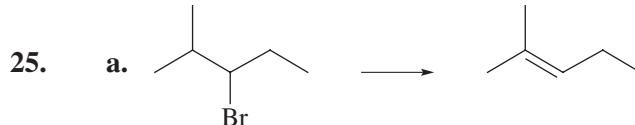


23. a. $\text{CH}_3\text{CH}=\text{CHCH}_3$ Removal of a hydrogen from the more substituted β -carbon forms the more stable “alkene-like” transition state.

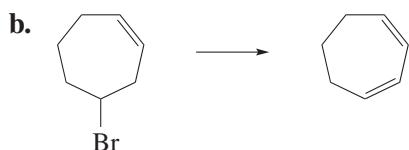


24. a.  The alkene (2-butene) that is formed is more stable than the alkene (1-butene) that is formed from the other alkyl halide.





It forms the more stable alkene (the alkene with the most substituents bonded to the sp^2 carbons), so it has the more stable transition state.



It forms the more stable alkene (the double bonds are conjugated, so it has the more stable transition state).

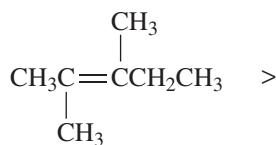
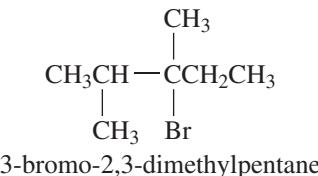


It has four hydrogens that can be removed to form an alkene with two substituents on the sp^2 carbons, so it has a greater probability of having an effective collision with the nucleophile than the other alkyl halide that has only two such hydrogens.

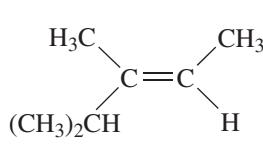


It forms the more stable alkene (the new double bond is conjugated with the phenyl substituent), so it has the more stable transition state.

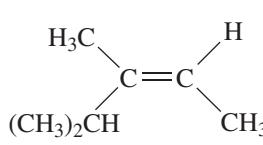
26.



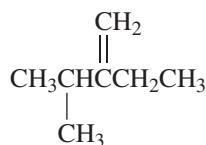
Four alkyl substituents are bonded to the sp^2 carbons.



Three alkyl substituents are bonded to the sp^2 carbons; the largest groups are on opposite sides of the double bond.



Three alkyl substituents are bonded to the sp^2 carbons; the largest groups are on the same side of the double bond.

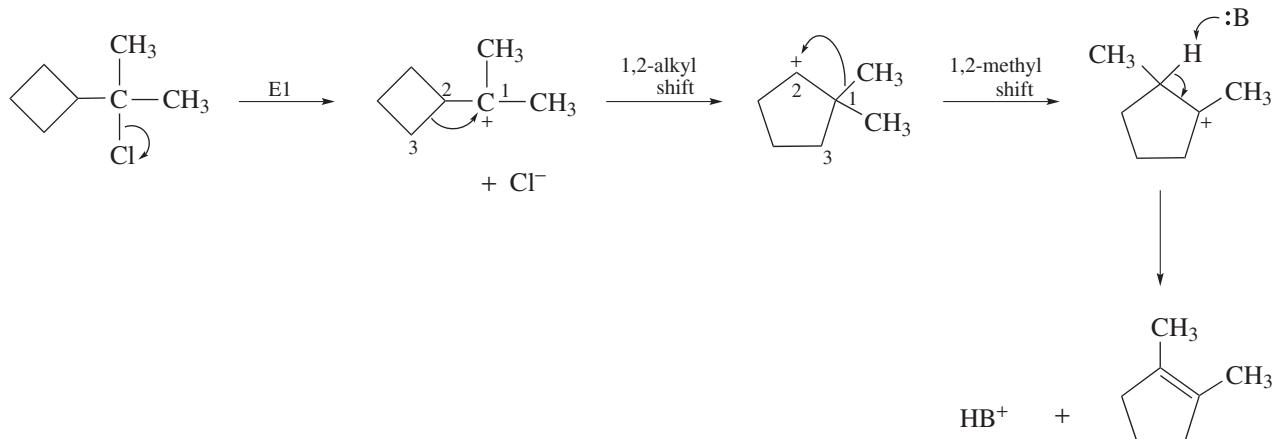


Two alkyl substituents are bonded to the sp^2 carbons.

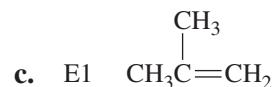
27. The major product is the one predicted by Zaitsev's rule, because the fluoride ion dissociates in the first step, forming a carbocation. Loss of a proton from the carbocation follows Zaitsev's rule, as it does in other E1 reactions.

- 28.
- B because it forms the more stable carbocation.
 - B because it forms the more stable alkene.
 - B because it forms the more stable carbocation.
 - A because it is less sterically hindered.

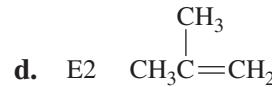
29. A tertiary carbocation with a strained four-membered ring is less stable than a secondary carbocation with an unstrained five-membered ring, so a carbocation rearrangement occurs. A second carbocation rearrangement forms a tertiary carbocation.



30. a. E2 $\text{CH}_3\text{CH}=\text{CHCH}_3$



- b. E2 $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$

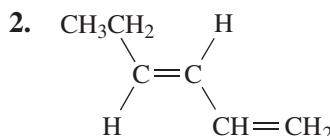


31. Solved in the text.

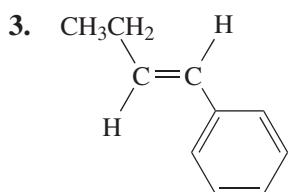
$$\frac{\text{E2}}{\text{E2} + \text{E1}} = \frac{7.1 \times 10^{-5} \times 2.5 \times 10^{-3}}{7.1 \times 10^{-5} \times 2.5 \times 10^{-3} + 1.50 \times 10^{-5}} = \frac{1.78 \times 10^{-7}}{1.78 \times 10^{-7} + 150 \times 10^{-7}} = \frac{1.78}{152} = 1.2\%$$

33. a. 1. $\text{CH}_3\text{CH}_2\text{CH}=\overset{\text{CH}_3}{\underset{|}{\text{C}}}=\text{CH}_3$

No stereoisomers are possible because there are two methyl groups on one of the sp^2 carbons.



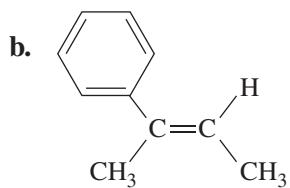
The major product is the conjugated diene with the larger group bonded to one sp^2 carbon on the opposite side of the double bond from the larger group bonded to the other sp^2 carbon.



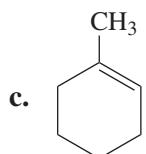
The major product is the conjugated alkene with the larger group bonded to one sp^2 carbon on the opposite side of the double bond from the larger group bonded to the other sp^2 carbon.

- b. In none of the reactions is the major product dependent on whether you start with the *R* or *S* enantiomer of the reactant.

34. Solved in the text.



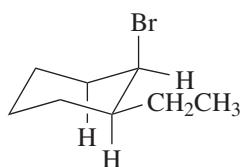
The larger substituent attached to one sp^2 carbon and the larger substituent attached to the other sp^2 carbon are on opposite sides of the double bond.



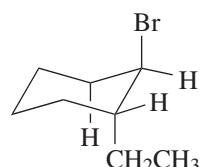
36. E2 elimination reactions from six-membered rings occur only when the substituents to be eliminated are both in axial positions.

In the cis isomer, when Br is in an axial position, there is an axial hydrogen on each of the adjacent carbons. The one bonded to the same carbon as the ethyl group is more apt to be the one eliminated with Br because the product formed is more stable and, therefore, more easily formed than the product formed when the other H is eliminated with Br. (Recall that when there is a choice, a hydrogen is removed from the β -carbon bonded to the fewest hydrogens.)

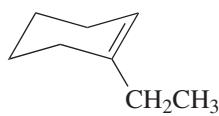
In the trans isomer, when Br is in an axial position, there is an axial hydrogen on only one adjacent carbon, and it is not the carbon that is bonded to the ethyl group. Therefore, a different product is formed. (Notice in this case there is no choice; there is only one hydrogen bonded by an axial bond to a β -carbon.)



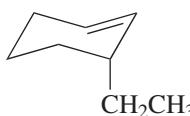
cis-1-bromo-2-ethylcyclohexane



trans-1-bromo-2-ethylcyclohexane



1-ethylcyclohexene

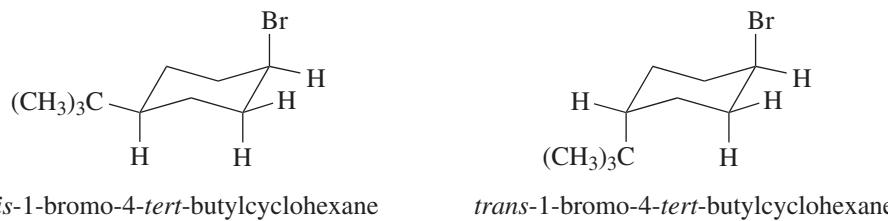


3-ethylcyclohexene

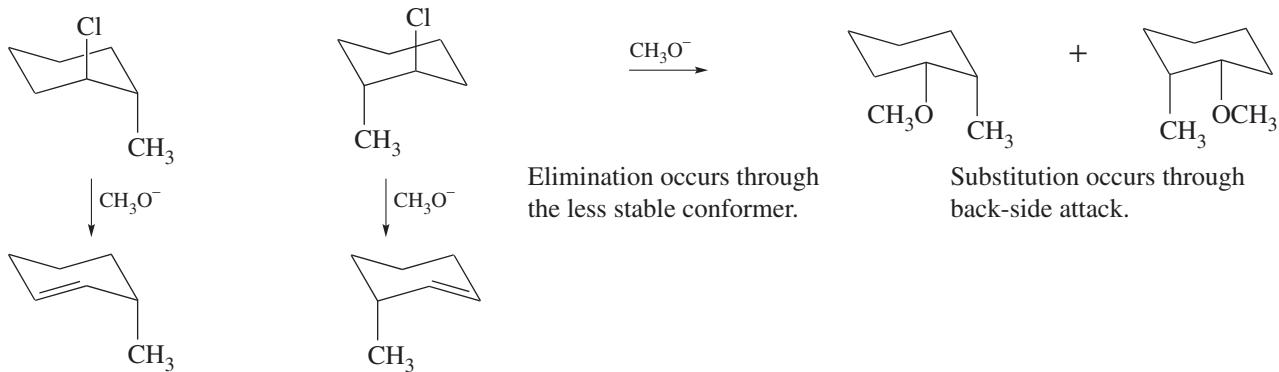
37. In order for a six-membered ring to undergo an E2 reaction, the substituents that are to be eliminated must both be in axial positions.

When bromine and an adjacent hydrogen are both in axial positions, the large *tert*-butyl substituent is in an equatorial position in the cis isomer and in an axial position in the trans isomer. The rate constant for the reaction is $k'K_{eq}$.

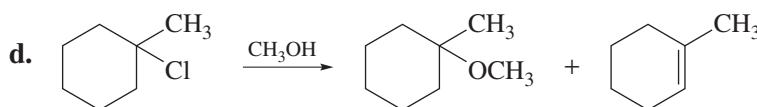
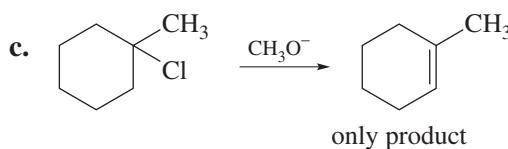
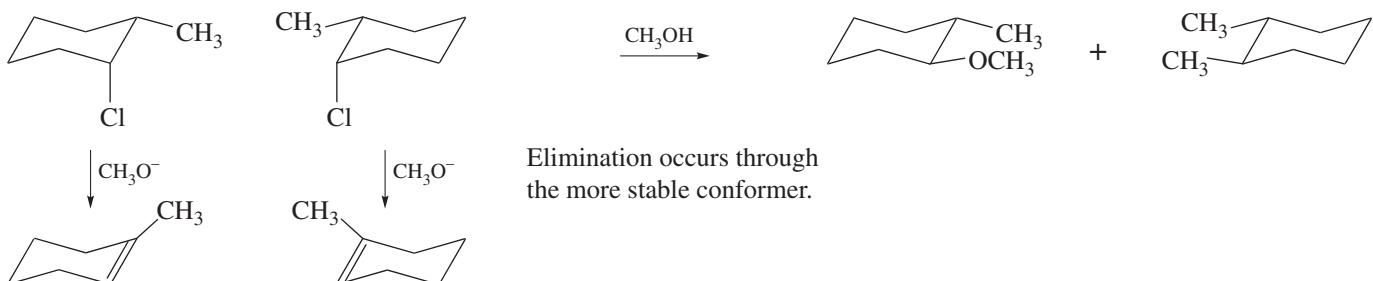
Because a large substituent is more stable in an equatorial position than in an axial position, elimination of the cis isomer occurs through its more stable chair conformer (K_{eq} is large; see page 427 of the text), whereas elimination of the trans isomer has to occur through its less stable chair conformer (K_{eq} is small). The cis isomer, therefore, reacts more rapidly in an E2 reaction.



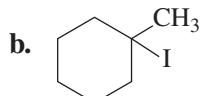
38. a. *trans*-1-Chloro-2-methylcyclohexane has two stereoisomers, and each forms a substitution product and an elimination product. Notice that the substitution products and the elimination products are enantiomers.



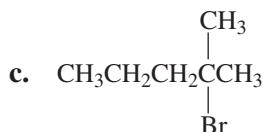
- b. *cis*-1-Chloro-2-methylcyclohexane has two stereoisomers, and each forms a substitution product and an elimination product. Notice that the substitution products and the elimination products are enantiomers.



39. a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ This compound has less steric hindrance.



I^- is a better leaving group (weaker base) than Br^- .

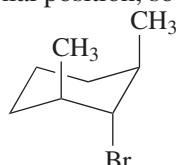


The tertiary alkyl halide because a secondary alkyl halide does not undergo $\text{S}_{\text{N}}1$ reactions.

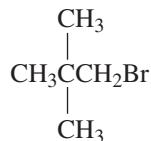
40. The reaction of an alkyl halide with an acetylide ion is an $\text{S}_{\text{N}}2$ reaction. Methyl and primary alkyl halides work best because they have the least steric hindrance to back-side attack. In addition, primary alkyl halides form mainly the desired substitution product and methyl halides form only the desired substitution product.

41. Because CH_3S^- is a better nucleophile in the protic polar solvent and a weaker base than CH_3O^- , the ratio of substitution (where Y^- reacts as a nucleophile) to elimination (where Y^- reacts as a base) increases when the nucleophile is changed from CH_3O^- to CH_3S^- .

42. In order to undergo an E2 reaction, the substituents to be eliminated (H and Br) must both be in axial positions. Drawing the compound in the chair conformation shows that when Br is in an axial position, neither of the adjacent β -carbons has a hydrogen in an axial position, so an elimination reaction cannot take place.



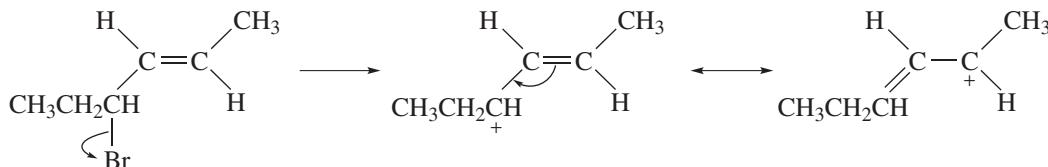
- 43.



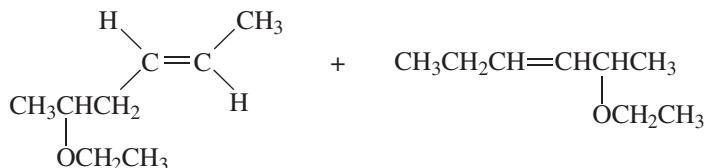
1-bromo-2,2-dimethylpropane

- a. The bulky *tert*-butyl substituent blocks the back side of the carbon bonded to the bromine to nucleophilic attack, making an $\text{S}_{\text{N}}2$ reaction difficult. An $\text{S}_{\text{N}}1$ reaction cannot occur because it requires formation of an unstable primary carbocation.
 b. It cannot undergo an E2 reaction, because the β -carbon is not bonded to a hydrogen.
 It cannot undergo an E1 reaction, because that requires the formation of a primary carbocation.

44. a. *trans*-4-Bromo-2-hexene (the compound on the right) is more reactive, because the carbocation that is formed is stabilized by electron delocalization. (It is a secondary allylic cation.) The other alkyl halide is a secondary alkyl halide and does not undergo an $\text{S}_{\text{N}}1$ reaction.

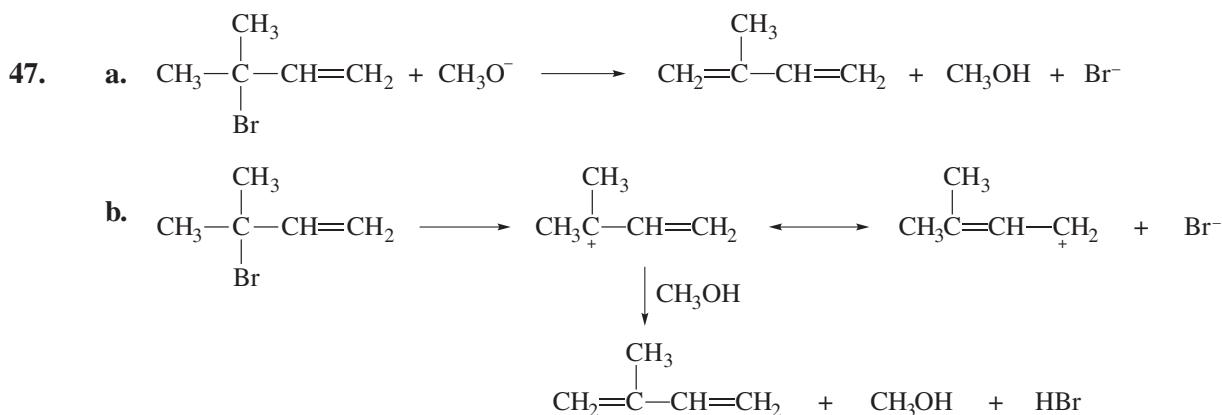


- b. For the compound on the left, a racemic mixture of the following compound would form.
The alkyl halide on the left does not undergo an S_N1 reaction.



45. Conjugated double bonds are more stable and, therefore, are easier to form than isolated double bonds.

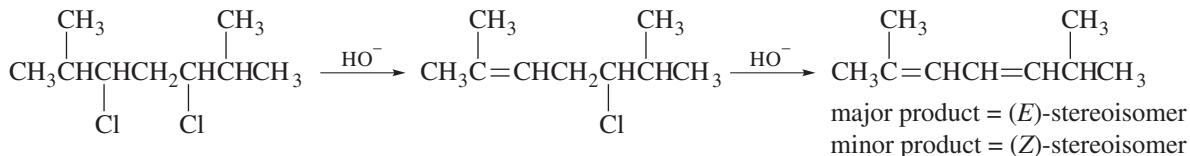
- a. b. c. $\text{CH}_2=\text{CHCH}(\text{CH}_3)=\text{CCH}_3$
46. a. c. $\text{CH}_2=\text{CHCH}(\text{CH}_3)=\text{CCH}_3 + \text{CH}_3\text{CH}=\text{CHC}(\text{CH}_3)=\text{CH}_2$
- b. The secondary alkyl halide does not undergo an E1 reaction.

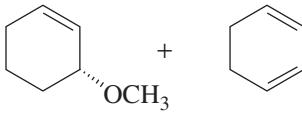
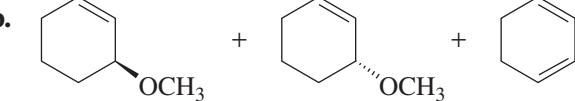


Only one elimination product is formed because elimination from the other resonance contributor would form a cumulated diene, which is much less stable and, therefore, much harder to form than a conjugated diene.

48. a. An aryl halide cannot undergo an S_N1 reaction because an aryl cation is too unstable to form.
- b. A vinyl halide cannot undergo an S_N1 reaction because a vinyl cation is too unstable to form.
49. a. An aryl halide cannot undergo an S_N2 reaction because it cannot undergo back-side attack.
- b. A vinyl halide cannot undergo an S_N2 reaction because it cannot undergo back-side attack.

- 50.** Because a cumulated diene is less stable than an alkyne, the transition state for its formation is less stable than that for the formation of the alkyne, so the cumulated diene is harder to make.
- 51.** Solved in the text.
- 52.** In the first elimination reaction, a hydrogen will be removed from the β -carbon bonded to the fewest hydrogens as expected. In the second elimination reaction, a hydrogen will be removed from the β -carbon that results in the formation of a conjugated double bond.



- 53.** a. 
- b. 

- 54.** Because both reactants in the rate-limiting step are neutral, the reaction will be faster if the polarity of the solvent is increased.
- 55.** a. Increasing the polarity decreases the rate of the reaction because the concentration of charge on the reactants is greater (the reactants are charged) than the concentration of charge on the transition state.
- b. Increasing the polarity decreases the rate of the reaction because the concentration of charge on the reactants is greater (the reactants are charged) than the concentration of charge on the transition state.
- c. Increasing the polarity increases the rate of the reaction because the concentration of charge on the reactants is less (the reactants are not charged) than the concentration of charge on the transition state.

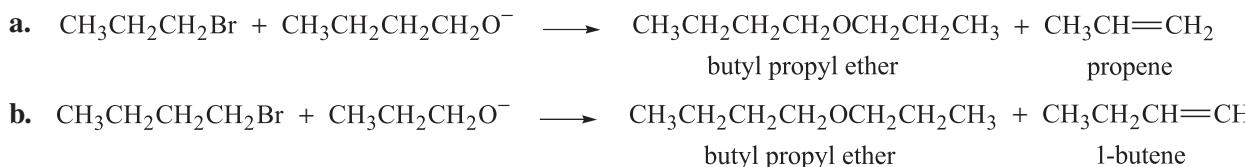
- 56.** a. $\text{CH}_3\text{Br} + \text{HO}^- \longrightarrow \text{CH}_3\text{OH} + \text{Br}^-$
 HO^- is a better nucleophile than H_2O .
- b. $\text{CH}_3\text{I} + \text{HO}^- \longrightarrow \text{CH}_3\text{OH} + \text{I}^-$
 I^- is a better leaving group than Cl^- .
- c. $\text{CH}_3\text{Br} + \text{NH}_3 \longrightarrow \text{CH}_3\text{NH}_3^+ + \text{Br}^-$
 NH_3 is a better nucleophile than H_2O .
- d. $\text{CH}_3\text{Br} + \text{HO}^- \xrightarrow{\text{DMSO}} \text{CH}_3\text{OH} + \text{Br}^-$
Unlike ethyl alcohol, DMSO does not stabilize the nucleophile (and, therefore, decrease the rate of the reaction) by hydrogen bonding.
- e. $\text{CH}_3\text{Br} + \text{NH}_3 \xrightarrow{\text{EtOH}} \text{CH}_3\text{NH}_3^+ + \text{Br}^-$
A more polar solvent stabilizes the transition state more than it stabilizes the reactants. (EtOH is ethanol.)

57. Solved in the text.

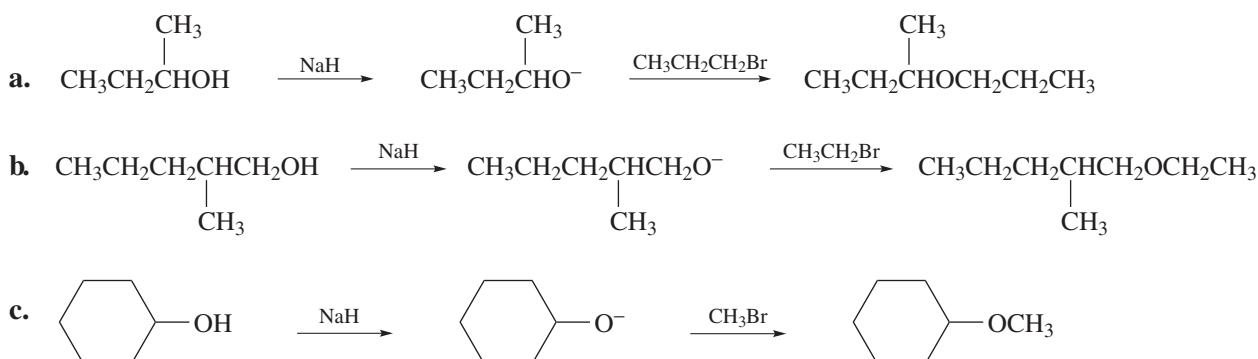
58. Acetate ion is a better nucleophile in dimethyl sulfoxide because dimethyl sulfoxide does not stabilize the negatively charged nucleophile by ion–dipole interactions, whereas methanol does stabilize it by ion–dipole interactions.

59. The only way the product with retention of configuration can be obtained is via an S_N1 reaction. An S_N1 reaction will be faster in the more polar solvent. So the reaction should be carried out in the 50% water/50% ethanol mixture.

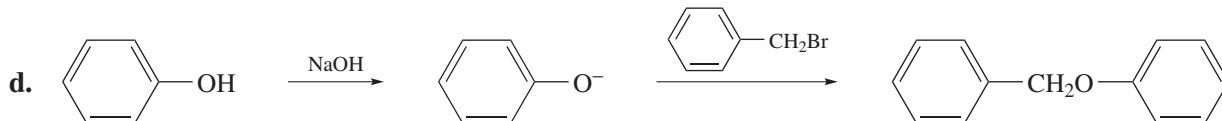
60. Because a strong base is used in the Williamson ether synthesis, the reaction is an S_N2 reaction, so a competing E2 reaction can also occur. The elimination product is a minor product because substitution is favored when the alkyl halide is primary.



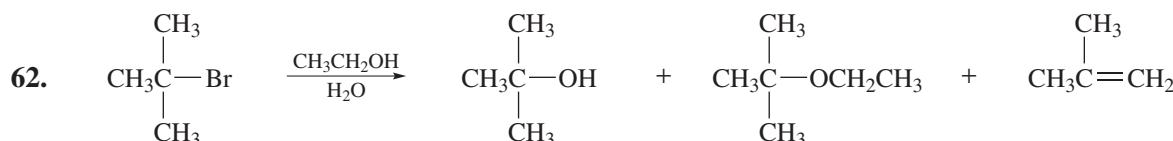
- 61.** To maximize the amount of ether formed in the S_N2 reaction, make sure the less hindered group is provided by the alkyl halide. In order to convert the alcohol ($pK_a \sim 15$) to an alkoxide ion in a reaction that favors products (in parts **a**, **b**, and **c**), a strong base (H^-) is needed.

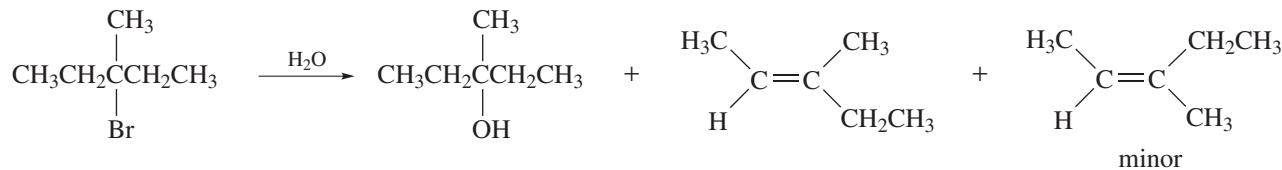
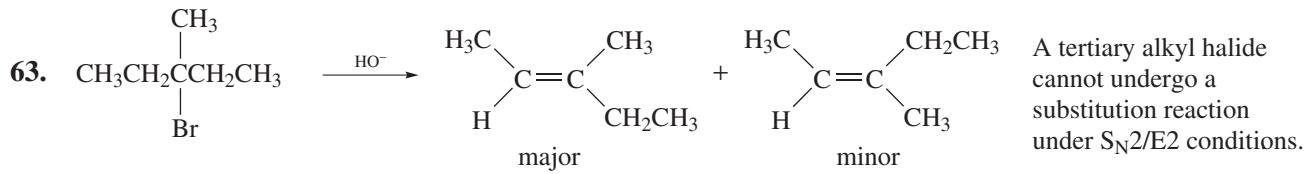


In part **d**, HO^- can be used to convert phenol ($\text{p}K_a \sim 15$) to phenoxide ion in a reaction that favors products, because phenol is a considerably stronger acid than an alcohol.

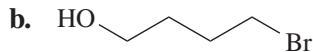


Remember that aryl halides cannot undergo S_N2 reactions.

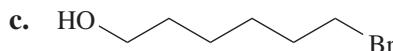




because it forms a six-membered ring, whereas the other compound would form a seven-membered ring. A seven-membered ring is more strained than a six-membered ring, so the six-membered ring is formed more easily. (See Table 3.8 on page 124 of the text.)

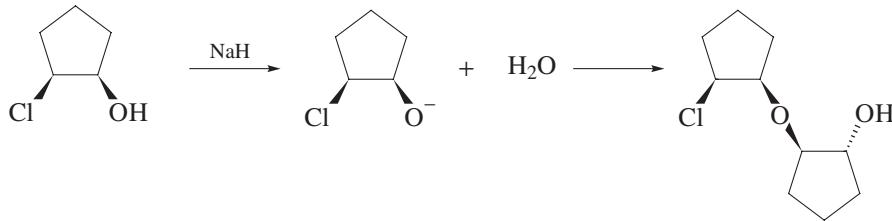


because it forms a five-membered ring, whereas the other compound would form a four-membered ring. A four-membered ring is more strained than a five-membered ring, so the five-membered ring is formed more easily.

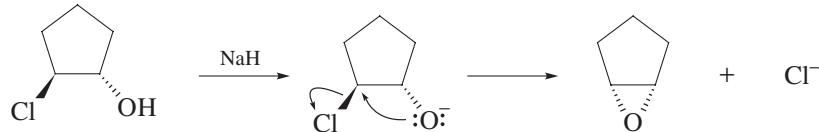


because it forms a seven-membered ring, whereas the other compound would form an eight-membered ring. An eight-membered ring is more strained than a seven-membered ring, so the seven-membered ring is formed more easily; also, the Br and OH in the compound that leads to the eight-membered ring are less likely to be in the proper position relative to each other for reaction because there are more bonds around which rotation to an unfavorable conformation can occur.

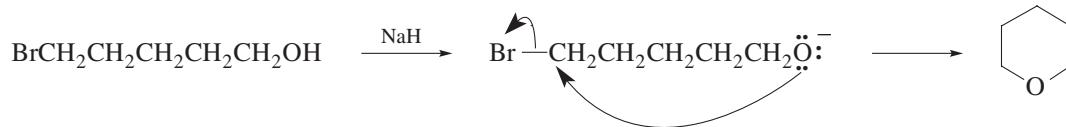
65. a. When hydride ion removes a proton from the OH group, the alkoxide ion cannot react in an intramolecular reaction with the alkyl chloride to form an epoxide, because it cannot reach the back side of the carbon attached to the chlorine. Therefore, the major product will result from an intermolecular reaction.



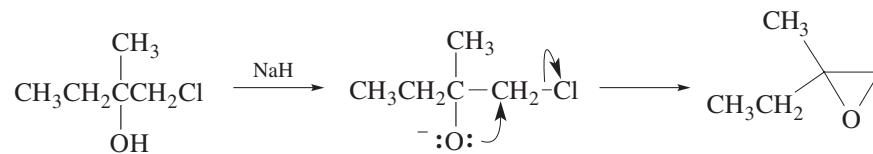
- b. Hydride ion removes a proton from the OH group more rapidly than it attacks the alkyl chloride. Once the alkoxide ion is formed, it attacks the back side of the alkyl chloride, forming an epoxide. (Removing a proton from an oxygen is always a fast reaction.)



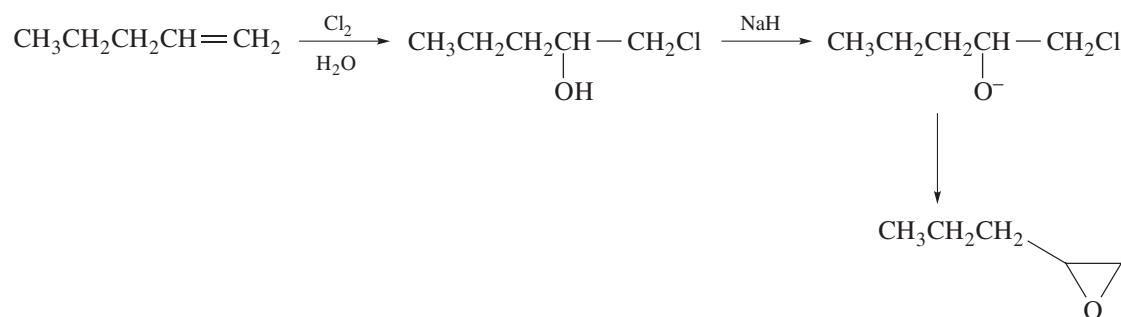
- c. Hydride ion removes a proton from the OH group and the alkoxide ion attacks the back side of the carbon attached to the bromine, forming a six-membered ring ether.



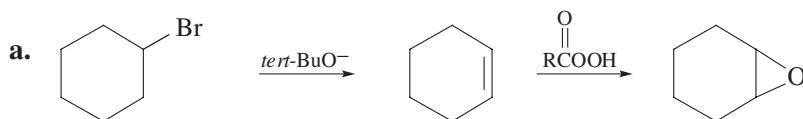
- d. Hydride ion removes a proton from the OH group and the alkoxide ion attacks the back side of the carbon attached to the chlorine, forming an epoxide.



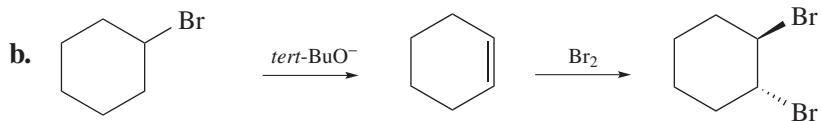
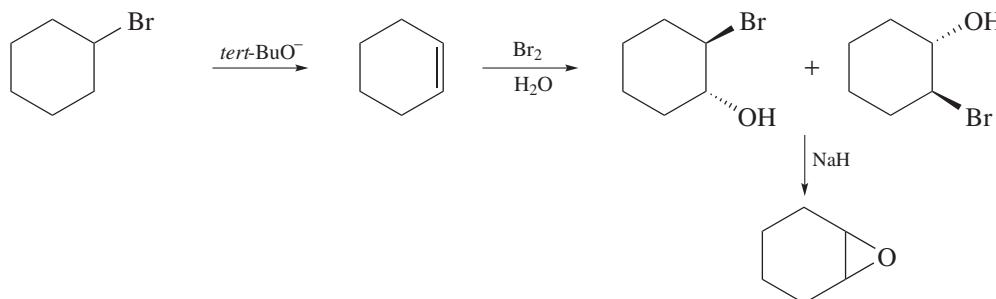
- e. After the halohydrin is formed, hydride ion removes a proton from the OH group and the alkoxide ion forms an epoxide.

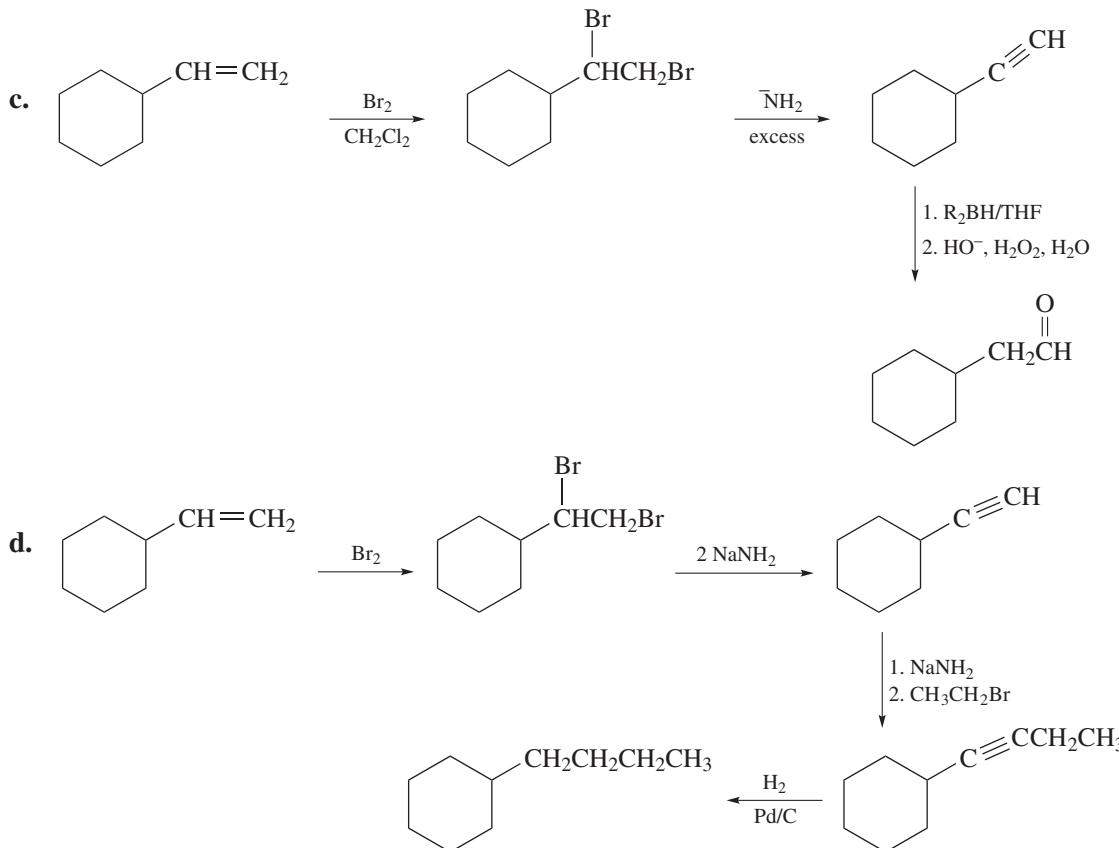


66. In parts **a** and **b**, a bulky base is used to encourage elimination over substitution.



or





67. a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ c. $\text{CH}_3\text{CH}_2\text{CH}_2\text{SCH}_3$ e. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3$
 b. $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ d. $\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$ f. $\text{CH}_3\text{CH}_2\text{CH}_2\overset{+}{\text{NH}_2}\text{CH}_3$

(Notice that the product in part c is not protonated because its pK_a is ~ -7 ; the product in f is protonated because its pK_a is ~ 11 . In part f, $\text{CH}_3\overset{+}{\text{NH}}(\text{CH}_2\text{CH}_2\text{CH}_3)_2$ and $\text{CH}_3\overset{+}{\text{N}}(\text{CH}_2\text{CH}_2\text{CH}_3)_3$ can also be formed, depending on the concentration of 1-bromopropane; see Problem 16 on page 404 of the text.)

68. If the atoms are in the same horizontal row of the periodic table, the stronger base is the better nucleophile. If the atoms are in the same column, the larger atom is the better nucleophile in the protic polar solvent because the solvent forms stronger hydrogen bonds with the smaller atom.

- a. HO^- c. H_2S e. I^-
 b. NH_3 d. HS^- f. Br^-

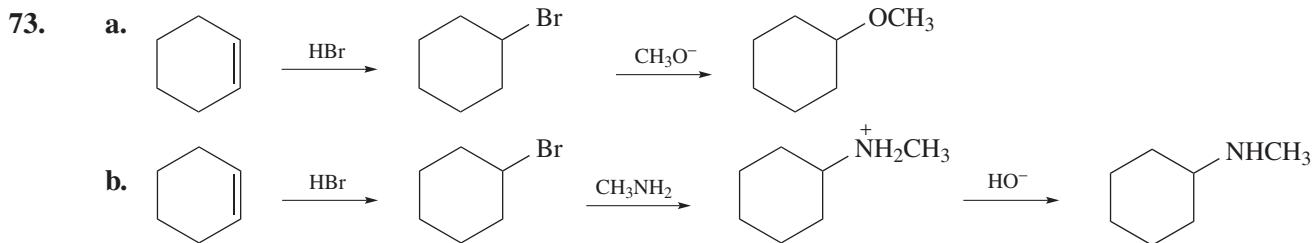
69. The weaker base is the better leaving group.

- a. H_2O c. H_2S e. I^-
 b. H_2O d. HS^- f. Br^-

70. a. HO^- c. CH_3NH_2 e. $\text{CH}_3\text{CH}_2\text{S}^-$ g. $\text{C}\equiv\text{N}^-$
 b. CH_3O^- d. HS^- f. $\text{CH}_3\overset{\text{O}}{\parallel}\text{CO}^-$ h. $\text{CH}_3\text{CH}_2\text{C}\equiv\text{C}^-$

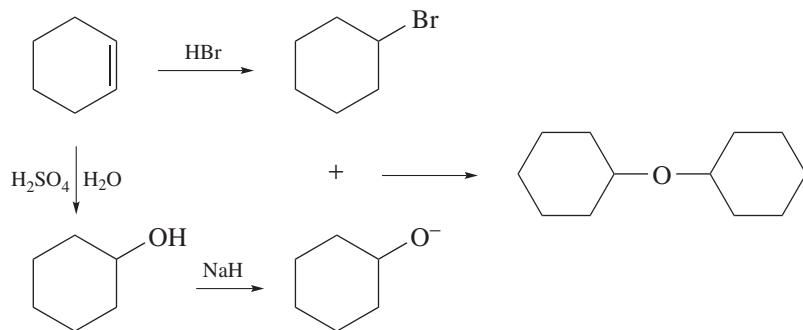
In part c, a tertiary amine and a quaternary ammonium ion can also form unless a large excess of CH_3NH_2 is used. (See Problem 16 on page 404 of the text.)

71. a. The rate will be increased nine-fold.
 b. The reaction will be slower because of the more polar solvent.
 c. The reaction will be slower because the leaving group will be poorer.
 d. The reaction will be slower because there will be more steric hindrance.
72. a. The reaction will be slower because the leaving group is poorer.
 b. The reaction will be slower because it will be an S_N2 reaction with a poor nucleophile, and the leaving group is poorer.



(A large excess of methylamine has to be used in the second step to minimize the formation of a tertiary amine and a quarternary ammonium ion.)

- c. Half of the cyclohexene is converted to bromocyclohexane, and half is converted to an alkoxide ion. The ether is formed from the reaction of bromocyclohexane with the alkoxide ion.

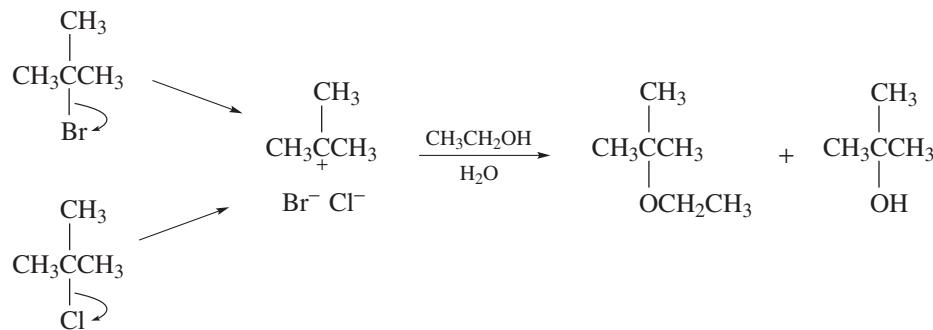


74. a. $\text{CH}_3\text{CH}_2\text{S}^- > \text{CH}_3\text{CH}_2\text{O}^- > \text{CH}_3\text{CO}^-$ c. $\text{NH}_3 > \text{H}_2\text{O}$
 b. $\text{C}_6\text{H}_5\text{O}^- > \text{C}_6\text{H}_5\text{OH}$ d. $\text{I}^- > \text{Br}^- > \text{Cl}^-$

75. The pK_a will increase (it will be a weaker acid) because of a decreased tendency to form a charged species in a less polar solvent. (See Problem 57 on page 442.)

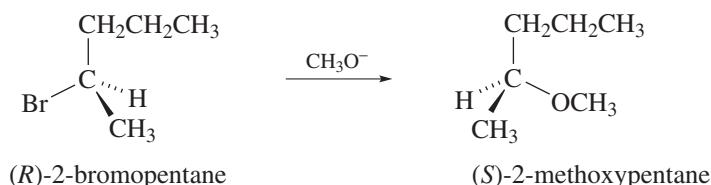
76.

a. CH

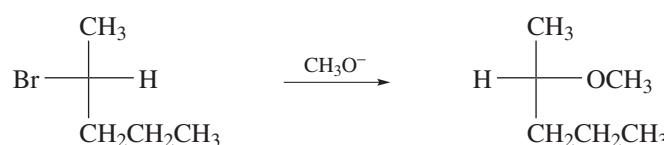


b. The products are obtained as a result of the nucleophiles reacting with the carbocation. 2-Bromo-2-methylpropane and 2-chloro-2-methylpropane form the same carbocation, so both alkyl halides form the same products.

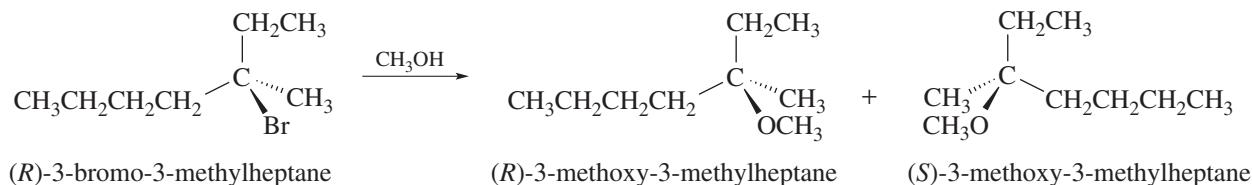
77. a. The S_N2 reaction takes place with inversion of configuration.



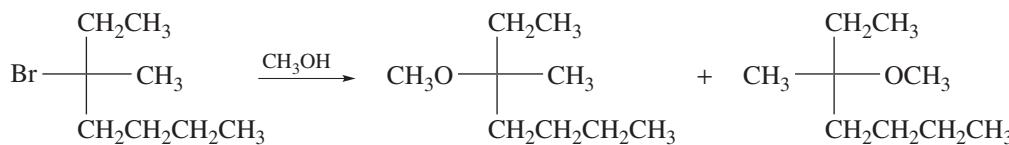
or



b. The S_N1 reaction takes place with inversion of configuration.



or



c.  $\xrightarrow{\text{CH}_3\text{CH}_2\text{OH}}$ 

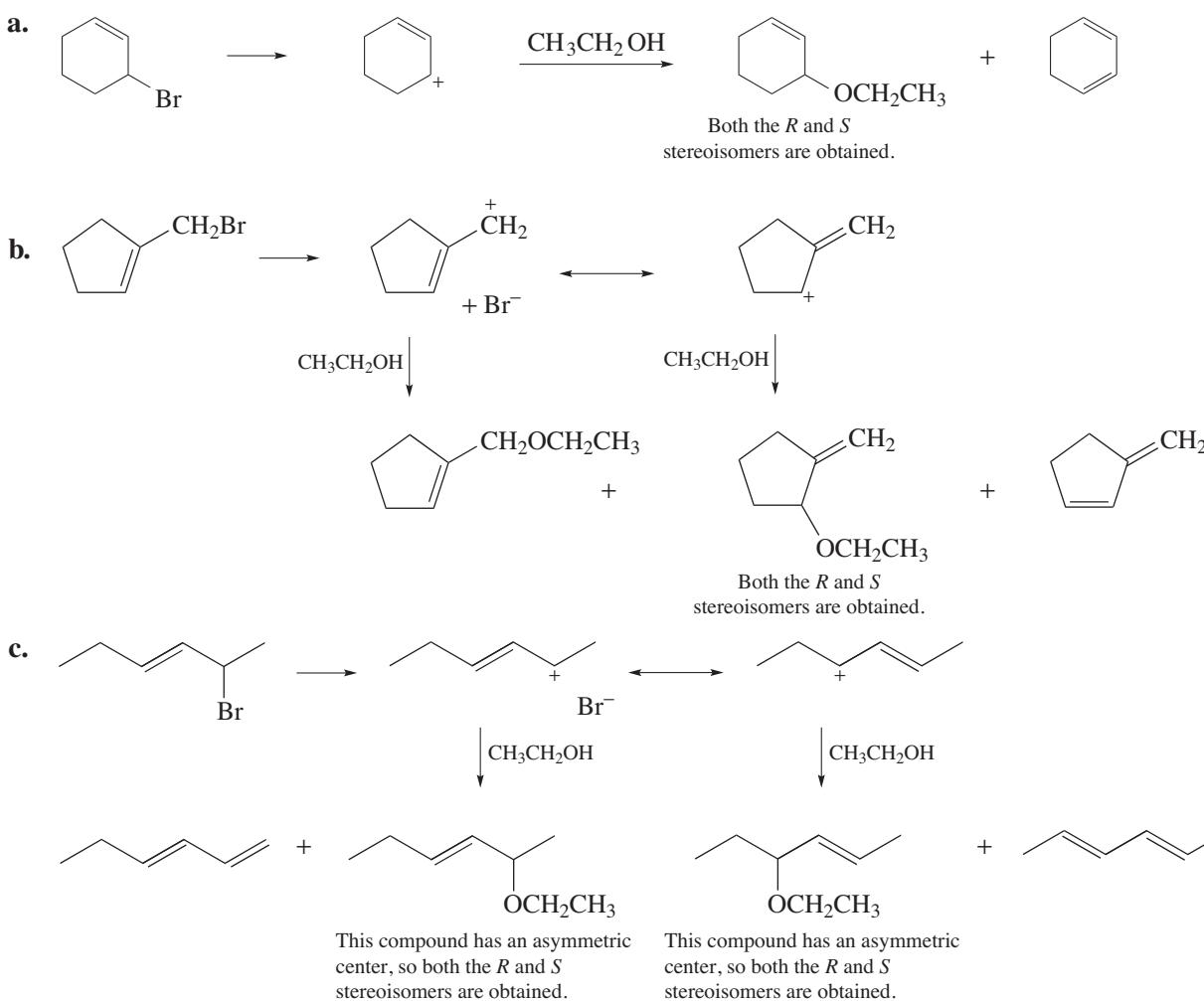
d. $\text{CH}_2=\text{CHCH}_2\text{Cl} \xrightarrow{\text{CH}_3\text{OH}} \text{CH}_2=\text{CHCH}_2\text{OCH}_3$

e. $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Br} \xrightarrow{\text{CH}_3\text{O}^-} \text{CH}_3\text{CH}=\text{CHCH}_2\text{OCH}_3$

f. $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Br} \xrightarrow{\text{CH}_3\text{OH}} \text{CH}_3\text{CH}=\text{CHCH}_2\text{OCl}$

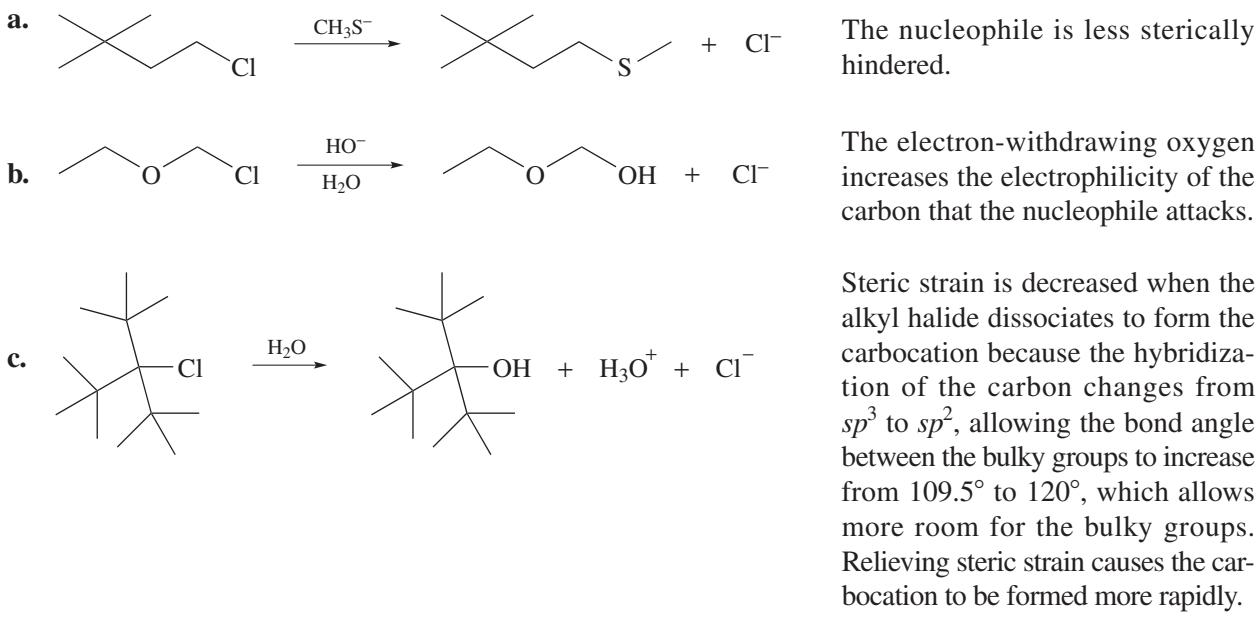
$$\text{OCH}_3$$

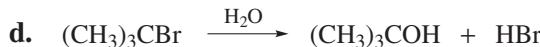
78.



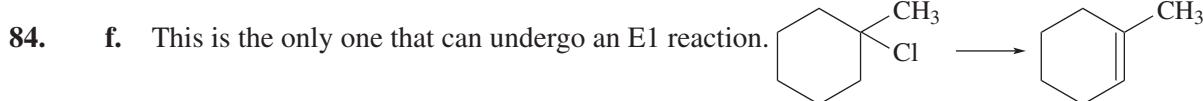
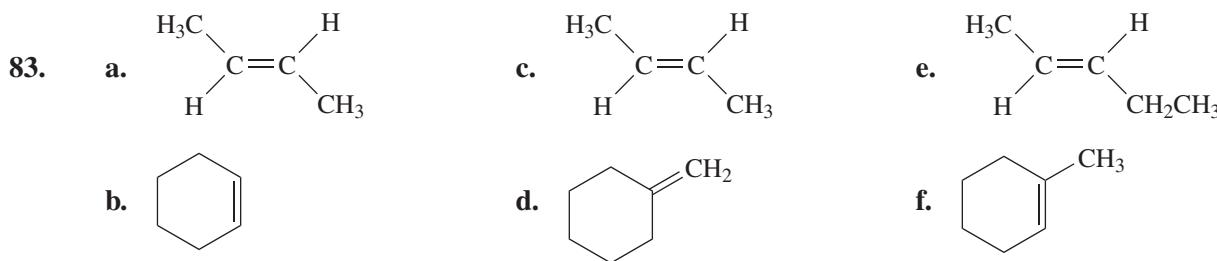
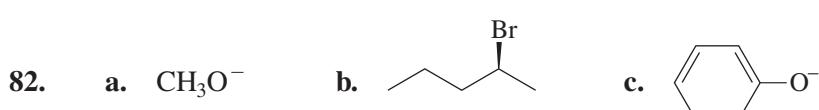
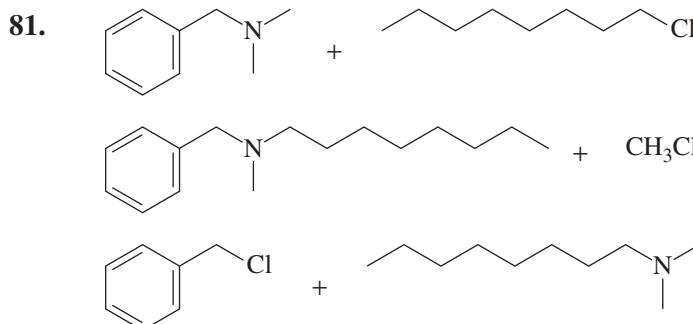
79. Methoxide ion is a better nucleophile in DMSO, because DMSO cannot stabilize the ion by ion–dipole interactions.

80.

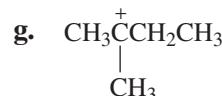
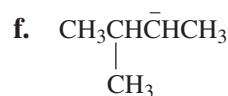
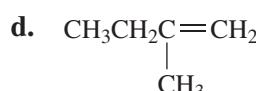
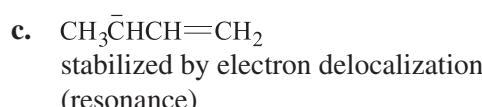
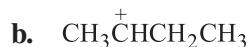




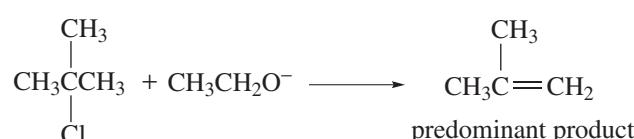
Because the reactants are neutral, the reaction is faster in the more polar solvent.



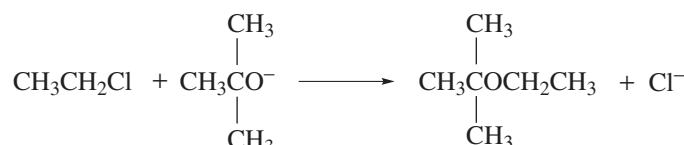
85. a. 1. An E1 reaction is not affected by the strength of the base but, if the reaction can take place by both an E1 and E2 reaction, a weak base will favor the E1 reaction by disfavoring an E2 reaction.
 2. An E1 reaction is not affected by the concentration of the base but, if the reaction can take place by both an E1 and E2 reaction, a low concentration of a base will favor the E1 reaction by disfavoring an E2 reaction.
 3. If the reactant is charged, an E1 reaction will be favored by the least polar solvent that will dissolve the reactant (generally an aprotic polar solvent). If the reactant is not charged, an E1 reaction will be favored by a protic polar solvent.
- b. 1. A strong base favors an E2 reaction.
 2. A high concentration of a base favors an E2 reaction.
 3. If one of the reactants is charged, an E2 reaction will be favored by the least polar solvent that will dissolve the reactant (generally an aprotic polar solvent). If neither of the reactants is charged, an E2 reaction will be favored by a protic polar solvent.



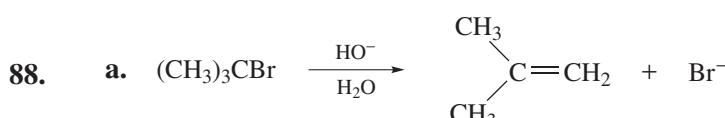
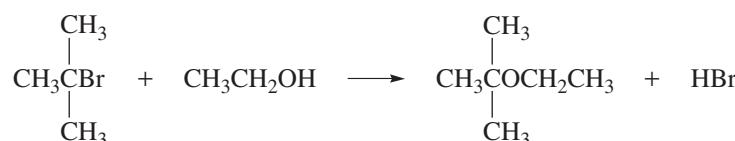
87. He obtained only the elimination product because a tertiary alkyl halide does not undergo an S_N2 reaction. Because of steric hindrance, only an E2 reaction occurs.



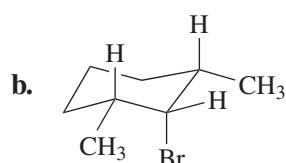
Rather than a tertiary alkyl halide and a primary alkoxide ion, he should have used a primary alkyl halide and a tertiary alkoxide ion. They will react in an S_N2 reaction to form the desired ether.



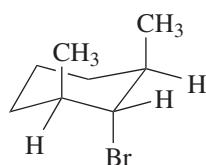
Although the Williamson ether synthesis (an S_N2 reaction) is the preferred way to synthesize an ether because it gives higher yields, the ether also could be synthesized using an S_N1 reaction.



because Br^- is a better leaving group than Cl^-

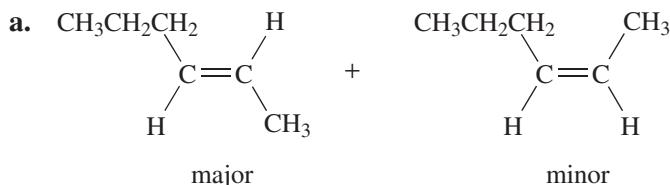


This compound is the only one that can undergo an E2 reaction because the other compound does not have an axial hydrogen bonded to a β -carbon.

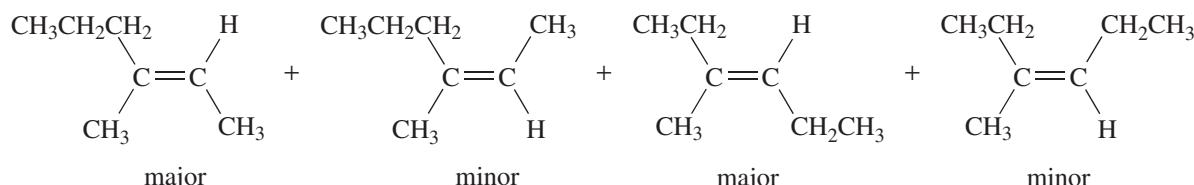


This compound will not be able to undergo an E2 reaction because it does not have an adjacent H and Br that are both attached to axial bonds.

- 89.** The very minor products that are obtained from “anti-Zaitsev” elimination (that is, the less substituted alkenes) are not shown.

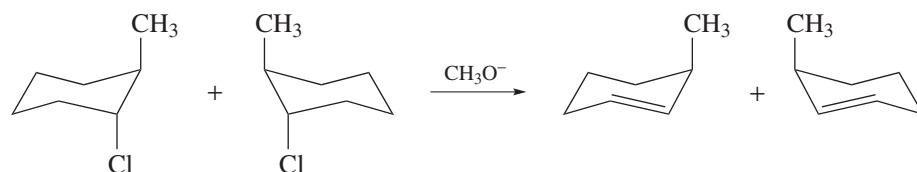


- b. The reactant has two β -carbons that are attached to two hydrogens, so the reaction is not regioselective. Therefore, two constitutional isomers can be formed. Each constitutional isomer has *E* and *Z* stereoisomers.

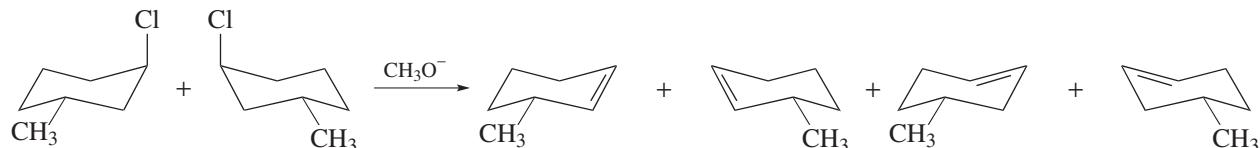


- c. *trans*-1-Chloro-2-methylcyclohexane has two stereoisomers.

A hydrogen cannot be removed from the β -carbon bonded to the fewest hydrogens because that hydrogen is not attached to an axial bond.



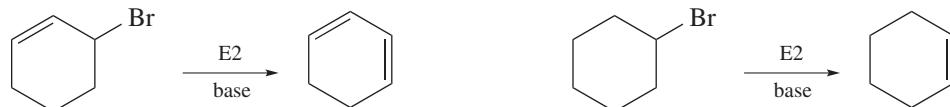
- d. *trans*-1-Chloro-3-methylcyclohexane has two stereoisomers, and each can form two elimination products.



- e. 

- f. $\begin{array}{c} \text{CH}_3\text{CH}_2 \\ & \diagup \quad \diagdown \\ & \text{C} = \text{C} \\ & \diagdown \quad \diagup \\ \text{CH}_3 & & \text{CH}_3 \end{array}$ + $\begin{array}{c} \text{CH}_3\text{CH}_2 \\ & \diagup \quad \diagdown \\ & \text{C} = \text{C} \\ & \diagdown \quad \diagup \\ \text{CH}_3 & & \text{CH}_3 \\ & & \text{H} \end{array}$

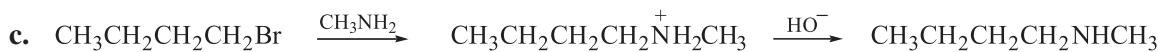
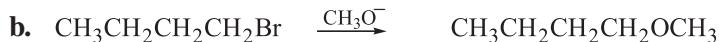
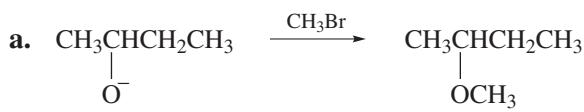
90. a. 3-Bromocyclohexene forms 1,3-cyclohexadiene; bromocyclohexane forms cyclohexene. 3-Bromocyclohexene reacts faster in an E2 reaction, because a conjugated double bond is more stable than an isolated double bond. So the transition state leading to formation of the conjugated double bond is more stable and, therefore, the conjugated double bond is easier to form.



- b. 3-Bromocyclohexene, because it forms a relatively stable secondary allylic cation. The other compound is a secondary alkyl halide, so it does not undergo an E1 reaction.

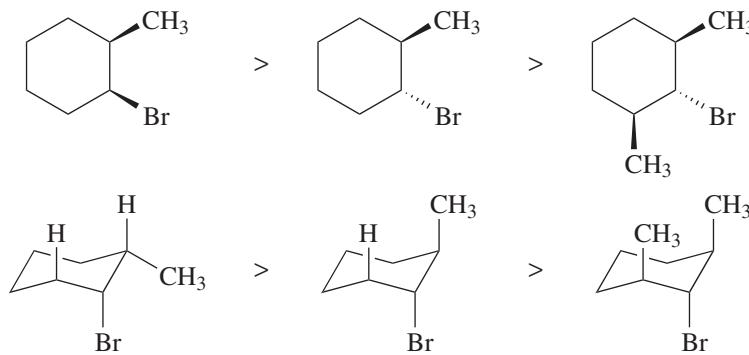


91. That fact that the change from hydrogen to deuterium affects the rate of the reaction tells us that the C–H (or C–D) bond is broken in the rate-limiting step. This is consistent with the mechanism for an E2 reaction but not for the mechanism for an E1 reaction.
92. Alkyl chlorides and alkyl iodides could also be used. Do not use alkyl fluorides because they have the poorest leaving groups and cannot undergo S_N2 reactions.

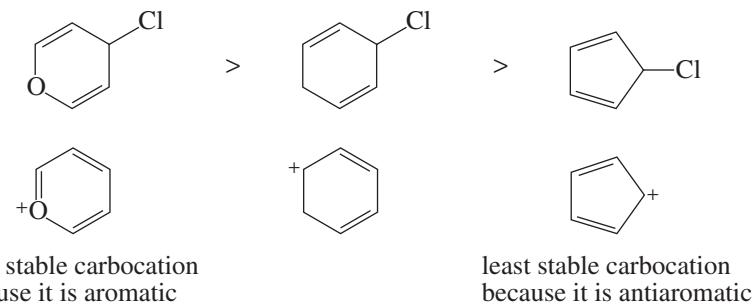


93. a. ethoxide ion, because elimination is favored by bulky bases and *tert*-butoxide ion is bulkier than ethoxide ion
 b. SCN^- because elimination is favored by strong bases and OCN^- is a stronger base than SCN^-
 c. Br^- because elimination is favored by strong bases and Cl^- is a stronger base than Br^-
 d. CH_3S^- because elimination is favored by strong bases and CH_3O^- is a stronger base than CH_3S^-

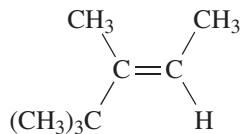
94. The first compound listed below is the most reactive compound because it has two axial hydrogens attached to β -carbons. The second compound has one axial hydrogen attached to a β -carbon, but it cannot form the more substituted (more stable) alkene that can be formed by the first compound. The last compound cannot undergo an E2 reaction because it does not have an axial hydrogen attached to a β -carbon.



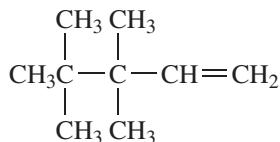
- 95.** Draw the carbocation that each compound forms in an S_N1 reaction. Because carbocation formation is the rate-limiting step, the more stable the carbocation, the faster is the rate of the S_N1 reaction.



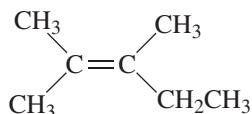
- 96.** a. The stereoisomer formed in greatest yield is the one in which the larger group attached to one sp^2 carbon and the larger group attached to the other sp^2 carbon are on opposite sides of the double bond.



- b. No stereoisomers are possible for this compound because one of the sp^2 carbons is bonded to two hydrogens.

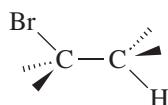


- c. No stereoisomers are possible for this compound because one of the sp^2 carbons is bonded to two methyl groups.

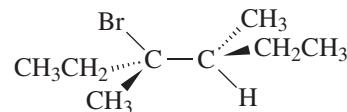


- d. Because it is an E2 reaction and only one hydrogen is attached to the β -carbon, the stereoisomer formed in greater yield depends on the configuration of the reactant. The reactant can have four different configurations: *S,S*; *S,R*; *R,R*; and *R,S*. To determine the product of the reaction:

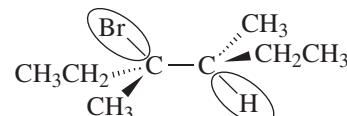
1. Draw the skeleton of a perspective formula, putting the groups to be eliminated on the solid lines. Notice that on each carbon, the solid wedge is below the hatched wedge.



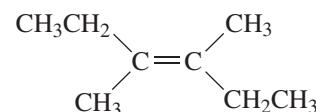
2. Add the remaining groups to the structure in a way that gives the asymmetric centers the desired configurations. For example, the structure below is (*3S,4S*)-3-bromo-3,4-dimethylhexane.

(3*S,4S*)-3-bromo-3,4-dimethylhexane

3. Because the groups to be eliminated are both attached to solid lines, they are anti to each other.

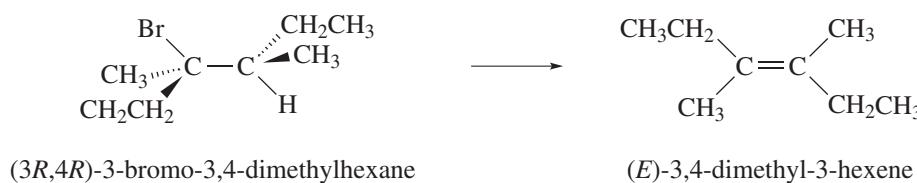
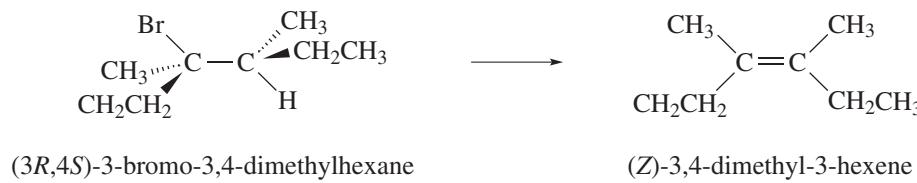


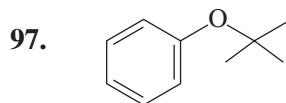
4. Once the groups are eliminated, you can draw the structure of the alkene product. (The groups attached to the solid wedges are on the same side of the double bond, and the groups attached by hatched wedges are on the other side of the double bond.)



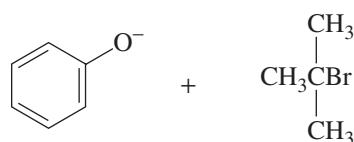
(E)-3,4-dimethyl-3-hexene

The configuration of the elimination product obtained from each of the other three stereoisomers can be determined in the same way.

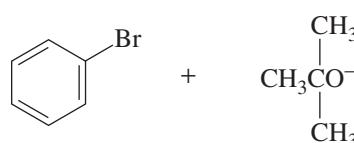
(3*S,4R*)-3-bromo-3,4-dimethylhexane (Z)-3,4-dimethyl-3-hexene(3*R,4R*)-3-bromo-3,4-dimethylhexane (E)-3,4-dimethyl-3-hexene(3*R,4S*)-3-bromo-3,4-dimethylhexane (Z)-3,4-dimethyl-3-hexene



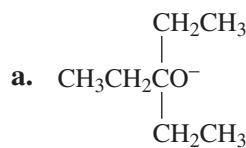
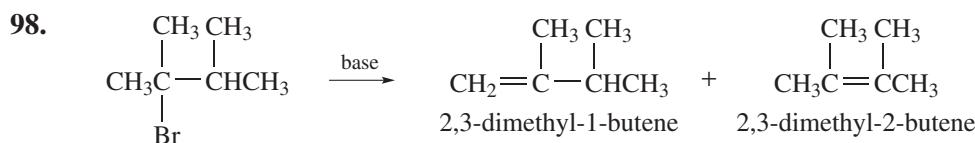
This ether cannot be made by a Williamson ether synthesis.



These reagents cannot be used because the tertiary alkyl halide undergoes only an elimination reaction.



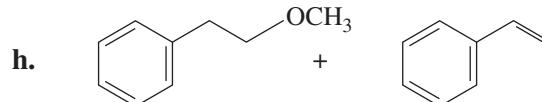
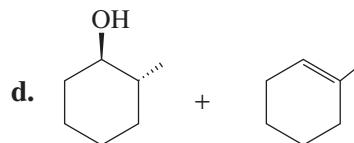
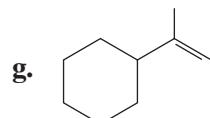
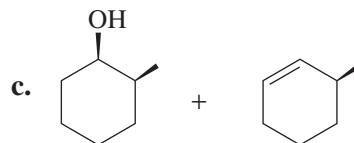
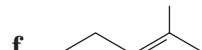
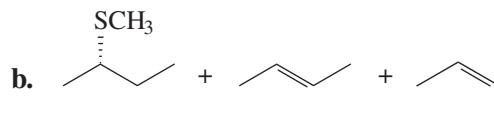
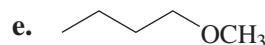
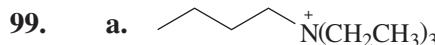
These reagents cannot be used because the aryl halide cannot undergo a substitution reaction.



Because it is the most sterically hindered base, **B** gives the highest percentage of the less stable 1-alkene because it is easier for it to remove the most accessible hydrogen.

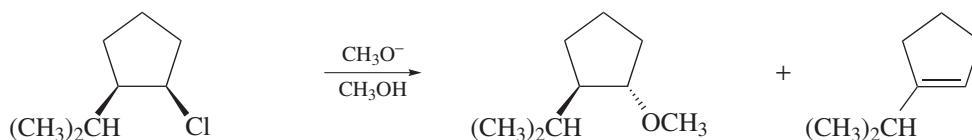
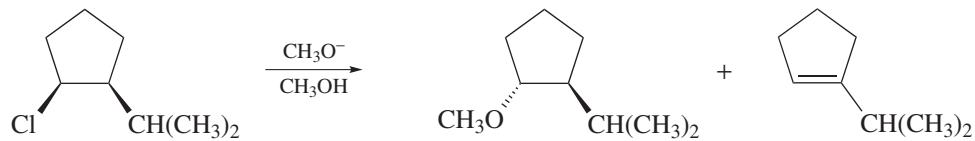


Because it is the least sterically hindered base, **C** gives the highest percentage of the more stable 2-alkene.

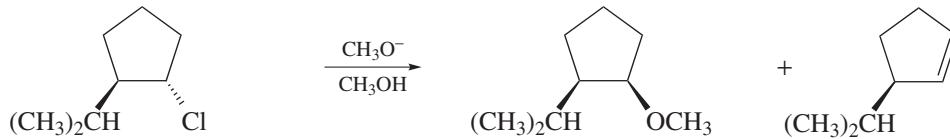
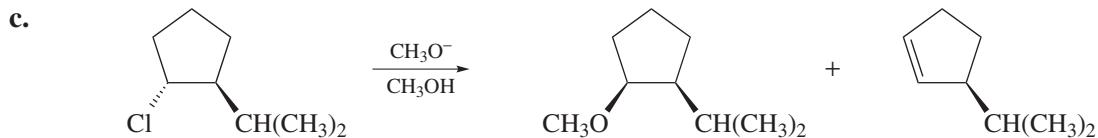


This primary alkyl halide forms more than the usual amount of elimination product because the new double bond is conjugated with the benzene ring. Its greater stability makes it easier to form.

100. a. These are S_N2/E2 reactions, because the alkyl halide is secondary.

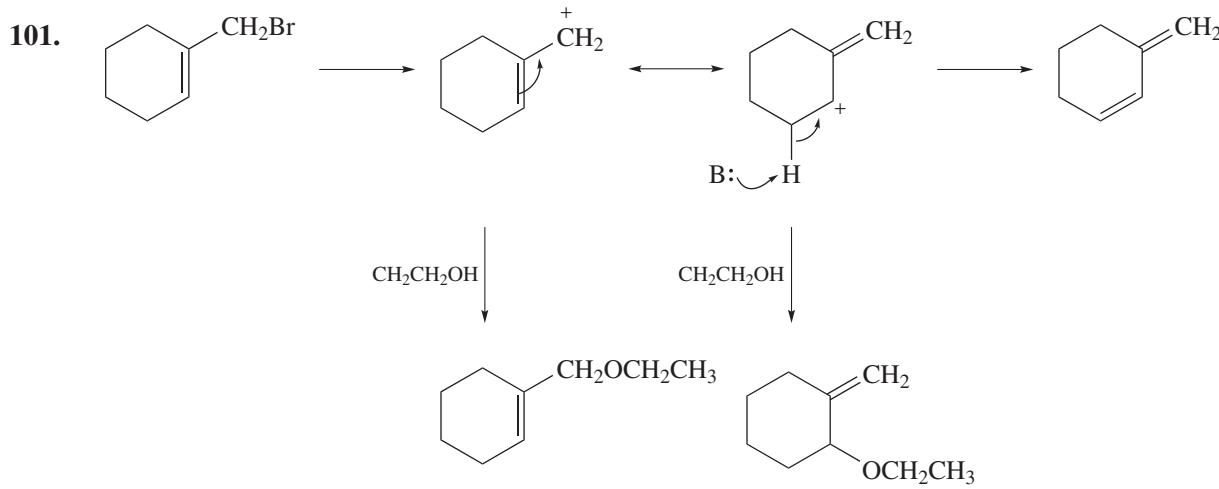


- b. Only the substitution products are optically active; the elimination product does not have an asymmetric center.



All the products are optically active.

- d. The cis enantiomers form the substitution products more rapidly, because there is less steric hindrance from the adjacent substituent to back-side attack by the nucleophile.
- e. The cis enantiomers form the elimination products more rapidly, because the alkenes formed from the cis enantiomers are more substituted and, therefore, more stable. The more stable the alkene, the lower the energy of the transition state leading to its formation and the more rapidly it is formed.

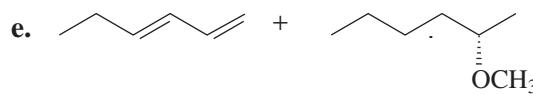
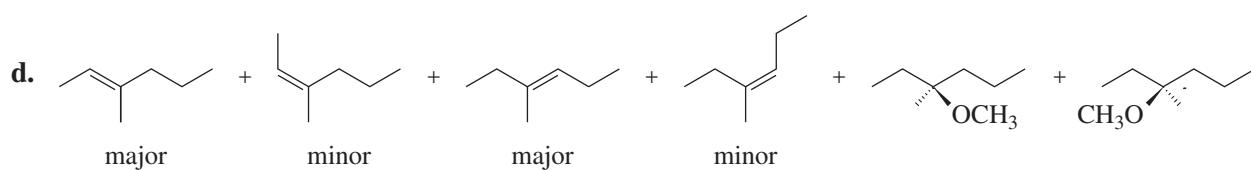
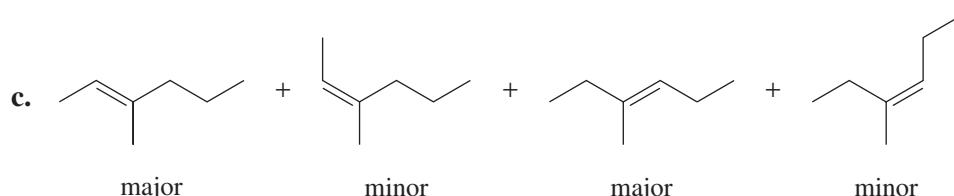
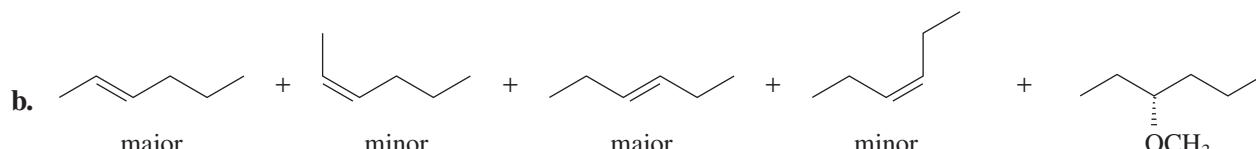
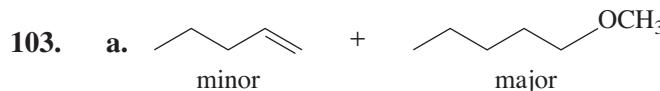
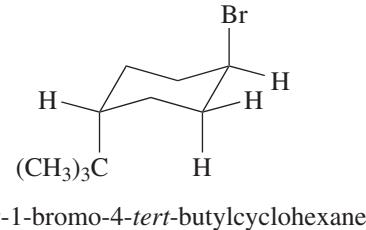
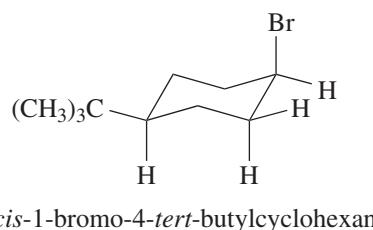


102. In an E2 reaction, both groups to be eliminated must be in axial positions.

When the bromine is in the axial position in the cis isomer, the *tert*-butyl substituent is in the more stable equatorial position.

When the bromine is in the axial position in the trans isomer, the *tert*-butyl substituent is in the less stable axial position.

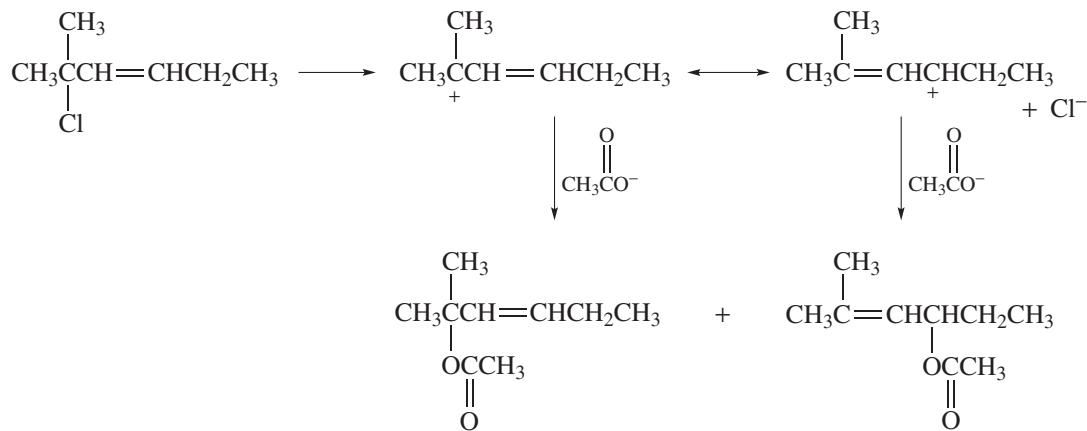
Therefore, elimination takes place via the most stable conformer in the cis isomer and via the less stable chair conformer in the trans isomer, so the cis isomer undergoes elimination more rapidly.



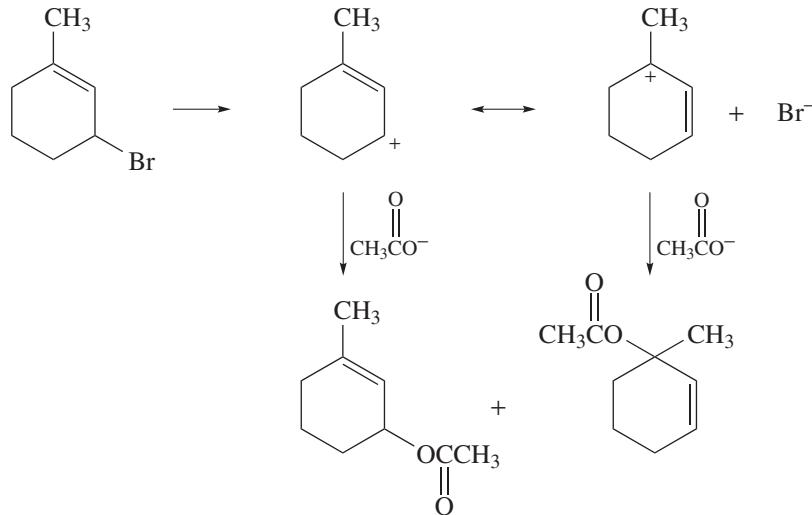
f. no substitution or elimination reaction

104. The reactants are neutral. Therefore, increasing the polarity of the solvent increases the rate of the reactions. Therefore, the reaction is faster in formic acid, the more polar of the two solvents.

105. a. We can predict that this is an S_N1 reaction because acetate ion is a relatively poor nucleophile.



- b. We can predict that this is an S_N1 reaction because acetate ion is a relatively poor nucleophile.



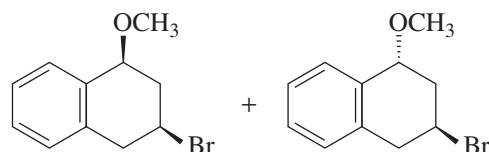
106. a. CH₃CH₂CH₂Br + HC≡C⁻ → CH₃CH₂CH₂C≡CH $\xrightarrow[\text{Pd/C}]{\text{H}_2}$ CH₃CH₂CH₂CH₂CH₃
- b. CH₃CH₂CH₂Br + HC≡C⁻ → CH₃CH₂CH₂C≡CH $\xrightarrow[\text{H}_2\text{O}]{\text{H}_2\text{SO}_4, \text{HgSO}_4}$ CH₃CH₂CH₂C(=O)CH₃
- c. CH₃CH₂CH₂Br + HC≡C⁻ → CH₃CH₂CH₂C≡CH $\xrightarrow[2. \text{HO}^-, \text{H}_2\text{O}_2, \text{H}_2\text{O}]{1. \text{R}_2\text{BH/THF}}$ CH₃CH₂CH₂CH₂C(=O)CH₃
- d. CH₃CH₂CH₂Br + HC≡C⁻ → CH₃CH₂CH₂C≡CH $\xrightarrow[\text{Na/NH}_3(\text{liq})]{\text{H}_2, \text{Lindlar catalyst or Na/NH}_3(\text{liq})}$ CH₃CH₂CH₂CH=CH₂ $\xrightarrow{\text{RCOOH}}$ CH₃CH₂CH₂CH(OH)CH₂

107. The equilibrium constant is given by the relative stabilities of the products and reactants. Therefore, any factor that stabilizes the products increases the equilibrium constant.

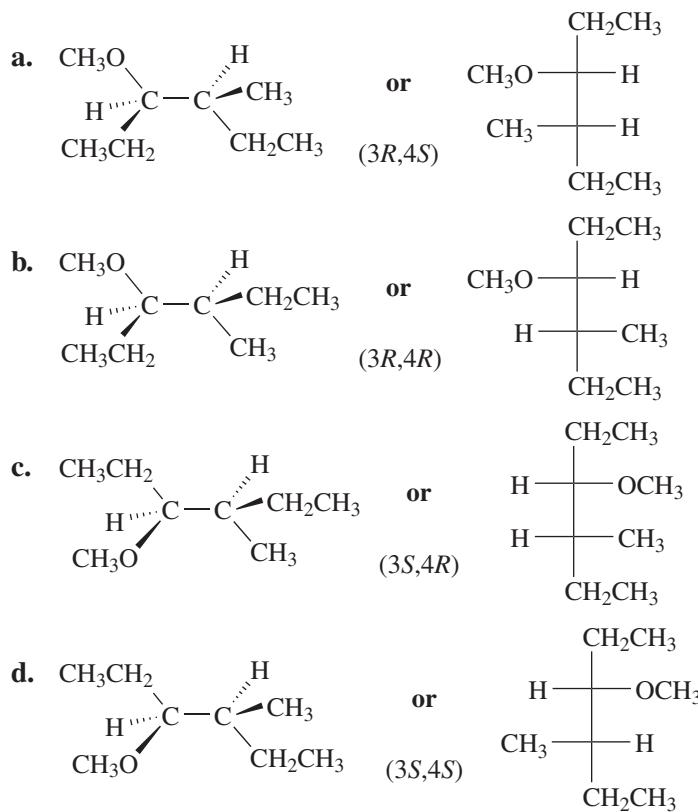
$$K_{\text{eq}} = \frac{[\text{products}]}{[\text{reactants}]}$$

Ethanol will stabilize the charged products more than will diethyl ether because ethanol is a more polar solvent. Therefore, the equilibrium will lie farther to the right (toward products) in ethanol.

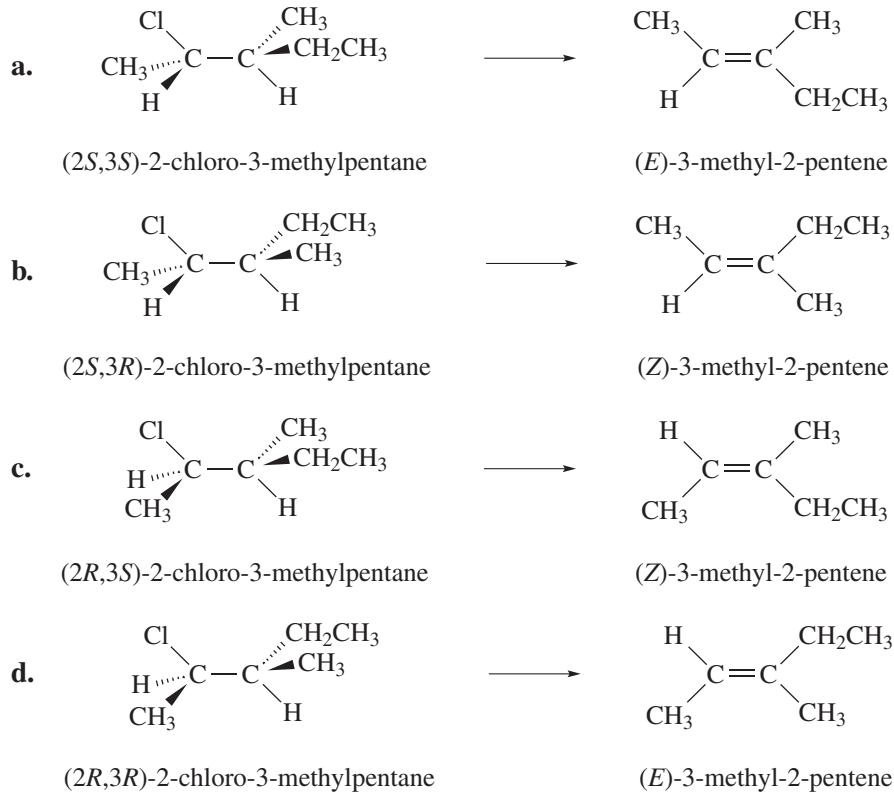
108. a. The reaction with quinuclidine had the larger rate constant because quinuclidine is less sterically hindered as a result of the substituents on the nitrogen being pulled back into a ring structure.
 b. The reaction with quinuclidine had the larger rate constant for the same reason given in part a.
 c. Isopropyl iodide exhibits the larger difference in rate constants and, therefore, the larger $k_{\text{quinuclidine}}/k_{\text{triethylamine}}$ ratio. Because it is more sterically hindered than methyl iodide, it is more affected by differences in the amount of steric hindrance in the nucleophile.
109. Because methanol is a poor nucleophile, it is an S_N1 reaction. The bromine that departs is the one that forms a secondary benzylic cation and not the one that would form a secondary carbocation. The nucleophile can approach from the top or bottom of the planar carbocation.



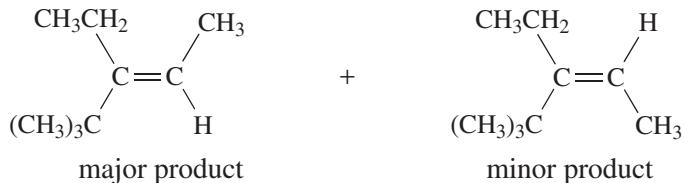
110. Because all the reactions are S_N2 reactions, the configuration of the asymmetric center attached to the Br in the reactant is inverted in the product.



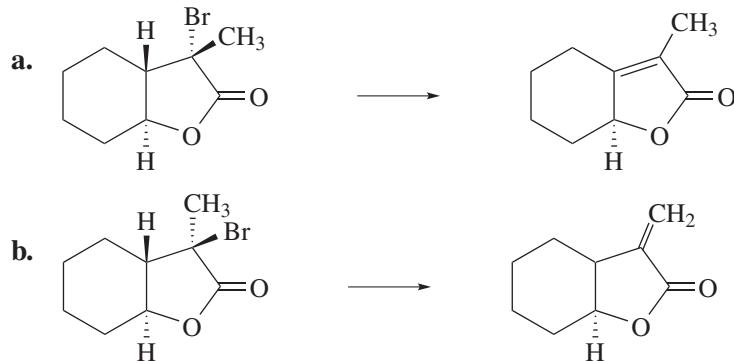
- 111.** In reactions **a–d**, the β -carbon from which the hydrogen is to be removed is bonded to only one hydrogen. Therefore, the configuration of the reactant determines the configuration of the product of the E2 reaction. To determine the configuration of the product, see the instructions in the Problem-Solving Strategy on page 425.



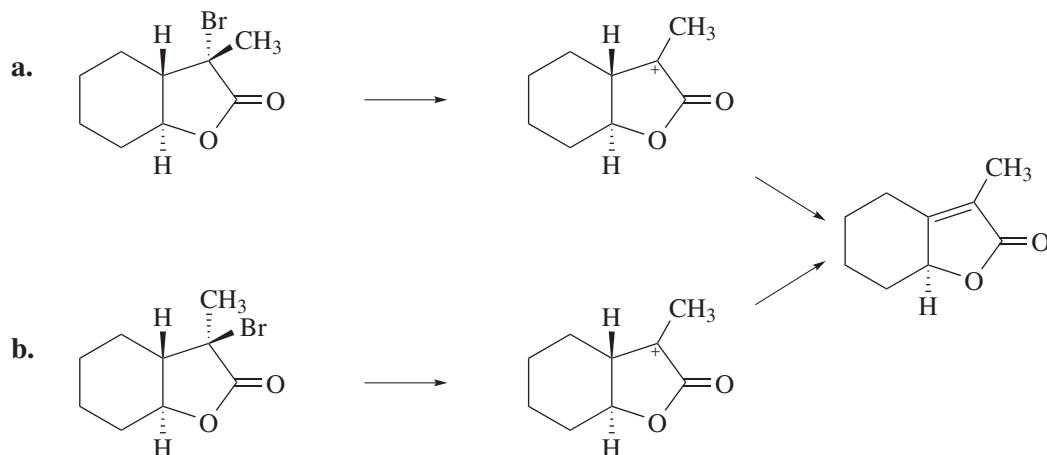
- e. This reactant has two hydrogens bonded to the β -carbon, so both *Z* and *E* stereoisomers are formed.



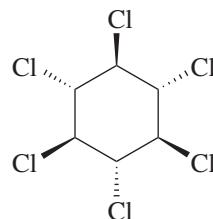
- 112.** The two tertiary alkyl halides form different products when they react with a strong base (an E2 reaction) because the H and Br attached to the ring can be eliminated only if they are anti to each other. Because the H and Br are on the same side of the ring in **b**, a hydrogen has to be removed from the other β -carbon (that is, from the methyl group).



The two tertiary alkyl halides form the same product when they react with a weak base (an E1 reaction) because both form the same carbocation.



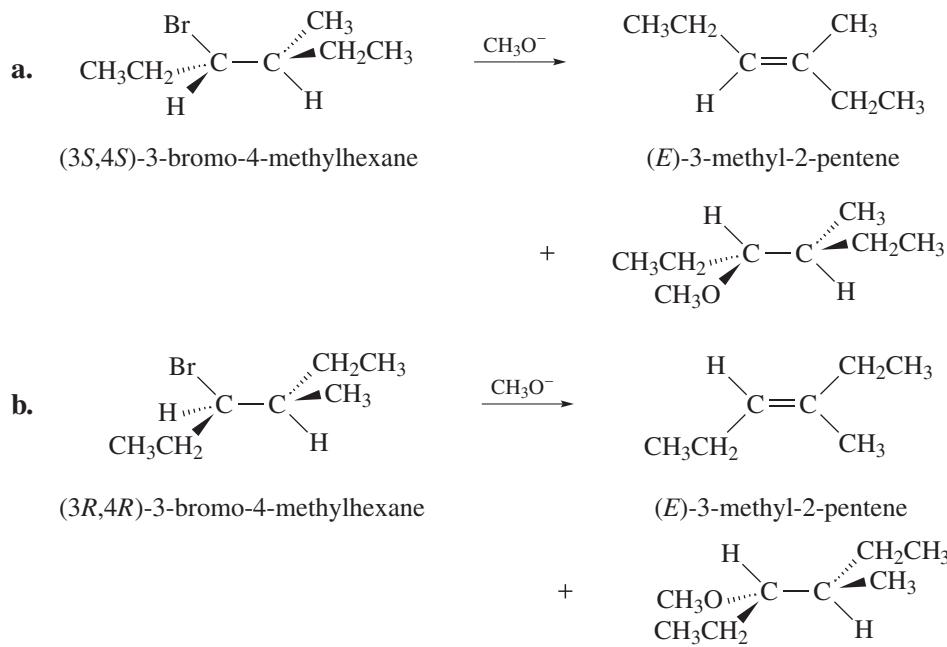
113. In order to undergo an E2 reaction, a chlorine and a hydrogen bonded to an adjacent carbon must be trans to each other so they can both be in the required axial positions. Every Cl in the following compound has a Cl trans to it, so no Cl has a hydrogen trans to it. Therefore, it is the least reactive of the isomers; it cannot undergo an E2 reaction.

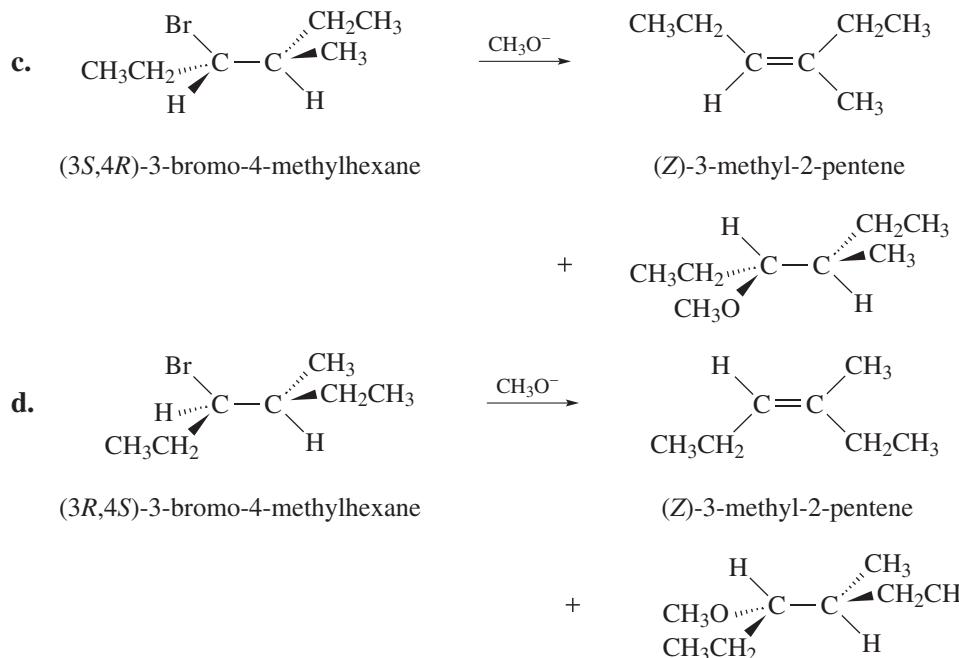


114. The silver ion increases the ease of departure of the halogen atom by sharing one of bromine's lone pairs, which weakens the carbon–bromine bond.

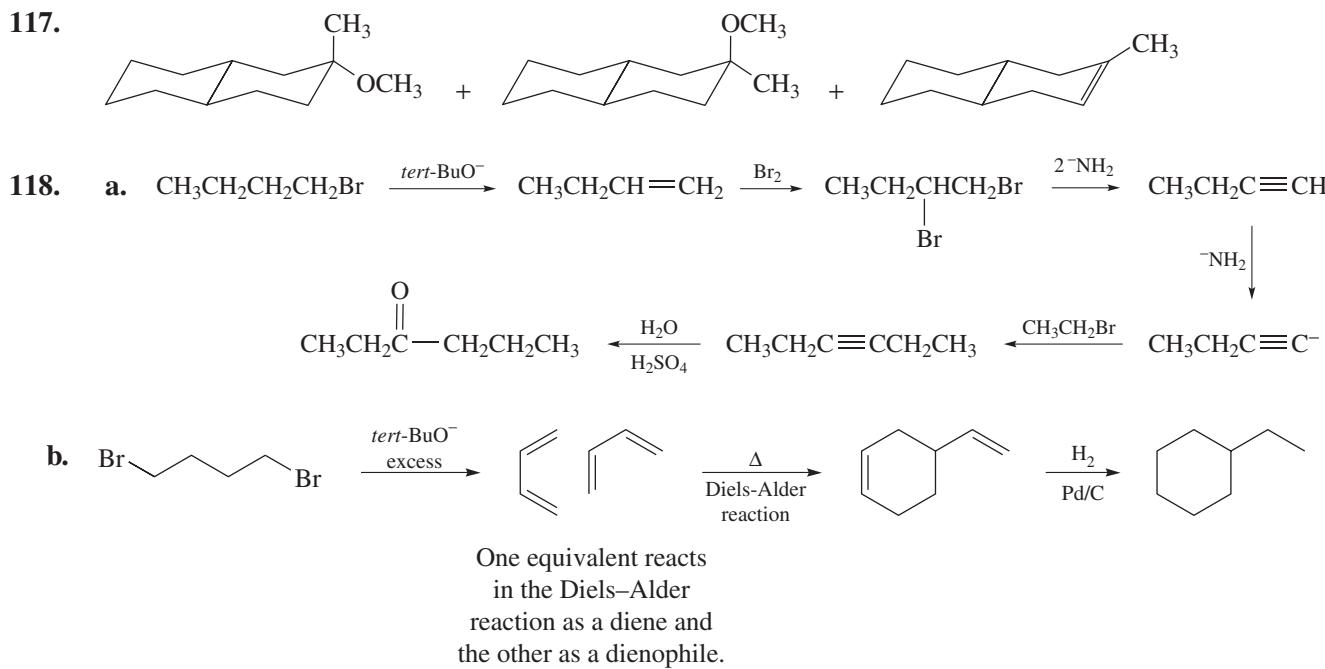


115. For a description of how to do this problem, see the Problem-Solving Strategy on page 425.

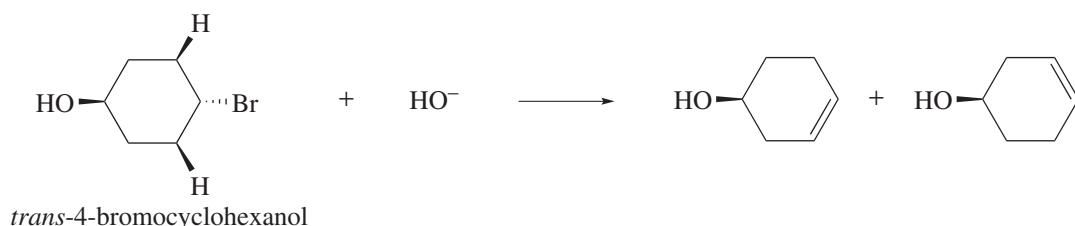
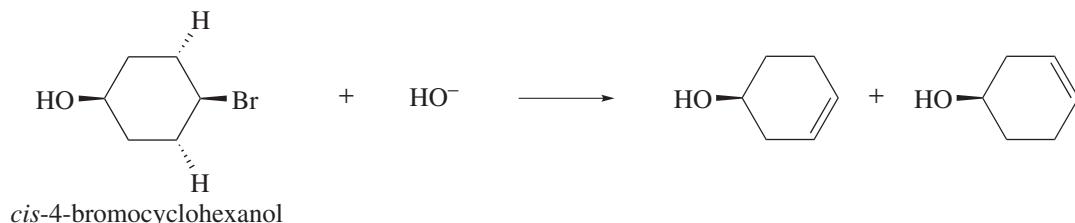




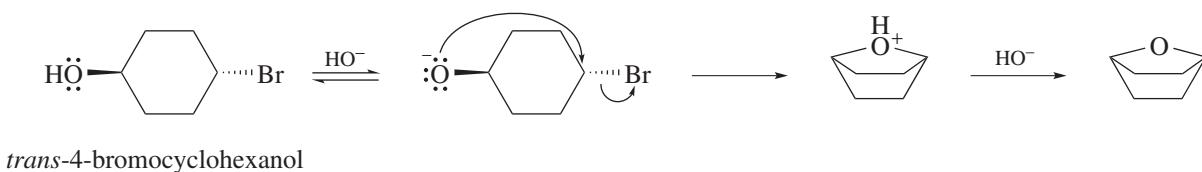
116. a. $\text{CH}_3\text{CH}_2\text{CD}=\text{CH}_2$ and $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$
b. The deuterium-containing compound results from elimination of HBr, whereas the non-deuterium-containing compound results from elimination of DBr. The deuterium-containing compound is obtained in greater yield, because a C—H bond is easier to break than a C—D bond.



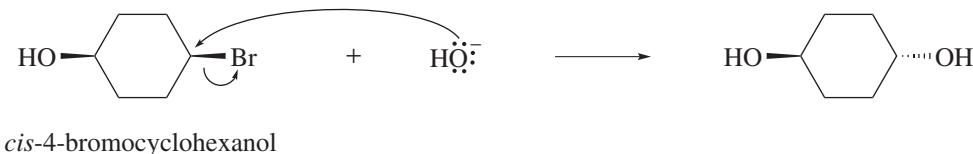
- 119.** **a.** Both compounds form the same elimination products because they both have hydrogens bonded to the same β -carbons that are anti to the bromine.



- b.** Only the *trans* isomer can undergo an intramolecular substitution reaction because the S_N2 reaction requires back-side attack.



The *cis* isomer can undergo only an intermolecular substitution reaction.



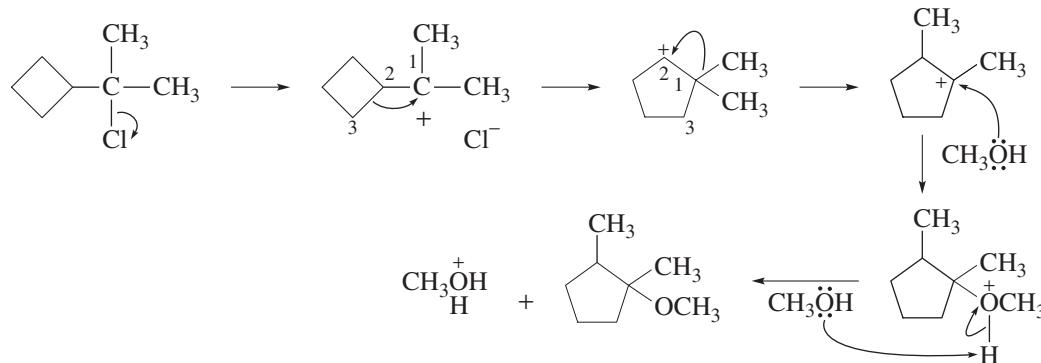
- c.** The elimination reaction forms a pair of enantiomers because the reaction creates an asymmetric center in the product. Both substitution reactions form a single stereoisomer, because the reaction does not create an asymmetric center in the product.

- 120.** **a.** 1. $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CCH}_2\text{CH}_3$ 2. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3$

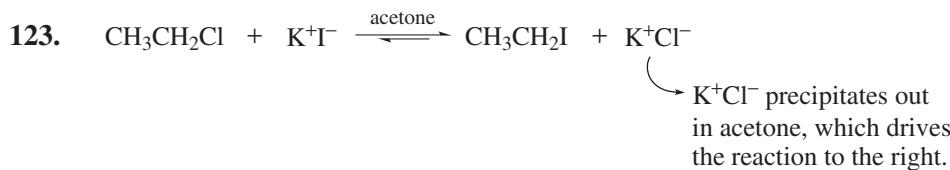
- b.** $\text{CH}_3\text{CH}_2\text{C}\equiv\text{C}^- + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}^- + \text{CH}_3\text{CH}_2\text{Br}$

- c.** $\text{CH}_3\text{CH}_2\text{O}^- + \text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{Br}$ or $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{O}^- + \text{CH}_3\text{CH}_2\text{Br}$

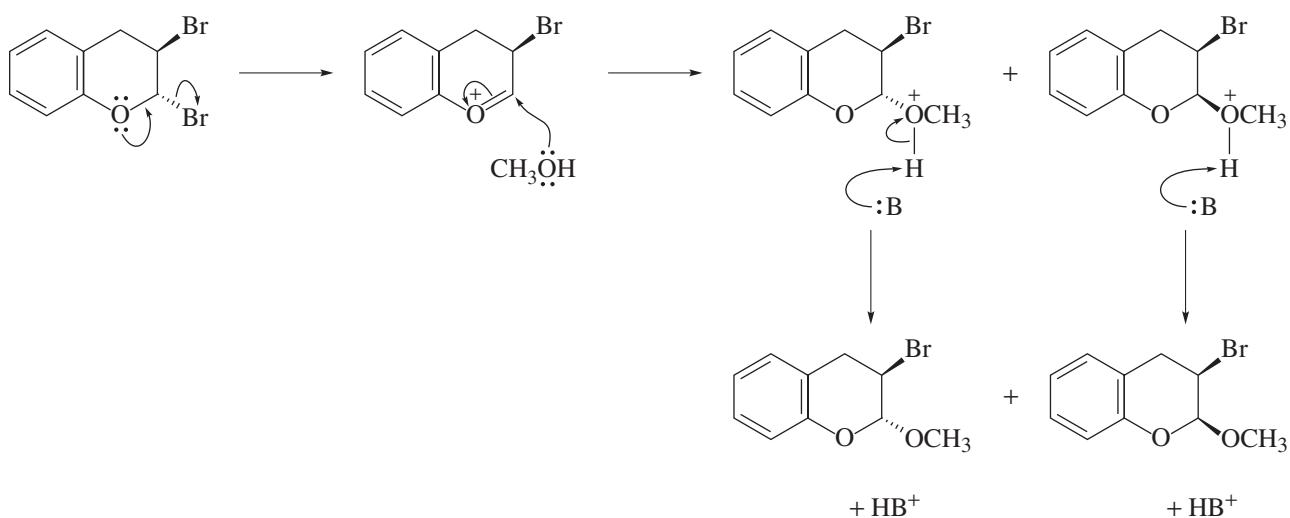
- 121.** A tertiary carbocation with a strained four-membered ring is less stable than a secondary carbocation with an unstrained five-membered ring, so a carbocation rearrangement occurs. A second carbocation rearrangement forms a tertiary carbocation.



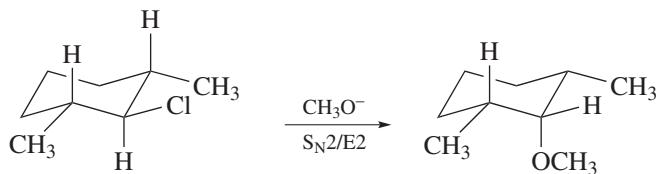
- 122.** Tetrahydrofuran can solvate a charge better than diethyl ether can, because the floppy ethyl substituents of diethyl ether provide steric hindrance, making it difficult for the nonbonding electrons of the oxygen to approach the positive charge that is to be solvated.



- 124. a.**

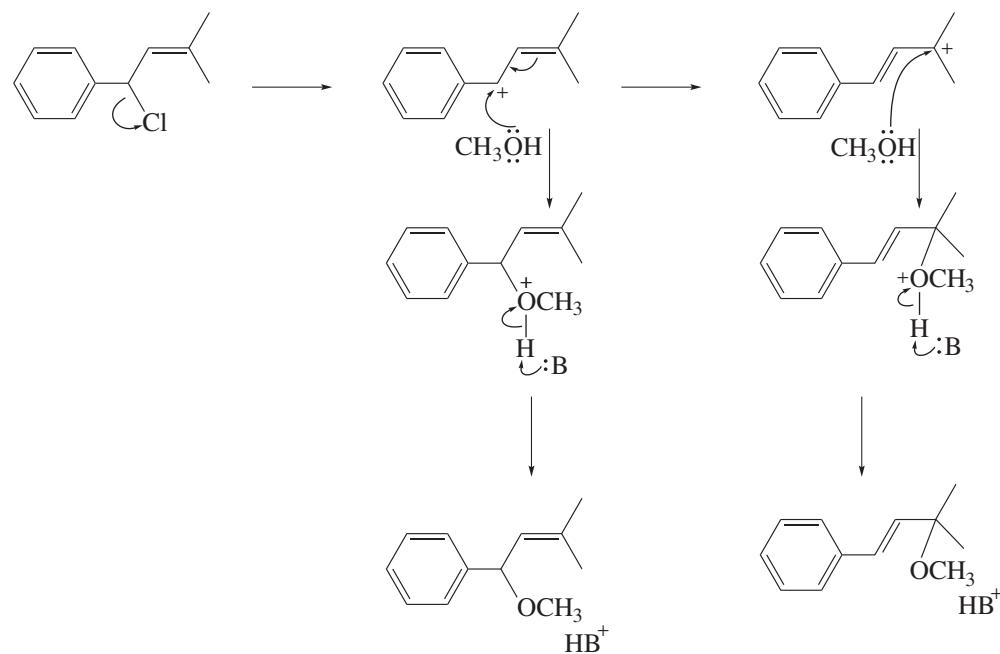
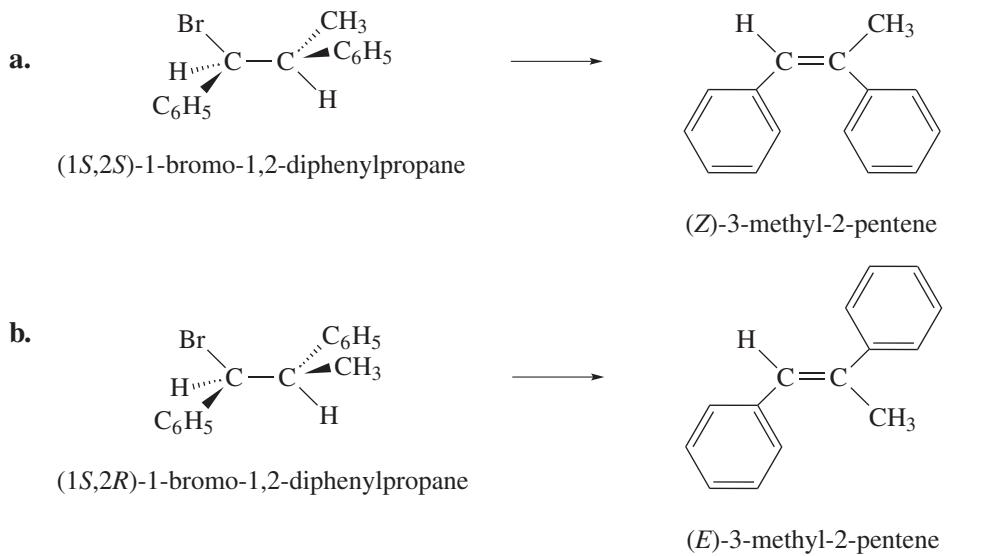


- b.** Two products are obtained because methanol can add to the top or bottom of the planar double bond.
c. One bromine is eliminated with the help of one of oxygen's lone pairs, forming a species in which the positive charge is shared by a carbon and an oxygen. The oxygen cannot help eliminate the other bromine.

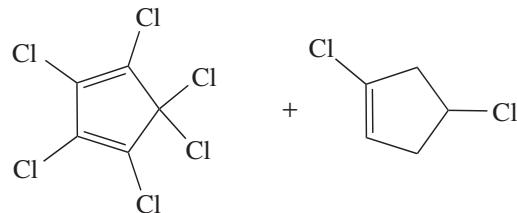
125.

There is only a substitution product.

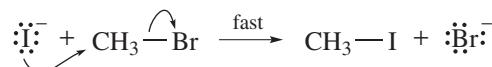
The reactant does not undergo elimination because when Cl is in an axial position, neither of the β -carbons is bonded to an axial hydrogen.

126.**127.**

128. A Diels–Alder reaction between hexachlorocyclopentadiene and 1,4-dichlorocyclopentene forms chlordane.

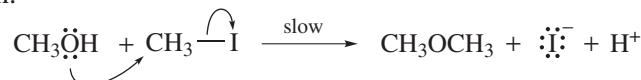


129. I^- is a good nucleophile in a polar solvent such as methanol, so it reacts rapidly with methyl bromide, causing the concentration of I^- to decrease rapidly.



I^- is a good leaving group, so methyl iodide undergoes an $\text{S}_{\text{N}}2$ reaction with methanol.

Methanol is a poor nucleophile, so the $\text{S}_{\text{N}}2$ reaction is slow. Therefore, iodide ion returns slowly to its original concentration.



130. It does not undergo an $\text{S}_{\text{N}}2$ reaction, because of steric hindrance to back-side attack.
It does not undergo an $\text{S}_{\text{N}}1$ reaction, because the carbocation that would be formed is unstable; the ring structure prevents it from achieving the 120° bond angles required for an sp^2 carbon.

131. The equation needed to calculate K_{eq} from the change in free energy is given in Section 5.6.

$$\ln K_{\text{eq}} = \frac{-\Delta G^\circ}{RT}$$

$$\ln K_{\text{eq}} = \frac{-(-21.7 \text{ kcal mol}^{-1})}{0.001986 \text{ kcal mol}^{-1} \text{ K}^{-1} \times 303 \text{ K}} = \frac{21.7}{0.60}$$

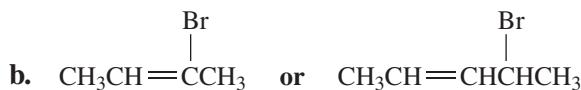
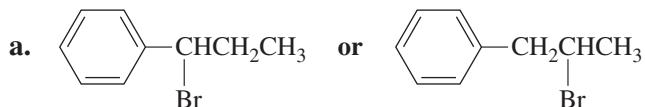
$$\ln K_{\text{eq}} = 36.1$$

$$K_{\text{eq}} = 4.8 \times 10^{15}$$

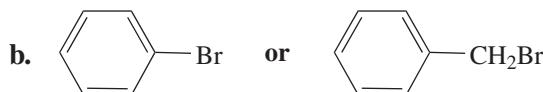
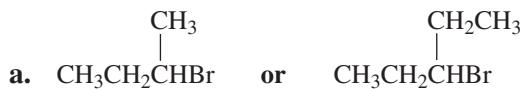
As expected, this highly exergonic reaction has a very large equilibrium constant.

Chapter 9 Practice Test

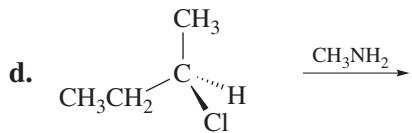
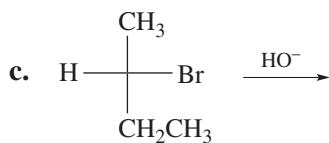
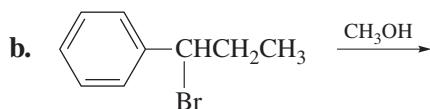
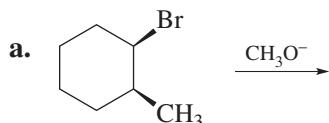
1. Which of the following is more reactive in an S_N1 reaction?



2. Which of the following is more reactive in an S_N2 reaction?

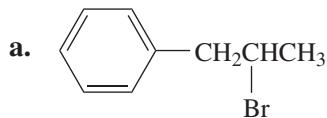


3. Draw the product(s) of the following reactions, showing the stereoisomers that are formed:

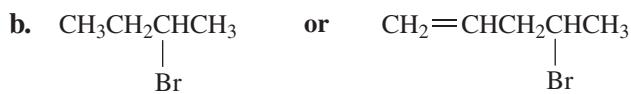
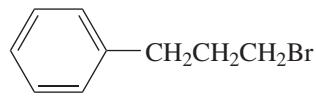


- 4.** Indicate whether each of the following statements is true or false:
- a. Increasing the concentration of the nucleophile favors an S_N1 reaction over an S_N2 reaction. T F
 - b. Ethyl iodide is more reactive than ethyl chloride in an S_N2 reaction. T F
 - c. In an S_N1 reaction, the product with the retained configuration is obtained in greater yield. T F
 - d. The rate of a substitution reaction in which none of the reactants is charged will increase if the polarity of the solvent is increased. T F
 - e. An S_N2 reaction is a two-step reaction. T F
 - f. The pK_a of a carboxylic acid is greater in water than it is in a less polar solvent. T F
 - g. 4-Bromo-1-butanol forms a cyclic ether faster than does 3-bromo-1-propanol. T F
- 5.** Answer the following:
- a. Which is a stronger base, CH₃O⁻ or CH₃S⁻?
 - b. Which is a better nucleophile in an aqueous solution, CH₃O⁻ or CH₃S⁻?
- 6.** For each of the following pairs of S_N2 reactions, indicate the one that occurs with the greater rate constant (that is, occurs faster):
- a. CH₃CH₂CH₂Cl + HO⁻ or CH₃CH(CH₃)₂ + HO⁻
 - b. CH₃CH₂CH₂Cl + HO⁻ or CH₃CH₂CH₂I + HO⁻
 - c. CH₃CH₂CH₂Br + HO⁻ or CH₃CH₂CH₂Br + H₂O
 - d. CH₃CH(CH₃)₂ $\xrightarrow[\text{H}_2\text{O}/\text{CH}_3\text{OH}]{\text{CH}_3\text{O}^-}$ or CH₃CH(CH₃)₂ $\xrightarrow[\text{CH}_3\text{OH}]{\text{CH}_3\text{O}^-}$
 - e. BrCH₂CH₂CH₂CH₂NHCH₃ or BrCH₂CH₂CH₂NHCH₃
- 7.** Circle the aprotic solvents.
- a. dimethyl sulfoxide
 - b. diethyl ether
 - c. ethanol
 - d. hexane
- 8.** How does increasing the polarity of the solvent affect the following?
- a. the rate of the S_N2 reaction of methylamine with 2-bromobutane
 - b. the rate of the S_N1 reaction of methylamine with 2-bromo-2-methylbutane
 - c. the rate of the S_N2 reaction of methoxide ion with 2-bromobutane
 - d. the pK_a of acetic acid
 - e. the pK_a of phenol

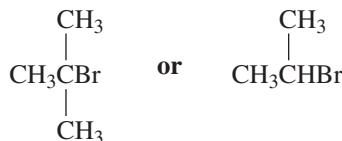
9. Which of the following is more reactive in an E2 reaction?



or

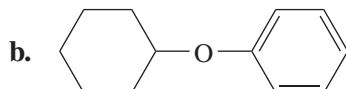
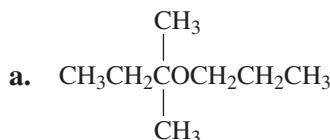


10. Which of the following gives the greater amount of substitution product when it reacts with a good nucleophile/strong base?

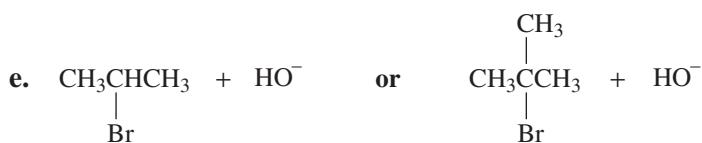
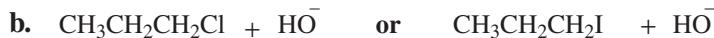
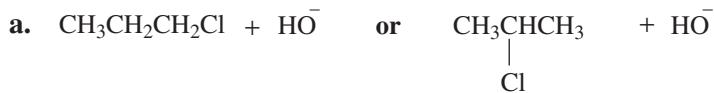


11. What products are obtained when (*R*)-2-bromobutane reacts with $\text{CH}_3\text{O}^- / \text{CH}_3\text{OH}$ under conditions that favor $\text{S}_{\text{N}}2/\text{E2}$ reactions? Include the configuration of the products.

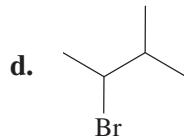
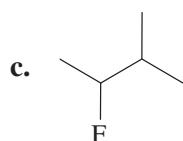
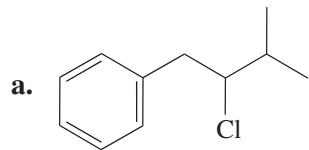
12. What alkoxide ion and what alkyl bromide should be used to synthesize the following ethers?



13. For each of the following pairs of E2 reactions, indicate the one that occurs with the greater rate constant:



14. What is the major product obtained from the E2 reaction of each of the following compounds with hydroxide ion?



15. Which is more reactive in an E2 reaction, *cis*-1-bromo-2-methylcyclohexane or *trans*-1-bromo-2-methylcyclohexane?