CHAPTER 9

ELIMINATION REACTIONS

Contents

The details of the elimination reactions

Elimination vs. substitution

9.1 The General Reaction

⇒ This reaction is termed as 1,2-elimination or β-elimination

⇒ There are two mechanisms for the elimination reactions; E1 and E2

9.2 Bimolecular elimination; E2 reaction

⇒ common reaction between alkyl halides and strong bases

⇒ The strong bases are also nucleophiles, the E2 competes with S_N2

$$\text{rate} = k[\text{EtO}^{\ominus}][t\text{-BuBr}].$$

Concerted reaction involves breaking and forming several bonds simultaneously

The bond dissociation Energy of C-D bond is about 1.2 Kcal/mol larger than that for C-H bond

C-D bond is being broken during the RDS !

Almost same rate
C-D bond is not being broken during the RDS !

9.3 Stereochemistry of the E2 reaction

Stereoelectronic requirements of E2

⇒Two sigma bonds (C-H and C-L) should lie in the same plane, because these two bonds overlap to form a pi bond.

⇒More stable conformation is desirable

Two possible conformations

⇒ anti-coplaner conformation is more stable, therefore <u>anti elimination is prefered</u> in the E2 reaction.

⇒ Syn elimination is rare, while possible when –H & -L are held syn-coplaner (eclipsed or nearly eclipsed)

Example; elimination reactions of the diastereomers of 1-bromo-1,2- diphenylpropane

only (*Z*)-1,2-diphenyl-1-propene is produced

Enantiomer of this reactant also produce (*Z*)- alkene

only (*E*)-1,2-diphenyl-1-propene is produced

Enantiomer of this reactant also produce (*E*)-alkene

Trans-diaxial elimination

For the anti elimination of cyclohexane

⇒ The leaving group and the hydrogen must be trans

⇒ They also must be in the axial position

examples

two alkyl groups + one chloride are in the axial position; less stable conformation

two alkyl groups are in the equtorial position; more stable conformation

⇒ elimination of neomenthyl chloride is 40 times faster

However syn elimination does occur in rigid molecules when the living group and the hydrogen are held in an eclipsed conformation (Fig. 9.3)

9.4 Direction of Elimination; Zaitsev's rule

Zaitsev’s rule is an empirical rule based on experiments
⇒ Product development control

More stable alkene is a major product

Hoffmann elimination

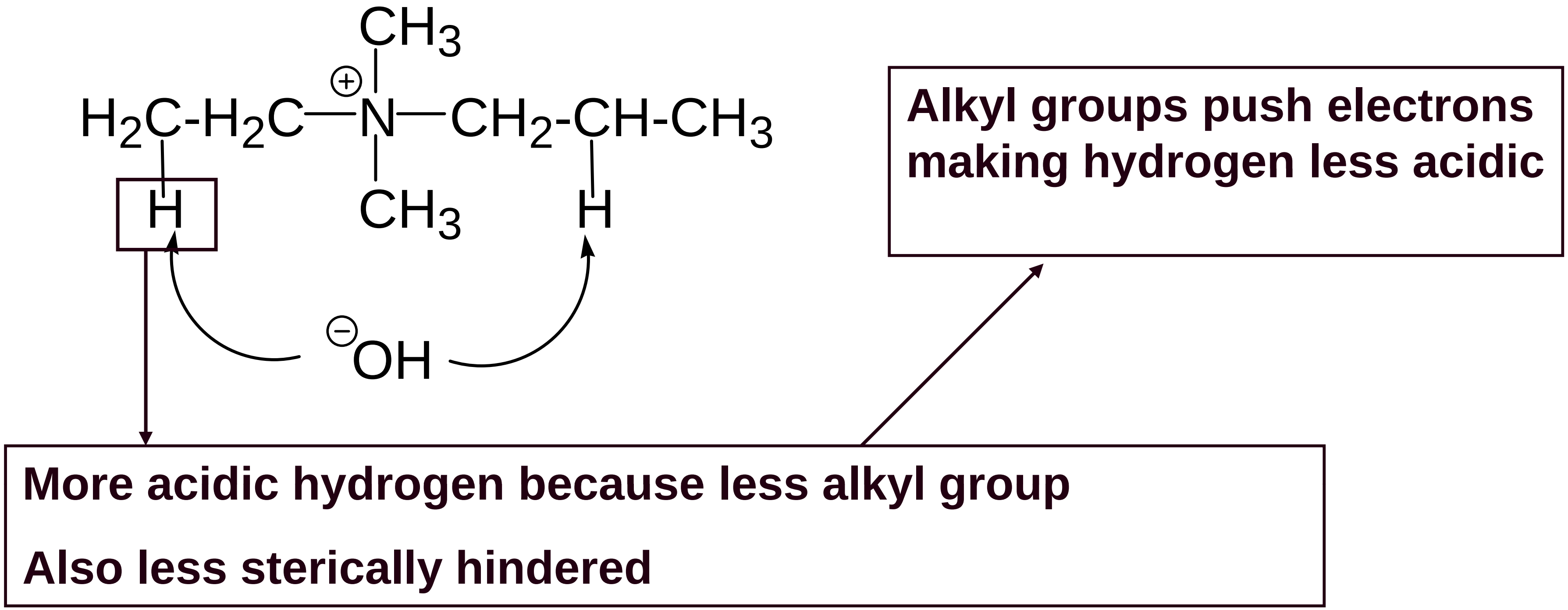
⇒ An exception to Zaitsev’s rule

ex) Elimination of 4° ammonium salt accords to Hoffmann’s rule; Less substituted product dominates.

Why Hoffmann elimination for the compounds with quaternary nitrogen?

⇒ The reaction involves a poor leaving group (trialkyl amine group) and a strong base. Then the breaking of C-H bond is more advanced in the Hoffmann elimination than in the E2.

⇒ Then acidity of the hydrogen determines the reactivity



Alkyl groups push electrons making hydrogen less acidic

More acidic hydrogen because less alkyl group

Also less sterically hindered

Steric effect of base

Hydrogens on less substituted C are more accessible especially for large base

Zaitsev’s rule

Hoffmann’s rule

Conjugation effect

⇒ Conjugated product more stable

9.5 Unimolecular elimination; E1

Reaction mechanisms of S_N1 and E1

1. RDS; the formation of carbocation

2. The transition state of the substitution is lower in energy; substitution is the major rxn

Investigating mechanisms

E1 or S_N1

Leaving groups do not affect the product ratio

⇒ first step is RDS

9.6 Regiochemistry and Stereochemistry of E1

1. **Stereochemistry of the leaving group and the hydrogen is not important in E1; need not coplanar**
2. **Product distribution follows** Zaitsev's rule

E2 using strong base, 2-menthene was 100 % (see p321)

9.7 Competition between Elimination & Substitution

S_N2 and E2

1. S_N2/E2 is favored over S_N1/E1 with good base or nucleophile; the strength of base ↑, the rate of both S_N2 and E2 ↑

   ex) using ethoxide, S_N2/E2 not S_N1/E1

2. Steric hindrance favors E2 over S_N2

   ex)

3. Among the bases, stronger base (Nu:) favors E2 over S_N2, and weaker base favors S_N2.

⇒ In elimination, hydrogen is easily abstracted by strong base

4. High temperature favors E2 over S_N2

⇒ $\Delta G = \Delta H - T\Delta S$; Temp ↑, ΔS *contribution* ↑.

S_N1 and E1

⇒ RDS of S_N1 and E1 involves the formation of carbocation.

1. S_N1 and E1 most commonly occur with tertiary (best) or secondary substrate in polar solvent and in absence of strong base (or nucleophile).
2. Difficult to control the ratio of E1 and S_N1

Competition on different substrate

Primary substrates; RCH_2L (1°)

⇒ Compounds with low steric hindrance

1. S_N2 with any nucleophile
2. E2 with bulky strong base which is not a good nucleophile such as *tert*-butoxide
3. S_N1 or E1 reaction does not occur because primary carbocation is very very unstable, while allylic and benzylic substrate S_N1 or E1 is possible.

Secondary substrates; R_2CHL (2°)

⇒ Four mechanisms are all possible

1. S_N2 with nucleophile that are not too basic
2. E2 with strong base such HO^- or RO^-
3. S_N1 (and/or E1) with weak nucleophile such as ROH; such reaction is called as solvolysis (alcohols are also solvents.

Tertiary substrates; R_3CL (3°)

1. S_N2 is impossible because they are too hindered
2. S_N1 (E1) with polar solvents and in the absence of strong base
3. E2 with strong base such as HO^- or RO^-

Nucleophilicity vs Basicity

- Nucleophilicity: ability to cause substitution rxn

$$H_2O < ROH < Cl^- < Br^- < OH^- < OR^- < I^- < CN^-$$

$$\longrightarrow$$

- Basicity: ability to accept proton in acid-base rxn

$$I^- < Br^- < Cl^- < ROH < H_2O < CN^- < OH^- < OR^-$$

$$\longrightarrow$$