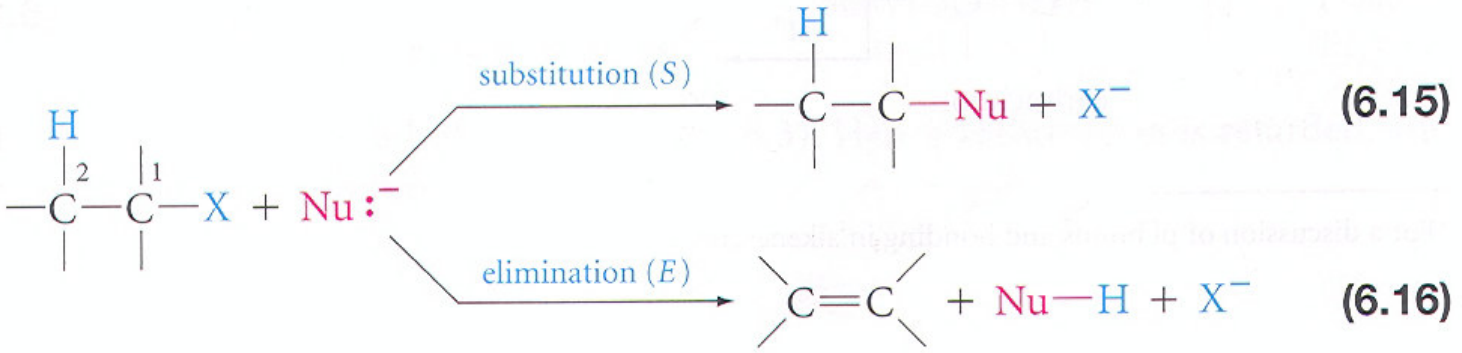
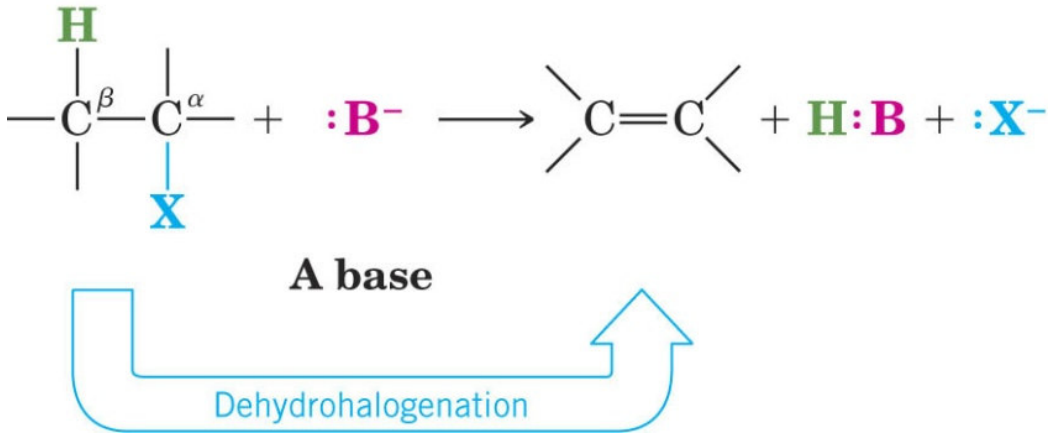
6.7 Dehydrohalogenation, an Elimination Reaction; the E2 and E1 Mechanisms

When an alkyl halide with a hydrogen attached to the carbon *adjacent* to the halogen-bearing carbon reacts with a nucleophile, two competing reaction paths are possible: substitution or **elimination**.



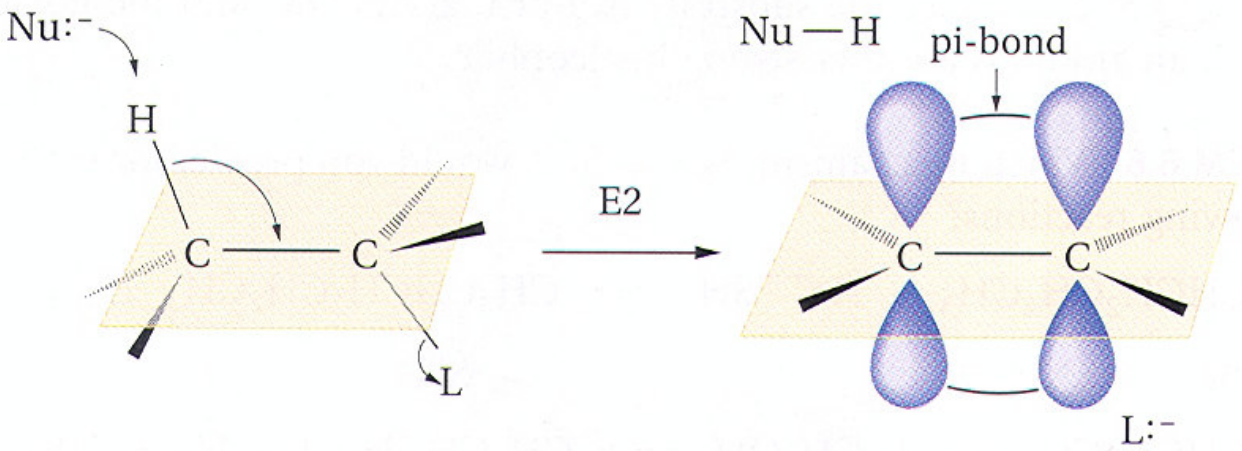
In the substitution reaction, the nucleophile replaces the halogen X. In the elimination reaction, the nucleophile acts as a base and removes a proton from carbon-2, the carbon next to the one that bears the halogen X. The halogen X and the hydrogen from the *adjacent* carbon atom are *eliminated*, and a new bond (a pi bond) is formed between carbons-1 and -2.* The symbol E is used to designate an elimination process. Since in this case a hydrogen halide is eliminated, the reaction is called **dehydrohalogenation**. Elimination reactions provide a useful way to prepare compounds with double or triple bonds.



Often substitution and elimination reactions occur simultaneously with the same set of reactants—a nucleophile and a substrate. One reaction type or the other may predominate, depending on the structure of the nucleophile, the structure of the substrate, and other reaction conditions. As with substitution reactions, *there are two main mechanisms for elimination reactions, designated E2 and E1*. To learn how to control these reactions, we must first understand each mechanism.

E2 Mechanism

Like the S_N2 mechanism, the **E2 mechanism** is a one-step process. The nucleophile, acting as a base, removes the proton (hydrogen) on a carbon atom adjacent to the one that bears the leaving group. At the same time, the leaving group departs and a double bond is formed. The bond breaking and bond making that occurs during an E2 reaction is shown by the curved arrows:



(6.17)

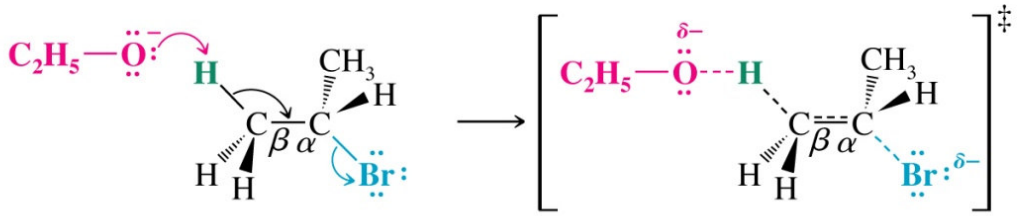
The preferred conformation for the substrate in an E2 reaction is also shown in eq. 6.17. The H—C—C—L atoms lie in a single plane, with H and L in an *anti*-arrangement. The reason for this preference is that the C—H and C—L bonds are parallel in this conformation. This alignment is needed to form the new pi bond as the C—H and C—L bonds break.

- The E2 Reaction
  - E2 reaction involves concerted removal of the proton, formation of the double bond, and departure of the leaving group
  - Both alkyl halide and base concentrations affect.

Reaction:

$$C_2H_5O^- + CH_3CHBrCH_3 \longrightarrow CH_2{=}CHCH_3 + C_2H_5OH + Br^-$$

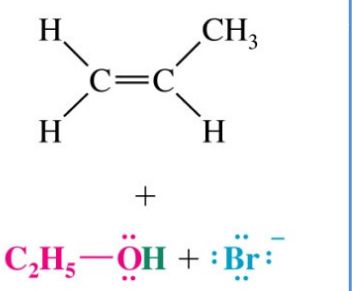
Mechanism:



The basic ethoxide ion begins to remove a proton from the β carbon using its electron pair to form a bond to it. At the same time, the electron pair of the β C—H bond begins to move in to become the π bond of a double bond, and the bromine begins to depart with the electrons that bonded it to the α carbon

Transition state

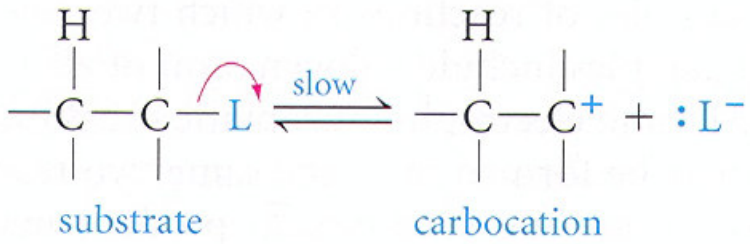
Partial bonds in the transition state extend from the oxygen atom that is removing the β hydrogen, through the carbon skeleton of the developing double bond, to the departing leaving group. The flow of electron density is from the base toward the leaving group as an electron pair fills the π bonding orbital of the alkene.



At completion of the reaction, the double bond is fully formed and the alkene has a trigonal planar geometry at each carbon atom. The other products are a molecule of ethanol and a bromide ion.

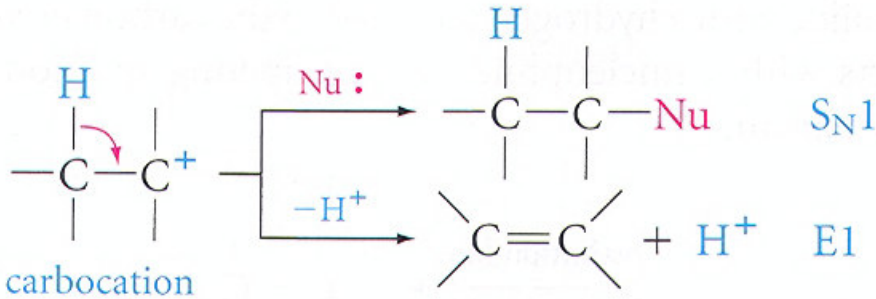
E1 Mechanism

The **E1 mechanism** is a two-step process and has the same first step as the S_N1 mechanism, the slow and rate-determining ionization of the substrate to give a carbocation (compare with eq. 6.12).



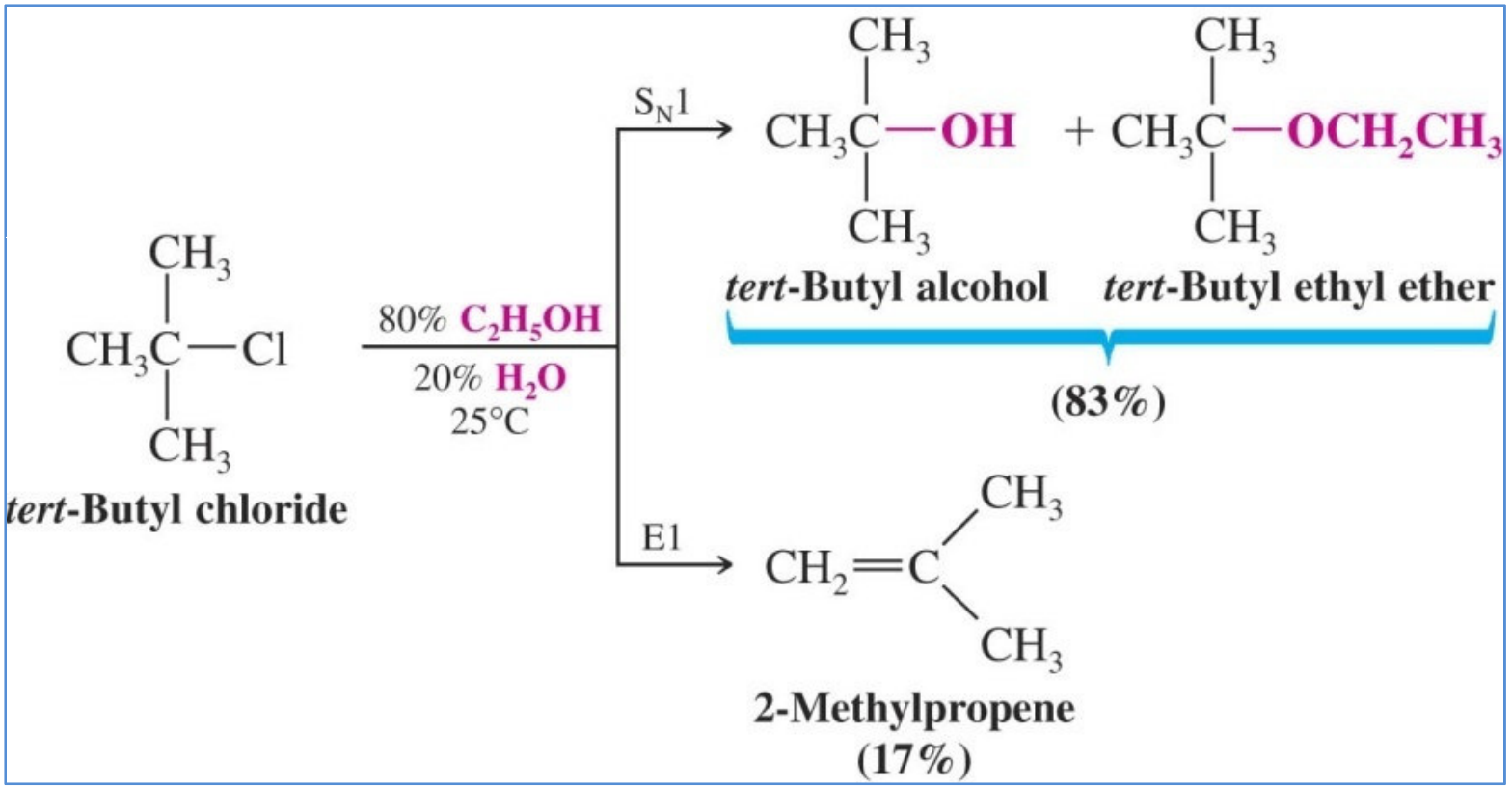
(6.18)

Two reactions are then possible for the carbocation. It may combine with a nucleophile (the S_N1 process), or it may lose a proton from a carbon atom adjacent to the positive carbon, as shown by the curved arrow, to give an alkene (the E1 process).

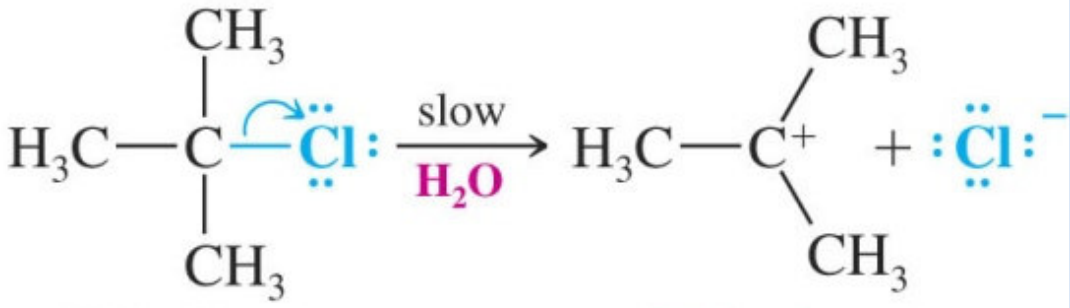


(6.19)

- # The E1 Reaction
  - The E1 reaction competes with the S_N1 reaction and likewise goes through a carbocation intermediate



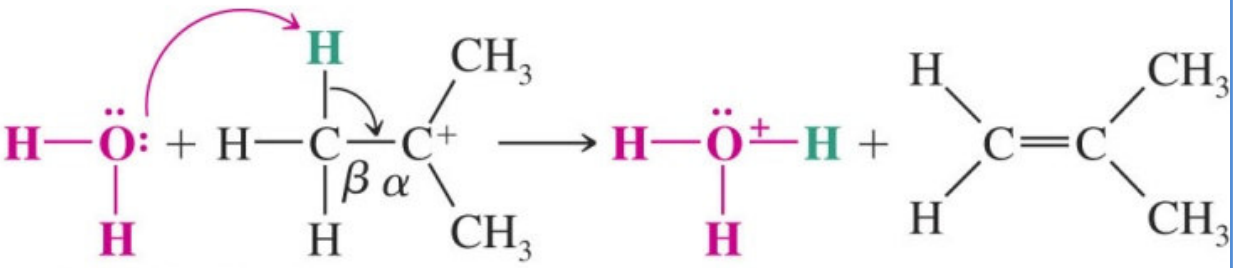
Step 1



Aided by the polar solvent, a chlorine departs with the electron pair that bonded it to the carbon.

This slow step produces the relatively stable 3° carbocation and a chloride ion. The ions are solvated (and stabilized) by surrounding water molecules.

Step 2



A molecule of water removes one of the hydrogens from the β carbon of the carbocation. These hydrogens are acidic due to the adjacent positive charge. At the same time an electron pair moves in to form a double bond between the α and β carbon atoms.

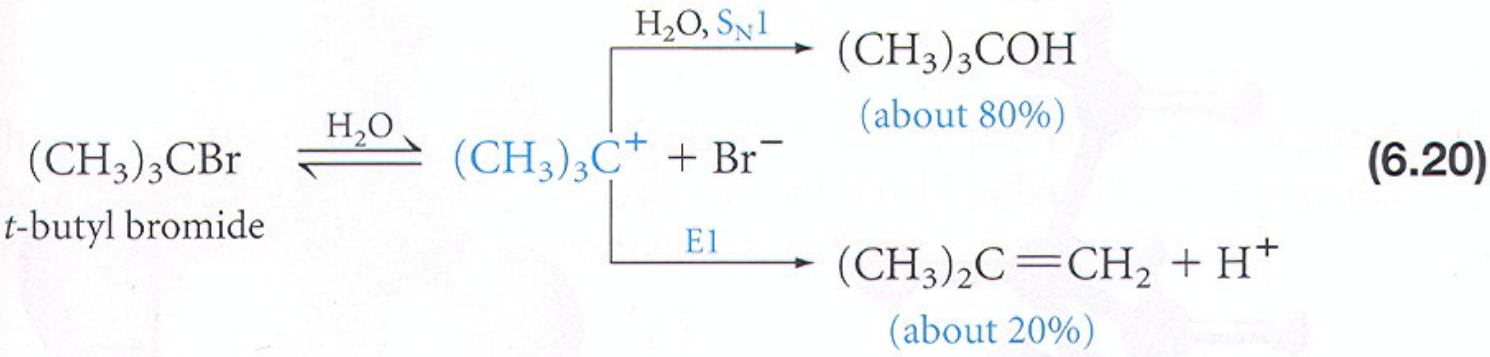
This step produces the alkene and a hydronium ion.

6.8 Substitution and Elimination in Competition

Now we can consider how substitution and elimination reactions compete with one another. Let us consider the options for each class of alkyl halide.

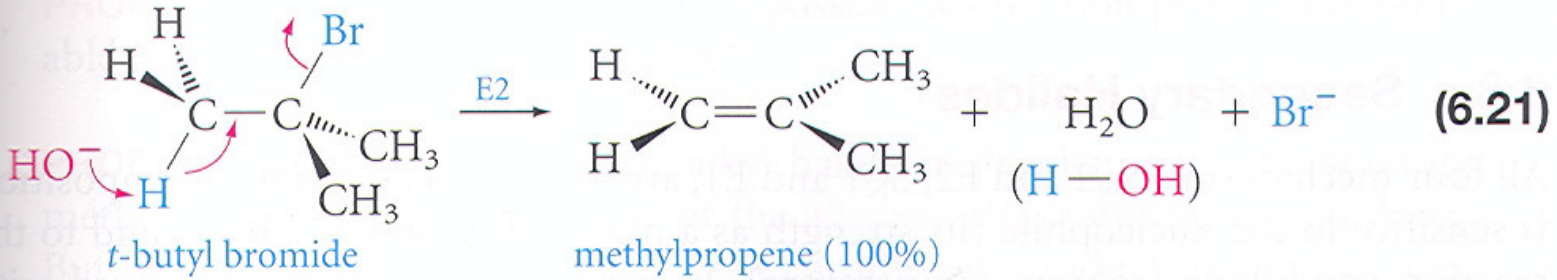
6.8.a Tertiary Halides

Substitution can only occur by the S_N1 mechanism, but elimination can occur by either the E1 or E2 mechanism. With weak nucleophiles and polar solvents, the S_N1 and E1 mechanisms compete. For example,

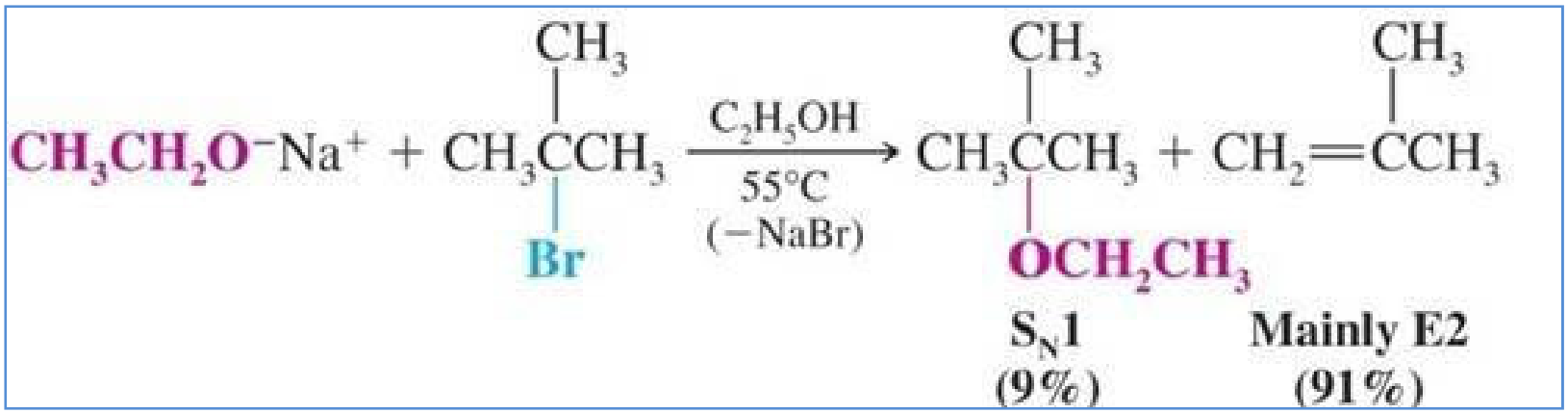


(6.20)

If we use a strong nucleophile (which can act as a base) instead of a weak one, and if we use a less polar solvent, we favor elimination by the E2 mechanism. Thus, with OH^- or CN^- as nucleophiles, only elimination occurs (eqs. 6.5 and 6.7), and the exclusive product is the alkene.



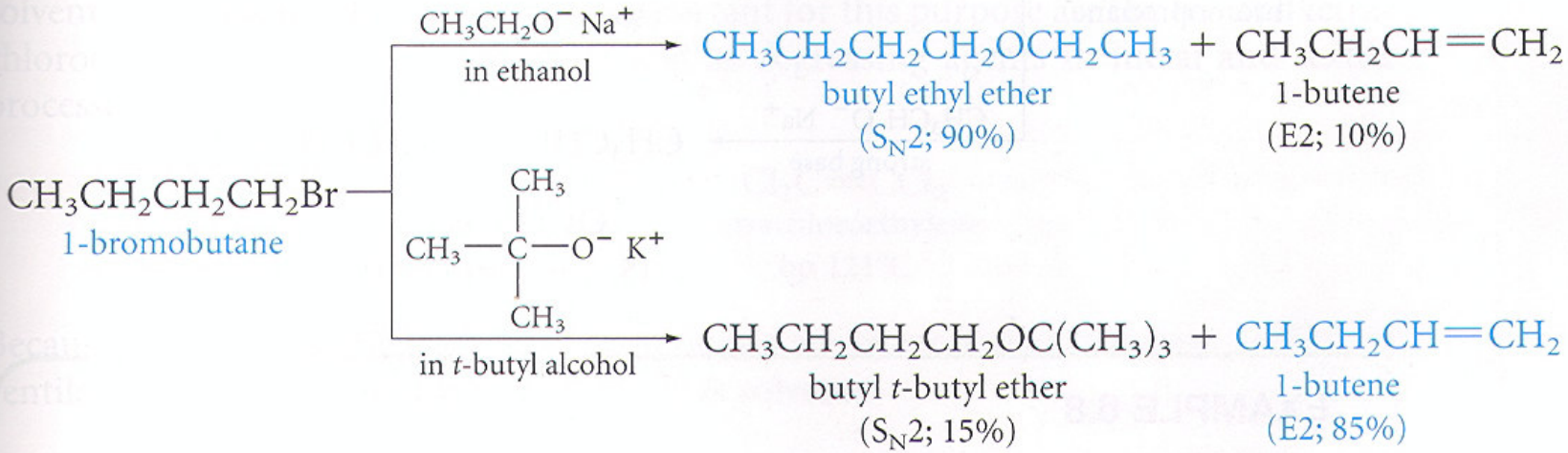
Because the tertiary carbon is too hindered sterically for S_N2 attack (eq. 6.11), substitution does not compete with elimination.



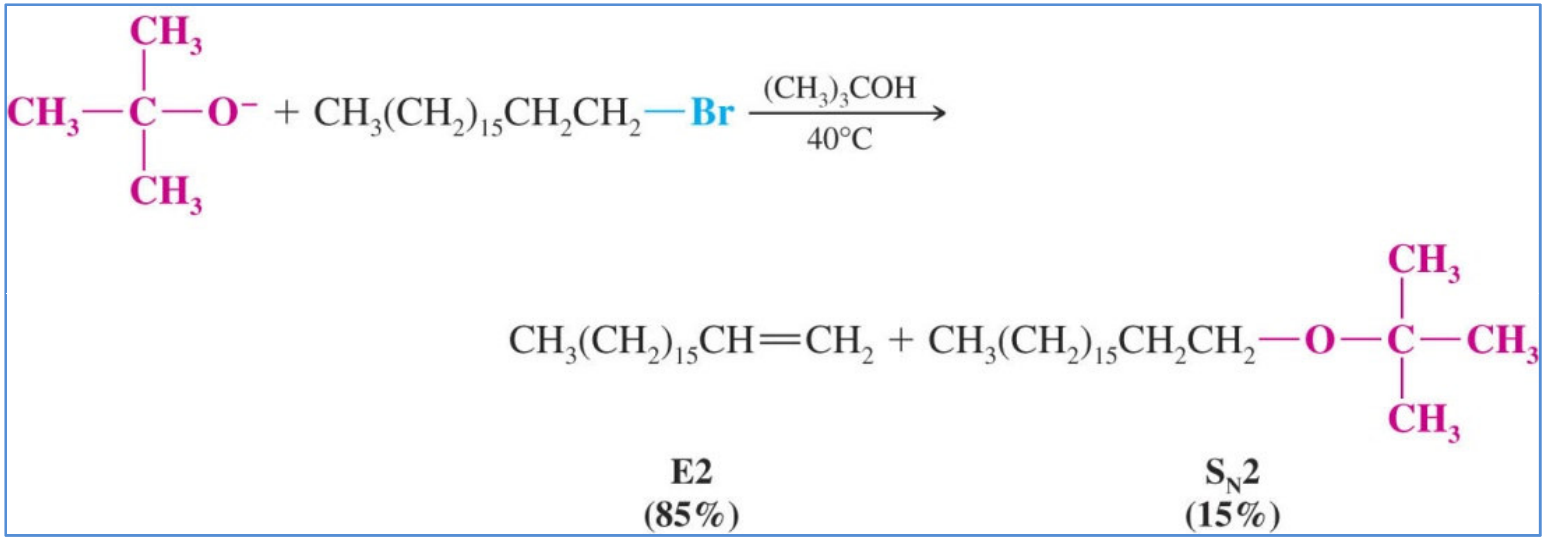
6.8.b Primary Halides

Only the S_N2 and E2 mechanisms are possible, because ionization to a primary carbocation, the first step required for the S_N1 or E1 mechanisms, does not occur.

With most nucleophiles, *primary halides give mainly substitution products* (S_N2). Only with very bulky, strongly basic nucleophiles do we see the E2 process favored. For example,



Potassium *tert*-butoxide is an extremely bulky base and is routinely used to favor E2 reaction



- If the base is small, S_N2 competes strongly because approach at carbon is unhindered

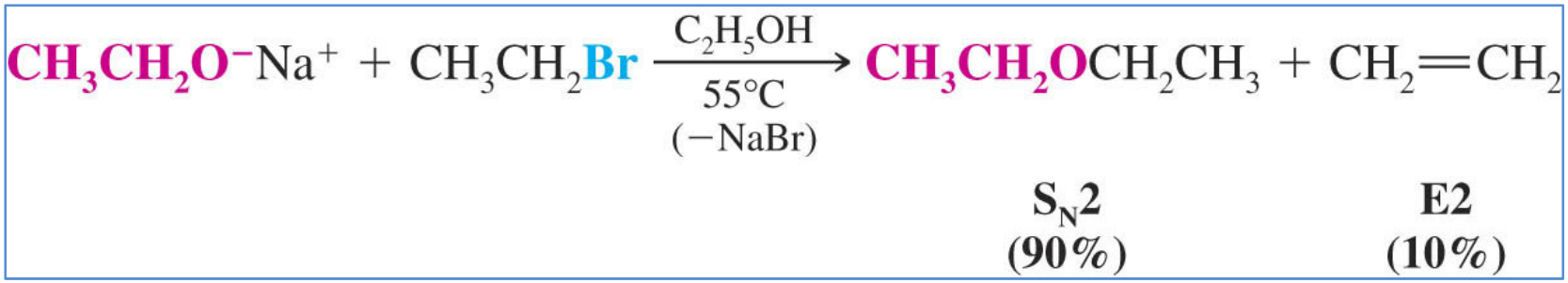
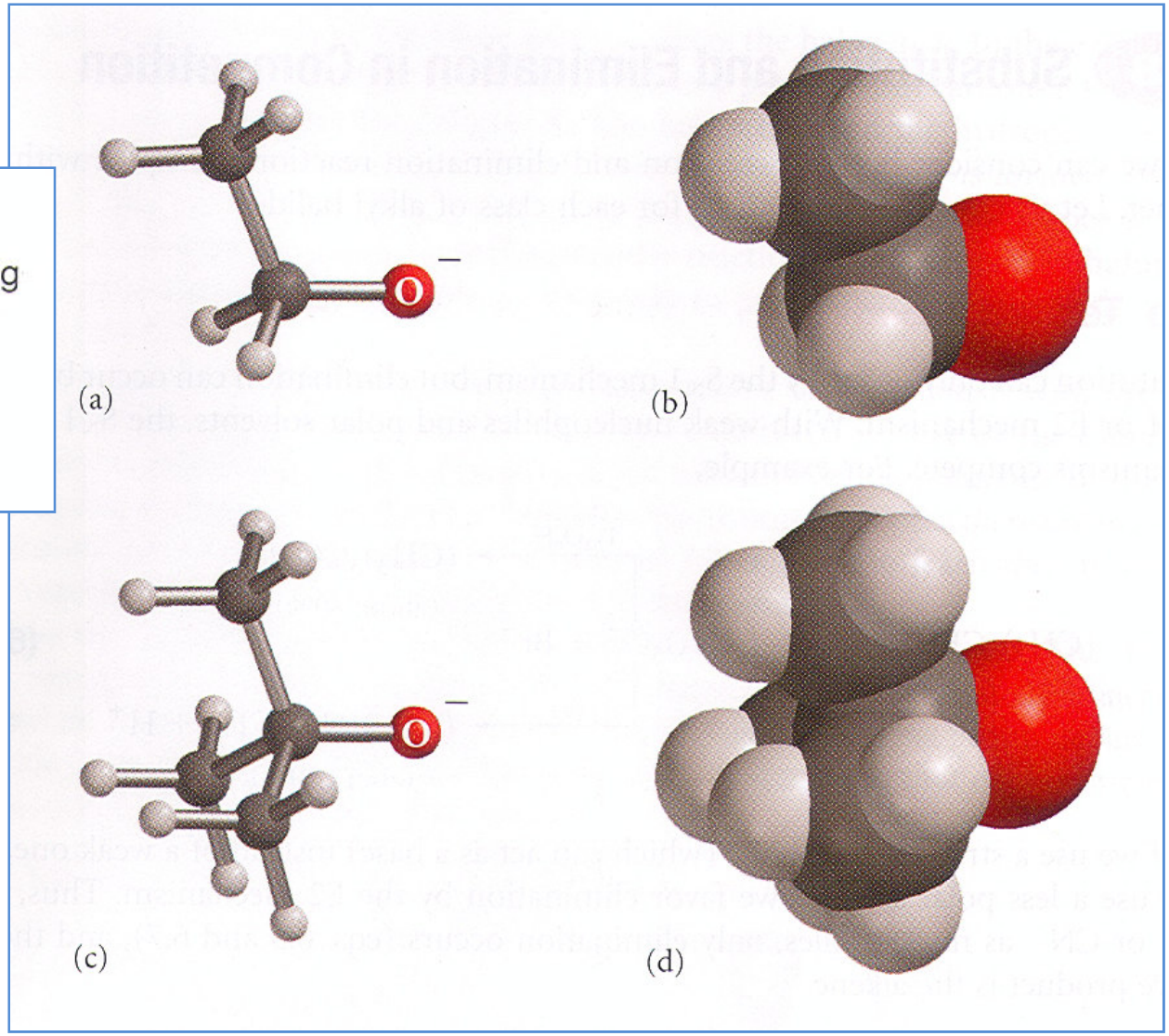


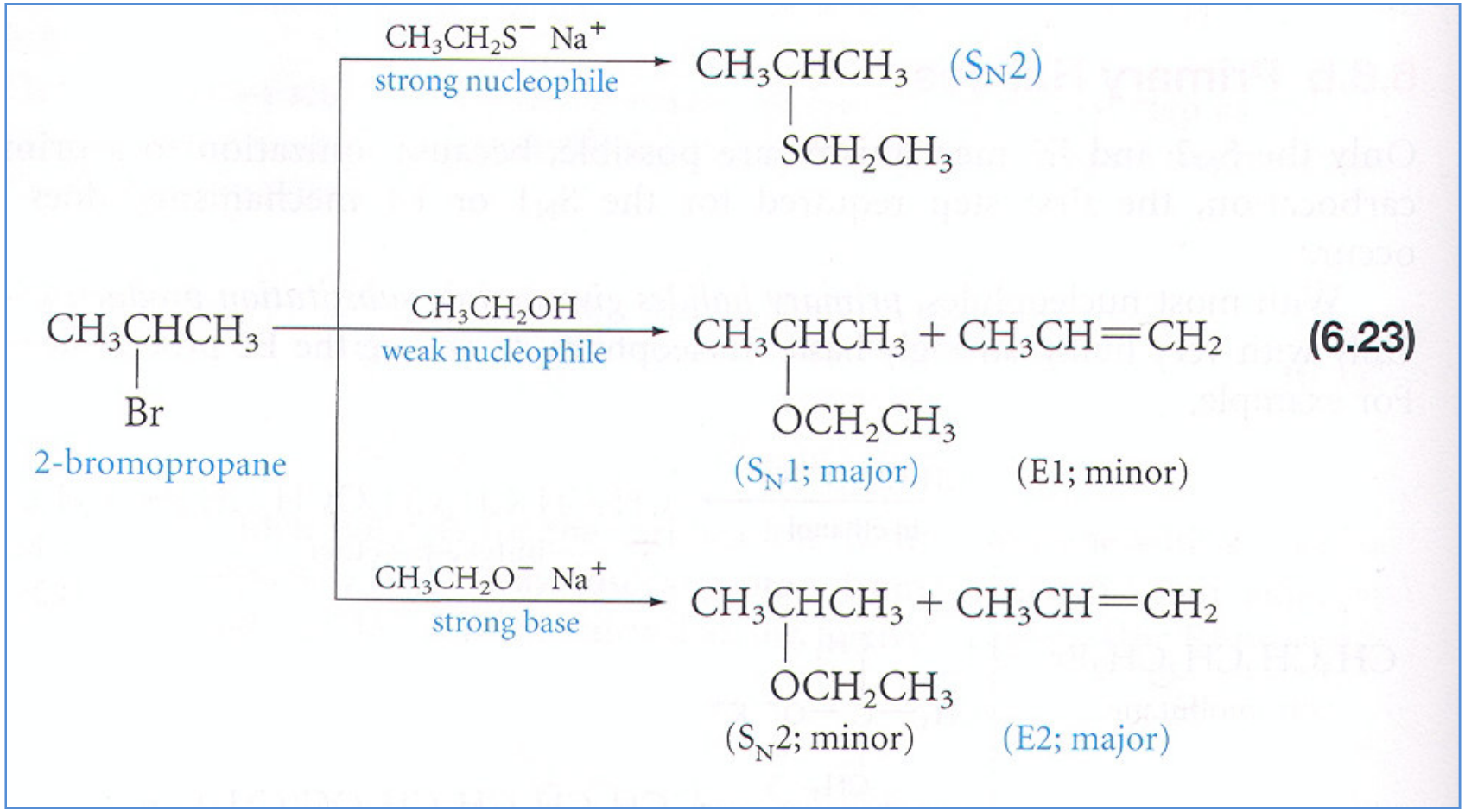
FIGURE 6.3

Ball-and-stick (a) and space-filling (b) structure for ethoxide ($CH_3CH_2O^-$) and for *t*-butoxide [$(CH_3)_3CO^-$] as ball-and-stick (c) and space-filling (d) models.



6.8.c Secondary Halides

All four mechanisms, S_N2 and E2, S_N1 and E1, are possible. The product composition is sensitive to the nucleophile (its strength as a nucleophile and as a base) and to the reaction conditions (solvent, temperature). In general, substitution is favored with stronger nucleophiles that are not strong bases (S_N2) or by weaker nucleophiles in polar solvents (S_N1), but elimination is favored by strong bases (E2).


CH3CH2S− Na+
strong nucleophile
CH3CHCH3
SCH2CH3
(SN2)
CH3CHCH3
Br
2-bromopropane
CH3CH2OH
weak nucleophile
CH3CHCH3 + CH3CH=CH2
OCH2CH3
(SN1; major)
(E1; minor)
(6.23)
CH3CH2O− Na+
strong base
CH3CHCH3 + CH3CH=CH2
OCH2CH3
(SN2; minor)
(E2; major)

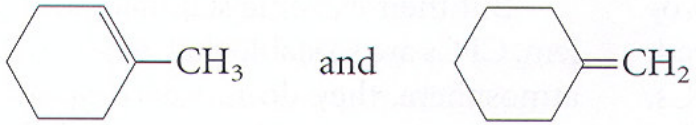
EXAMPLE 6.8

Predict the product of the reaction of 1-bromo-1-methylcyclohexane with

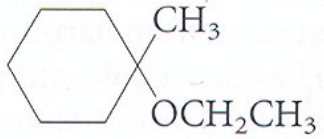
a. sodium ethoxide in ethanol.
b. refluxing ethanol.

SOLUTION The alkyl bromide is tertiary

a. The first set of conditions favors the E2 process, because sodium ethoxide is a strong base. Two elimination products are possible, depending on whether the base attacks a hydrogen on an adjacent CH_2 or CH_3 group.



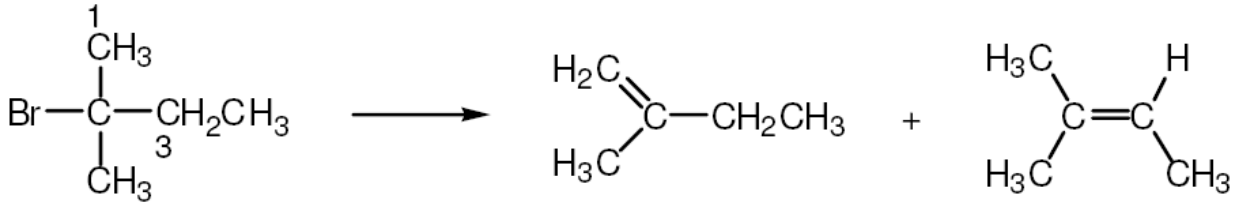
b. This set of conditions favors ionization, because the ethanol is neutral (hence a weak nucleophile) and, as a solvent, fairly polar. The S_N1 process predominates, and the main product is the ether.



Some of the above alkenes will also be formed by the E1 mechanism.

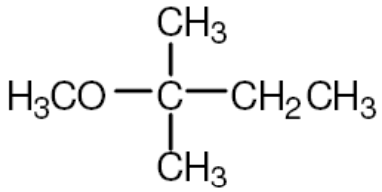
PROBLEM 6.9 Draw structures for *all* possible elimination products obtainable from 2-bromo-2-methylbutane.

6.9 Two products are possible. Removal of the hydrogen from carbon-1 gives 2-methyl-1-butene. Removal of the hydrogen from carbon-3 gives 2-methyl-2-butene.



PROBLEM 6.10 Treatment of the alkyl halide in Problem 6.9 with KOH in methanol gives mainly a mixture of the alkenes whose structures you drew. But treatment with only methanol gives a different product. What is it, and by what mechanism is it formed?

6.10



2-Bromo-2-methylbutane is a tertiary alkyl halide. It reacts with methanol, a weak nucleophile and polar solvent, to give an ether by an S_N1 mechanism.

Dr. Abdullah I. Saleh

END OF CHAPTER 6