

Chapter 9

Formation of Alkenes and Alkynes. Elimination Reactions

from Organic Chemistry

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Chapter Outline of the Book

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1. Organic Molecules and Chemical Bonding
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3. Haloalkanes, Alcohols, Ethers, and Amines
4. Stereochemistry
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9: Formation of Alkenes and Alkynes. Elimination Reactions

- Elimination Reactions*
- Mechanistic Competitions in Elimination Reactions*
- Alkynes and Allenes from Haloalkanes*
- Alkenes from Alcohols*
- Alkenes from Amines*

Preview

C=C and C≡C bonds form in **elimination reactions** in which atoms or groups of atoms are removed from two adjacent C's that are already bonded together. Reactants for *elimination reactions* can include *haloalkanes*, *alcohols*, or *amines*.

Most elimination reactions occur by **E1** or **E2** mechanisms that we shall see are analogous to S_N1 and S_N2 mechanisms. For example, the *E1* mechanism is a two-step reaction with an intermediate carbocation, while the *E2* mechanism is a single step process. Nucleophilic substitution (S_N) reactions frequently compete with *elimination reactions*. The carbon skeletons of *carbocations* formed during *E1* reactions sometimes rearrange.

9.1 Elimination Reactions

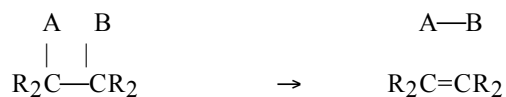
Elimination reactions form *alkenes* as well as *alkynes*. This section describes *alkene-forming* eliminations. *Alkyne-forming* elimination reactions are described in a subsequent section.

Common Features of Elimination Reactions (9.1A)

A variety of different types of substrates undergo *elimination reactions* to form alkenes, but many of these reactions have common features.

General Equations. We can represent elimination reactions that form alkenes with the following general equation where A and B are atoms or groups of atoms.

Figure 9.01

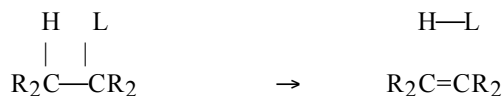


The C-A and C-B bonds break in the elimination reaction, and a second bond forms between the two C's to form a C=C bond. "A-B" in Figure 9.01 may not be an actual reaction product, but

we show it this way in this general example in order to keep the chemical bonds on both sides of the equation in balance. We call the reaction "elimination" because the C=C double bond forms by the overall "elimination" of A and B from the reactant.

In many elimination reactions that give alkenes, A (or B) is an H atom. In those cases we can represent the overall elimination reaction as we show below where we replace A by H, and B by the general leaving group symbol L.

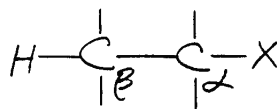
Figure 9.02



In this reaction, the loss of both an H and the leaving group L from adjacent C atoms leads to the formation of the C=C bond. Typically H is removed as a proton (H⁺) by a base, and L departs with its bonding electron pair as ⁻L. We clarify these details in the mechanisms that follow.

Haloalkane Substrates. A common method for formation of alkenes involves elimination of H-X (X = I, Br, Cl, or F) from a *haloalkane* or *halocycloalkane* (R-X).

Figure 9.03



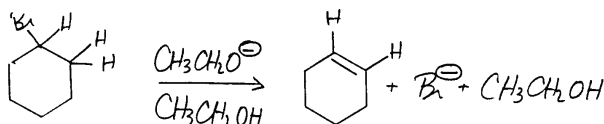
The leaving group L (Figure 9.02) is a halogen X. Because we refer to the C-X carbon as C_α, and its adjacent C-H carbon as C_β, we say that the H on C_β is a **β-hydrogen** or a **β-H**. The elimination reactions of *haloalkanes* illustrate the fundamental features and mechanisms of many elimination reactions that form alkenes.

Mechanisms for Elimination of H-X (9.1B)

Elimination reactions of H-X occur primarily by either an **E1** or **E2** mechanism. In a number of ways, these mechanisms are similar to the S_N1 and S_N2 mechanisms we described in Chapter 7.

The E2 Mechanism. We illustrate the E2 mechanism using the reaction of *bromocyclohexane* with *ethoxide ion* in the solvent *ethanol* that gives *cyclohexene* as the alkene product.

Figure 9.04



It is a single step reaction (Figure 9.05) with the transition state in Figure 9.06 [next page].

Figure 9.05

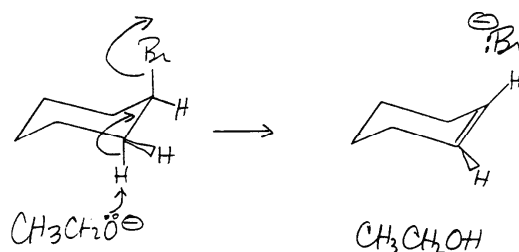
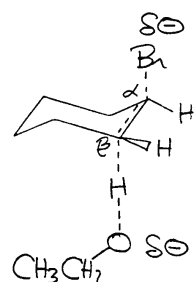


Figure 9.06



As the ethoxide ion removes the proton from C_β , the electron pair in the C-H bond forms the C=C π bond as the bromide ion (Br^-) leaves from C_α with its bonding electron pair.

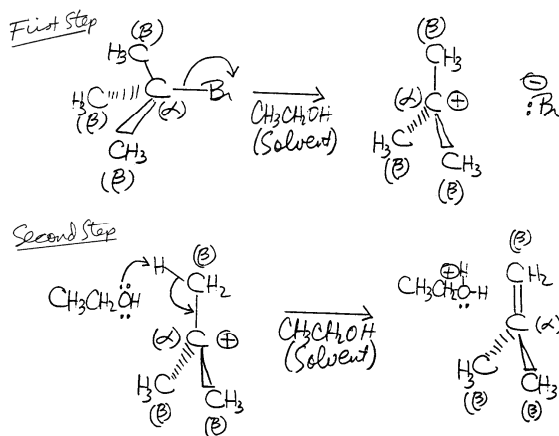
The designation *E2* stands for "*elimination (E)* with a *bimolecular (2)* transition state." The *E2* transition state is *bimolecular* because it contains both the *base* and the *haloalkane* substrate (Figure 9.06). The *rate law* for an *E2* reaction shows that its rate increases as we increase the concentration of the haloalkane *RX* and/or the concentration of base.

$$\text{Rate of E2 Elimination} = k[\text{RX}][\text{base}]$$

The *E2* mechanism is analogous to the S_N2 substitution mechanism (Chapter 7). Both are single step reactions and both have bimolecular rate laws.

The *E1* Mechanism. We illustrate the *E1* elimination mechanism using formation of 2-methylpropene from reaction of 2-bromo-2-methylpropane (*t*-butyl bromide) in ethanol.

Figure 9.07



The first step of this two step mechanism is ionization of *t-butyl bromide* to form a carbocation. This is followed by a step where *ethanol*, acting as a *base*, removes a proton from C β of the carbocation.

This *E1* mechanism is analogous to the two-step *S_N1 substitution* mechanism (Chapter 7). The "1" in *E1* indicates that the rate determining step of the reaction is unimolecular. This rate determining step is the ionization step (the first step) that involves only the haloalkane substrate (RX). The *E1* rate law has the same form as that for *S_N1* reactions because this ionization step is identical to the ionization step in the *S_N1* reaction.

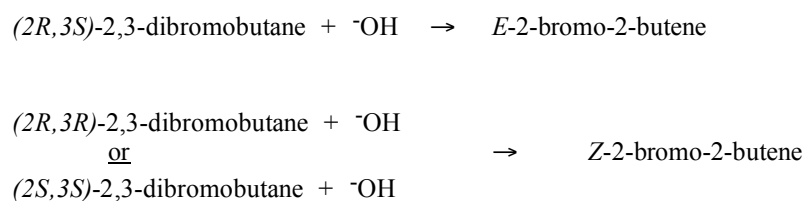
$$\text{Rate of E1 Elimination} = k[\text{RX}]$$

Stereochemistry of E1 and E2 Elimination (9.1C)

The *E1* and *E2* elimination reactions have distinctly different stereochemical results.

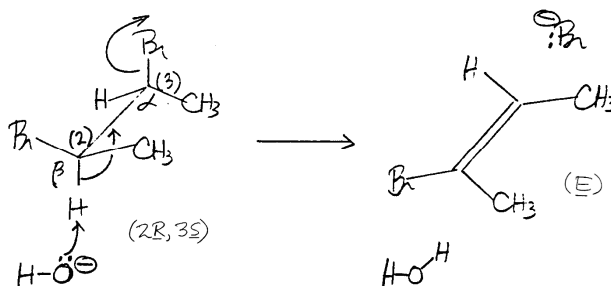
E2 Elimination. We saw in Figure 9.06 that the transition state for the *E2* elimination mechanism has the leaving group (X) and the β -H in a common plane and oriented in an *anti* staggered conformation (Chapter 2) with respect to each other. This so-called ***anti-periplanar*** orientation for the β -H and the leaving group (X) is the most favorable conformation for an *E2* elimination transition state. It gives *stereospecific* reaction products as we show in Figure 9.08 for reaction of the various stereoisomers of *2,3-dibromobutane* with the base :OH^- .

Figure 9.08



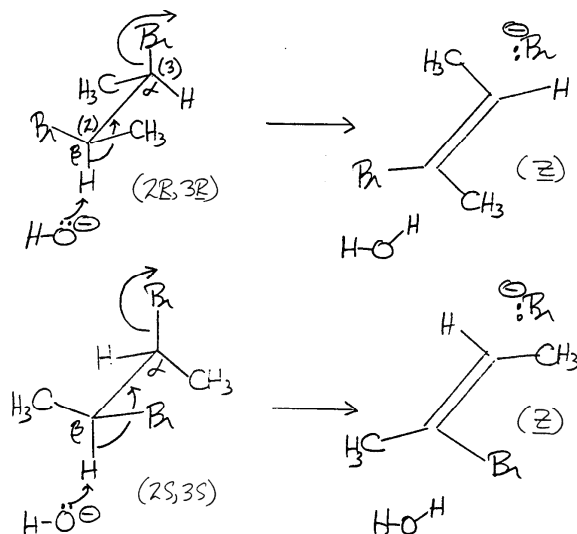
Using *(2R,3S)-2,3-dibromobutane* as the example in Figure 9.09, we show the staggered (*anti-periplanar*) conformation in which the H on C β , and the Br on C α , are *anti* to each other.

Figure 9.09



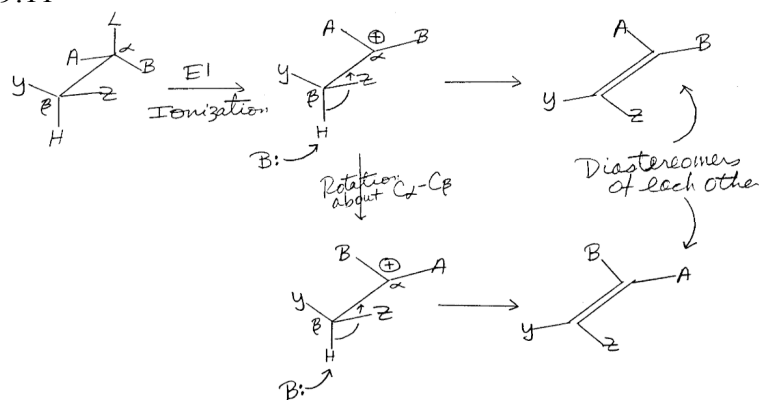
You can see that when an :OH^- removes the $\beta\text{-H}$, the simultaneous loss of Br^- gives the (*E*)-alkene as the other groups on C_α and C_β move into the alkene plane. Similarly, the staggered conformation of (*2R,3R*) or of (*2S,3S*)-2,3-dibromobutane (Figure 9.10), specifically gives the (*Z*)-alkene by the *anti-periplanar* E2 elimination of a $\beta\text{-H}$ and Br shown here.

Figure 9.10



E1 Elimination. Alkene formation in E1 reactions is not stereospecific. After the leaving group leaves, there is time for rotation about the $\text{C}_\alpha\text{-C}_\beta$ bond to occur in the intermediate carbocation before ethanol (acting as a base) removes a $\beta\text{-H}$ from that carbocation. As a result, the alkene product is a mixture of the two possible stereoisomers.

Figure 9.11

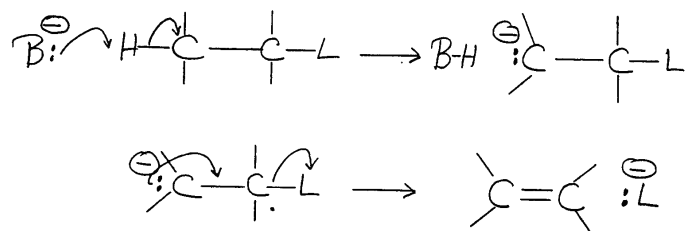


Other Elimination Reactions (9.1D)

There are other elimination mechanisms besides those of the E1 and E2 reactions. We describe some of the more important ones below.

The E1cb Mechanism. In an **E1cb** reaction, a base first removes a proton from the C_{α} carbon of the substrate to give an intermediate **carbanion** (a species with a negatively charged carbon).

Figure 9.12

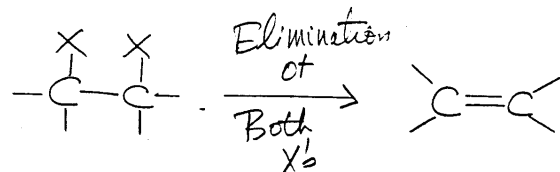


This *carbanion* then loses the leaving group (^-L) to form alkene product(s). The E1cb mechanism usually occurs with strong bases and with substrates where groups directly attached to the *carbanion* center can stabilize the negative charge on that *carbanion* center.

We have not yet introduced most groups that stabilize a C- center. However, we will present an example of an E1cb reaction later in the chapter.

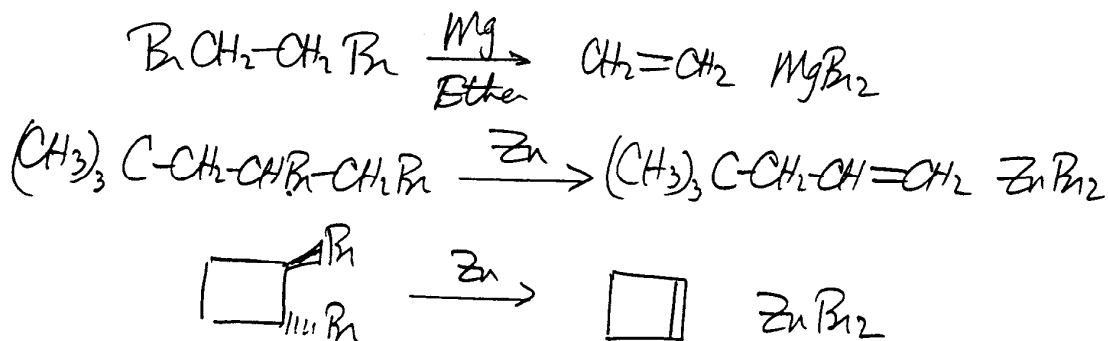
Elimination of X-X. Alkenes also form from the loss of both X's of a 1,2-dihaloalkane.

Figure 9.13



These dehalogenation reactions do not involve bases. They use metals such as Mg or Zn that react with the halogens (Cl, Br, and/or I) to form metal salts such as MgX_2 or ZnX_2 .

Figure 9.14



Their mechanisms probably involve formation of intermediate organometallic compounds on the metal surface that then eliminate ^+Mg-X or ^+Zn-X and X^- (Figures 9.15 and 9.16)[next page]

Figure 9.15

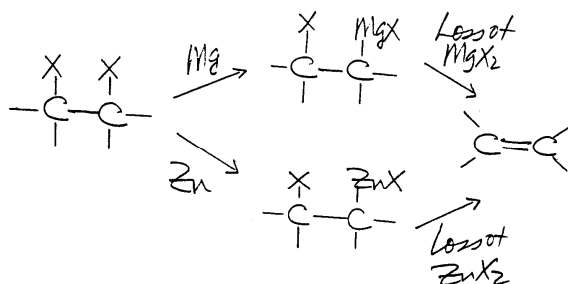
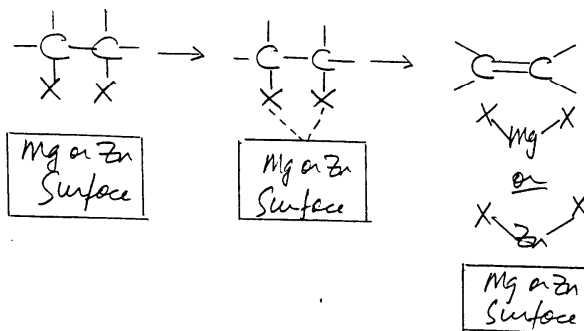


Figure 9.16



Since the C=C bond forms between the C's of the two C-X groups in the reactant, these reactions precisely place the C=C in the product. However, the dihaloalkane reactant is usually synthesized (Chapter 10) from the same alkene that it forms by elimination of X-X, so dehalogenation reactions are less synthetically useful than dehydrohalogenation.

α-Elimination to form Carbenes. (to be added later)

9.2 Mechanistic Competitions in Elimination Reactions

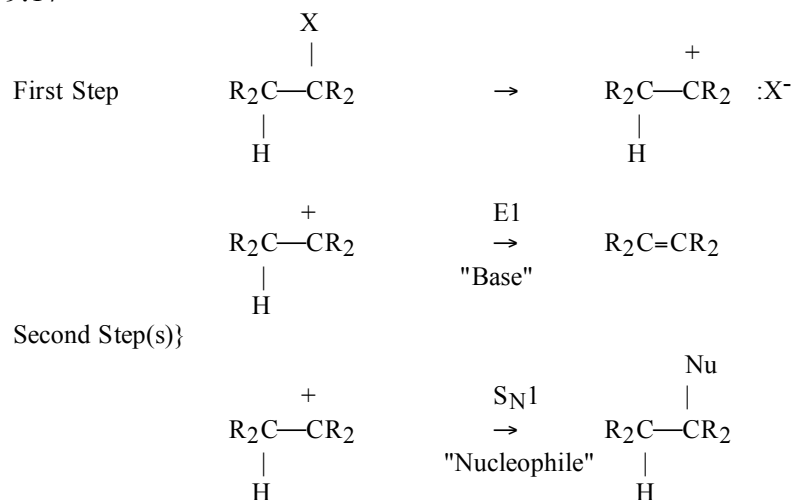
Depending on the choice of substrate, solvent, base, and other reaction variables, E1 and E2 reactions can compete with each other and they can also compete with nucleophilic substitution (S_N) reactions.

Substitution Competes with Elimination (9.2A)

We mentioned in Chapter 7 that *elimination* reactions often occur along with *substitution* reactions. Now that we have introduced elimination mechanisms, we can describe this competition.

S_N1 and E1 Reactions Compete. E1 elimination from haloalkanes only occurs with substrates (usually 3°) that ionize to form intermediate carbocations, and carbocation formation is the first step of an E1 reaction. Carbocation formation is also the first step of an S_N1 substitution reaction. As a result, the first steps of both E1 and S_N1 reactions are identical (Figure 9.17) [next page].

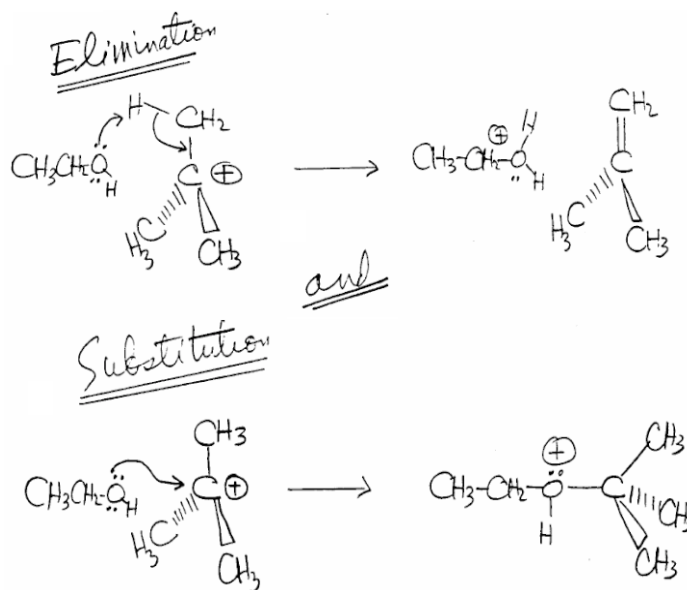
Figure 9.17



Whether we think of an overall reaction of a 3° substrate as *elimination*, *substitution*, or a *mixture* of the two reactions, depends on the subsequent reaction(s) of the carbocation as shown above.

We used the reactions of *t-butyl bromide* (2-bromo-2-methylpropane) with the solvent *ethanol* as our example of an *E1* reaction (Figure 9.07), and you may remember that we also used these same reactants for our example of an *S_N1* reaction in Chapter 7. In each of those presentations we ignored the fact that both *S_N1* and *E1* reactions occur simultaneously. *E1 elimination* occurs when ethanol acts as a *base* and removes a β -hydrogen from the intermediate C^+ . *S_N1 substitution* occurs when ethanol acts as a *nucleophile* and forms a C-O bond with the C^+ center in the intermediate carbocation.

Figure 9.18



Any 3° substrate that ionizes to form a carbocation and has β -H's (such as *t*-butyl bromide) can potentially undergo competitive S_N1 and E1 reactions. An example is 2-bromo-2-methylbutane that we compare with *t*-butyl bromide (2-bromo-2-methylpropane) in Table 9.1.

Table 9.1. Relative Amounts of Elimination and Substitution from Reaction of 3° Bromoalkanes in Ethanol (25°C).

R-Br	%Elimination (E1)	%Substitution (S_N1)
(CH ₃) ₃ C-Br	19	81
CH ₃ CH ₂ (CH ₃) ₂ C-Br	36	64

S_N2 and E2 Reactions Compete. 1° haloalkane substrates such as 1-bromoethane and 1-bromopropane cannot ionize to form carbocations so they give alkenes only by E2 elimination reactions (Figure 9.18a).

Figure 9.18a

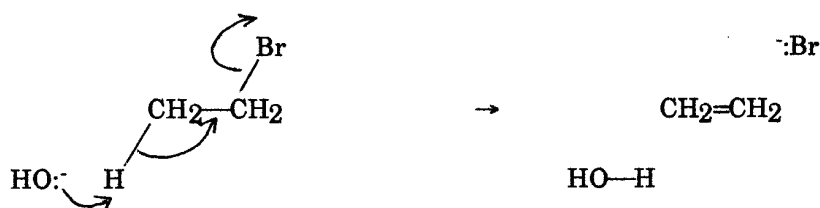
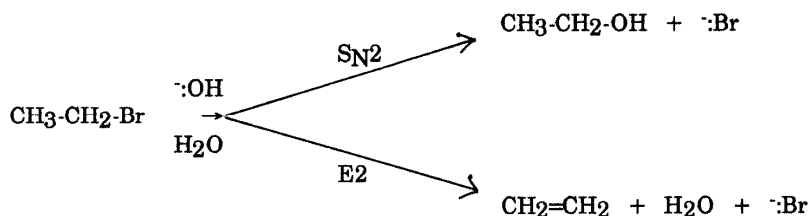


Figure 9.18b



For the same reason, these 1° haloalkanes are examples of substrates that give substitution products only by S_N2 reactions (Chapter 7). In fact, both alkene (elimination) and substitution products simultaneously form (Figure 9.18b) when we treat 1° haloalkanes with ethoxide ion in ethanol (Table 9.2).

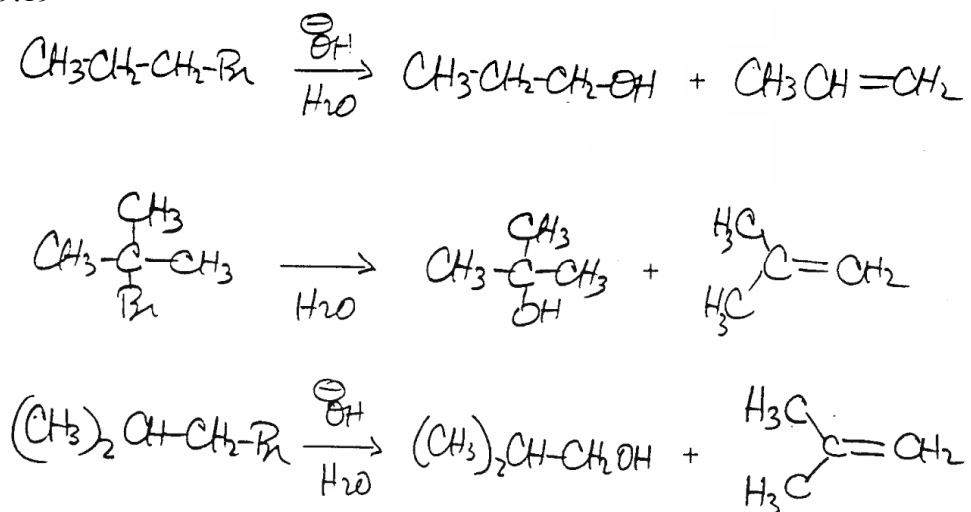
Table 9.2. Relative Amounts of Elimination and Substitution from Reaction of Bromoalkanes with Ethoxide Ion in Ethanol.

R-Br	T°C	%Elimination (Alkene)	%Substitution (Ether)
CH ₃ CH ₂ -Br (1°)	55	1	99
CH ₃ CH ₂ CH ₂ -Br (1°)	55	9	91
(CH ₃) ₂ CH-Br (2°)	25	80	20

The 2° haloalkane *2-bromopropane* (third entry in Table 9.2) can sometimes ionize to form a carbocation, but the alkene and substitution products that we show in this table arise from competing E2 and S_N2 reactions because ethoxide ion is both a strong *base* (for E2 reactions) and a strong *nucleophile* (for S_N2 reactions).

The results in Tables 9.1 and 9.2 show that substitution competes with elimination in both E1 and E2 reactions.

Figure 9.19



They also show that the relative amounts of elimination and substitution products vary significantly depending on the structure of the substrate.

Nucleophile versus Base. When *ethoxide* ion displaces a leaving group in a S_N2 reaction, we call it a *nucleophile*. When *ethoxide* ion removes a β-H in an E2 reaction we refer to it as a *base*. Ethoxide ion does not change its properties in these two reactions, it simply has the ability to do both reactions (Figure 9.18b). The same is true with respect to the behavior of *ethanol* in the competitive S_N1 and E1 reactions that we showed earlier.

The term *nucleophile* is more fundamental than the term *base*. A *nucleophile* is a species with an electron pair that uses that electron pair to form a new chemical bond to the atom it attacks. Based on this definition, you can see that *ethoxide ion*, as well as *ethanol*, serve as *nucleophiles* in both *substitution* and *elimination* reactions. However, not all nucleophiles (Nu:) that displace leaving groups from C in *substitution* reactions (and form C-Nu bonds) react with C-H protons to form Nu-H bonds. That is why we use the term "base" to describe *nucleophiles* that also remove protons from carbon in elimination reactions.

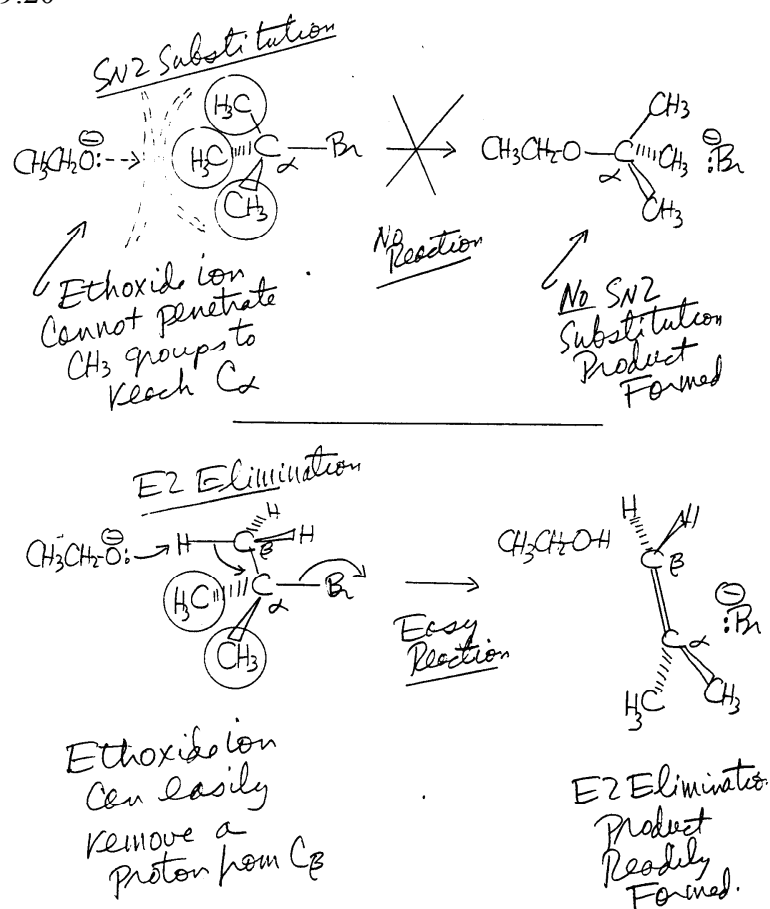
E1 and E2 Reactions Can Compete (9.2B)

E1 and E2 reactions may occur simultaneously with the same substrate. This differs markedly from substitution reactions (Chapter 7) where a substrate usually reacts exclusively by an S_N1 or by an S_N2 mechanism in a particular reaction.

E1 and E2 with 3° Haloalkanes. The base often determines whether *2-methylpropene* arises via an E1 or an E2 mechanism with the 3° haloalkane *t-butyl bromide* (*2-bromo-2-methylpropane*). In contrast, we learned in Chapter 7 that this 3° haloalkane substrate undergoes substitution only by an S_N1 mechanism.

t-Butyl bromide reacts by S_N1 mechanisms because it gives an energetically favorable 3° carbocation, and that 3° carbocation can also lose a proton to a weakly basic nucleophile to give *2-methylpropene* by an E1 reaction. *t-Butyl bromide* cannot undergo S_N2 substitution since CH_3 groups prevent backside approach of any nucleophile to its C-Br carbon. However, an E2 mechanism requires only that ^-OEt approach a β -H, and there are 9 β -H's on *t-butyl bromide* that are all easily accessible on its outer surface (Figure 9.20).

Figure 9.20



Strongly Basic Nucleophiles Favor E2 Over E1. Strongly basic nucleophiles such as EtO^- can make E2 elimination more important than E1 elimination for 3° substrates such as t-butyl bromide. This is because the rate of the E2 reaction increases with increasing concentration of the strong base, while the rate of an E1 reaction is independent of the concentration of the base as we saw earlier in the rate laws for E1 and E2 reactions.

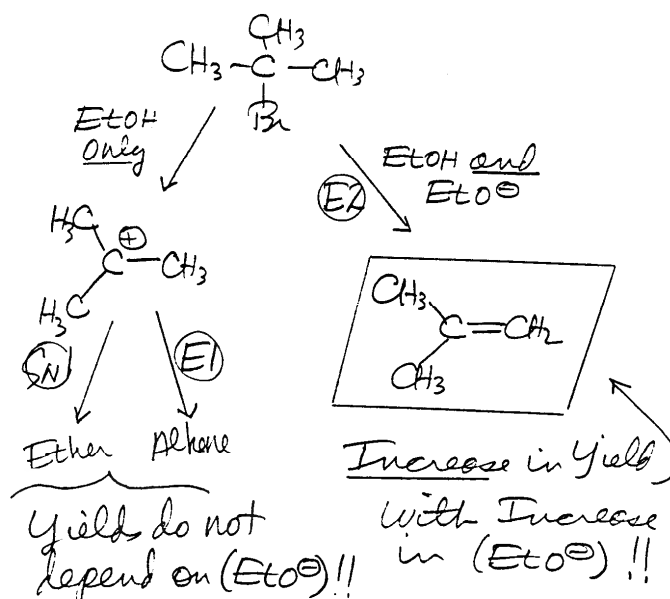
The product data in Table 9.3 are a result of this increase in E2 compared to E1 elimination with increasing base concentration.

Table 9.3. Effect of Ethoxide Ion Concentration on Products from Reaction of 2-Bromo-2-methylpropane in Ethanol (25°C).

[ethoxide ion], M	%Yield	
	2-methylpropene (elimination)	2-ethoxy-2-methylpropane (substitution)
0	19	81
0.02	26	74
0.05	46	54
1.0	91	9
2.0	93	7

The data in the first row of the table show the relative amounts of substitution and elimination when there is no ethoxide ion in the reaction mixture. As a result they illustrate the relative importance of *E1* elimination and S_N1 substitution. As the concentration of ethoxide ion increases, you can see that the relative amount of elimination compared to substitution increases. This increase in yield of 2-methylpropene is entirely due to E2 elimination increasing in importance compared to E1 elimination.

Figure 9.21



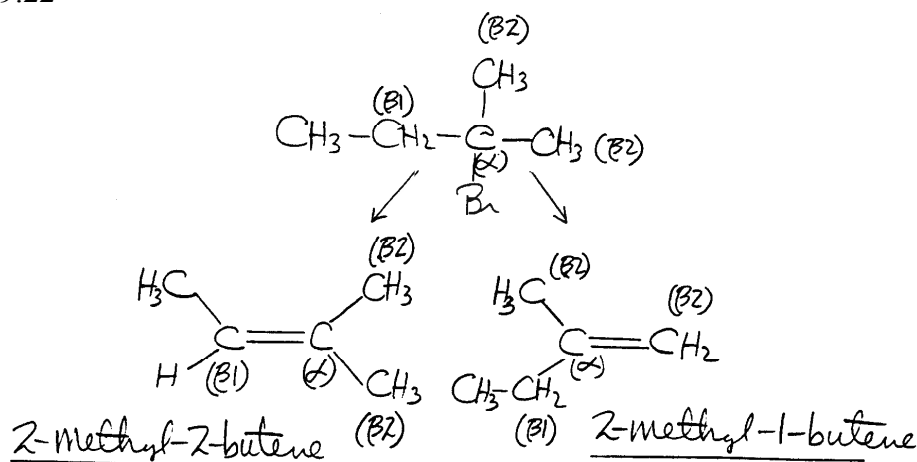
A More Detailed Analysis. When $[\text{EtO}^-] = 0 \text{ M}$ the only mechanisms are E1 and $\text{S}_{\text{N}}1$. However when $[\text{EtO}^-] = 0.02 \text{ M}$, the operable mechanisms include E2 in addition to E1 and $\text{S}_{\text{N}}1$. (Remember that $\text{S}_{\text{N}}2$ is not possible with this substrate). The amount of E2 elimination continues to increase with increasing $[\text{EtO}^-]$ until elimination becomes almost the exclusive reaction at $[\text{EtO}^-] = 2.0 \text{ M}$. Since the base EtO^- has no direct effect on rates of either the E1 or $\text{S}_{\text{N}}1$ reactions, the increase in $[\text{EtO}^-]$ causes E2 elimination to increase with respect to E1 elimination (Figure 9.21).

Different Alkene Products (9.2C)

When a substrate has more than one type of $\text{C}_{\beta}\text{-H}$, different alkenes may form in competition with each other in either E1 or E2 eliminations.

Effect of Alkene Stability. The substrate *2-bromo-2-methylbutane* has two different types of $\text{C}_{\beta}\text{-H}$ whose loss gives both *2-methyl-2-butene* as well as *2-methyl-1-butene* (Figure 9.22).

Figure 9.22



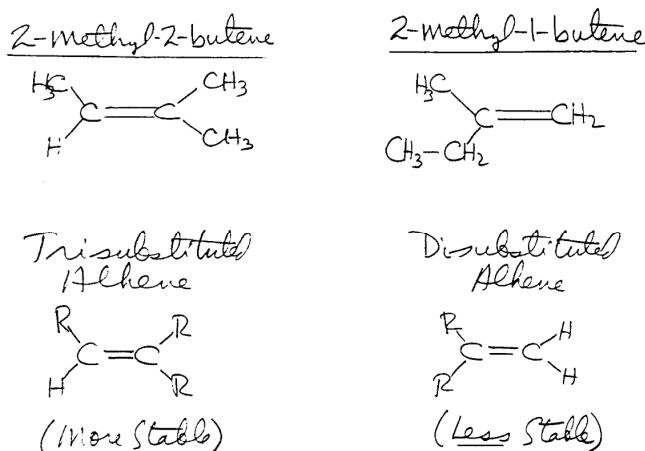
2-Methyl-2-butene arises from loss of a $\text{C}_{\beta 1}\text{-H}$, while *2-methyl-1-butene* forms by loss of a $\text{C}_{\beta 2}\text{-H}$. There are 6 $\text{C}_{\beta 2}\text{-H}$'s that a base can remove to give *2-methyl-1-butene*, but only 3 $\text{C}_{\beta 1}\text{-H}$'s that a base can remove to give *2-methyl-2-butene*. As a result, we might expect a higher yield of the *1-butene* than the *2-butene*, however the results are opposite that prediction for both E1 and E2 eliminations (Table 9.4).

Table 9.4. Relative Alkene Yields from Elimination Reactions of 2-Bromo-2-methylbutane in Ethanol (25°C).

(ethoxide ion), M	Mechanism	% Yield	
		2-methyl-2-butene	2-methyl-1-butene
0	E1	82	18
2.0	E2	72	28

These results occur because (1) the most stable alkene is usually the major product in elimination reactions of haloalkanes, and (2) the alkene 2-methyl-2-butene is more stable than 2-methyl-1-butene. We learned in Chapter 8 that alkene stability depends on the extent of substitution on the C=C bond, and 2-methyl-2-butene (with the general structure $R_2C=CHR$) is more highly substituted than 2-methyl-1-butene (with the general structure $R_2C=CH_2$).

Figure 9.23



Zaitsev's Rule. When an elimination reaction gives predominantly the most stable alkene, we say that the reaction follows **Zaitsev's rule**. This rule, named after the Russian chemist A. N. Zaitsev (1841-1910), states that the most highly substituted alkene is the major product in an elimination reaction where more than one alkene can form. However, not all elimination reactions follow Zaitsev's rule, and we discuss these later in this Chapter.

Rules and Their Names. When elimination reactions were first described as "obeying" or "not obeying" Zaitsev's rule, chemists did not fully understand the correlation between alkene *substitution* and alkene *stability*. Since chemists now know the direct correlation between alkene stability and substitution, *Zaitsev's rule* is equivalent to saying that an elimination reaction preferentially gives the most stable alkene product(s).

While it would be better for us to simply state that an elimination gives the most stable alkene, rather than say "it follows *Zaitsev's rule*", the use of *Zaitsev's rule* to describe an elimination reaction is a part of the vocabulary of organic chemistry that we cannot ignore. We will encounter other similar examples throughout this text.

You may see the name *Zaitsev* also spelled *Saytzeff*, *Saytsef*, or *Saytzev*. These variations result from taking a name originally written in the Russian alphabet and writing it in our alphabet.

Other Halide Leaving Groups (9.2D)

We have used bromoalkanes (R-Br) to illustrate elimination reactions, however the other halide ions also serve as leaving groups.

Relative Reactivity. I, Br, Cl, and F, can all serve as leaving groups in $E2$ elimination. All except F are also leaving groups in $E1$ reactions. The reactivity of the various haloalkanes in eliminations is $R-I > R-Br > R-Cl \gg R-F$ and we saw this same order in Chapter 7 for S_N reactions. It is a direct result of the relative C-X bond strengths (Chapter 3) that are $C-F \gg C-Cl > C-Br > C-I$.

The specific halogen has a relatively small effect on the ratio of elimination to substitution products. This is not surprising for $E1$ reactions and their competing S_N1 reactions because the elimination *versus* substitution ratio is determined by reactions of the carbocation after loss of the halide ion. However, the data in Table 9.5 show that X also has a relatively small effect on the competition between $E2$ and S_N2 reactions (Figure 9.24).

Figure 9.24

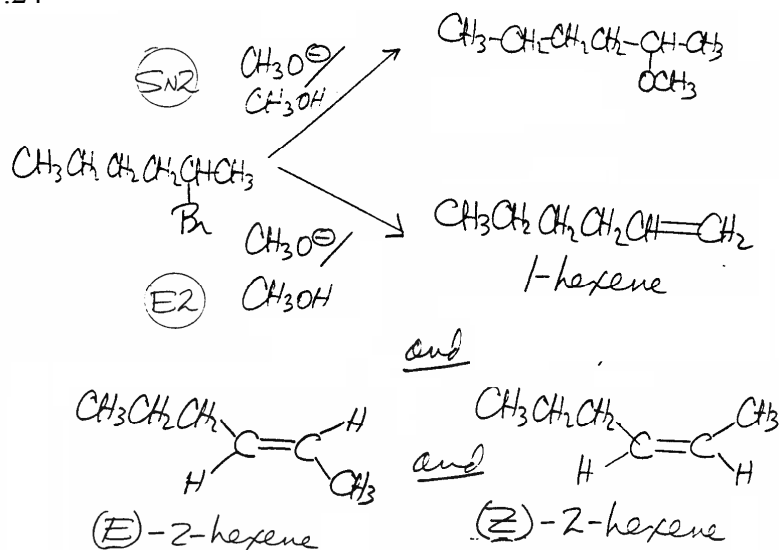


Table 9.5. Relative Amounts of $E2$ Elimination and S_N2 Substitution for Reaction of 2-Haloalkanes (R-X) with $^-OCH_3$ in CH_3OH .

<u>R-X</u>	<u>T, °C</u>	<u>%-Substitution</u>	<u>%-Elimination</u>
R-I	99	16	84
R-Br	99	25	75
R-Cl	99	35	65
R-F	130	35	65

Alkene Product Distribution. In contrast, X has a larger effect on the ratio of different alkenes formed from a single substrate by E2 elimination (Table 9.6).

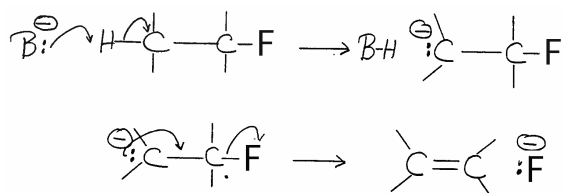
Table 9.6. Relative Amounts of Alkene Products from Reaction of 2-Haloalkanes (R-X) with OCH_3^- in CH_3OH .

<u>R-X</u>	<u>T, °C</u>	<u>1-Hexene</u>	<u>% Yield</u>	
			<u>(E)-2-hexene</u>	<u>(Z)-2-hexene</u>
R-I	99	19	63	18
R-Br	99	28	54	18
R-Cl	99	33	50	17
R-F	130	72	20	8

(E)-2-hexene is the most stable alkene in this group and is the major product when X = Cl, Br, and I, however this is not the case for X = F.

Organic chemists explain this difference for X = F by proposing that the elimination mechanism for reaction of fluoroalkanes is *E1cb* rather than E2 (see section 9.1D).

Figure 9.25



Carbanion stability (R_3C^-) follows the order $1^\circ > 2^\circ > 3^\circ$ so in an E1cb mechanism we expect the alkene arising from the least substituted carbanion (e.g. 1-hexene) to predominate as it does in elimination of H-F from 2-fluorohexane.

The Type of Base (9.2E)

A variety of different nucleophilic species can serve as bases in elimination reactions.

Alkoxide and Amide Ions. We show the bases most commonly used to prepare alkenes from haloalkanes in Table 9.7 [next page]. In each case, the basic atom is a negatively charged O or N, and the solvent is usually the conjugate acid (B-H) of the negatively charged base (B:⁻).

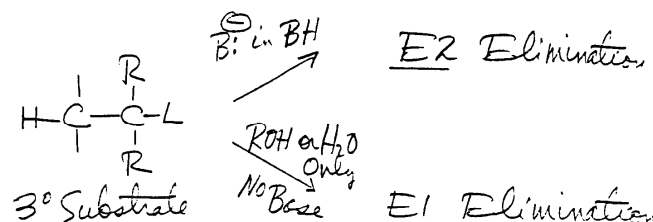
Table 9.7. Important Types of Bases for Elimination Reactions

<u>Base</u>	<u>Solvent</u>	<u>R Group</u>
:OH^-	H_2O or ROH	Me, Et
:OR^-	ROH	Me, Et, i-Pr, t-Bu
:NH_2^-	NH_3	
:NR_2^-	NHR_2	i-Pr

With these strong bases, the elimination mechanism with a 3° substrate is usually E2 even though the substrate could in principle react *via* an E1 mechanism.

In the absence of alkoxide (RO⁻) or hydroxide ion, 3° haloalkane substrates react by E1 elimination when they are heated in a hydroxylic solvent (ROH or H₂O) (Figure 9.26).

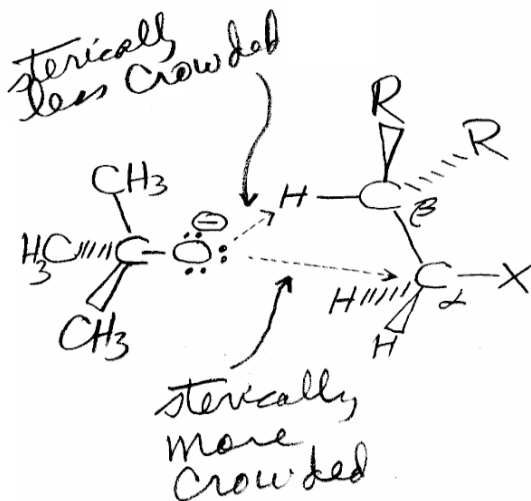
Figure 9.26



However the solvents NH₃ and R₂NH are sufficiently basic to cause E2 elimination even if :NH_2 or :NR_2 are not present.

Effect on E2/S_N2 Competition. Bases that are "sterically bulky", such as (CH₃)₃C-O⁻ (abbreviated t-BuO⁻) and ((CH₃)₂CH)₂N⁻ (abbreviated i-Pr₂N⁻) (Table 9.7), favor E2 reactions over competing S_N2 reactions. The O⁻ and N⁻ atoms are both strongly basic and strongly nucleophilic, but the large R groups attached to O and N in t-Bu-O⁻ and i-Pr₂N⁻ make it difficult for them to approach the backside of a C-X carbon in most S_N2 reactions even on 1° and 2° substrates (e.g. see Figure 9.27).

Figure 9.27



Other Bases. Other nucleophilic species besides those in Table 9.7, such as halide ions (X⁻), cyanide ion (CN⁻), carbonate ion (CO₃²⁻), and LiAlH₄ (a source of hydride ion ("H⁻")) (see Chapter 7), can act as bases in certain elimination reactions. We illustrate their use later in the text.

The Solvent and The Temperature (9.2F)

Both *solvents* and *temperature* affect the rates and products of elimination reactions.

Solvents. Elimination reactions can occur in a variety of solvents and some that are most useful are included in Table 9.7. We can also use *polar aprotic solvents* such as *dimethyl sulfoxide* ($(\text{CH}_3)_2\text{S}=\text{O}$) that we described in Chapter 7. *Polar aprotic solvents* make nucleophilic species such as halide ions and cyanide ion more effective as *bases* just as they make them more nucleophilic as we explained in Chapter 7.

Temperature. An increase in reaction temperature generally increases rates of all reactions. But rates of elimination reactions generally increase faster with increasing temperature than those of competing substitution reactions. As a result, we find that elimination becomes increasingly favored over substitution with an increase in reaction temperature.

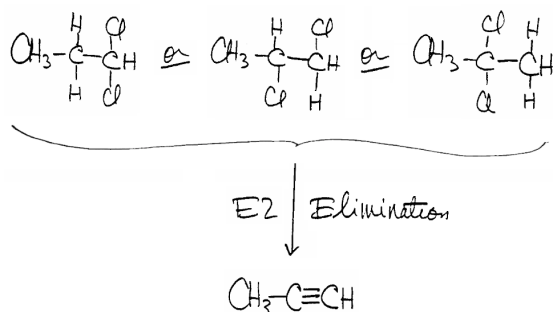
9.3 Alkynes and Allenes from Haloalkanes

Alkynes with a $\text{C}\equiv\text{C}$ bond and *allenes* with a $\text{C}=\text{C}=\text{C}$ group can be prepared from haloalkanes by elimination reactions analogous to those that give alkenes.

Dehydrohalogenation (9.3A)

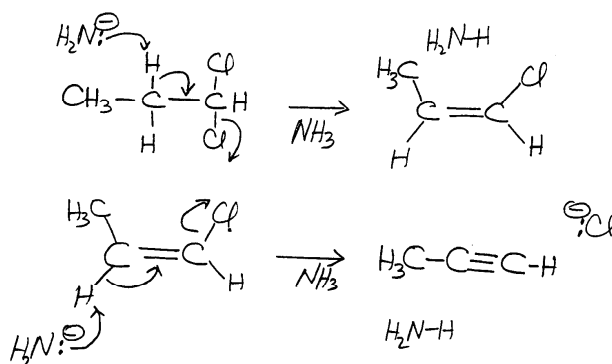
In order to form *alkynes* or *allenes* by *dehydrohalogenation*, we start with dihaloalkanes and eliminate two molecules of H-X as we illustrate using the reactants *1,1-dichloropropane*, *1,2-dichloropropane*, and *2,2-dichloropropane* (Figure 9.28).

Figure 9.28



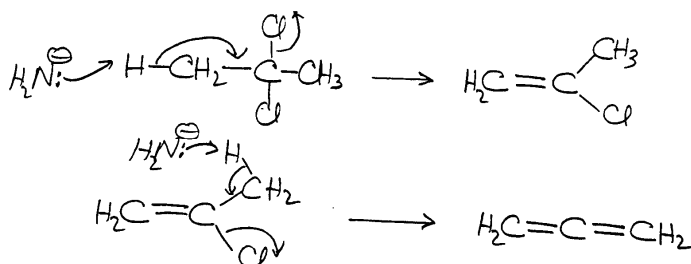
These transformations from dihaloalkanes to *alkynes* and *allenes* involve two successive E2 eliminations. A *haloalkene* intermediate forms in the first step as we show here for reaction of *1,1-dichloropropane* with the strong base *sodium amide* (Figure 9.29).

Figure 9.29



Although *propyne* is the only reaction product we expect from E2 elimination on *1,1-dichloropropane*, dehydrohalogenation of *1,2-dichloropropane* or *2,2-dichloropropane* can give the allene $\text{CH}_2=\text{C}=\text{CH}_2$ (*1,2-propadiene*) as well as *propyne* (Figure 9.30).

Figure 9.30

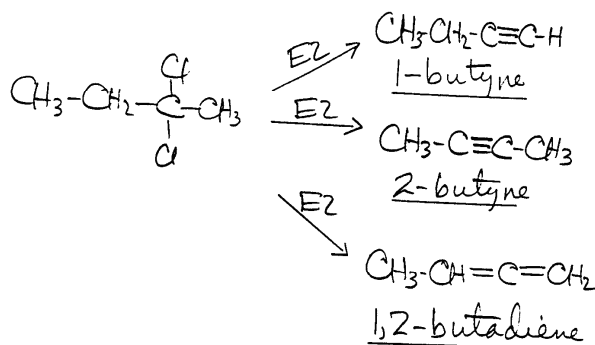


Generally when *alkyne* and *allene* formation compete, the *alkyne* product is preferentially formed because it is more stable. *Allenes* also isomerize to *alkynes* under E2 reaction conditions as we describe in the next section.

Different Alkyne Products (9.3B)

Reaction of *2,2-dichlorobutane* with a base gives both *1-butyne* and *2-butyne* (Figure 9.31).

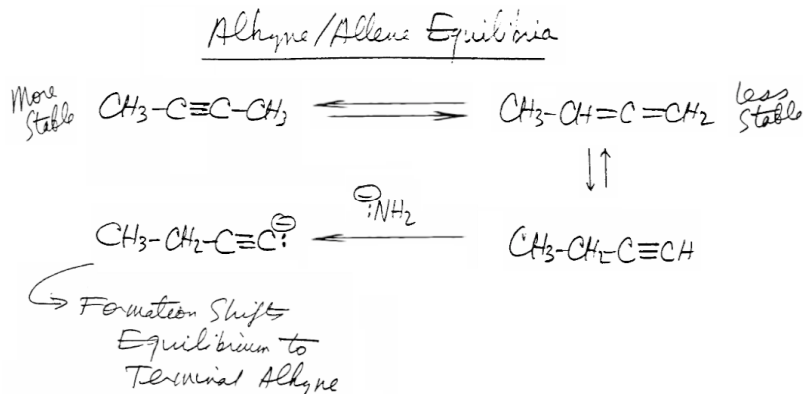
Figure 9.31



2-Butyne is more stable than *1-butyne*, as we described in Chapter 8, and 2-butyne is the major product when *2,2-dichlorobutane* reacts with :OH^- in an alcohol solvent. However, reaction of *2,2-dichlorobutane* with the much stronger base :NH_2^- gives primarily *1-butyne*. This is because

:NH_2 is sufficiently basic to remove the weakly acidic proton (section 8.2D) from a $\text{C}\equiv\text{C-H}$ group (Figure 9.32) and this shifts the equilibrium entirely toward the 1-butyne anion ($\text{CH}_3\text{CH}_2\text{C}\equiv\text{C}^-$).

Figure 9.32



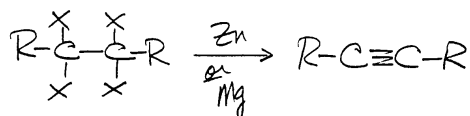
The *allene 1,2-butadiene* is an intermediate in this isomerization reaction (Figure 9.32).

In contrast to these *alkyne/allene isomerizations*, we do not see $\text{C}=\text{C}$ bond isomerizations with alkenes under E2 elimination reaction conditions. The $\text{C}=\text{C-H}$ protons are much less acidic than $\text{C}\equiv\text{C-H}$ protons and do not react with :NH_2 (section 8.2D).

Elimination of X-X (9.3C)

We saw in section 9.1D that 1,2-dihaloalkanes react with metals such as Mg or Zn to give alkenes. Similarly, reaction of polyhaloalkanes with Zn or Mg also gives alkynes.

Figure 9.33

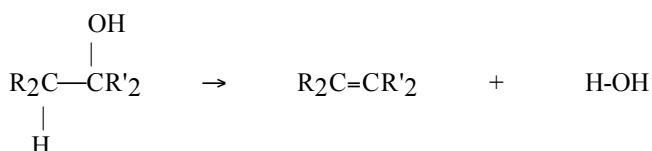


The same limitations exist with these reactions as we described for alkene formation since the polyhaloalkane starting material is best made from the alkyne product that it forms when it reacts with metals.

9.4 Alkenes from Alcohols

Alcohols can also be substrates in elimination reactions. We refer to these elimination reactions as **dehydration** because the overall reaction to form the alkene involves the loss of H_2O .

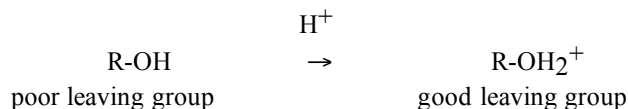
Figure 9.33a



Acid Catalyzed Dehydration (9.4A)

We learned in Chapter 7 that the OH group of an alcohol cannot leave as :OH , but we can protonate it (Figure 9.34) to form the OH_2^+ group that is a good leaving group in elimination reactions as well as in nucleophilic substitution reactions (Chapter 7).

Figure 9.34



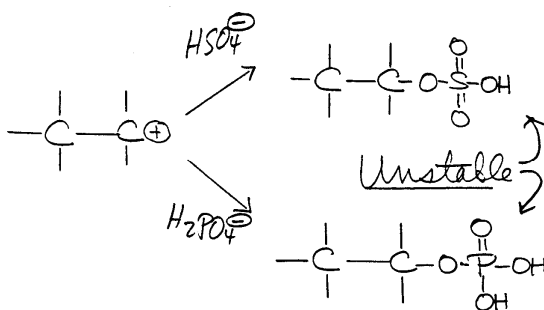
H_2SO_4 or H_3PO_4 . The best acids for dehydration reactions of alcohols are *sulfuric acid* (H_2SO_4) or *phosphoric acid* (H_3PO_4). Mineral acids (HCl, HBr, or HI) give substitution products (iodoalkanes, bromoalkanes, or chloroalkanes) rather than alkenes because the I^- , Br^- or Cl^- ions formed after the alcohol is protonated are very nucleophilic (Chapter 7) and react with R-OH_2^+ ($\text{S}_{\text{N}}2$) or R^+ arising from loss of H_2O .

Figure 9.34a



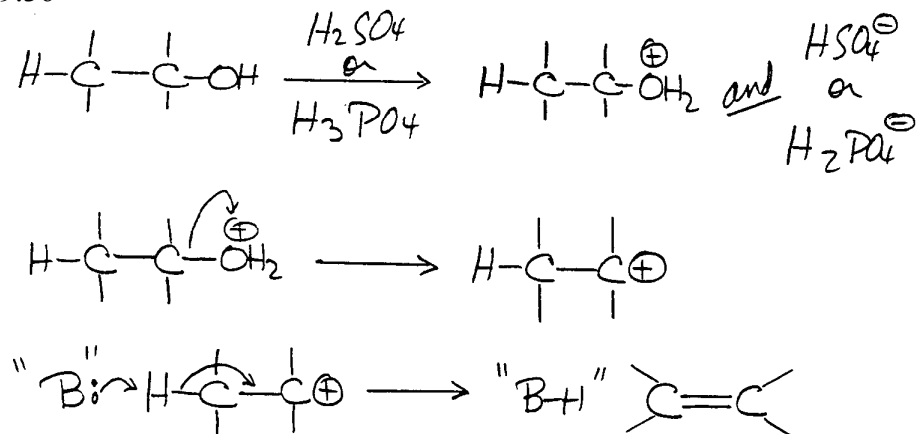
In contrast, HSO_4^- or H_2PO_4^- anions, formed when H_2SO_4 or H_3PO_4 protonate alcohols, are not good nucleophiles and do not displace OH_2^+ groups. Either HSO_4^- or H_2PO_4^- can combine with intermediate carbocations that may form in E1 reactions (Figure 9.35), but the resultant products are unstable and either undergo elimination reactions to form alkenes, or revert to alcohols by substitution.

Figure 9.35



Dehydration Mechanism. Acid catalyzed dehydration reactions take place exclusively by E1 mechanisms. This is because E2 mechanisms require a strong base that cannot exist in the highly acidic medium required to protonate the OH group. In the first step, the alcohol is protonated on O. In the second step the resulting OH_2^+ group leaves as a water molecule (OH_2) to give a carbocation (Figure 9.36) [next page].

Figure 9.36



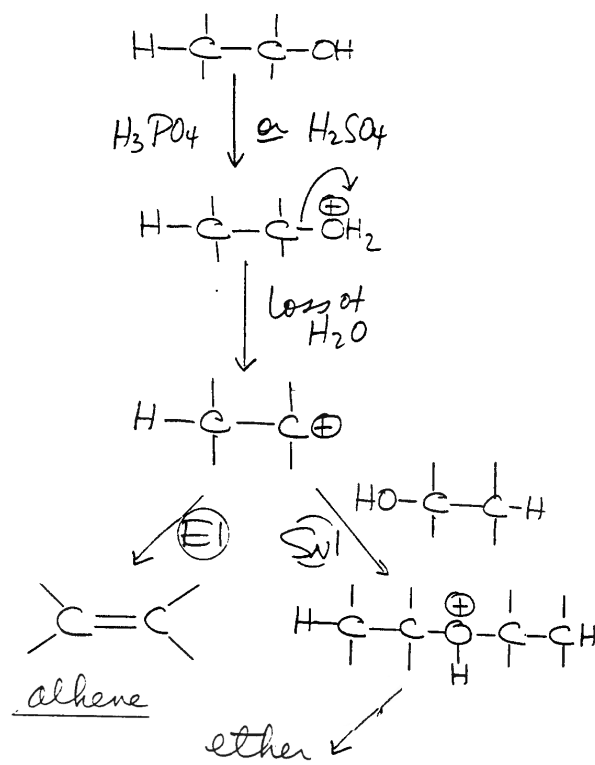
A β -H on the intermediate carbocation is removed as a proton by some species B: that acts as a base (eg. HSO_4^- or H_2PO_4^- , the solvent, or another alcohol molecule). (We show B: (and its conjugate acid B-H) without a charge since B: can be either neutral or negative.) We call B: a base because it removes the β -H, but none of the possible bases that we just mentioned are very basic. They remove β -H's (as protons) from carbocations because these β -H's are very acidic and can be removed by even weak bases.

Alcohol Structure. Since *acid catalyzed dehydration* occurs by an E1 mechanism, 3° alcohols react most readily. However, we can dehydrate 2° or even 1° alcohols if we carry out the reaction at a high temperature. The relative reactivity of alcohols to acid catalyzed dehydration is 3° > 2° > 1°. This order reflects the relative stability of the carbocations formed by loss of H_2O from the protonated alcohol $\text{R}-\text{OH}_2^+$.

Caution! It is important for you to understand that protonated 1° alcohols do not lose water to give 1° carbocations! We explained in Chapter 7 that this was not possible in $\text{S}_{\text{N}}1$ reactions and it does not occur here either. We will see below in section 9.4B that the carbocation that forms from a 1° alcohol is a 2° or 3° carbocation that arises from a rearrangement reaction that occurs as H_2O leaves the protonated 1° alcohol.

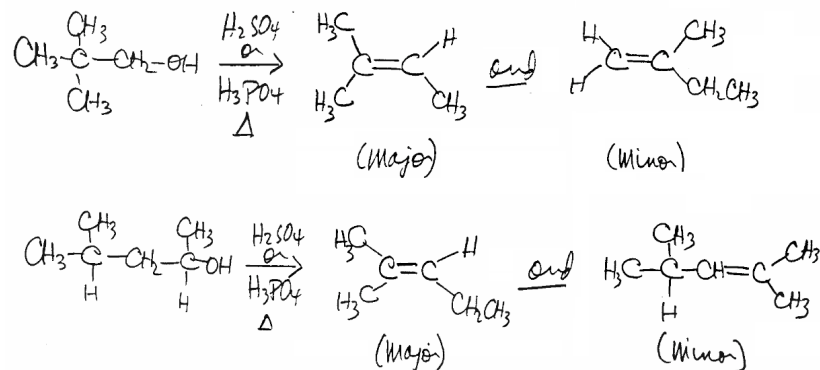
Substitution Can Compete. The formation of an *ether* ($\text{R}-\text{O}-\text{R}$) substitution product by reaction of the intermediate carbocation with unreacted alcohol, can compete with alkene formation (Figure 9.37) [next page]. We can minimize ether formation by this $\text{S}_{\text{N}}1$ mechanism, if we use a low concentration of alcohol. This causes addition of unprotonated alcohol to the carbocation to be slower than deprotonation of the carbocation to form alkene.

Figure 9.37

**Rearranged Alkene Products (9.4B)**

Dehydration of alcohols can give alkenes with **rearranged** carbon skeletons (Figure 9.38).

Figure 9.38

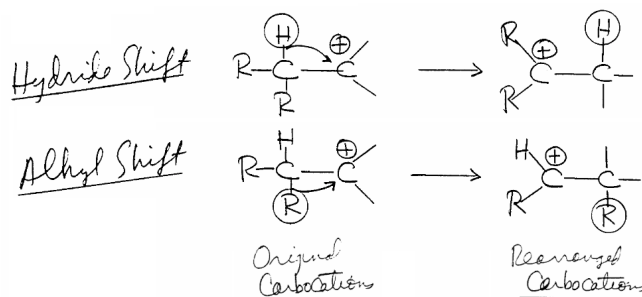


Rearranged alkenes usually result from rearrangements of the intermediate *carbocation* that first forms when OH_2^+ leaves the protonated alcohol. However, the rearranged alkenes can also form by a *direct rearrangement* of the carbon skeleton of the protonated alcohol at the same time the OH_2^+ group leaves the protonated alcohol.

Carbocation Rearrangements. Rearrangement of an intermediate C^+ takes place by the **shift** of an H with its electron pair (a **hydride shift**) from a carbon directly adjacent to the C^+ center, or by a *shift* of an *alkyl group* with its bonding electron pair from a carbon adjacent to the C^+

center. The *hydride* or *alkyl group migrates* to the C⁺ center forming a new *rearranged* carbocation (Figure 9.39).

Figure 9.39

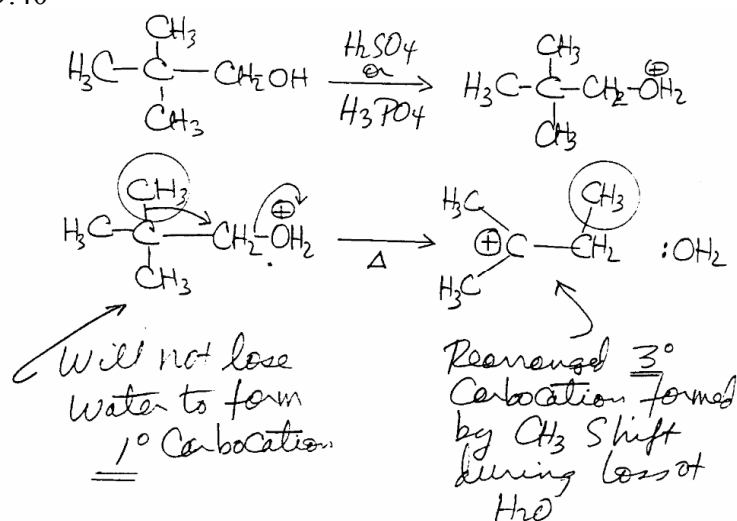


A **driving force** for such *hydride* or *alkyl* shifts is formation of a new carbocation that is more stable than the original one. For example a 2° carbocation (formed from loss of H₂O from a protonated 2° alcohol) rearranges to a 3° carbocation when possible. However, it is also possible for a 2° carbocation to rearrange to another 2° carbocation, or a 3° carbocation to rearrange to another 3° carbocation.

Endothermic Hydride Shifts. Rearrangements that increase the energy of the carbocation (for example 3° to 2°, or 3° to 1°, or 2° to 1°) do not occur under normal reaction conditions. However hydride shifts to give less stable carbocation intermediates can occur when alcohols are dehydrated at high temperatures. These less stable carbocations rapidly rearrange again to more stable carbocations.

1° Alcohol Dehydration. We explained in Chapter 7 that it is very energetically unfavorable to form a 1° carbocation, so dehydration of a protonated 1° alcohol does not directly give a 1° carbocation. An *alkyl* or *hydride* shift occurs simultaneously with loss of H₂O from a protonated 1° alcohol leading directly to a 2° or 3° carbocation (Figure 9.40).

Figure 9.40



These resulting 2° or 3° carbocations can then undergo additional rearrangements before proton loss from C_β gives the alkene product(s).

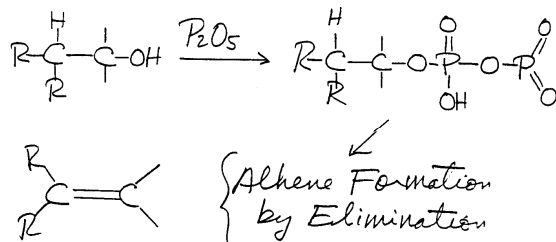
Rearrangements of Carbocations from Other Sources. Carbocations that are intermediates in S_N1 and E1 reactions of *haloalkanes* can also rearrange to give both rearranged alkenes and rearranged substitution products. However, such rearrangements are less important in elimination and substitution reactions of haloalkanes because those reactions are carried out at lower temperatures than alcohol dehydration. In addition, 2° and 1° haloalkanes usually react by S_N2 and/or E2 mechanisms that have no intermediate carbocation. Carbocations from other sources can also rearrange and we will see examples in later chapters.

Other Dehydration Reagents (9.4C)

Besides dehydration catalyzed by acids, we can dehydrate alcohols to form alkenes using **metal oxides** such as P₂O₅, Al₂O₃, Cr₂O₃, TiO₂, and WO₃. The use of these metal oxides minimizes formation of substitution products and rearranged alkenes. They can be used not only for reactions in solution, but they dehydrate alcohols that are passed over them in the vapor phase.

Their dehydration mechanisms probably involve reaction of the alcohol OH group with a "metal" atom of the reagent (e.g. Al, Cr, Ti, W, or P) as a first step as we show in Figure 9.41 using P₂O₅.

Figure 9.41

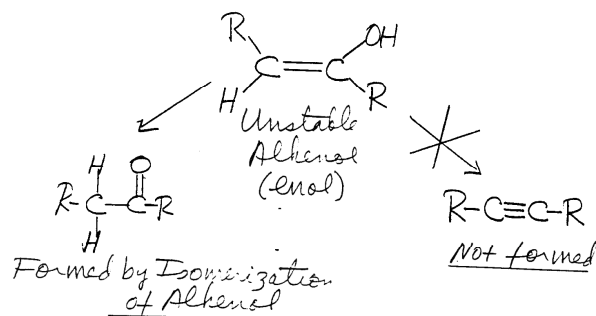


The resulting intermediate subsequently gives the product alkenes directly without intermediate carbocation formation.

Alkynes Are Not Formed by Alcohol Dehydration (9.4D)

While alkynes form by *dehydrohalogenation* of *haloalkanes*, we cannot form alkynes by *dehydration* of *alcohols*. The required *alkenol* precursor (Figure 9.42) is not a stable compound.

Figure 9.42



These *alkenols* (more properly referred to as **enols**), rapidly isomerize to more stable compounds (structural isomers) containing a C=O functional group (*ketones* or *aldehydes*) as we mentioned in Chapter 8 (see Figure 8.35a). We will learn about *enols* and their isomerizations to C=O compounds in later chapters after we discuss compounds containing the C=O group in Chapter 13.

9.5 Alkenes from Amines

Neither the NH₂ group of amines (R-NH₂), nor the NH₃⁺ group of protonated amines (R-NH₃⁺), are leaving groups in elimination reactions. This partially contrasts with the behavior of alcohols that we just discussed. While neither OH (in R-OH) nor NH₂ (in R-NH₂) are leaving groups, we have seen that the OH₂⁺ of R-OH₂⁺ is a good leaving group. Nevertheless, we can modify *amines* so that they are precursors in two important elimination reactions as we describe here.

Quaternary Aminium Hydroxides (9.5A)

Quaternary aminium hydroxides (R-NR₃⁺ ·OH) that contain the structural element H-C-C-N(CH₃)₃⁺ undergo elimination reactions to give alkenes.

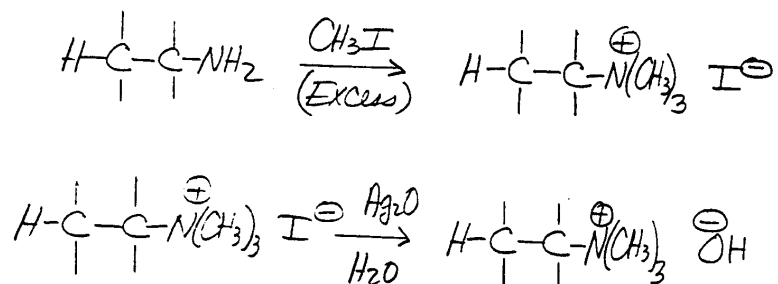
Hofmann Amine Degradation. In the presence of a strong base such as ⁻OH, the N(CH₃)₃⁺ group (the *trimethylaminium* group) serves as a leaving group for alkene formation in an E₂ elimination reaction (Figure 9.43).

Figure 9.43



We can synthesize the starting *alkyltrimethylaminium hydroxide* (Figure 9.43) from an unsubstituted amine (R-NH₂) (Figure 9.44) by *methylation* (a nucleophilic substitution reaction) that we described in Chapter 7.

Figure 9.44

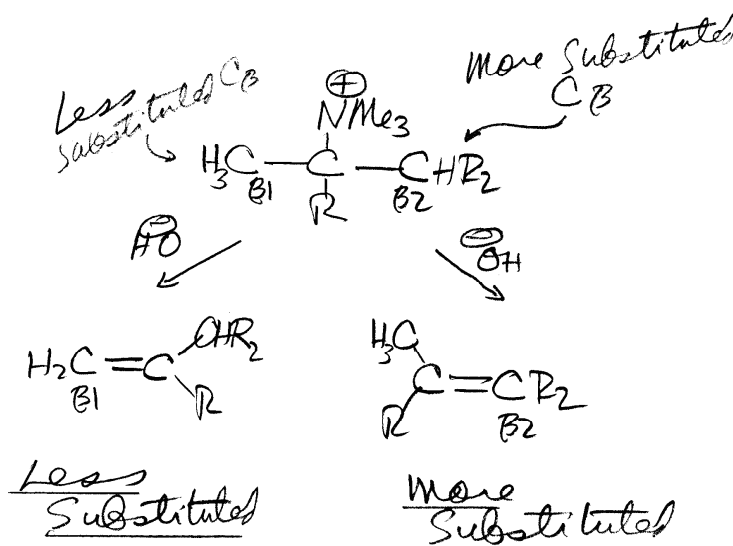


Alkene forms when we vigorously heat the final *trimethylaminium hydroxide* product (Figure 9.43).

We call this overall process (Figures 9.27 and 9.26) the **Hofmann degradation** of amines. It is important to note that the aminium ion leaving group must be fully methylated ($\text{N}(\text{CH}_3)_3^+$). Otherwise OH^- will remove a proton from an aminium ion with an H on N (for example $\text{NH}(\text{CH}_3)_2^+$) rather than react with the $\text{C}_\beta\text{-H}$.

Alkene Product. The alkene product that forms in highest yield during the *Hofmann degradation* (Figure 9.43) is often the least substituted (least stable) of the various possible alkene products (Figure 9.45a).

Figure 9.45a

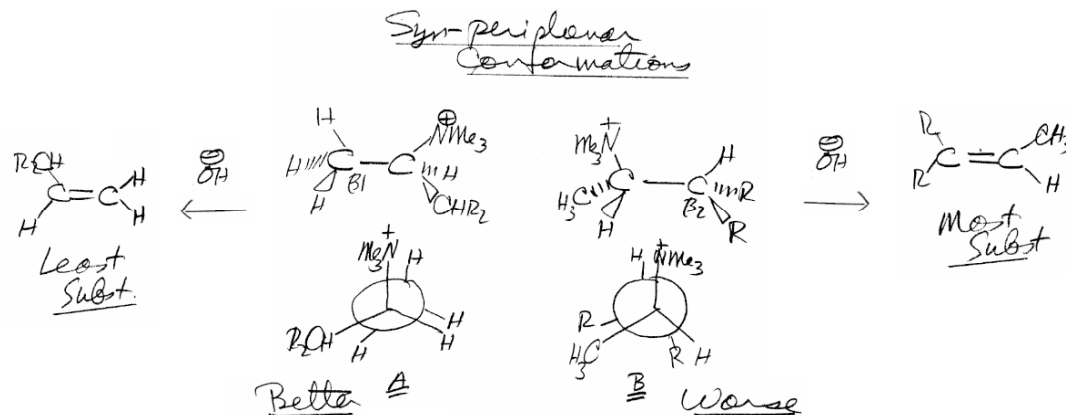


As a result, this and other elimination reactions that give the least substituted alkene product in the highest yield are all generally referred to as **Hofmann eliminations** in order to contrast them with *Zaitsev eliminations* (section 9.2C) that give the most substituted alkene in greatest yield. While it is confusing, you need to be aware that the very last step of the *Hofmann amine degradation* is also specifically called the Hofmann elimination reaction.

Why the Least Stable Alkene? The least substituted alkene probably predominates in Hofmann elimination reactions due to a combination of steric and electronic properties of the $-N(CH_3)_3^+$ group. This group is relatively large and one explanation is that this large steric size favors approach of the hydroxide ion to β -H's that are on the least substituted C's (see Figure 9.45a).

The size of the $-N(CH_3)_3^+$ group may also raise the energies of staggered conformations causing normally unfavorable syn-periplanar conformations (Figure 9.45b) to become available for elimination.

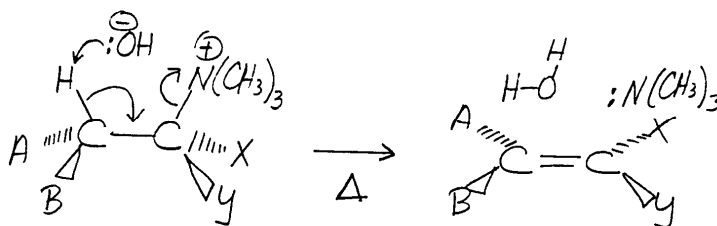
Figure 9.45b



Of the two shown above, we expect the one leading to the least substituted alkene to be the lower energy conformation.

A third possible factor is that the Hofmann elimination reaction is carried out under conditions where there is little solvent to solvate either the ^-OH ion or the $N(CH_3)_3^+$ group. As a result, the negatively charged ^-OH ion remains close to the positively charged $N(CH_3)_3^+$ group causing the ^-OH to react mainly with a $C\beta$ -H that is *syn* to the $N(CH_3)_3^+$ group (Figure 9.45c).

Figure 9.45c

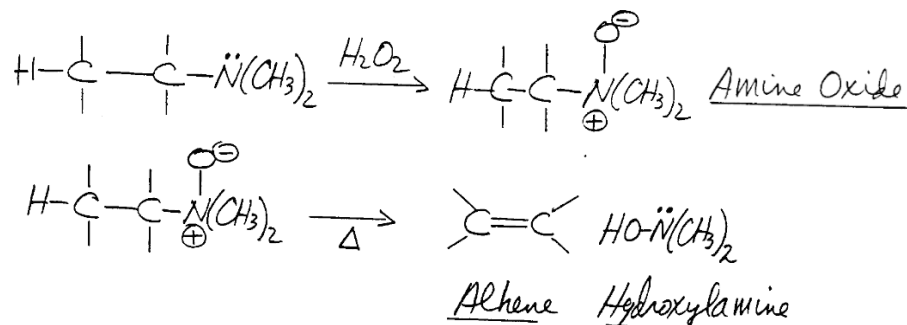


Finally, we can rationalize predominant formation of the least substituted alkene if the Hofmann elimination reaction follows an E1cb mechanism (section 9.1D). We will learn in a later chapter that the $-N(CH_3)_3^+$ group is expected to increase the acidity of β -H's and an increase in C-H acidity would favor an E1cb mechanism. Since C-H acidity is greatest for least substituted C's (section 9.2D), we would expect the least substituted intermediate carbanion to predominate leading to predominant formation of the least substituted alkene.

Amine Oxides Give Alkenes (9.5B)

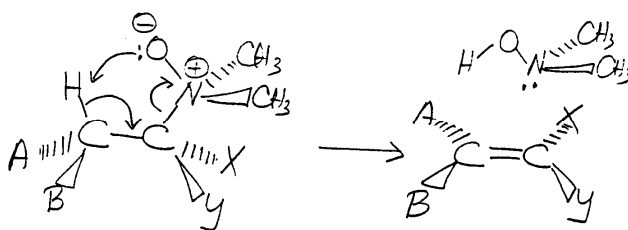
Amines also serve as precursors to alkenes by the reaction sequence outlined in Figure 9.46 called the **Cope elimination**.

Figure 9.46



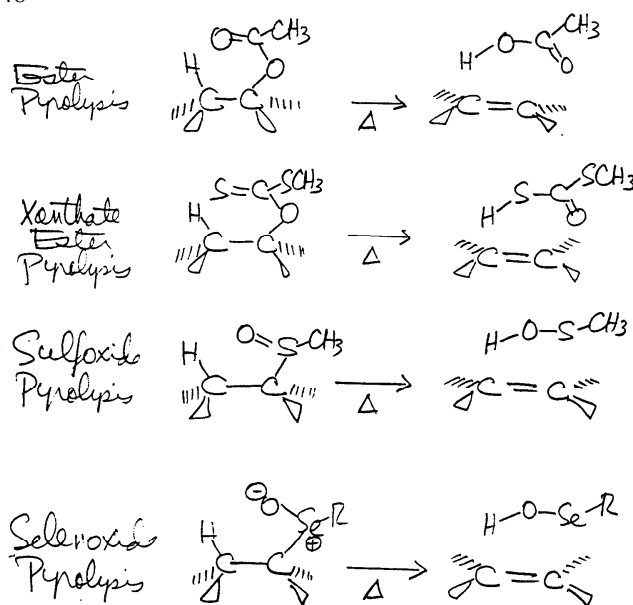
We convert a 3° *N,N*-dimethylamine into an ***N,N*-dimethylamine oxide** that subsequently undergoes an *intramolecular Cope elimination reaction* to give an *alkene* and a **hydroxylamine**.

Figure 9.47



Other Elimination Reactions. Besides the elimination reactions included in this chapter, there are a number of others. Four of these are similar to the Cope elimination because they involve intramolecular *syn* elimination transition states (Figure 9.48).

Figure 9.48



The **ester pyrolysis reaction** involves an *ester* functional group that we introduce later in this text. The other reactive functional groups in Figure 9.48 are specialized groups that organic chemists have developed because they work well in these reactions.

There are also a number of E1 and E2 elimination reactions that are analogous to those described for the haloalkanes (and alcohols), but that involve substrates with leaving groups other than a halide ion (or OH_2^+). Some of these other groups were mentioned in the chapter on nucleophilic substitution reactions.

The most important leaving groups for E1 and E2 eliminations are those that are described in this chapter.

Chapter Review

Elimination Reactions

(1) Elimination reactions form alkenes ($\text{R}_2\text{C}=\text{CR}_2$) by loss of the atoms or groups A and B from compounds with the general structure $\text{R}_2\text{CA}-\text{CBR}_2$. (2) Haloalkanes where $\text{A} = \text{H}$ and $\text{B} = \text{X}$ ($\text{R}_2\text{CH}-\text{CXR}_2$) are common substrates for elimination reactions. (3) E1 eliminations of haloalkanes have a two-step mechanism in which an intermediate carbocation $\text{R}_2\text{CH}^+-\text{CR}_2$ formed by loss of $^-:\text{X}$ transfers its CH proton to a base. (4) E2 eliminations have a single step mechanism in which a base removes H as a proton and X leaves a halide ion (X^-). (5) E1 eliminations are usually not stereospecific, but E2 eliminations of haloalkanes are stereospecific with anti-periplanar transition states. (6) The E1cb elimination mechanism has two steps in which a base removes the CH proton from $\text{R}_2\text{CH}-\text{CLR}_2$ to give an intermediate carbanion that subsequently loses an L^- leaving group. (7) Metallic magnesium or zinc dehalogenate 1,2-dihaloalkanes ($\text{R}_2\text{CX}-\text{CXR}_2$) to give alkenes. (8) (add α -elimination)

Mechanistic Competitions in Elimination Reactions

(1) Nucleophilic substitution reactions often compete with elimination reactions. (2) 1° haloalkanes ($\text{R}_2\text{CH}-\text{CH}_2\text{X}$) or 2° haloalkanes ($\text{R}_2\text{CH}-\text{CHXR}$) usually undergo E2 elimination and the required strong bases (B^-) can also competitively displace X^- by an S_2 mechanism to give substitution products ($\text{R}_2\text{CH}-\text{CH}_2\text{B}$ or $\text{R}_2\text{CH}-\text{CHBR}$). (3) 3° haloalkanes ($\text{R}_2\text{CH}-\text{CXR}_2\text{X}$) give substitution products ($\text{R}_2\text{CH}-\text{CR}_2\text{B}$) by $\text{S}_\text{N}1$ reactions that compete with E1 elimination. (4) 1° haloalkanes ($\text{R}_2\text{CH}-\text{CH}_2\text{X}$) give substitution reactions by $\text{S}_\text{N}2$ reactions that compete with E2 elimination. (5) 2° haloalkanes ($\text{R}_2\text{CH}-\text{CHXR}$) can give substitution products in competition with elimination and the mechanisms might be $\text{S}_\text{N}1/\text{E1}$ or $\text{S}_\text{N}2/\text{E2}$ depending on the substrate structure and reaction conditions. (6) In the presence of strong bases (B^-), 3° haloalkanes can also undergo E2 elimination in competition with E1 and $\text{S}_\text{N}1$ reactions. (7) When two or more alkene products are possible, haloalkanes generally give the most substituted (most stable) alkene product by E1 or E2 eliminations. (8) Elimination reactivity order of haloalkanes is $\text{RI} > \text{RBr} > \text{RCI} > \text{RF}$. (9) The halogen leaving group X has relatively little effect on products in E1 reactions, but the substitution/elimination ratio as well as the relative amount of the less substituted (less stable) alkene both increase in E2 reactions in the order $\text{RI} < \text{RBr} < \text{RCI} < \text{RF}$. (10) Strong bases for E2 reactions include alkoxide ions (RO^-) and amide ions (R_2N^-). (11) Sterically bulky R groups in bases favor elimination over substitution. (9) Solvents include polar protic solvents such as alcohols as well as polar aprotic solvents such as dimethylsulfoxide.

Alkynes and Allenes from Haloalkanes

(1) Dehydrohalogenation of 1,1-dihaloalkanes ($\text{RCX}_2\text{-CH}_2\text{R}$) or 1,2-dihaloalkanes (RCHX-CHXR) with strong bases gives alkynes and/or allenes. (2) Internal alkynes ($\text{RC}\equiv\text{CR}$) are more stable than terminal alkynes ($\text{RC}\equiv\text{CH}$), but terminal alkynes predominate when amide bases ($\text{R}_2\text{N:}^-$) are used because they deprotonate terminal alkynes to give the acetylide ion ($\text{RC}\equiv\text{C:}^-$).

(??)(Add more here and add section about alkyne acidity)(??)

(3) Allene intermediates rearrange to alkynes under basic dehydrohalogenation conditions. (4) Zn and Mg metal dehalogenate tetrahaloalkenes ($\text{RCX}_2\text{-CX}_2\text{R}$) to give alkynes.

Alkenes from Alcohols

(1) Sulfuric or phosphoric acid dehydrate alcohols to give alkenes. (2) A protonated alcohol intermediate R-OH_2^+ loses water by an E1 mechanism to form an intermediate carbocation R^+ that loses a proton. (3) The alcohol reactivity order is $3^\circ > 2^\circ > 1^\circ$ that reflects carbocation stability. (4) Intermediate carbocations (R^+) may react with their alcohol precursors (ROH) to give ethers (R-OR). (5) The intermediate carbocation often undergoes hydride or alkyl shifts under the reaction conditions causing the alkene product to have a rearranged skeleton. (5) 1° alcohols rearrange during loss of water to give 2° or 3° carbocations rather than directly forming the highly unstable 1° carbocations. (6) Metal oxides such as P_2O_5 and Al_2O_3 also dehydrate alcohols to give alkenes. (7) Alkynes cannot be formed by alcohol dehydration because the required precursor alkenols (enols) are unstable.

Alkenes from Amines

(1) Quaternary aminium hydroxides with the general structure ($\text{H}_\beta\text{-CR}_2\text{-CR}_2\text{-N(CH}_3)_3^+ \text{ } ^-\text{:OH}$) react to form alkenes ($\text{R}_2\text{C}=\text{CR}_2$) at high temperatures by loss of water (H-O-H β) and trimethylamine ($\text{N(CH}_3)_3$). (2) This reaction (the Hofmann elimination reaction) generally gives the least substituted amine *via* a syn-periplanar transition state. (3) Amine oxides with the general structure ($\text{H}_\beta\text{-CR}_2\text{-CR}_2\text{-N(O)(CH}_3)_2$) thermally decompose to give alkenes ($\text{R}_2\text{C}=\text{CR}_2$) and N,N-dimethylhydroxylamine ($\text{H}_\beta\text{-O-N(CH}_3)_2$) in a reaction called the Cope elimination.