

# Chapter 6

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## *Elimination Reactions*

Until now, discussions have focused only on how **carbanions** and **carbocations** behave under conditions favorable for nucleophilic substitutions. However, these species may undergo other types of reactions in which unsaturation is introduced into the molecule. Such reactions are called **elimination reactions** and should be considered whenever charged species are of importance to the mechanistic progression of a molecular transformation. In previous chapters,  $S_N1$  and  $S_N2$  reactions were discussed. In this chapter, the corresponding **E1** and **E2** elimination mechanisms are presented.

### 6.1 E1 ELIMINATIONS

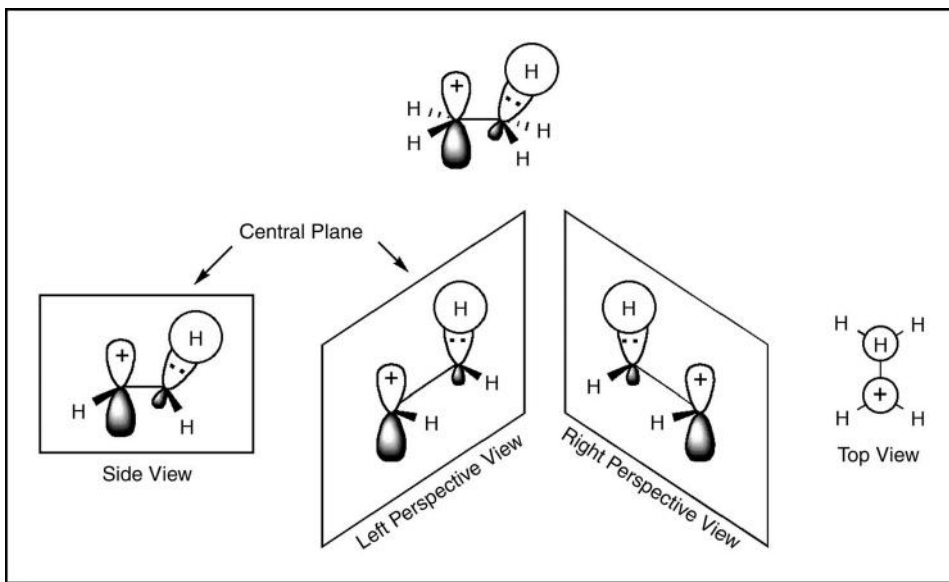
Having addressed the chemistry of carbocations and associated  $S_N1$  reaction mechanisms, it is appropriate to begin discussions of elimination reactions with the related E1 mechanism. As addressed in Chapter 5, carbocations generated from solvolysis reactions can undergo various types of rearrangements that include hydride and alkyl shifts. Furthermore, these shifts were rationalized when the empty  $p$  orbital associated with the positive charge is aligned in the same plane with the migrating group. Figure 6.1 reiterates the process of hyperconjugation necessary for these shifts to occur. Furthermore, Figure 6.2 reiterates that hyperconjugation can be viewed as introducing **double-bond character** to a carbocation. Carrying this rationale one step further, if the double-bond character in a given carbocation becomes stabilized through full **dissociation** of a proton, the result, illustrated in Scheme 6.1, is formation of a full double bond through an E1 elimination mechanism.

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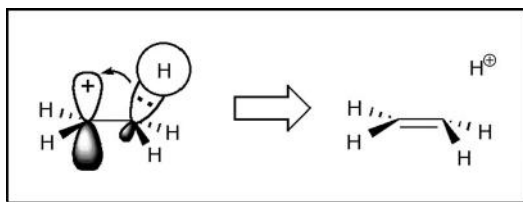
*Arrow Pushing in Organic Chemistry: An Easy Approach to Understanding Reaction Mechanisms.*

By Daniel E. Levy

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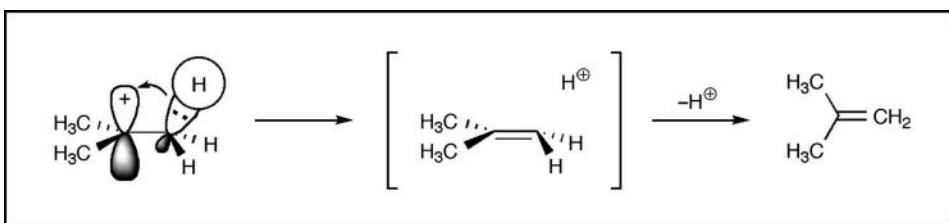


**Figure 6.1** Hyperconjugation occurs when a carbon–hydrogen bond lies in the same plane as a carbocation’s vacant p orbital.

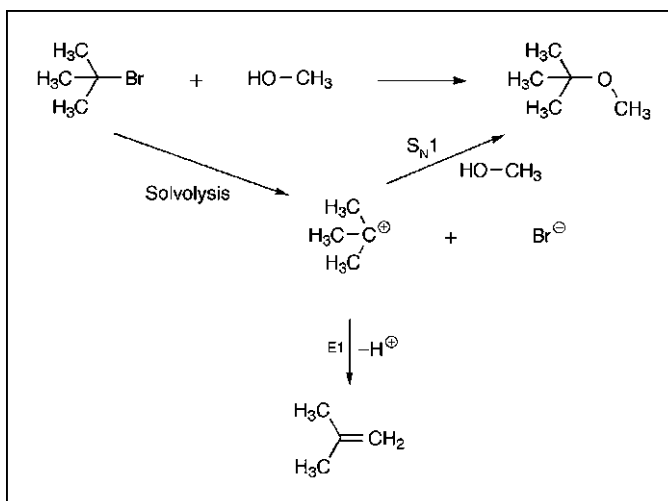


**Figure 6.2** Hyperconjugation can be viewed as formation of a “pseudo-double-bond.”

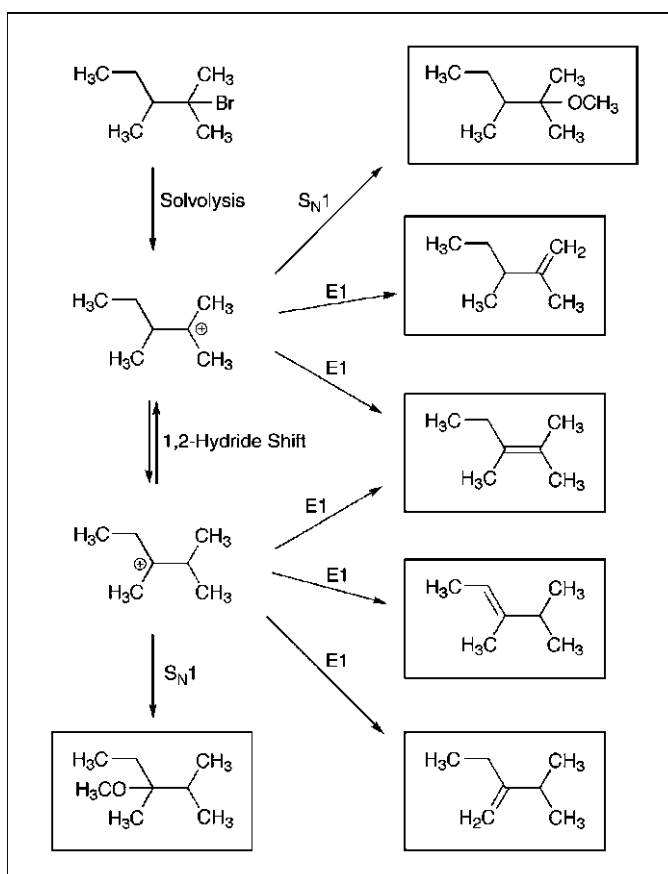
As alluded to above, E1 reactions are integrally related to  $S_N1$  reactions by virtue of the carbocations common to both mechanisms. Thus, revisiting the solvolysis reaction leading to the conversion of *tert*-butyl bromide to MTBE illustrated in Scheme 6.2, we understand how formation of isobutylene occurs. Formation of isobutylene only occurs through the E1 process and comprises approximately 20 percent of the reaction mixture.



**Scheme 6.1** Dissociation of a proton through hyperconjugation completes the final stage of an E1 elimination mechanism.



**Scheme 6.2** E1 mechanisms explain additional products observed during  $\text{S}_{\text{N}}1$  reactions.



**Scheme 6.3** Solvolysis of 2-bromo-2,3-dimethylpentane in methanol leads to formation of up to six different products via multiple mechanistic pathways.

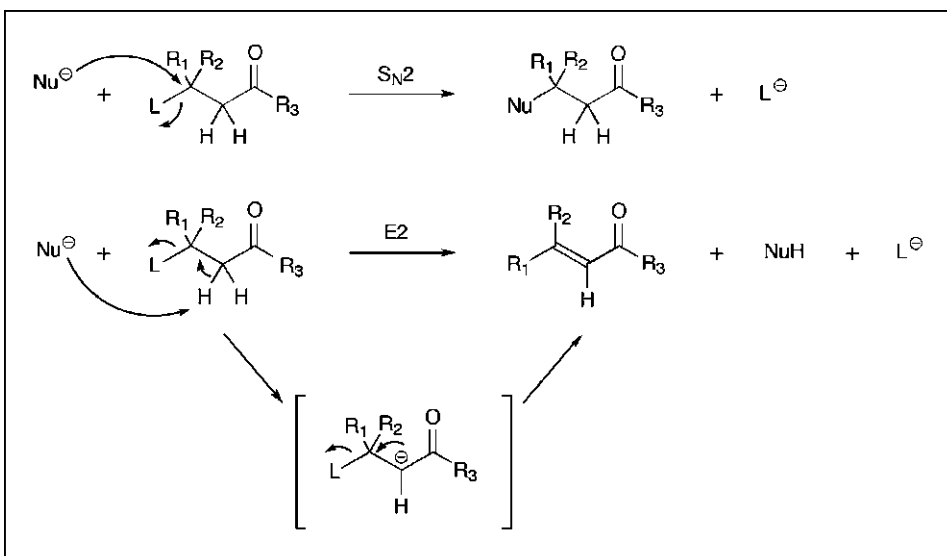
As can be deduced from discussions presented above and in Chapter 5, it is very important to recognize that when designing reactions involving carbocations, both **migration reactions** and **elimination reactions** can complicate the outcome of intended  $S_N1$  transformations. An example illustrating the potential formation of multiple side products is shown in Scheme 6.3 with the solvolysis of 2-bromo-2,3-dimethylpentane in methanol.

Returning to Scheme 6.1, we recognize that an  $E1$  reaction proceeds with the **E**limination of a leaving group, leading to the **E** designation. Because this mechanism proceeds with the initial dissociation of a single starting material forming a carbocation, this process is considered a unimolecular reaction. The involvement of only **1** species in the initial phase of the reaction enhances the mechanistic designation to **E1**.

## 6.2 E2 ELIMINATIONS

To this point, considerable time has been spent discussing acids, bases, nucleophiles, and leaving groups. These were ultimately all presented in the context of  $S_N2$  reactions. Like the complicating side reactions associated with carbocations formed during  $S_N1$  reactions, depending upon the nature of substituents adjacent to acidic protons,  $S_N2$  reaction conditions can induce similar complications. For example, consider a molecule with an acidic proton and a leaving group, L, on the carbon adjacent to the acidic proton. Consider also that nucleophiles are bases. As shown in Scheme 6.4, an alternative to **nucleophilic displacement** of the leaving group is found in initial **deprotonation**. Subsequent displacement of the leaving group by the resulting anion results in formation of an **olefin**.

In studying Scheme 6.4, we recognize that an  $E2$  reaction proceeds through initial extraction of a proton by a base or nucleophile leading to **E**limination of a leaving group, justifying the **E** designation. Because this mechanism proceeds through the interaction of two species (substrate and base/nucleophile),  $E2$  reactions are recognized



**Scheme 6.4**  $S_N2$  Substitution reactions can occur in competition with  $E2$  elimination reactions.

as bimolecular. Thus, the involvement of 2 species in the initial phase of the reaction enhances the mechanistic designation to **E2**. Finally, it is important to note that while E1 reactions proceed through cationic intermediates, E2 reactions proceed through anionic intermediates.

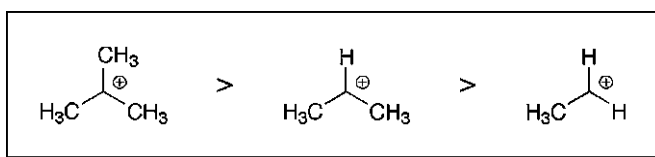
### 6.3 HOW DO ELIMINATION REACTIONS WORK?

In addressing the mechanistic basis behind elimination reactions, we must refer to discussions surrounding carbocations in the context of  $S_N1$  reactions. Furthermore, consideration of carbocation-associated hydride/alkyl shifts and E1 related products is essential. Recall that carbocations are stabilized by phenomena such as hyperconjugation. Furthermore, recall that hydride shifts, alkyl shifts, and E1 eliminations are dependent upon the planar alignment of an empty  $p$  orbital and an adjacent bond bearing either a migrating group or a dissociable hydrogen atom as illustrated in Figure 6.1.

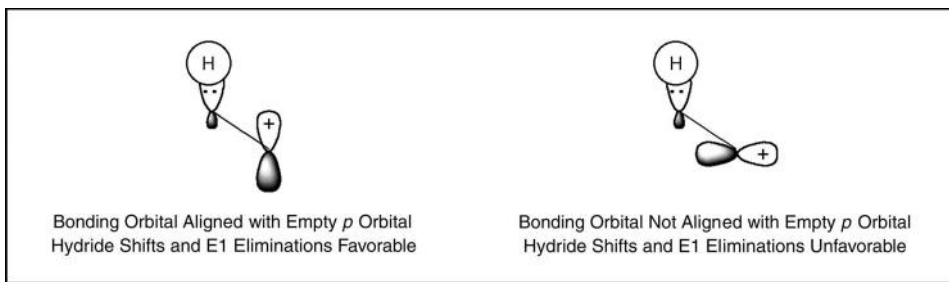
The mechanistic basis behind the stability and reactivity of carbocations, regardless of the reaction outcome, depends on the alignment of an empty  $p$  orbital and the orbitals comprising an adjacent bond. Specifically, if there are no **planar alignments**, then hyperconjugation, hydride/alkyl shifts, or eliminations cannot occur. Perhaps there is no better illustration of this fact than a comparison of the stability of primary, secondary, and tertiary carbocations. As reiterated from Chapter 5, Figure 6.3 illustrates the order of stability from most stable to least stable. This trend in stability is directly related to the number of adjacent carbon–hydrogen bonds available for hyperconjugation.

Looking at the structures shown in Figure 6.3, we notice that the *tert*-butyl carbocation possesses nine carbon–hydrogen bonds adjacent to the cation, while the secondary carbocation possesses six, and the primary carbocation possesses only three. This tabulation of bonds is relevant in that the more adjacent carbon–hydrogen bonds, the more opportunities there are for hyperconjugation to occur. In this discussion, the term *opportunities* is important because single bonds employing  $sp^3$  orbitals are not rigid and can rotate around the bond axis as shown in Figure 6.4 in much the same way a wheel rotates on an axle. Thus, when empty  $p$  orbitals and adjacent bonds are not in alignment, there can be no associated **orbital overlap** and the observed reactions are only possible due to the intermittent alignment of a system that is continually in motion.

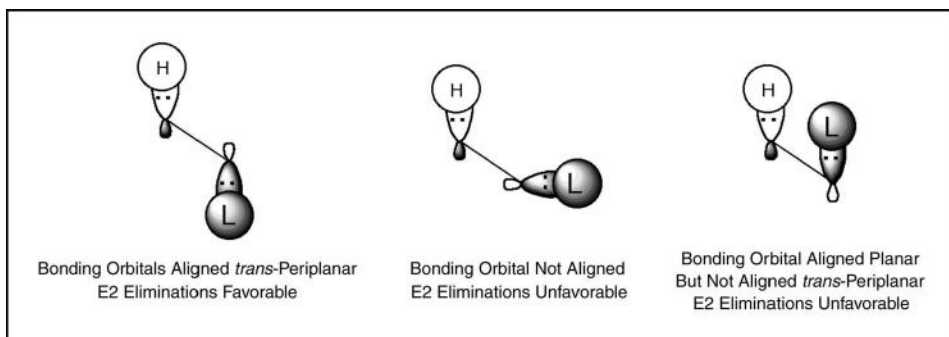
As already discussed, E1 and E2 eliminations differ, in part, by the electronic nature of the mechanism. Specifically, E1 eliminations depend on **cationic** intermediates, whereas E2 eliminations depend on **anionic** intermediates. This difference, however, does not eliminate the mechanistic similarities of these reactions as related to the necessary alignment of adjacent chemical bonds. While, as shown in Figure 6.4, E1 eliminations require alignment of a carbon–hydrogen bond with an adjacent empty  $p$  orbital, E2 eliminations, as shown in



**Figure 6.3** Tertiary carbocations are more stable than secondary carbocations, and secondary carbocations are more stable than primary carbocations.

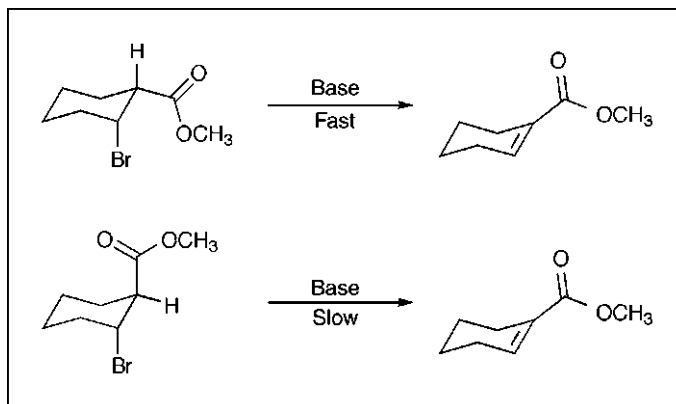


**Figure 6.4** When a carbon–hydrogen (or carbon–alkyl) bond is aligned with an empty  $p$  orbital, 1,2-hydride/alkyl shifts and E1 eliminations are favorable.

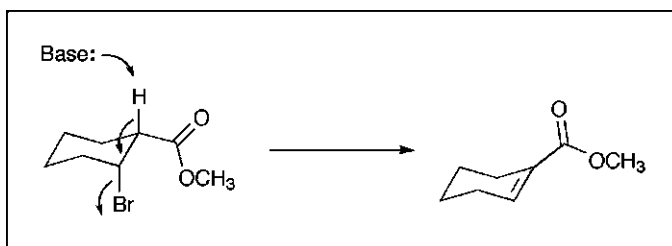


**Figure 6.5** When a carbon–hydrogen bond is aligned *trans*-periplanar with a carbon-leaving group bond, E2 eliminations are favorable.

Figure 6.5, require alignment of a carbon–hydrogen bond with an adjacent carbon-leaving group bond. Furthermore, as shown in Figure 6.5, the relationship between these bonds is critical for elimination to occur. Specifically, the relevant bonds must adopt a *trans* relationship within the same plane. This relationship is referred to as ***trans*-periplanar**.

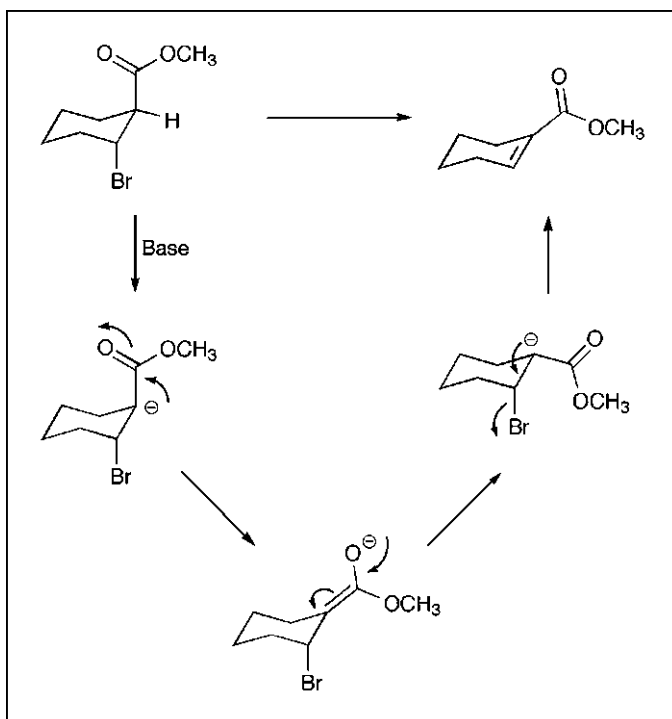


**Scheme 6.5** Rates and reactivity of substrates for potential E2 eliminations are influenced by the presence of *trans*-periplanar relationships.



**Scheme 6.6** *trans*-Periplanar relationships lead to direct E2 eliminations.

A practical example demonstrating the importance of the *trans*-periplanar relationship between protons and leaving groups is illustrated in Scheme 6.5. As shown, when treated with base, the 1,2-*cis*-substituted cyclohexane analog rapidly converts to the illustrated cyclohexene. However, the same reaction conditions applied to the 1,2-*trans* analog results in conversion to the cyclohexene analog at a much slower rate. These observations are mechanistically explained in Schemes 6.6 and 6.7. As shown in Scheme 6.6, the 1,2-*cis* analog, possessing a *trans*-periplanar relationship, reacts through a direct E2 elimination mechanism. However, as shown in Scheme 6.7, the 1,2-*trans* analog must first proceed through deprotonation followed by delocalization of the resulting anion into the ester



**Scheme 6.7** E2 eliminations can proceed in the absence of a *trans*-periplanar relationship in the reaction substrate if reaction intermediates can obtain conformations that are favorable for elimination reactions to occur.

functionality. Once the negative charge is delocalized into the ester, the anion can displace the bromide through the intermediate double bond as illustrated with arrow pushing.

## 6.4 SUMMARY

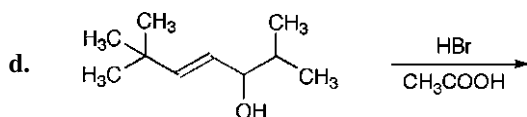
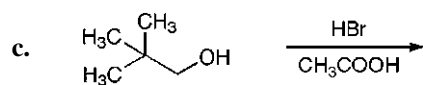
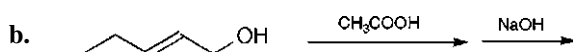
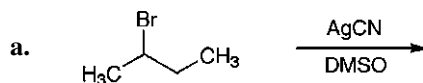
In this chapter, elimination reactions were presented both independently and in association with their related **nucleophilic substitution** mechanisms. Furthermore, the processes by which molecules undergo both E1 and E2 eliminations were presented and explained using **bonding** and **nonbonding orbitals** and their required relationships to one another. While much emphasis was placed on the planar relationships of orbitals required for both elimination reaction mechanisms, the special case of *trans*-periplanar geometries were described as necessary for efficient E2 eliminations to occur.

While *trans*-periplanar relationships are important to E2 elimination reactions, it is important to remember that, as illustrated in Schemes 6.6 and 6.7, E2 elimination reaction mechanisms do not have to occur in a **concerted** manner. After deprotonation, if the relevant orbitals do not line up, elimination will not occur until they do. Furthermore, recall that **rotation** around an acyclic **single bond**, as illustrated in Figures 6.4 and 6.5, occurs readily. Therefore, elimination reactions should not be removed from consideration if a molecule is drawn in a conformation that makes these reactions appear unfavorable. When looking at any type of nucleophilic reaction, initial identification of relevant *trans*-periplanar relationships will aid in the identification of potential side products and their respective mechanisms of formation.

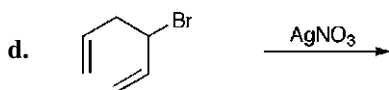
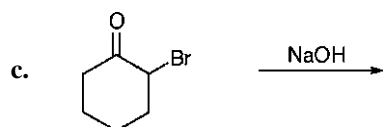
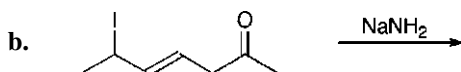
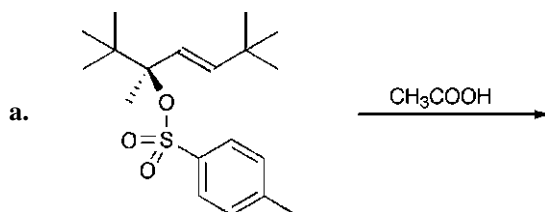




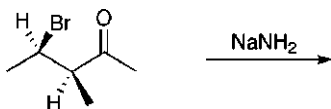
3. With an understanding of E1 mechanisms, one may realize that under  $S_N1$  reaction conditions multiple products may form. In addition to the products predicted in Chapter 5 for the following molecules, predict plausible elimination products.



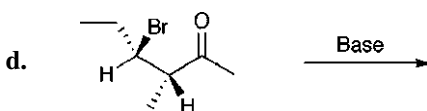
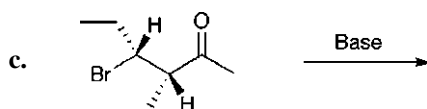
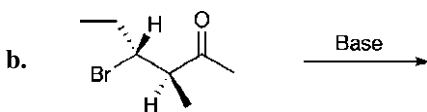
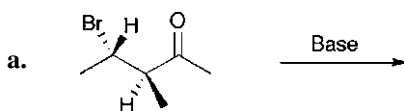
4. Presently, several different organic reaction mechanisms have been presented. Keeping all of these in mind, predict all of the possible products of the following reactions and list the mechanistic type or types from which these products result.



5. As mentioned earlier, stereochemistry is not of great concern in this book. However, certain mechanistic types will show specific stereochemical consequences when acting on chiral molecules. With this in mind, predict the product resulting from the E2 elimination of HBr when the shown isomer of 4-bromo-3-methyl-2-pentanone is treated with sodamide. Show all stereochemistry and explain your answer.



6. Based on the answer to Problem 5, predict the product of the following reactions and show all stereochemistry:



7. Explain the results of the following experiment:

