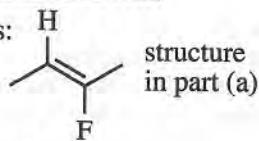


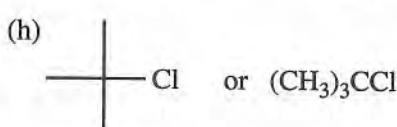
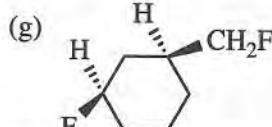
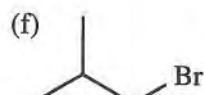
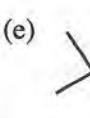
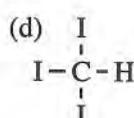
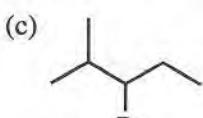
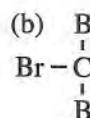
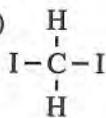
CHAPTER 6—ALKYL HALIDES; NUCLEOPHILIC SUBSTITUTION

6-1 In problems like part (a), draw out the whole structure to detect double bonds:

- (a) vinyl halide (b) alkyl halide (c) alkyl halide
 (d) alkyl halide (e) vinyl halide (f) aryl halide



6-2 (a)

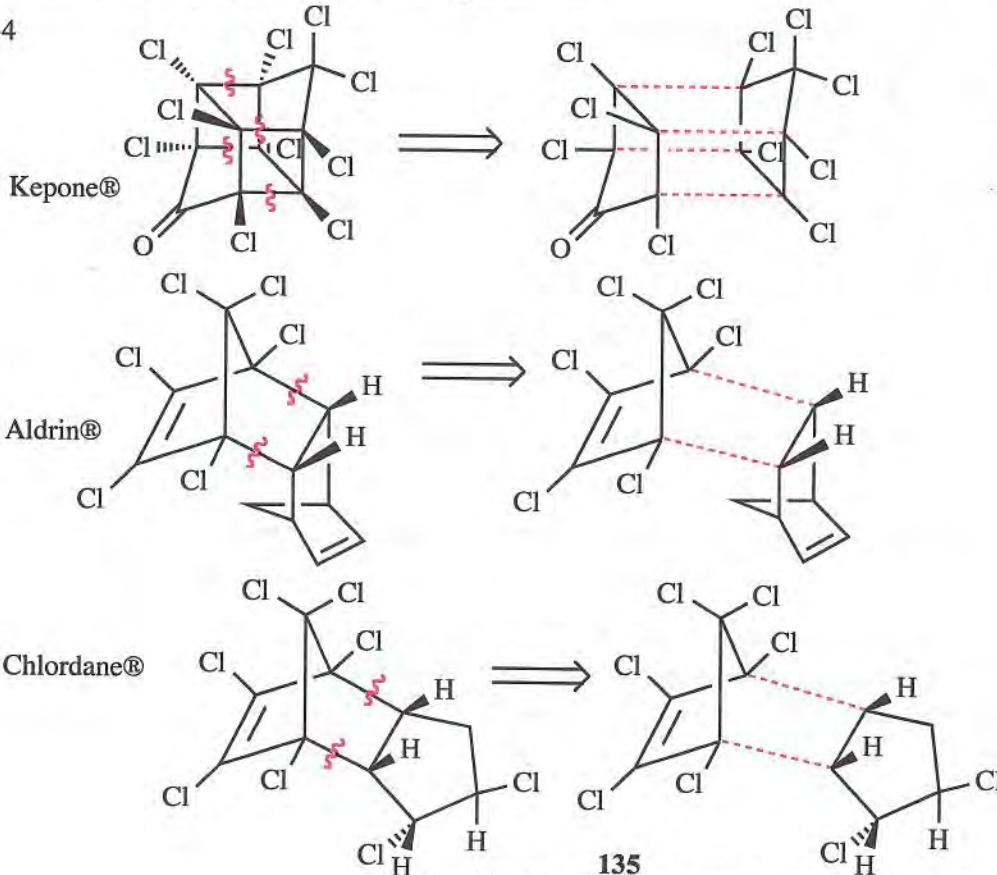


You may have drawn the other enantiomer. Either is correct.

6-3 IUPAC name; common name; degree of halogen-bearing carbon

- (a) 1-chloro-2-methylpropane; isobutyl chloride; 1° halide
 (b) 2-bromo-2-methylpropane; *tert*-butyl bromide; 3° halide
 (c) 1-chloro-2-methylbutane; no common name; 1° halide
 (d) 4-fluoro-1,1-dimethylcyclohexane; no common name; 2° halide
 (e) 4-bromo-3-methylheptane; no common name; 2° halide
 (f) *cis*-1-bromo-2-chlorocyclobutane; no common name; both 2° halides;
 also correct is (1*R*,2*S*)-1-bromo-2-chlorocyclobutane

6-4



6-5

- (a) Table 6-1 shows that in all cases, the iodide has the lowest dipole moment of all four halides. Even though the C—I bond length is longer than C—Cl, the larger electronegativity of Cl makes a more significant contribution to the dipole moment. Ethyl chloride has a larger dipole moment.
- (b) 1-Bromopropane has a polar C—Br bond and has a large dipole moment. Cyclopropane has no electronegative atom and has essentially zero dipole moment.
- (c) The isomer with two bromine atoms *cis* to each other will have a large dipole moment. The *trans* isomer has the individual bond dipole moments pointing in opposite directions, so *trans*-2,3-dibromobut-2-ene has essentially zero dipole moment.
- (d) Two chlorine atoms *cis* to each other on a ring like *cis*-1,2-dichlorocyclobutane will have a large molecular dipole moment. When two chlorine atoms point in opposite directions in a molecule as in *trans*-1,3-dichlorocyclobutane, they effectively cancel and the molecular dipole moment is essentially zero.

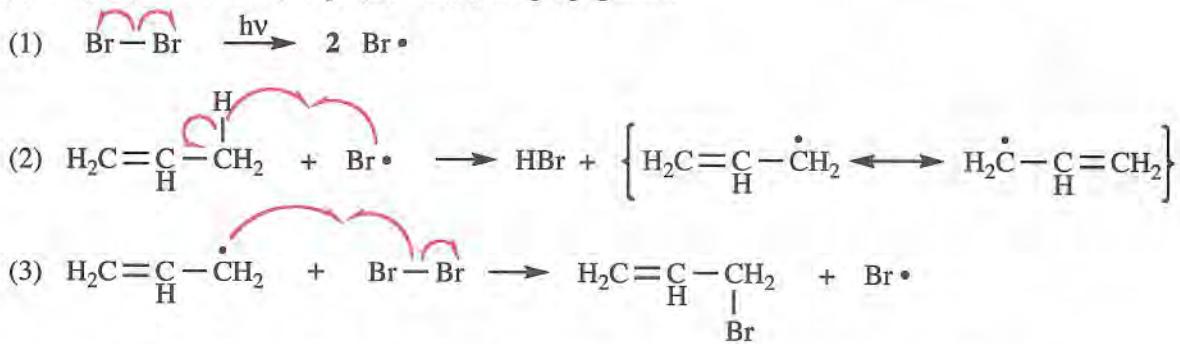
6-6

- (a) *n*-Butyl bromide (1-bromobutane) has a higher molecular weight and less branching, and boils at a higher temperature than isopropyl bromide.
- (b) *tert*-Butyl bromide has a higher molecular weight and a larger halogen, and despite its greater branching, boils at a higher temperature than isopropyl chloride.
- (c) 1-Bromobutane has a higher molecular weight and a larger halogen, and boils at a higher temperature than 1-chlorobutane.

6-7 From Table 3-2, the density of hexane is 0.66; it will float on the water layer (ρ 1.00). From Table 6-2, the density of chloroform is 1.50; water will float on the chloroform. Water is immiscible with many organic compounds; whether water is the top layer or bottom layer depends on whether the other material is less dense or more dense than water. (This is an important consideration to remember in lab procedures.) Water and ethanol are miscible, so only one phase would appear after shaking these two together.

6-8

- (a) Step (1) is initiation; steps (2) and (3) are propagation.



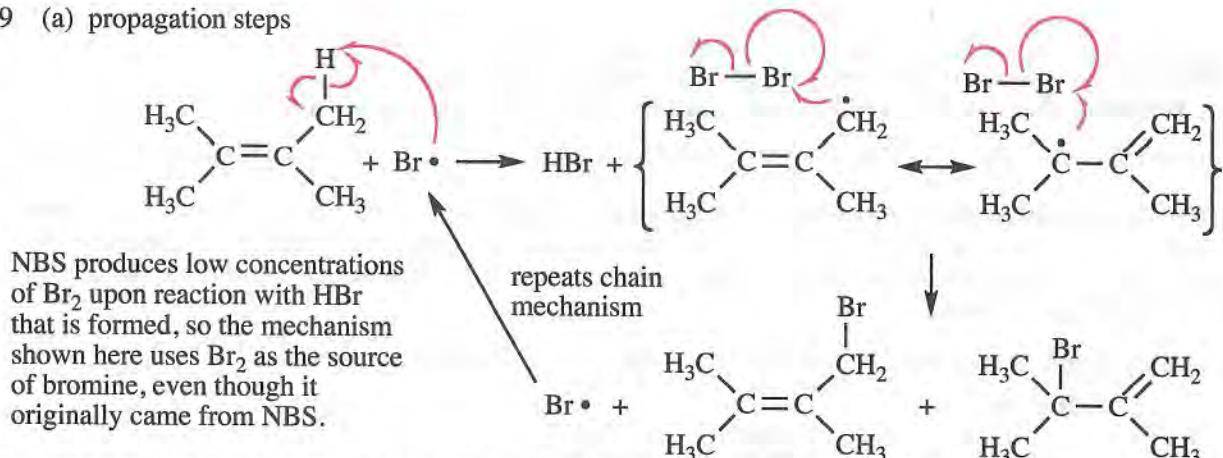
- (b) Step (2): break allylic C—H, make H—Br: kJ/mole: $+372 - (+366) = +6$ kJ/mole
kcal/mole: $+89 - (+88) = +1$ kcal/mole

Step (3): break Br—Br, make allylic C—Br: kJ/mole: $+190 - (+280) = -90$ kJ/mole
kcal/mole: $+45 - (+67) = -22$ kcal/mole

$$\Delta H^0_{\text{overall}} = +6 + (-90) = -84 \text{ kJ/mole} \quad (+1 + -22 = -21 \text{ kcal/mole})$$

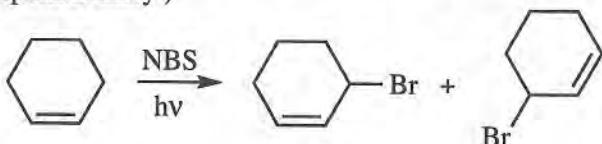
This is a very exothermic reaction; it is reasonable to expect a small activation energy in step (2), the first propagation step, so this reaction should be very rapid.

6-9 (a) propagation steps

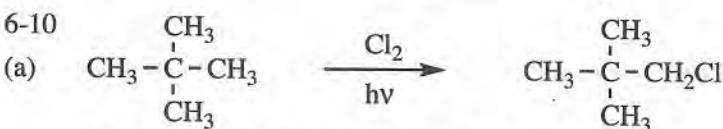


The resonance-stabilized allylic radical intermediate has radical character on both the 1° and 3° carbons, so bromine can bond to either of these carbons producing two isomeric products.

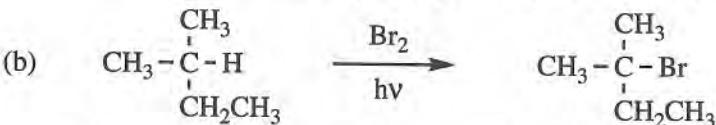
(b) Allylic bromination of cyclohexene gives 3-bromocyclohex-1-ene regardless of whether there is an allylic shift. Either pathway leads to the same product. If one of the ring carbons were somehow marked or labeled, then the two products could be distinguished. (We will see in following chapters how labeling is done experimentally.)



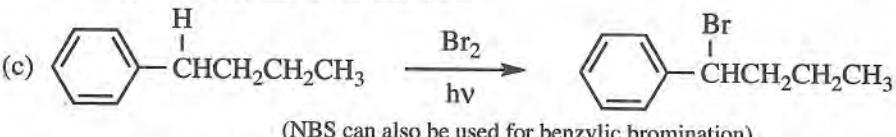
This second structure from the allylic shift is *identical* to the first structure—only one compound is produced here.



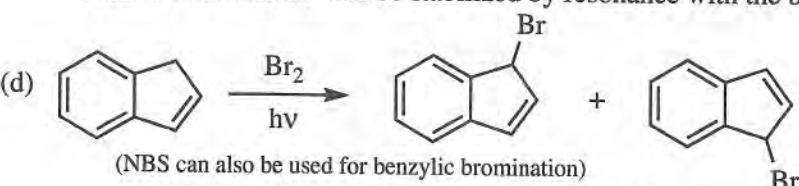
This compound has only one type of hydrogen—only one monochlorine isomer can be produced.



Bromination has a strong preference for abstracting hydrogens that give the most stable radical intermediates, like 3° in this case.



The bromine atom will abstract the hydrogen giving the most stable radical; in this case, the radical intermediate will be stabilized by resonance with the benzene ring.



This second structure from the allylic shift is *identical* to the first structure—only one compound is produced here.

The bromine atom will abstract the hydrogen giving the most stable radical; in this case, the radical intermediate will be stabilized by resonance with the benzene ring.

6-11

- (a) Substitution— Br^- is the leaving group; CH_3O^- is the nucleophile.
 - (b) Elimination—when OH is protonated, H_2O is the leaving group.
 - (c) Elimination—both Br atoms are lost; iodide ion is a nucleophile that reacts at Br.

6-12 (a) $\text{CH}_3(\text{CH}_2)_4\text{CH}_2 - \text{OCH}_2\text{CH}_3$ (b) $\text{CH}_3(\text{CH}_2)_4\text{CH}_2 - \text{CN}$ (c) $\text{CH}_3(\text{CH}_2)_4\text{CH}_2 - \text{OH}$

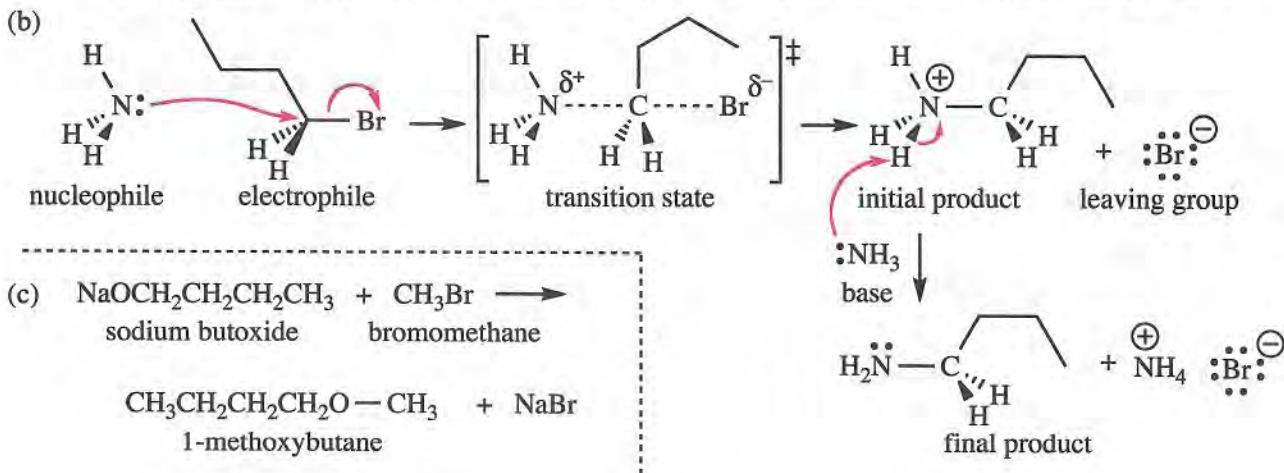
6-13 (a) The rate law is first order in both 1-bromobutane, C_4H_9Br , and methoxide ion. If the concentration of C_4H_9Br is lowered to one-fifth the original value, the rate must decrease to one-fifth; if the concentration of methoxide is doubled, the rate must also double. Thus, the rate must decrease to two-fifths of the original rate, 0.02 mole/L per second:

A completely different way to answer this problem is to solve for the rate constant k , then put in new values for the concentrations.

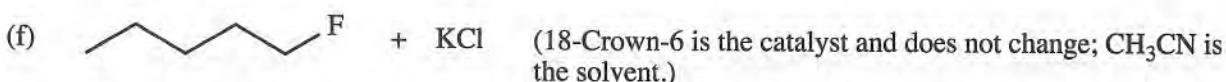
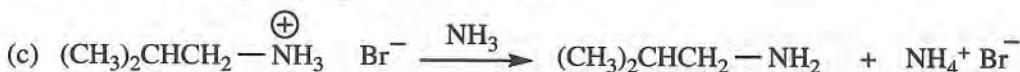
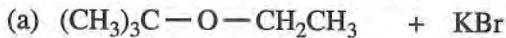
$$\text{rate} = k [\text{C}_4\text{H}_9\text{Br}] [\text{NaOCH}_3] \longrightarrow 0.05 \text{ mole L}^{-1} \text{ sec}^{-1} = k (0.5 \text{ mol L}^{-1}) (1.0 \text{ mol L}^{-1}) \longrightarrow$$

$$\text{rate constant } k = 0.1 \text{ L mol}^{-1} \text{ sec}^{-1}$$

$$\text{rate} = k [\text{C}_4\text{H}_9\text{Br}] [\text{NaOCH}_3] = (0.1 \text{ L mol}^{-1} \text{ sec}^{-1}) (0.1 \text{ mol L}^{-1}) (2.0 \text{ mol L}^{-1}) = 0.02 \text{ mole L}^{-1} \text{ sec}^{-1}$$



6-14 Organic and inorganic products are shown here for completeness.



6-15 All reactions in this problem follow the same pattern; the only difference is the nucleophile (:Nuc). Only the nucleophile is listed below. (Cations like Na^+ or K^+ accompany the nucleophile but are simply spectator ions and do not take part in the reaction; they are not shown here.)



- (a) HO^- (b) F^- from KF/18-crown-6 (c) I^- (d) $\text{^-\text{CN}}$ (e) $\text{HC}\equiv\text{C}:\text{\Theta}$
 (f) $\text{^-\text{OCH}_2\text{CH}_3}$ (g) excess NH_3 (or $\text{^-\text{NH}_2}$)

6-16

- (a) $(\text{CH}_3\text{CH}_2)_2\text{NH}$ is a better nucleophile—less hindered.

(b) $(\text{CH}_3)_2\text{S}$ is a better nucleophile—S is larger, more polarizable than O.

(c) PH_3 is a better nucleophile—P is larger, more polarizable than N.

(d) CH_3S^- is a better nucleophile—anions are better than neutral atoms of the same element.

(e) $(\text{CH}_3)_3\text{N}$ is a better nucleophile—less electronegative than oxygen, better able to donate an electron pair.

(f) CH_3COO^- is a better nucleophile—more basic, electrons less delocalized than in CF_3COO^- because of inductive effect of F substituents.

(g) $\text{CH}_3\text{CH}_2\text{CH}_2\text{O}^-$ is a better nucleophile—less branching, less steric hindrance.

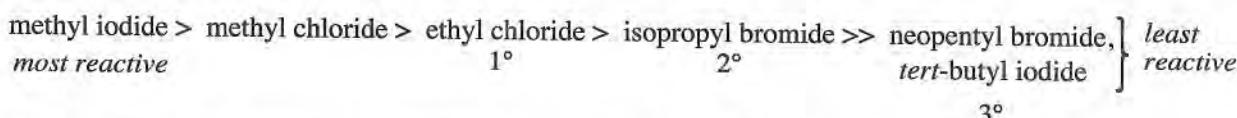
(h) I^- is a better nucleophile—larger, more polarizable than Cl $^-$.

6-17 A mechanism uses arrows to show *electron movement*. An arrow must begin at either a bond or an unshared electron pair (or a single electron in radical reactions). "Et" is the abbreviation for an ethyl group.



Protonation converts OCH_2CH_2 to a good leaving group so that bromide can effect substitution.

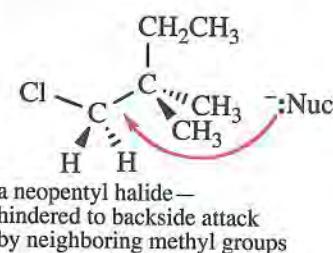
6-18 The type of carbon with the halide, and relative leaving group ability of the halide, determine the reactivity.



Predicting the relative order of neopentyl bromide and *tert*-butyl iodide would be difficult because both would be extremely slow.

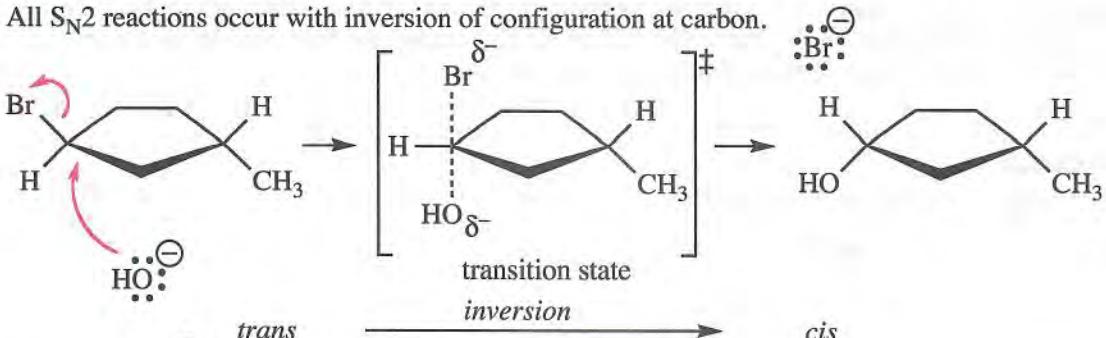
6-19 In all cases, the less hindered structure is the better S_N2 substrate.

- (a) 2-methyl-1-iodopropane (1° versus 3°)
 - (b) cyclohexyl bromide (2° versus 3°)
 - (c) isopropyl bromide (no substituent on neighboring carbon)
 - (d) 2-chlorobutane (Even though this is a 2° halide, it is easier than the 1° neopentyl type in 1-chloro-2,2-dimethylbutane—see and the solution to Problem 6-18.)
 - (e) 1-iodobutane (1° versus 2°)

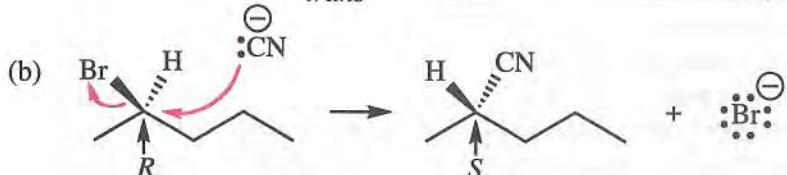


6-20 All S_N2 reactions occur with inversion of configuration at carbon.

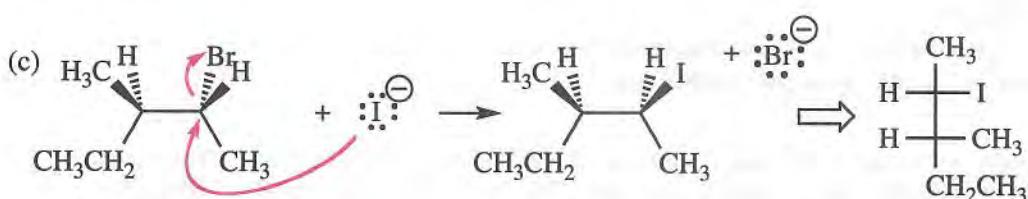
(a)



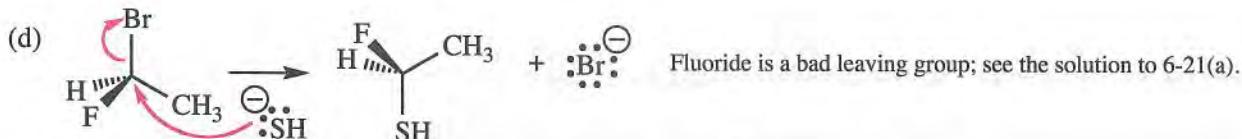
(b)



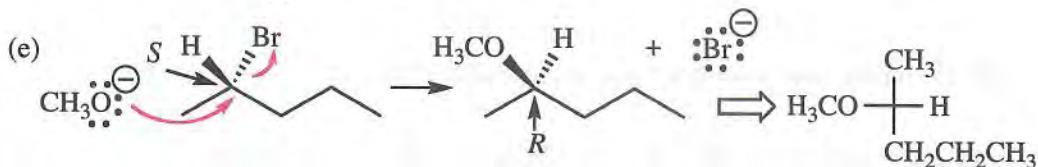
(c)



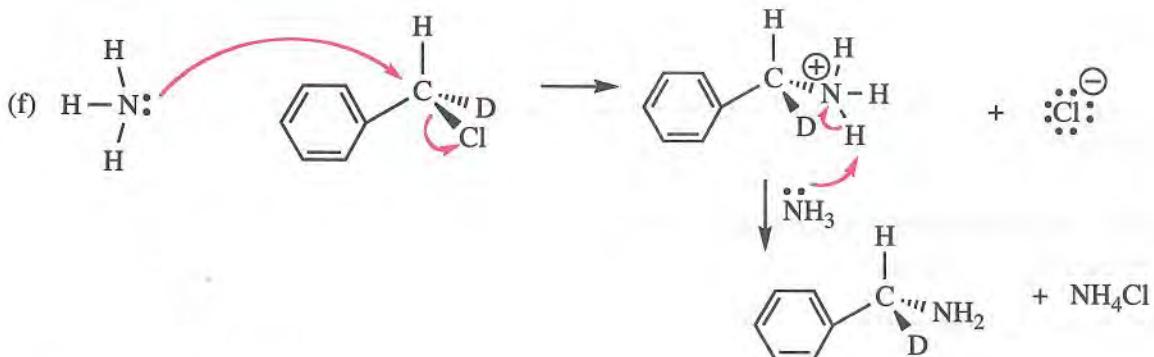
(d)



(e)



(f)

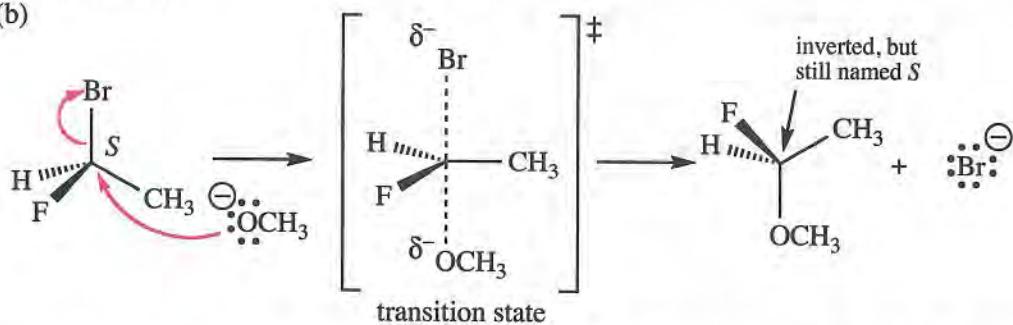


6-21

- (a) The best leaving groups are the weakest bases. Bromide ion is so weak it is not considered at all basic; it is an excellent leaving group. Fluoride is moderately basic, by far the most basic of the halides. It is a terrible leaving group. Bromide is many orders of magnitude better than fluoride in leaving group ability.

6-21 continued

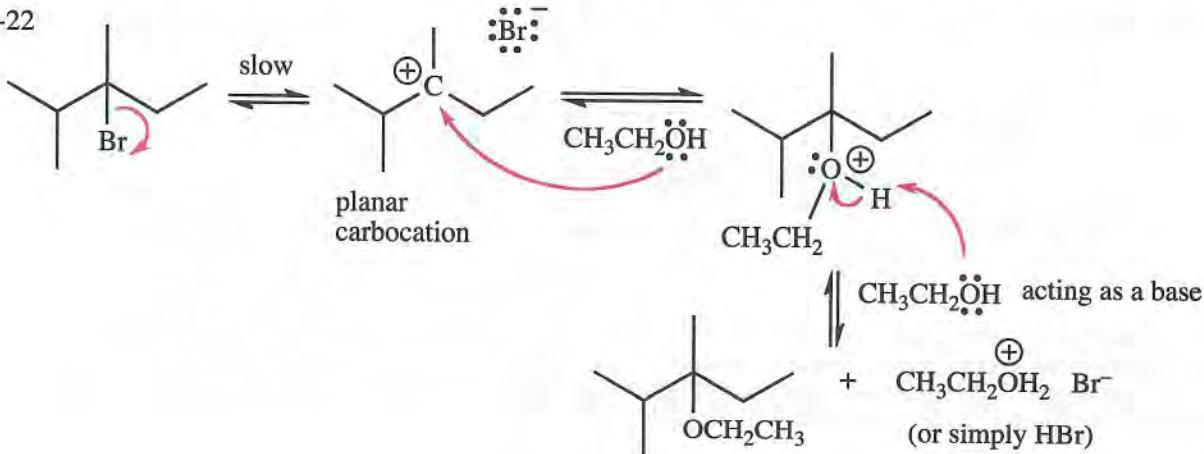
(b)



(c) As noted on the structure above, the configuration is inverted even though the designations of the configuration for both the starting material and the product are *S*; the oxygen of the product has a lower priority than the bromine it replaces. Refer to the solution to problem 5-38 for the caution about confusing absolute configuration with the *designation* of configuration.

(d) The result is perfectly consistent with the S_N2 mechanism. Even though both the reactant and the product have the *S* designation, the configuration has been inverted: the nomenclature priority of fluorine changes from second (after bromine) in the reactant to first (before oxygen) in the product. While the designation may be misleading, the structure shows with certainty that an inversion has occurred.

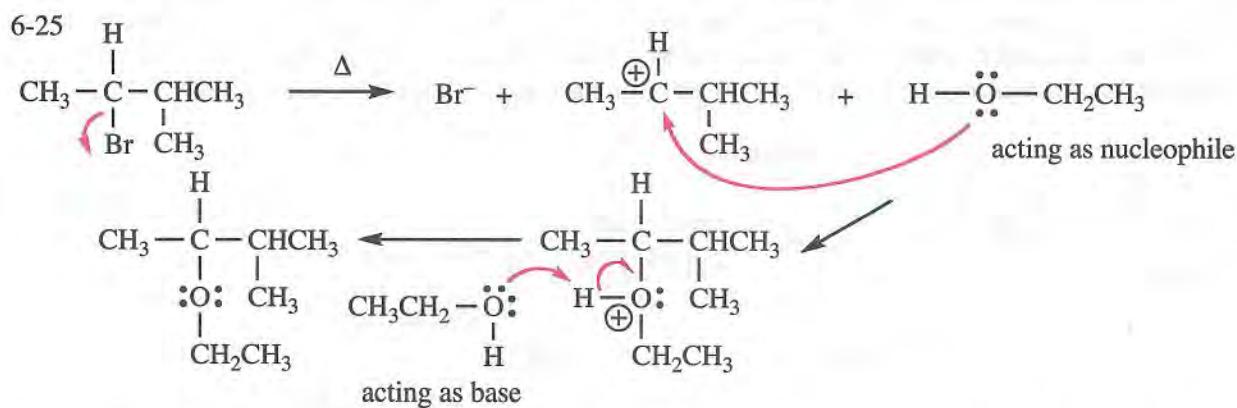
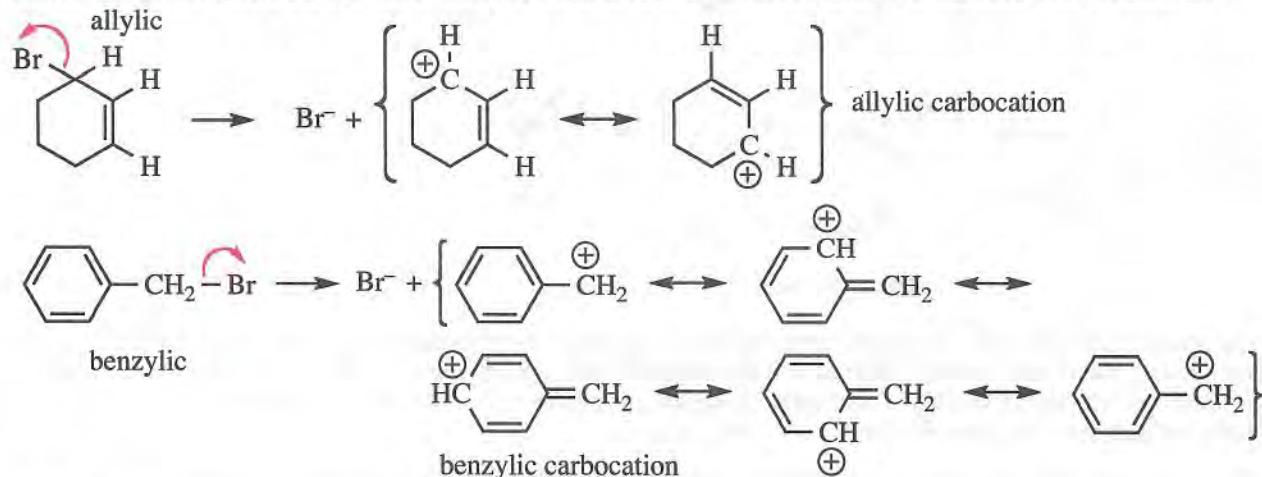
6-22



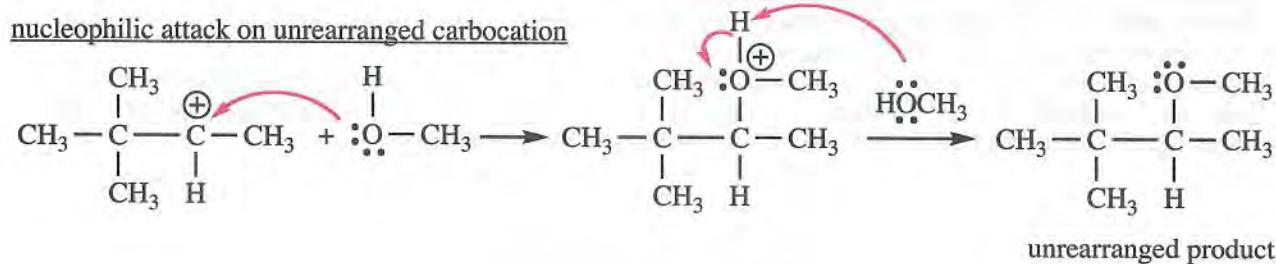
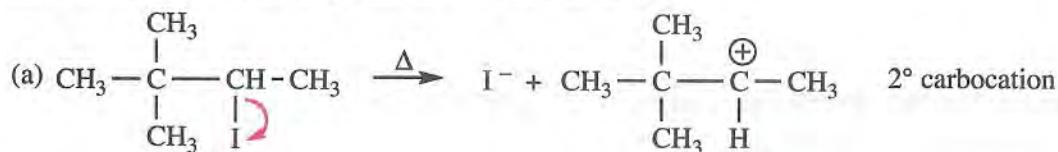
6-23 The structure that can form the more stable carbocation will undergo S_N1 faster.

- 2-Bromopropane: will form a 2° carbocation.
- 2-Bromo-2-methylbutane: will form a 3° carbocation.
- Allyl bromide is faster than propyl bromide: allyl bromide can form a resonance-stabilized intermediate.
- 2-Bromopropane: will form a 2° carbocation.
- 2-Iodo-2-methylbutane is faster than *tert*-butyl chloride (iodide is a better leaving group than chloride).
- 2-Bromo-2-methylbutane (3°) is faster than ethyl iodide (1°); although iodide is a somewhat better leaving group, the difference between 3° and 1° carbocation stability dominates.

6-24 Ionization is the rate-determining step in S_N1. Anything that stabilizes the carbocation intermediate will speed the reaction. Both of these compounds form resonance-stabilized intermediates.



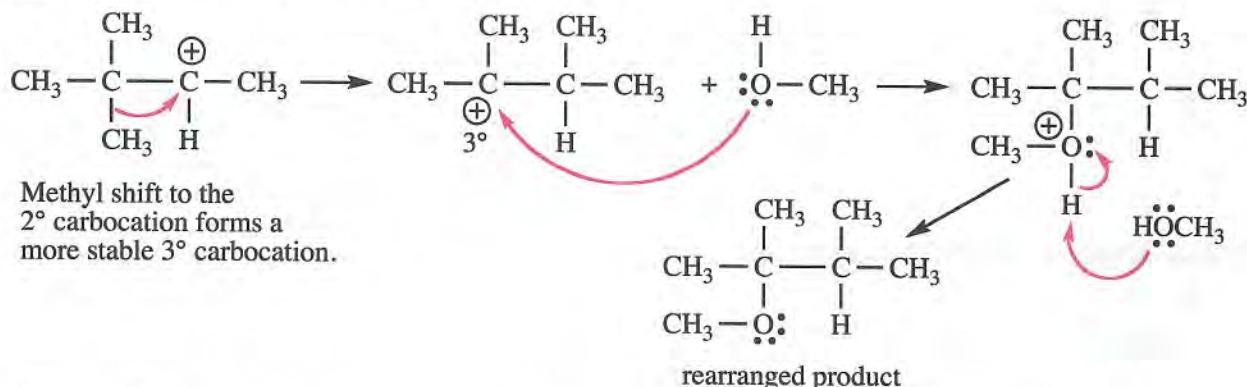
6-26 It is important to analyze the structure of carbocations to consider if migration of any groups from adjacent carbons will lead to a more stable carbocation. As a general rule, if rearrangement would lead to a more stable carbocation, a carbocation will rearrange. (Beginning with this problem, only those unshared electron pairs involved in a particular step will be shown.)



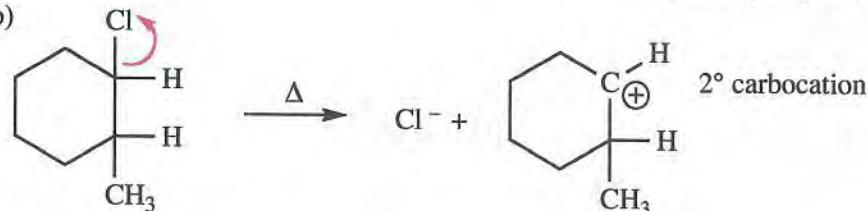
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6-26 (a) continued

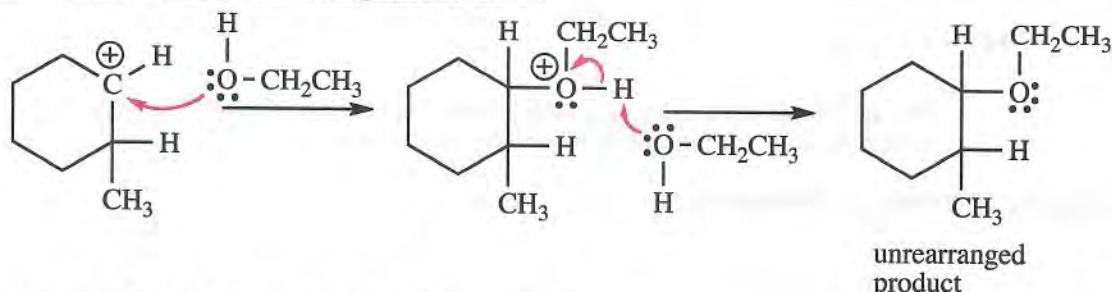
nucleophilic attack after carbocation rearrangement



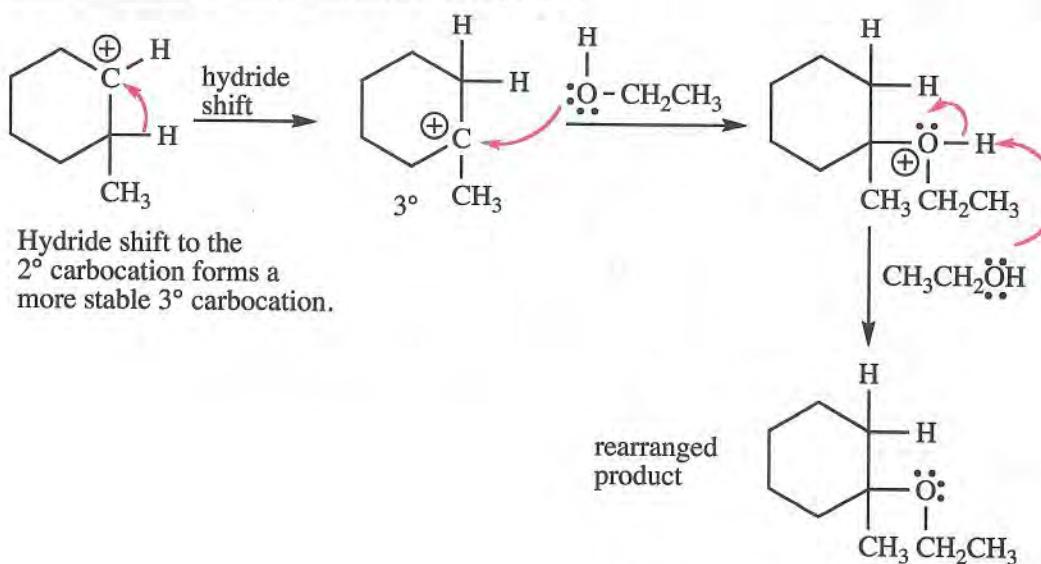
(b)



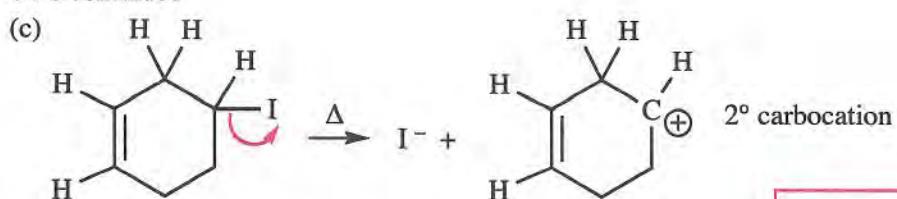
nucleophilic attack on unrearranged carbocation



nucleophilic attack after carbocation rearrangement

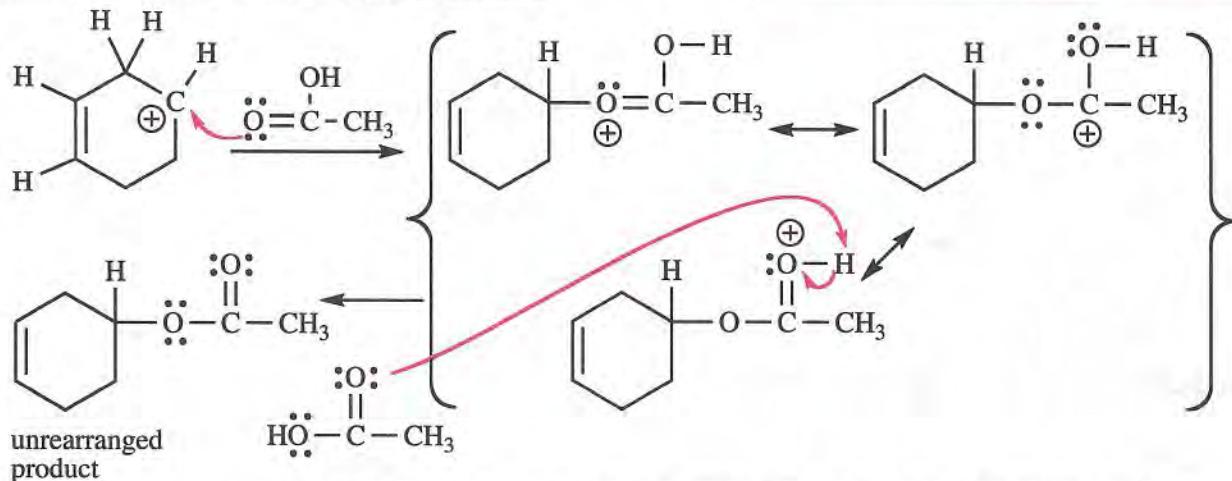


6-26 continued



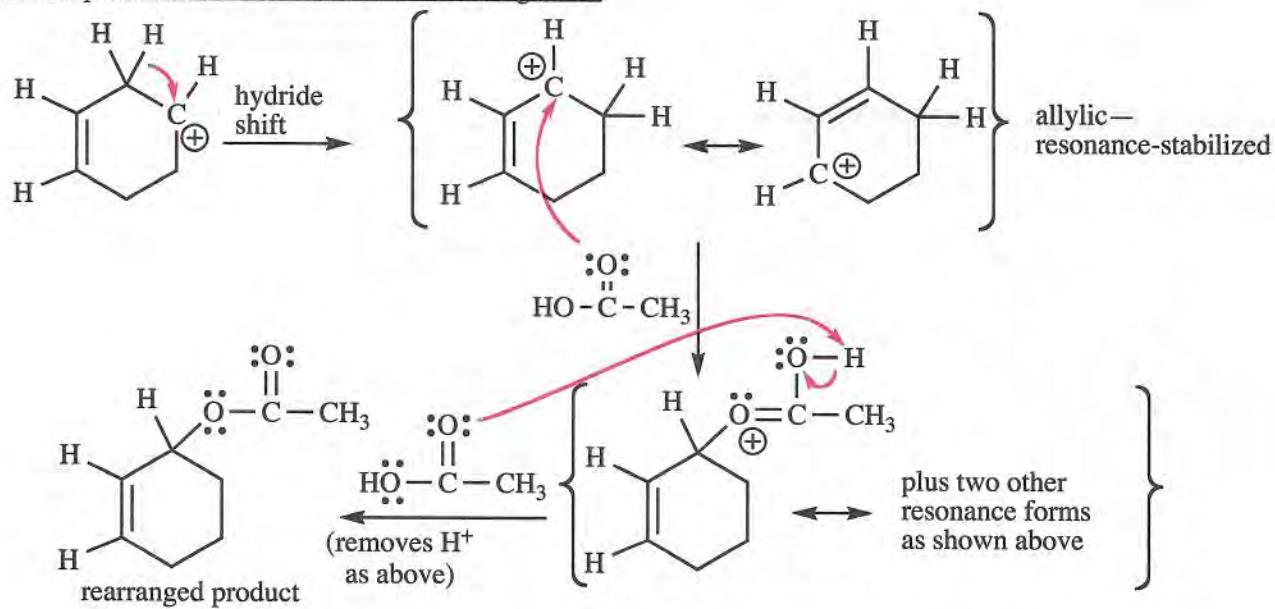
Note: braces are used to indicate the ONE chemical species represented by multiple resonance forms.

nucleophilic attack on unrearranged carbocation



The most basic species in a mixture is the most likely to remove a proton.
In this reaction, acetic acid is more basic than iodide ion.

nucleophilic attack after carbocation rearrangement



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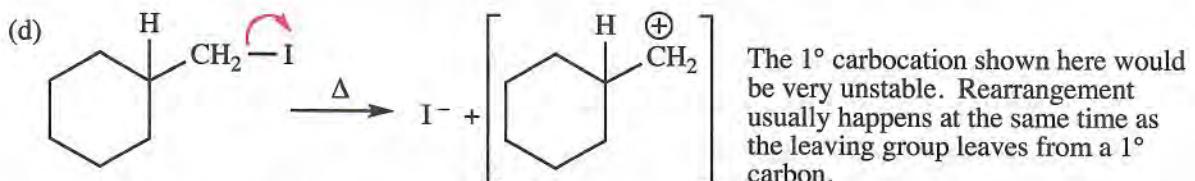
6-26(c) continued

Comments on 6-26(c)

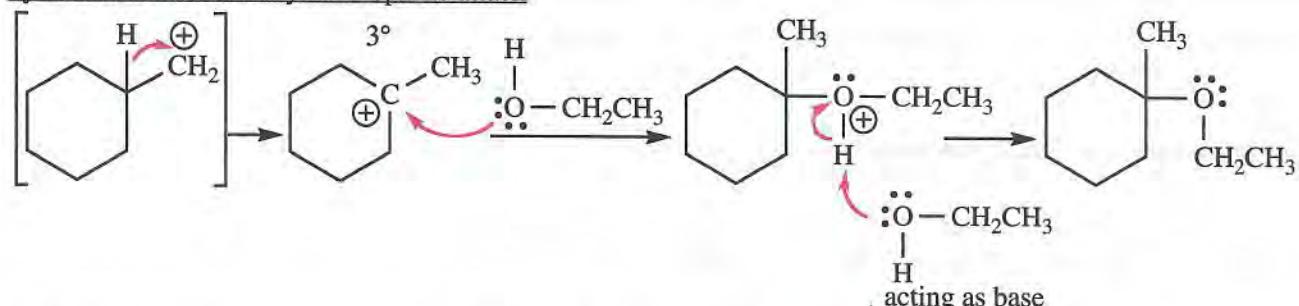
(1) The hydride shift to a 2° carbocation generates an allylic, resonance-stabilized 2° carbocation.

(2) The double-bonded oxygen of acetic acid is more nucleophilic because of the resonance forms it can have after attack. (See the solution to Problem 2-20.)

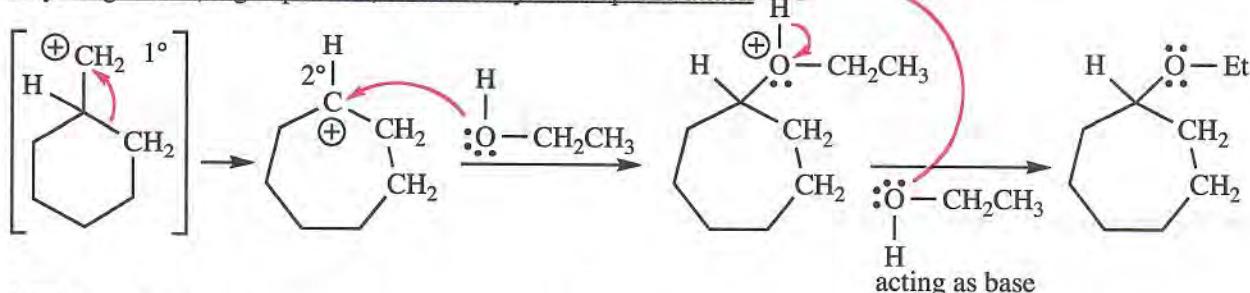
(3) Attack on only one carbon of the allylic carbocation is shown. In reality, both positive carbons would be attacked in equal amounts, but they would give the identical product *in this case*. In other compounds, however, attack on the different carbons might give different products. **ALWAYS CONSIDER ALL POSSIBILITIES.**



hydride shift followed by nucleophilic attack

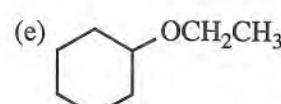


alkyl migration (ring expansion) followed by nucleophilic attack



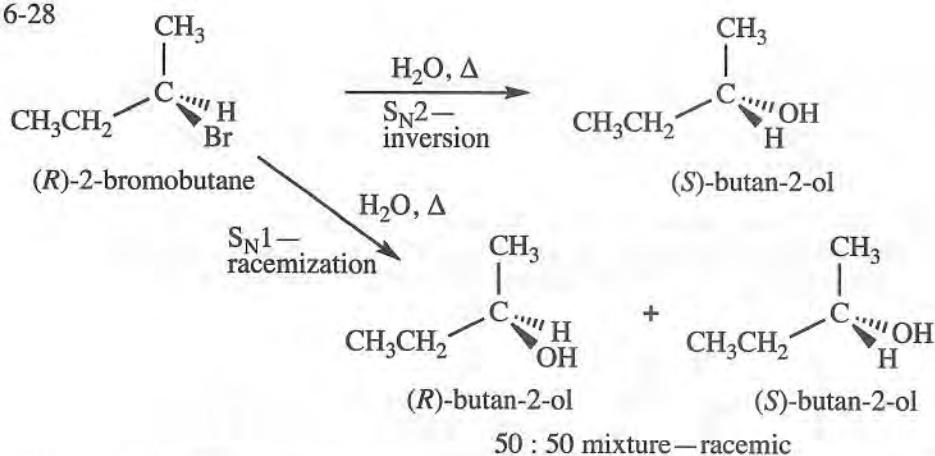
6-27

- | | | | |
|--|--|--|--|
| $\begin{array}{c} \text{CH}_3 & \text{O} \\ & \\ \text{CH}_3-\text{C}-\text{O}-\text{C}-\text{CH}_3 \\ & \\ \text{CH}_2\text{CH}_3 & \end{array}$ | $\begin{array}{c} \text{CH}_3-\text{CHCH}_2\text{OCH}_3 \\ \\ \text{CH}_3 \end{array}$ | $\begin{array}{c} \text{CH}_3 \\ \\ \text{OCH}_2\text{CH}_3 \end{array}$ | $\begin{array}{c} \text{OCH}_3 \\ \\ \text{C}_6\text{H}_5 \end{array}$ |
| (a) | (b) | (c) | (d) |
- S_N1 on 3° C,
weak nucleophile
- S_N2 on 1° C,
strong nucleophile
- S_N1 on 3° C,
weak nucleophile
- S_N1 on 2° C,
weak nucleophile



S_N2 on 2° C, strong
nucleophile

6-28



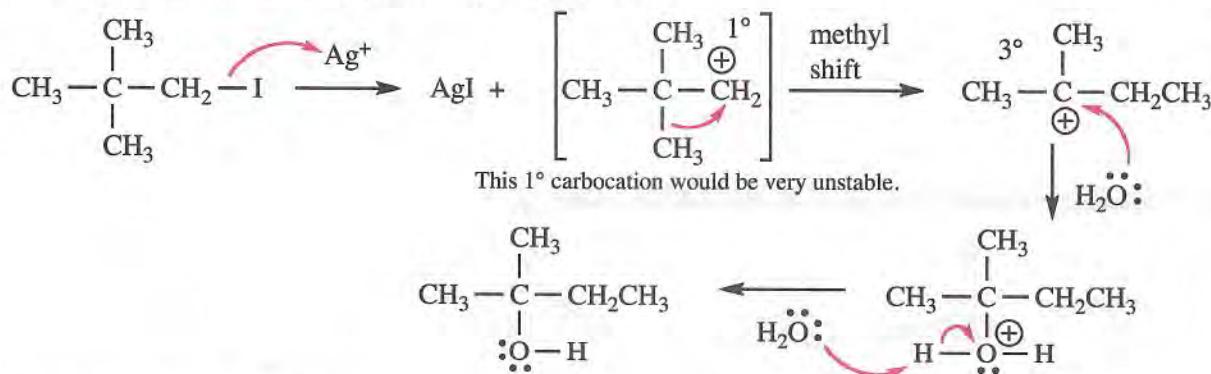
If $\text{S}_{\text{N}}1$, which gives racemization, occurs exactly twice as fast as $\text{S}_{\text{N}}2$, which gives inversion, then the racemic mixture (50 : 50 *R* + *S*) is 66.7% of the mixture and the rest, 33.3%, is the *S* enantiomer from $\text{S}_{\text{N}}2$. Therefore, the excess of one enantiomer over the racemic mixture must be 33.3%, the enantiomeric excess. (In the racemic mixture, the *R* and *S* "cancel" each other algebraically as well as in optical rotation.)

The optical rotation of pure (S)-butan-2-ol is $+13.5^\circ$. The optical rotation of this mixture is:

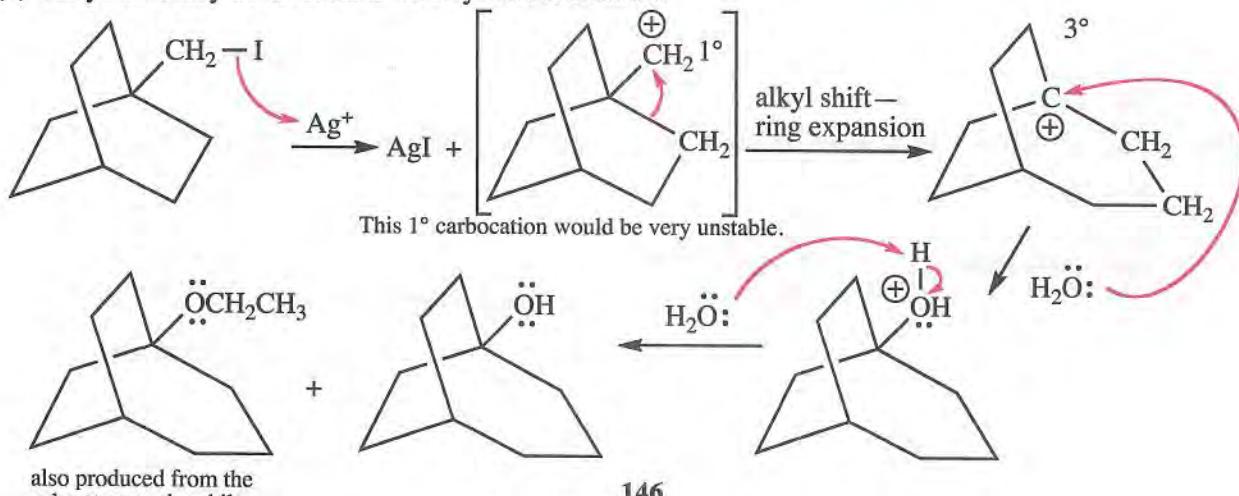
$$33.3\% \times +13.5^\circ = +4.5^\circ$$

6-29

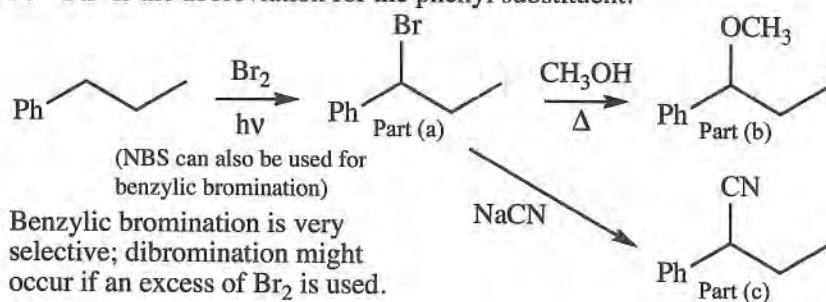
(a) Methyl shift may occur simultaneously with ionization.



(b) Alkyl shift may occur simultaneously with ionization.

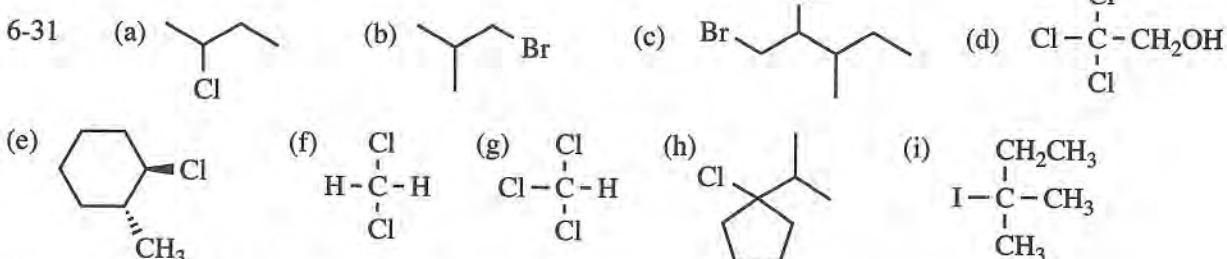


6-30 "Ph" is the abbreviation for the phenyl substituent.



Solvolytic conditions— $\text{S}_{\text{N}}1$ —should give a clean product with no rearrangement.

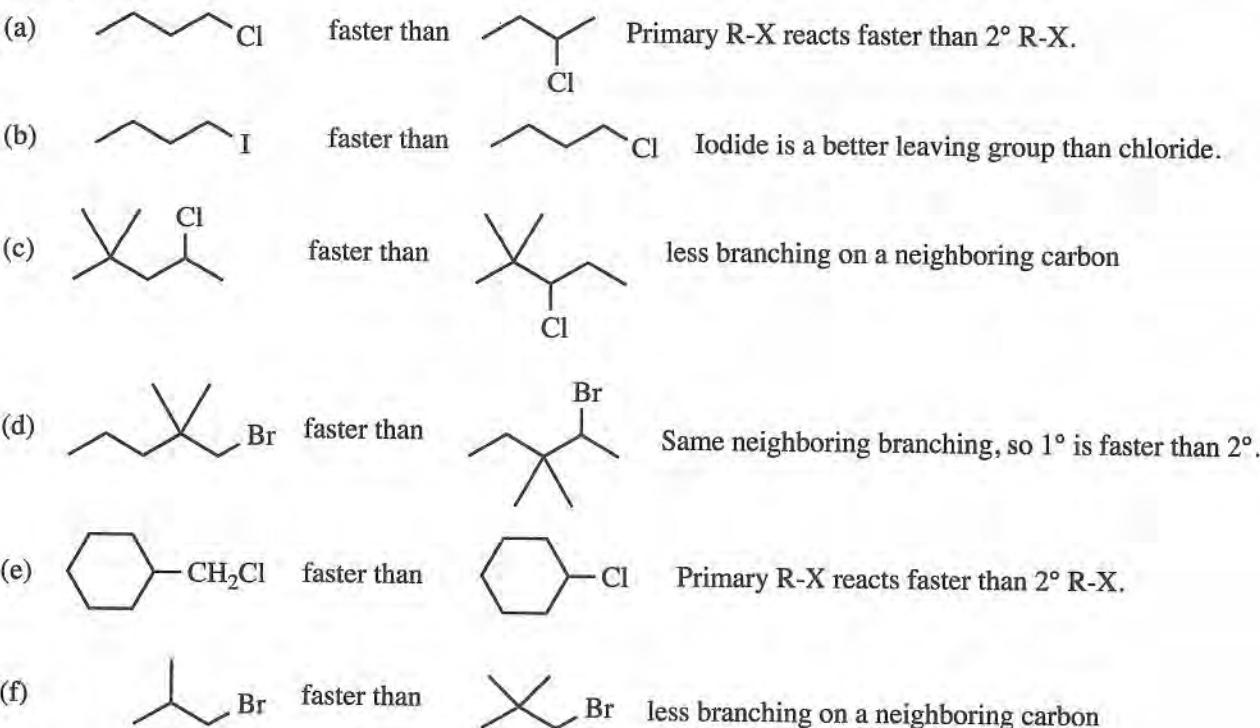
Benzylic positions give clean $\text{S}_{\text{N}}2$ reactions.



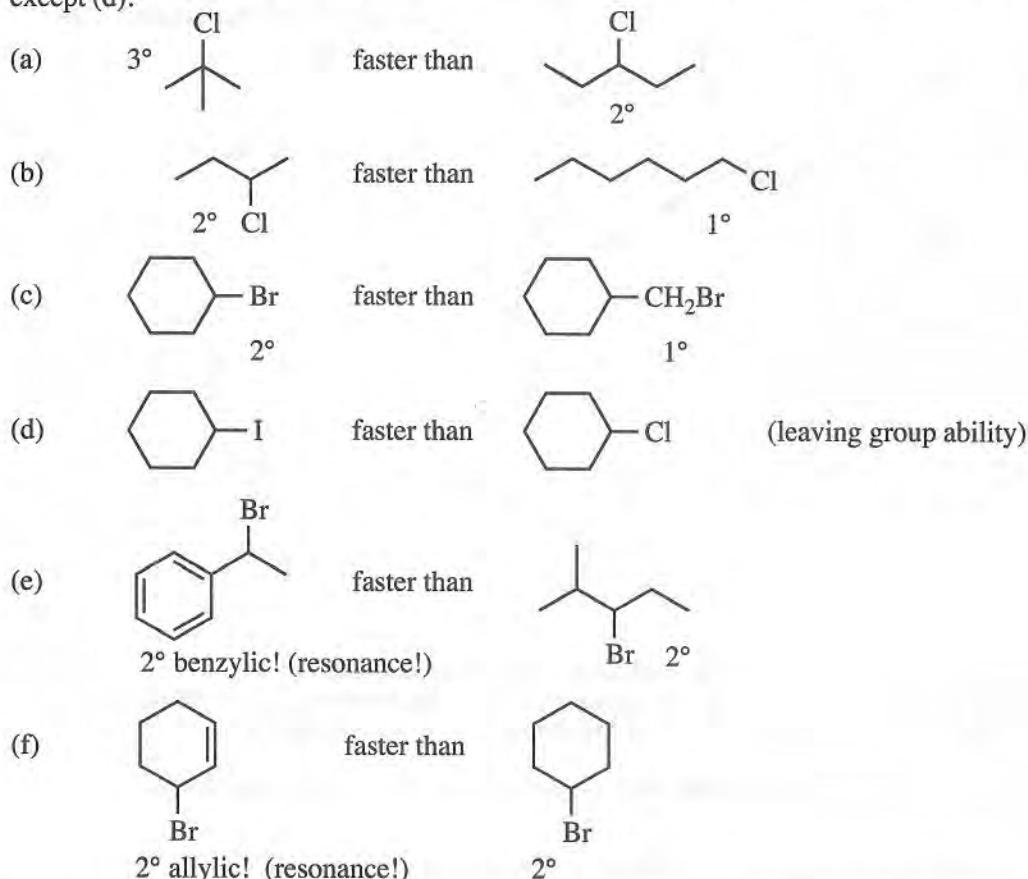
6-32

- | | |
|--|---|
| (a) 2-bromo-2-methylpentane | (b) 1-chloro-1-methylcyclohexane |
| (c) 1,1-dichloro-3-fluorocycloheptane | (d) 4-(2-bromoethyl)-3-(fluoromethyl)-2-methylheptane |
| (e) 4,4-dichloro-5-cyclopropyl-1-iodoheptane | (f) <i>cis</i> -1,2-dichloro-1-methylcyclohexane |

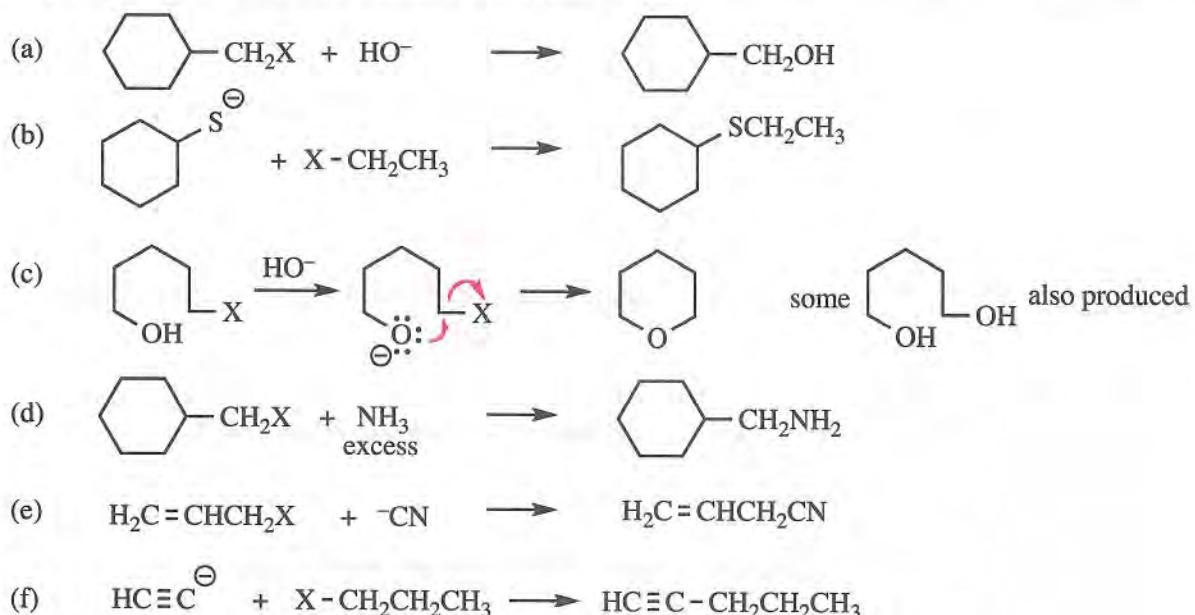
6-33 Ease of backside attack (less steric hindrance) decides which undergoes $\text{S}_{\text{N}}2$ faster in all these examples except (b).



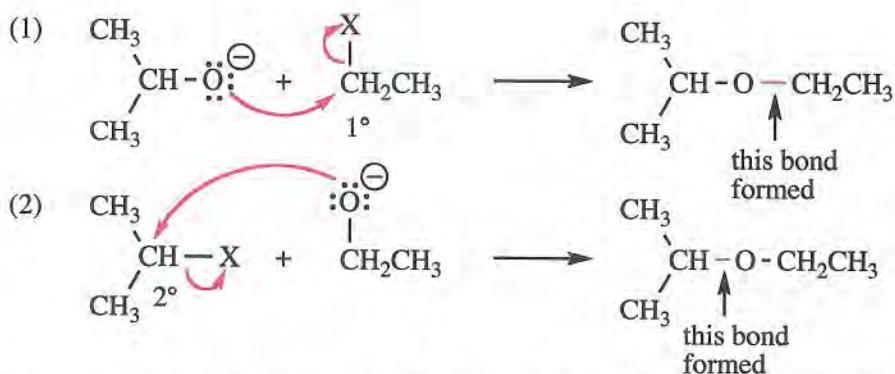
6-34 Formation of the more stable carbocation decides which undergoes S_N1 faster in all these examples except (d).



6-35 For S_N2, reactions should be designed such that the nucleophile attacks the least highly substituted alkyl halide. ("X" stands for a halide: Cl, Br, or I.)



6-36



Synthesis (1) would give a better yield of the desired ether product. (1) uses S_N2 attack of a nucleophile on a 1° carbon, while (2) requires attack on a more hindered 2° carbon. Reaction (2) would give a lower yield of substitution, with more elimination.

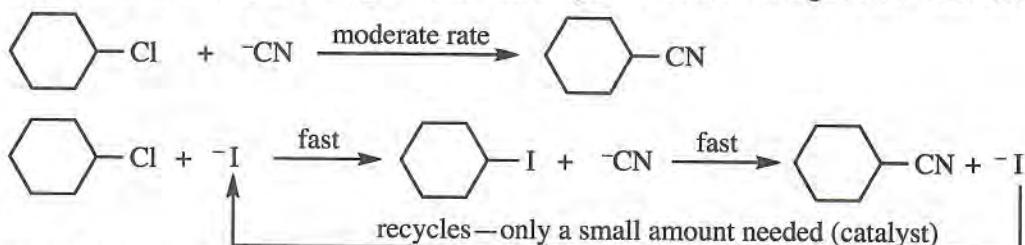
6-37

- (a) S_N2 —second order: reaction rate doubles: rate = $k [EtBr] [KO-t-Bu]$
- (b) S_N2 —second order: reaction rate increases six times
- (c) Virtually all reaction rates, including this one, increase with a temperature increase.

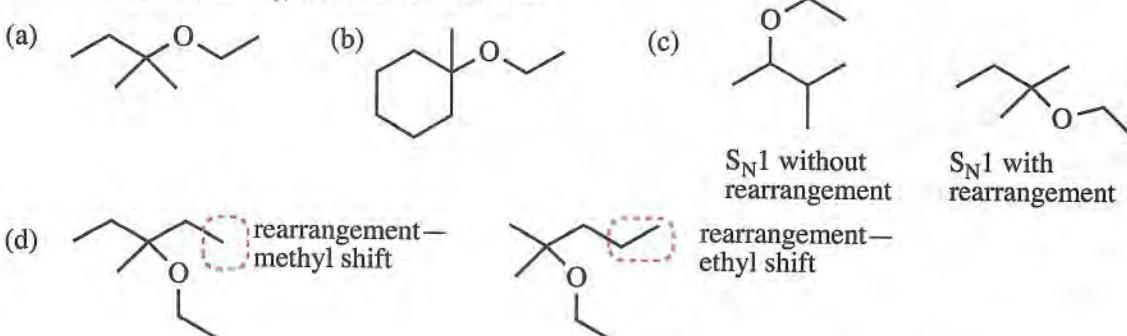
6-38 This is an S_N1 reaction; the rate law depends only on the substrate concentration, not on the nucleophile concentration: rate = $k [C_4H_9Br]$

- (a) no change in rate
- (b) the rate triples, dependent only on [tert-butyl bromide]
- (c) Virtually all reaction rates, including this one, increase with a temperature increase.

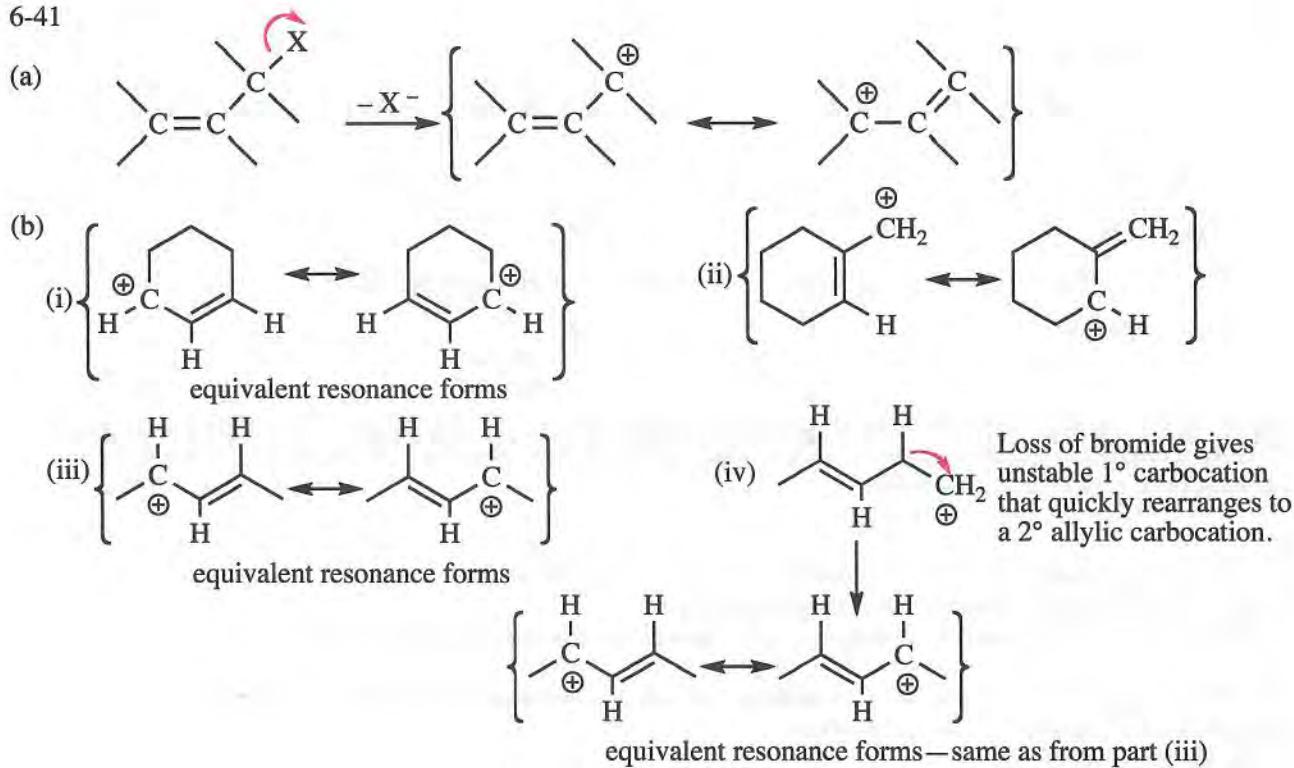
6-39 The key to this problem is that iodide ion is both an excellent nucleophile AND leaving group. Substitution on chlorocyclohexane is faster with iodide than with cyanide (see Table 6-3 for relative nucleophilicities). Once iodocyclohexane is formed, substitution by cyanide is much faster on iodocyclohexane than on chlorocyclohexane because iodide is a better leaving group than chloride. So two fast reactions involving iodide replace a slower single reaction, resulting in an overall rate increase.



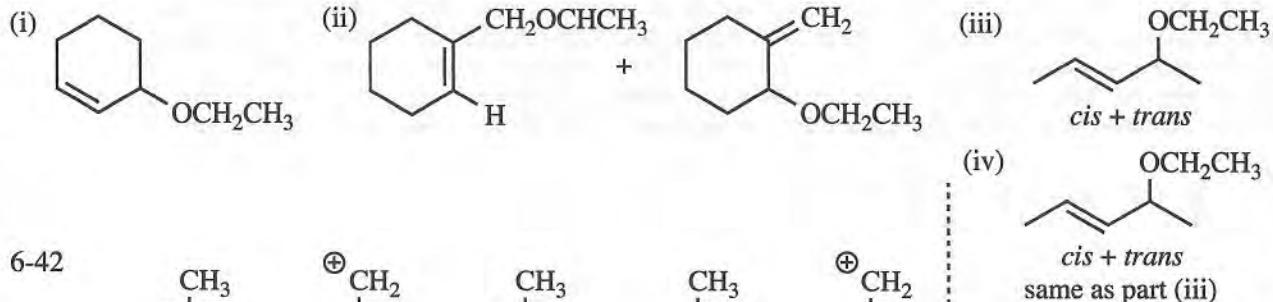
6-40 The solvolysis (S_N1) products are shown.



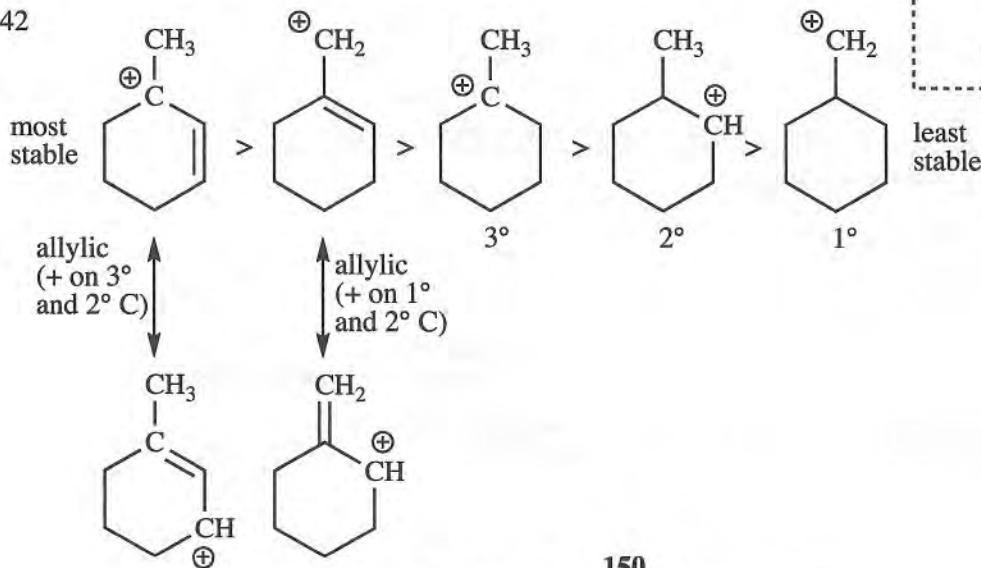
6-41



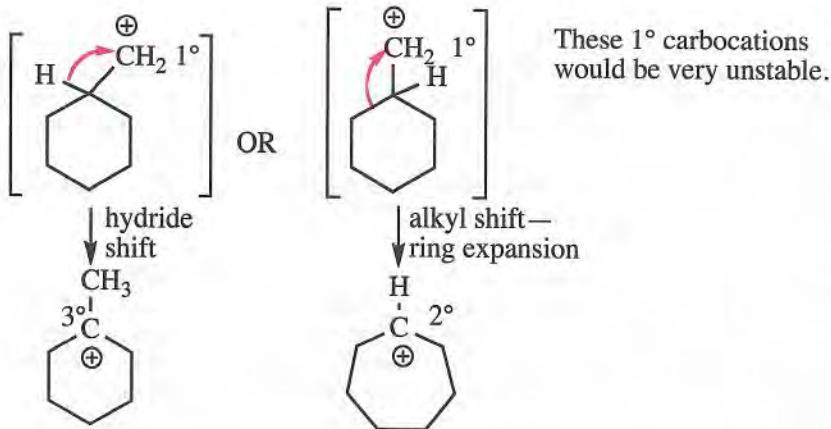
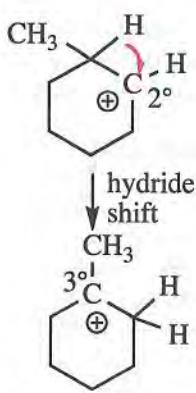
(c) Only one substitution product arises from equivalent resonance forms.



6-42

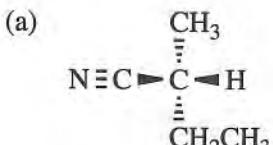


6-43

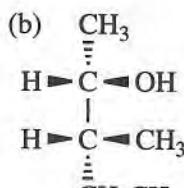


These 1° carbocations would be very unstable.

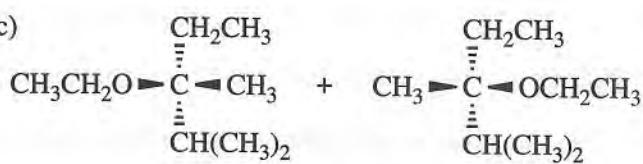
6-44



S_N2 gives inversion:
only product

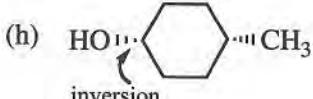
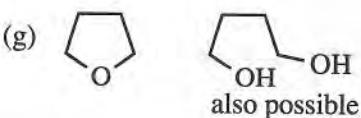
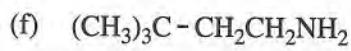
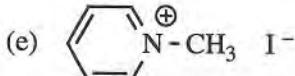
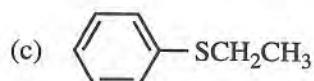
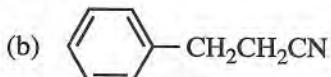
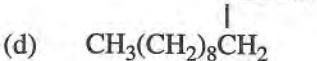
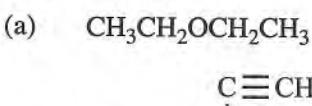


S_N2 only
with inversion

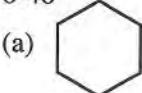


solvolysis, S_N1, racemization

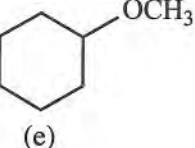
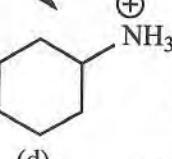
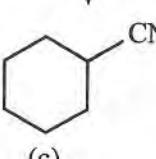
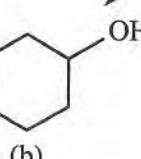
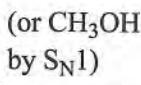
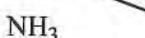
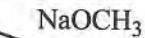
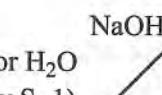
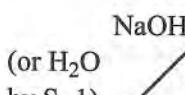
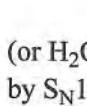
6-45



6-46



Use this as the starting material for the other four parts.



6-47

The use of methyl bromide (bromomethane) as a soil sterilant has been controversial: it is effective in killing soil organisms that are pathogenic to agricultural crops, especially strawberries, but its toxicity is not specific to soil organisms. It is acutely toxic to most plants and animals, including humans, and is a potent mutagen which is typical of alkylating agents. (Alkylated DNA bases are mutations.) It is also a potent disrupter of stratospheric ozone; one estimate is that the C—Br bond is about 50 times more effective at destroying ozone than is a C—Cl bond.

Methyl iodide (iodomethane) is more toxic because iodide is a better leaving group than bromide; therefore, methyl iodide is faster to alkylate any nucleophile that it contacts. On the other hand, methyl iodide is a liquid at room temperature, although it evaporates quickly; methyl bromide is a gas and diffuses more readily than methyl iodide. The other "benefit" of methyl iodide is that because it is more reactive than methyl bromide, it reacts in the soil or in the atmosphere more rapidly, so it is much less likely to reach the stratosphere than is methyl bromide—all because iodide is a better leaving group than bromide.

6-48

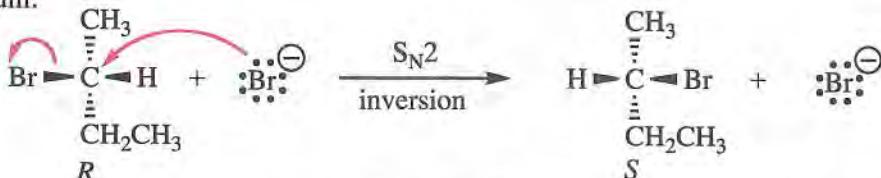
$$(a) \frac{+15.58^\circ}{+15.90^\circ} \times 100\% = 98\% \text{ of original optical activity} = 98\% \text{ e.e.}$$

Thus, 98% of the *S* enantiomer and 2% racemic mixture gives an overall composition of 99% *S* and 1% *R*.

(b) The 1% of radioactive iodide has produced exactly 1% of the *R* enantiomer. Each substitution must occur with inversion, a classic S_N2 mechanism.

6-49

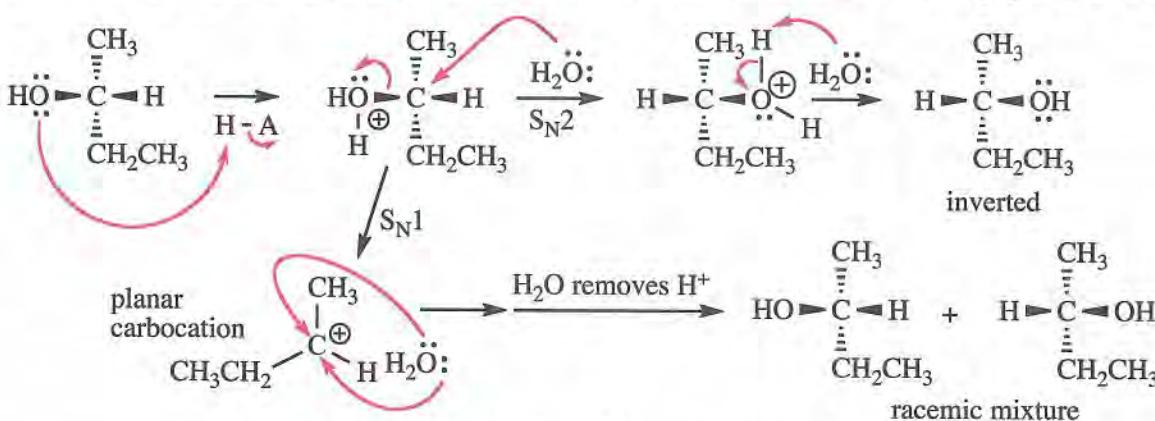
(a) An S_N2 mechanism with inversion will convert *R* to its enantiomer, *S*. An accumulation of excess *S* does not occur because it can also react with bromide, regenerating *R*. The system approaches a racemic mixture at equilibrium.



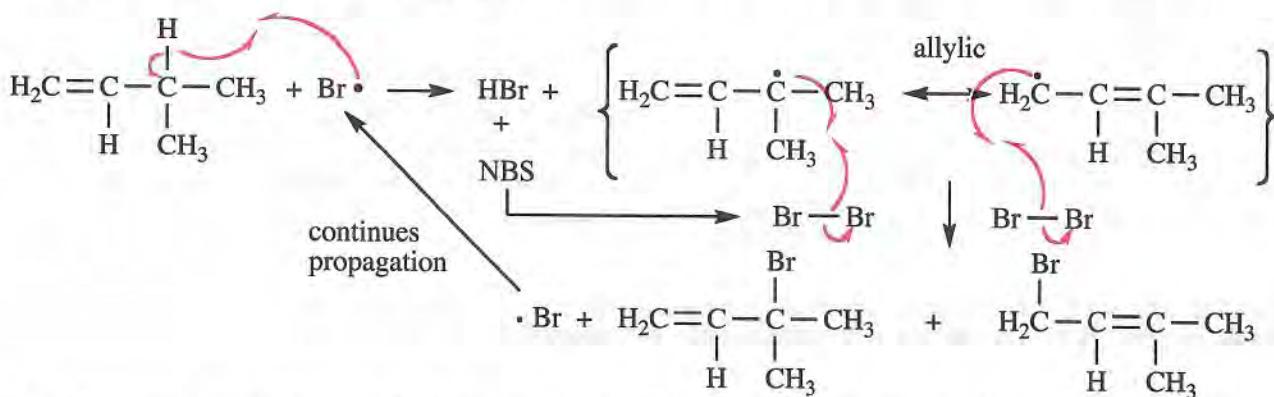
(b) In order to undergo substitution and therefore inversion, HO⁻ would have to be the leaving group, but HO⁻ is never a leaving group in S_N2. No reaction can occur.

(c) Once the OH is protonated, it can leave as H₂O. Racemization occurs in the S_N1 mechanism because of the planar, achiral carbocation intermediate which "erases" all stereochemistry of the starting material. Racemization occurs in the S_N2 mechanism by establishing an equilibrium of *R* and *S* enantiomers, as explained in part (a).

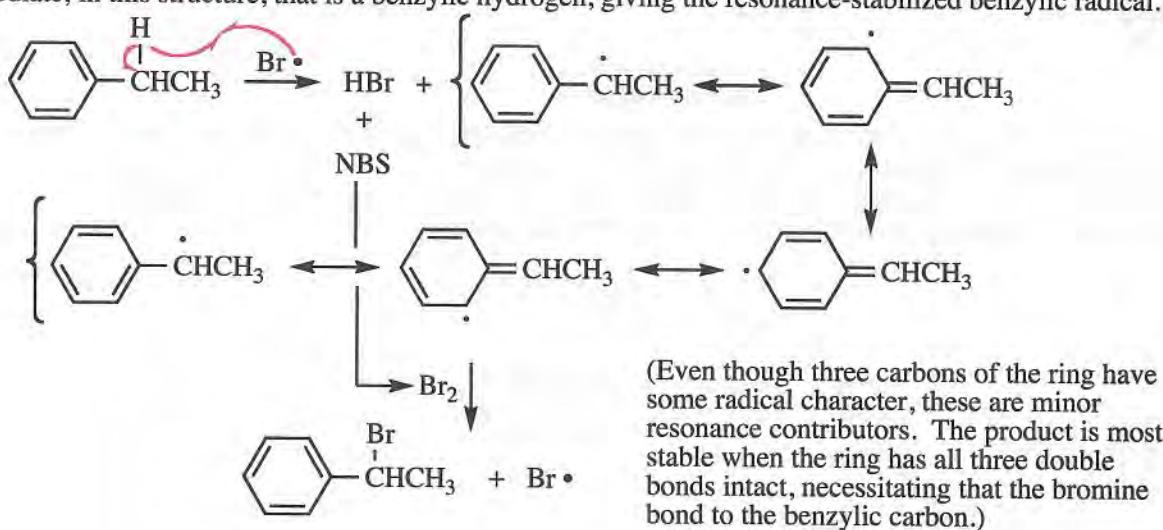
The symbol H—A is used for a generic acid, usually a catalyst in a mechanism. The conjugate base is A⁻.



6-50 NBS generates bromine which produces bromine radical. Bromine radical abstracts an allylic hydrogen, resulting in a resonance-stabilized allylic radical. The allylic radical can bond to bromine at either of the two carbons with radical character.



6-51 The bromine radical from NBS will abstract whichever hydrogen produces the most stable intermediate; in this structure, that is a benzylic hydrogen, giving the resonance-stabilized benzylic radical.

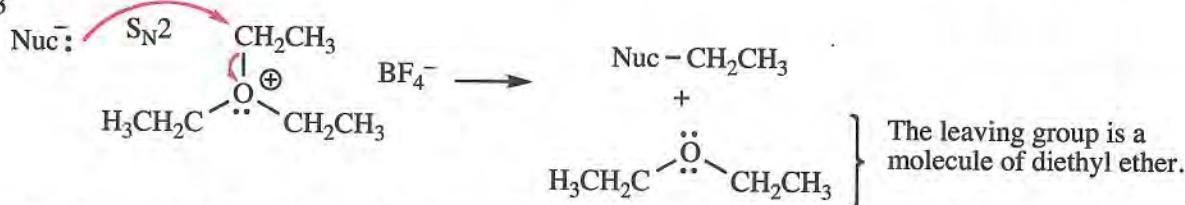


(Even though three carbons of the ring have some radical character, these are minor resonance contributors. The product is most stable when the ring has all three double bonds intact, necessitating that the bromine bond to the benzylic carbon.)

6-52 Two related factors could explain this observation. First, as carbocation stability increases, the leaving group will be less tightly held by the carbocation for stabilization; the more stable carbocations are more "free" in solution, meaning more exposed. Second, more stable carbocations will have longer lifetimes, allowing the leaving group to drift off in the solvent, leading to more possibility for the incoming nucleophile to attack from the side that the leaving group just left.

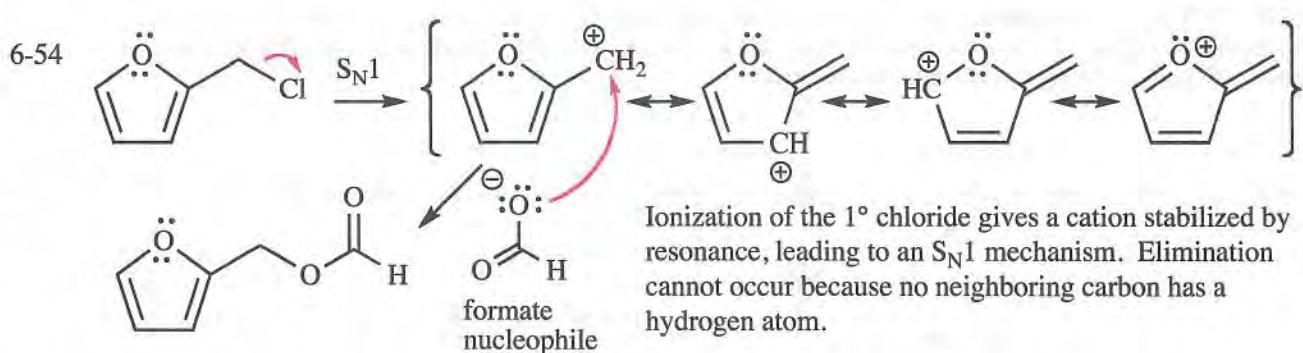
The less stable carbocations hold tightly to their leaving groups, preventing nucleophiles from attacking this side. Backside attack with inversion is the preferred stereochemical route in this case.

6-53

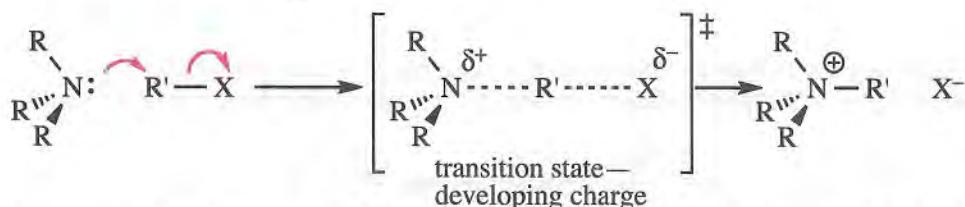


The leaving group is a molecule of diethyl ether.

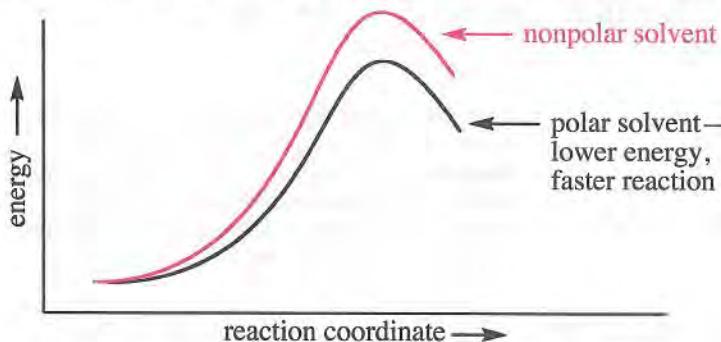
From Table 6-2, all of the ethyl halides are liquids. Triethyloxonium tetrafluoroborate is a solid which is easier to handle and often safer.



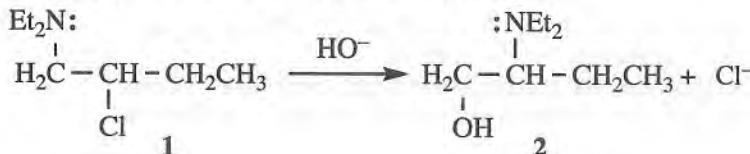
6-55 The energy, and therefore the structure, of the transition state determines the rate of a reaction. Any factor that lowers the energy of the transition state will speed the reaction.



This example of S_N2 is unusual in that the nucleophile is a neutral molecule—it is not negatively charged. The transition state is beginning to show the positive and negative charges of the products (ions), so the transition state is more charged than the reactants. The polar transition state will be stabilized in a more polar solvent through dipole-dipole interactions, so the rate of reaction will be enhanced in a polar solvent.



6-56 The problem is how to explain this reaction:



facts

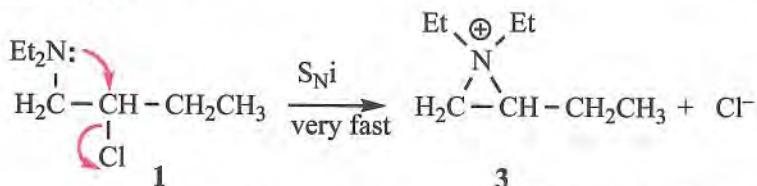
- 1) second order, but several thousand times faster than similar second-order reactions without the NEt_2 group
 - 2) NEt_2 group migrates

See explanation on next page.

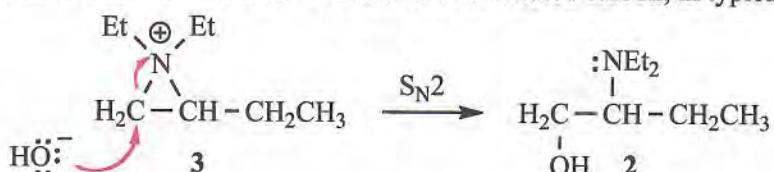
6-56 continued

Solution

Clearly, the NET_2 group is involved. The nitrogen is a nucleophile and can do an internal nucleophilic substitution ($\text{S}_{\text{N}}\text{i}$), a very fast reaction for entropy reasons because two different molecules do not have to come together.



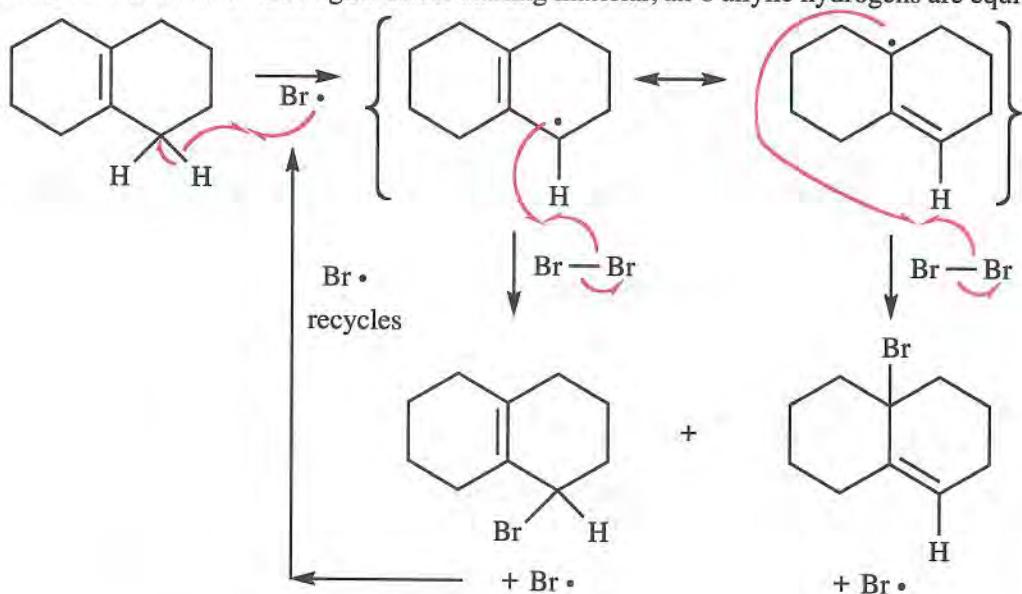
The slower step is attack of HO⁻ on intermediate 3; the N is a good leaving group because it has a positive charge. Where will HO⁻ attack 3? On the less substituted carbon, in typical S_N2 fashion.



This overall reaction is fast because of the *neighboring group assistance* in forming **3**. It is second order because the HO⁻ group and **3** collide in the slow step (not the *only* step, however). And the NEt₂ group "migrates", although in two steps.

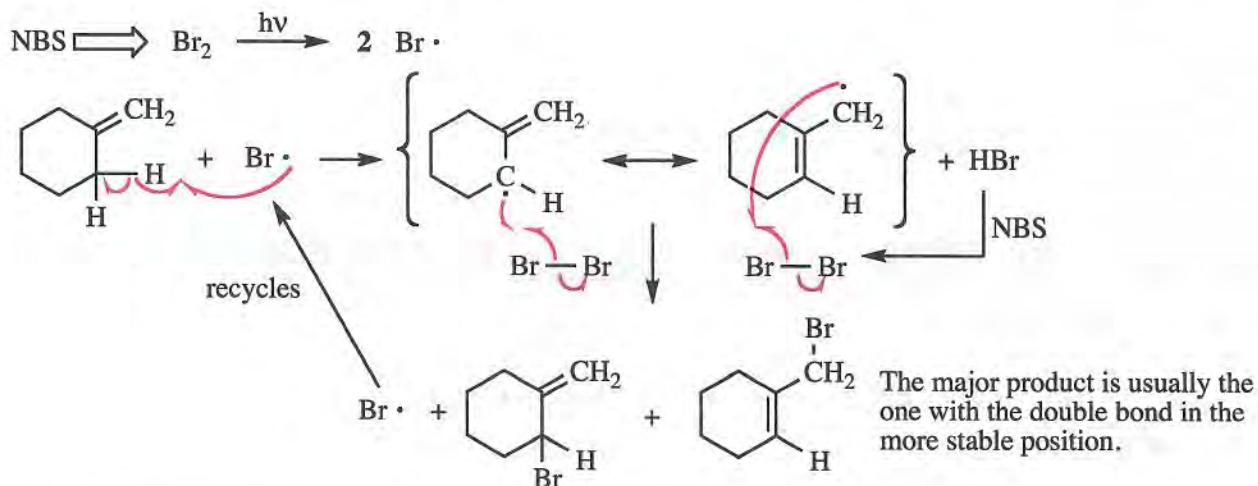
6-57

- (a) Only the propagation steps are shown. NBS provides a low concentration of Br_2 which generates bromine radical in ultraviolet light. In the starting material, all 8 allylic hydrogens are equivalent.

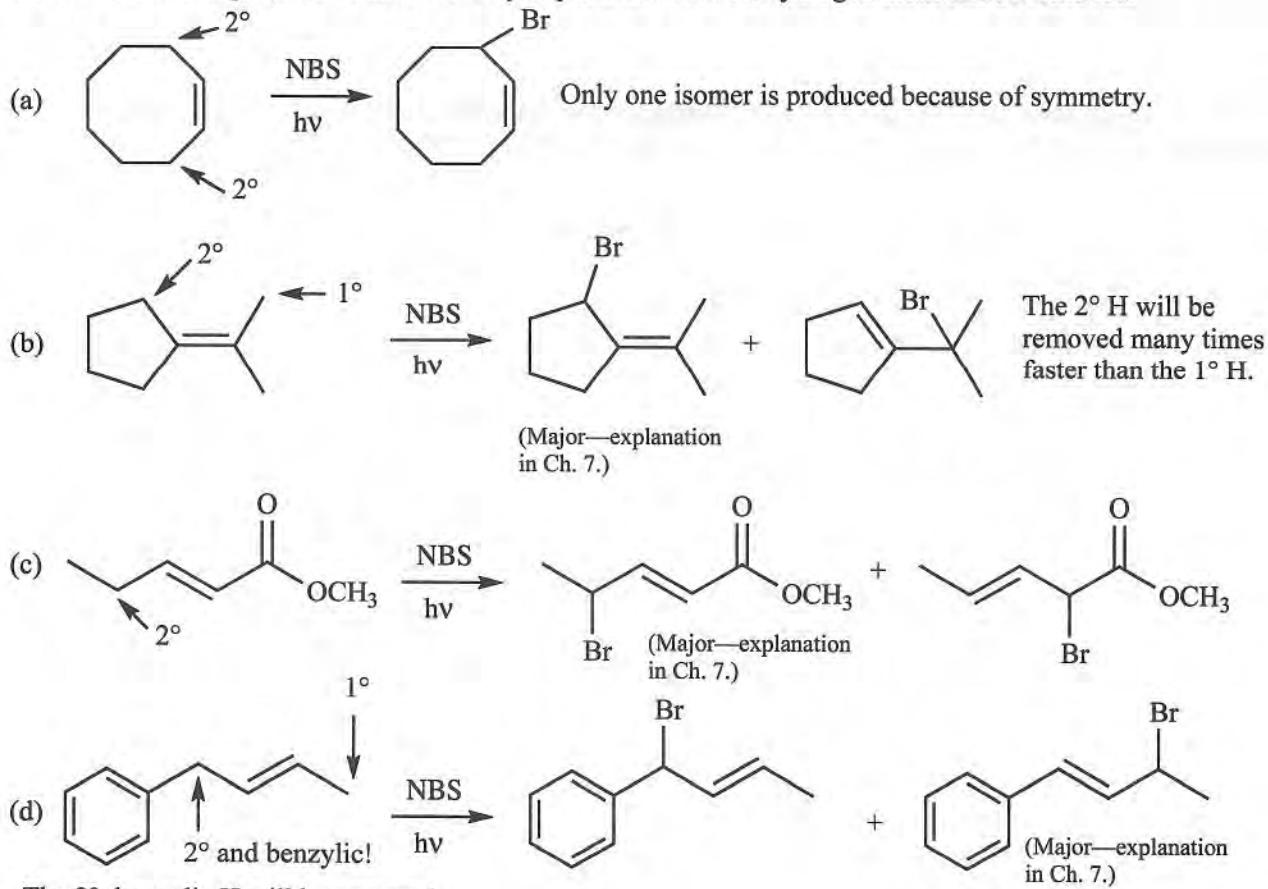


6-57 continued

(b) NBS contains traces of bromine; when combined with HBr, NBS produces more bromine. Bromine contains small amounts of bromine radical. Bromine radical abstracts an allylic hydrogen, resulting in a resonance-stabilized allylic radical. The allylic radical can bond to bromine at either of the two carbons with radical character.

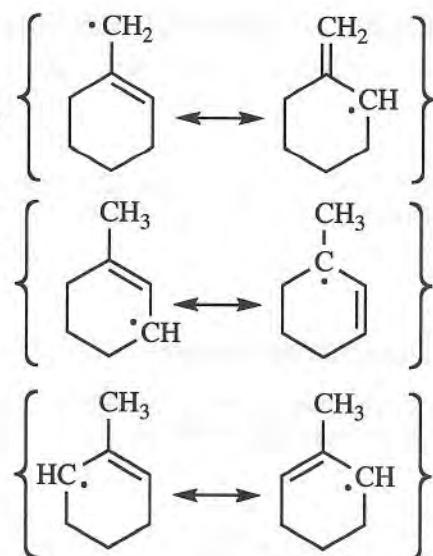
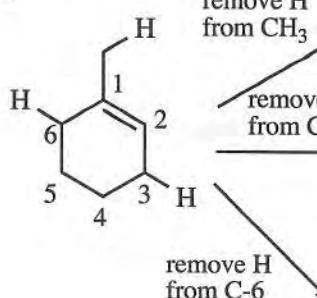


6-58 In each example, arrows show the allylic positions where a hydrogen atom can be removed.



6-59

(a)



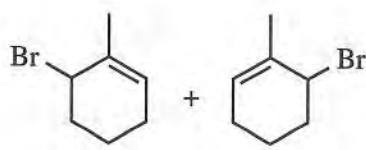
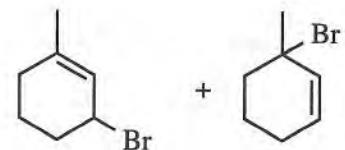
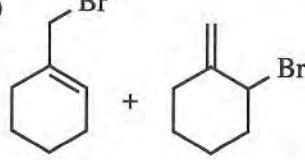
(b)

Radical character on 1° and 2° carbons—least stable of these three (will be slowest to form).

Radical character on 2° and 3° carbons—most stable of these three (will be fastest to form).

Radical character on two 2° carbons, equivalent resonance forms—almost as stable as the $2^\circ/3^\circ$ radical.

(c)



Two products from the $1^\circ/2^\circ$ radical; so minor that only trace quantities might be detected.

Two products from the $2^\circ/3^\circ$ radical.

SAME COMPOUND

Only ONE compound is produced from the $2^\circ/2^\circ$ radical.