# **Organic Reaction Mechanisms-IV** (Elimination reactions of Alkyl halides & Alcohols)

### Introduction :

In an elimination reaction two atoms or groups (YZ) are removed from the substrate and generally resulting into formation of  $\pi$  bond.



 $\alpha$ -elimination : When two groups are lost from the same carbon atom to give a carbone (or nitrene). This is also called 1,1 elimination.



**β-elimination :** When two groups are lost from adjacent atoms so that a new  $\pi$  bond is formed. This is also called 1,2 elimination.



 $\gamma$ -elimination : It is also called 1,3 elimination, In this a three membered ring is formed.



Type of  $\beta$ -elimination reactions :

(I) E1 (II) E2 (III) E1cB

# Section (A) : Unimolecular elimination (E1) reaction of alkyl halides

In  $\beta$  elimination reaction two atoms or groups (YZ) are removed from the substrate and generally resulting into formation of  $\pi$  bond.



Proton and leaving group depart in two different steps in E1 reaction.

Mechanism of E1 :

Step-1 : Formation of the carbocation (r.d.s.)

$$\begin{array}{c} | & | & | & | \\ -C - C - & -C - C \oplus + \stackrel{\circ}{X} \\ | & | & \rangle \\ H & X^2 \rightleftharpoons H \end{array}$$

Step-2 : Weak base  $(\stackrel{\Theta}{B})$  abstracts a proton (fast step)

### Kinetics :

- Rate ∝ [Alkylhalide]
- It is an unimolecular and first order reaction.
- Reaction intermediate is carbocation, so rearrangment is possible

### **Energetics:**

The free energy diagram for the E1 reaction is similar to that for the S<sub>N</sub>1 reaction.



### **Reactivity Order :**

Similar to  $S_N 1$  becuase carbocation intermediate is formed in the rds step.

In case of alkyl halide  $S_N 1$  product is generally more than E1 product at room temperature, but elimination product may be more at higher temperature.

### Saytzeff alkene is the major product in E1 reaction.





# Section (B) : Bimolecular elimination (E2) reaction of alkyl halides

- This is a single step concerted process.
- No carbocation intermediate is formed, hence there is no rearrangement but a transition state is achieved.

### Mechanism :

• Orientation of eliminated proton and leaving group should be antiperiplanar to each other because in anti conformation the transition state is more stable due to minimum electronic repulsion.



• E2 reaction is stereospecific anti elimination.

#### Kinetics :

- Rate  $\propto$  [R X] [Base]
- It is a second order reaction because rate of reaction depends upon both conc. of substrate as well as base.
- More favourable substrate is tertiary alkyl halide because it will give more stable alkene according to saytzeff rule.

#### Saytzeff rule (Positional orientation of elimination) :

In most E1 and E2 eliminations where there are two or more possible elimination products, the product with highly substituted double bond will predominate. This is called the saytzeff or zaitsev rule. **Energetics :** 

P.E. diagram for dehydrohalogenation of 2-bromo-2-methylbutane.



Progress of reaction



Example:

### **Reactivity order:**

• Reactivity of E2 reaction  $\propto$  Stability of formed alkene.

• R–I > R–Br > R–Cl > R–F

### Major product :

E2 reaction product depends upon size of base which decides major or minor products.



#### **Stereospecific E2 reactions**

The E2 reaction is stereospecific because it normally goes through an anti periplanar transition state.



### Some important terms :

(a) **Regioselective reaction :** Those reaction in which more than one structural isomeric products are possible, said to be regioselective reaction.

CH<sub>3</sub>-CH<sub>2</sub>-CH-CH<sub>3</sub>

 $\operatorname{Br}^{I}$   $\operatorname{CH}_{3}$   $\operatorname{CH}_{3}$   $\operatorname{CH}_{3}$   $\operatorname{CH}_{3}$   $\operatorname{CH}_{2}$   $\operatorname{CH$ 

**Examples :** E1, E2, electrophilic addition of alkene/alkyne, electrophilic substitution of substituted benzene.

(b) Regiospecific reaction : Those reaction in which only one structural isomer product is formed out of the possible products, said to be regiospecific reaction.

Examples : E1 & E2

(c) Stereoselective : Those reactions in which mixture of two stereoisomeric products are formed with one major product.

Examples : S<sub>N</sub>1, S<sub>N</sub>2 and E2

(d) Stereospecific reaction : Those reactions in which two stereoisomeric reactants give two different stereoisomeric products, are called as stereospecific reactions.

Examples : S<sub>N</sub>2 and E2

### Note : All stereospecific reactions are stereo selective generally.

### Comparison between E1 and E2 reactions :

	E1	E2
Base	Weak base	Strong base required
Substrate	3° > 2° > 1°	3° > 2° > 1°
Leaving group	Better one required	Better one required
Kinetics	K [R – X], first order	K [R – X] [Base] second order
Orientation (major product)	Saytzeff alkene	Depends upon size of base

### Dehalogenation of dihalo-alkane :

It is removal of X<sub>2</sub> from dihalo alkane.

**Reagent**: NaI in acetone or zinc in presence of acetic acid or ethanol or  $Zn/\Delta$ 

### Dihalides are of two types :

### (a) Vicinal dihalide or Alkylene dihalides



Mech. With NaI in acetone :

**Remark :** Both are E2 elimination and stereospecific antielimination.

### (b) Gem-dihalide or Alkylidene halides

### **Ex**: CH<sub>3</sub>—CHCl<sub>2</sub> (ethylidene chloride)

When gem dihalide is heated with Zinc dust at 300°C then higher alkenes are formed, which is based on free radical mechanism.



### Double dehydrohalogenation of gem and vicinal dihalides :

(a) Vicinal dihalides :



NaNH<sub>2</sub> is more basic than alc. KOH.

### (b) Gem dihalides :

 $\begin{array}{c} \mathsf{R} - \overset{\mathsf{I}}{\mathsf{C}} = \mathsf{C} - \mathsf{R} \quad \underbrace{\overset{\mathsf{NaNH}_2, \Delta}{-\mathsf{HBr}}} \mathsf{R} - \mathsf{C} \equiv \mathsf{C} - \mathsf{R} \\ \mathsf{Br} \\ \overset{\mathsf{heat}}{\mathsf{alc.KOH}} \end{array} \\ \xrightarrow{\mathsf{No} \text{ reaction}} \mathsf{No} \text{ reaction} \end{array}$ R - C - C - Rн Br + alc. KOH -HBr

**Note:** At higher temperature ( $\approx 200^{\circ}$ C) elimination of vinylhalide is possible with alc.KOH also. Mechanism :



### Step 2 :

# Section (C) : Elimination reaction of alcohols (a) E1 reaction of alcohols

Dehydration requires an acidic catalyst to protonate the hydroxyl group of the alcohol and convert it to a good leaving group. Loss of water, followed by loss of proton, gives an alkene. An equilibrium is established between reactants and products.

For E1 mechanism reagents are : (i) conc.H<sub>3</sub>PO<sub>4</sub>,  $\Delta$ (ii) conc.  $H_2SO_4$ ,  $\Delta$ 

$$\begin{array}{c|c} -C - C - \\ -C - C - \\ H OH \underline{acid} - C = C - + H_2O \end{array}$$

(Rearrangement may occur)

Mechanism :







### **Remarks :**

- In first step (an acid-base reaction) a proton is rapidly transferred from the acid to one of the unshared electon pairs of the alcohol.
- In second step the carbon oxygen bond breaks and water as the leaving group removed from the molecule.
- Finally, in third step the carbocation transfers a proton to a molecule of water. The result is the formation of a hydronium ion and an alkene.

### Reactivity of ROH towards elimination : 3° > 2° > 1° Alcohols :



• With Al<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub> Saytzeff alkene is major product but with ThO<sub>2</sub> and WO<sub>3</sub> Hofmann alkene is major product.



# Section (D) : Miscellaneous elimination reactions (a) E1cB Reaction :

It is two step reaction.

### Mechanism :

In first step base takes proton from adjacent carbon atom of leaving group bearing carbon and generate carbanion intermediate.



In second step there is loss of leaving group by carbanion to get alkene :



Ex.

### Remarks :

- $\beta$ -hydrogen atom should be more acidic. Which is possible only if carbon atom having  $\beta$ -hydrogen atom linked with electron withdrawing group (–M, –I group).
- E1cB reaction is prefer if leaving group is more electronegative (because it also increases acidity of β-hydrogen atom).
- Experimentally it is found that Ist step i.e. formation of carbanion intermediate is fast step and second step i.e. removal of leaving group is slow step thus r.d.s. in E1cB is second step.

# (b) Hofmann elimination in quaternary ammonium salts :

In Hofmann degradation of quaternary ammonium salts, Hofmann alkene [less substitued alkene] is formed as major product

$$CH_2 - CH_-CH_3$$

$$H_2 - CH_2 - CH_3$$

$$CH_3 - CH_2 - CH_3$$

$$H_2 - CH_2 - CH_3$$

$$CH_2 - CH_2 - CH_3$$

$$CH_2 - CH_2 - CH_3$$

$$CH_2 - CH_2 - CH_3 - CH_2 - CH_3 - H_2O$$

Ex.1







Note : For unsymmetrical diol that –OH group will be replaced first which will generate stable carbocation as below.





### (d) Ei Reaction of ester (Pyrolysis of Esters)

Thermal cleavage of an ester involves formations of a six membered ring in the transition state leading to the elimination of an acid leaving behind an alkene.



As a direct consequence of cyclic transition state, both the leaving groups namely proton and carboxylate ion are eliminated from the cis position.

It is an example of **syn elimination**.

It is a regioselctive reaction, generally Hofmann alkene is the major product.

 $H_2O/H^+$ 

(e) Acid hydrolysis followed by heating of  $\beta$ -Ketoester :



β-ketoester



 $-CH_3 + CO_2$ 

**Note** : It is β-ketoacid which decarboxylate more readily as it proceeds via six membered cyclic transition-state.



### (f) Cope-reaction:

Tertiaryamine oxides on heating form alkene, if there is  $\beta$ -hydrogen atom in it.



**Note :** In the above reaction it is necessary that the four halogen atoms must be attached at vicinal carbons. If they are attached at the two ends then the product cyclo alkene is obtained.

# (i) Reaction of trihaloalkanes :

Acetylene can be prepared from CHCl<sub>3</sub> with Ag dust.

$$H - C \boxed{Cl_3 + 6Ag + Cl_3} - CH \xrightarrow{-6AgCl} H - C \equiv C - H$$
  
2CH<sub>3</sub>--Cl<sub>3</sub> + 6Ag CH<sub>3</sub>--CC--CH<sub>3</sub> + 6Agl

# Section (E) : Chloroform/ CCl₄/Freon/Ethylene glycol/Glycerol

(a) Reactions of chloroform :



- Purity of chloroform (presence of phosgene) can be tested before use as anaesthetic by treating with aqueous solution of AgNO<sub>3</sub> because the presence of COCl<sub>2</sub> may cause cardiac failure.
- Chloroform is stored in dark colour bottle containing small amount of ethyl alcohol. (It converts phosgene into diethylcarbonate).

# (b) Carbon tetrachloride (pyrene) :

### Preparations & reactions :



- CCl<sub>4</sub> is stable to heat and its vapours do not catch fire thus it is used as fire extinguisher.
- CCl<sub>4</sub> used as medicine for elimination of hook worms.

# (c) Freons (Polychlorofluoro alkane)

(i)  $CCl_4 + HF \xrightarrow{SbCl_4F} CCl_3F + HCl$ 

(Freon-11)

(ii)  $CCI_3F + HF \longrightarrow CCI_2F_2 + HCI$ (Freon-12)

(iii)  $C_2CI_6 + 2HF \longrightarrow C_2CI_4F_2 + 2HCI$ (Freon-112)

### Nomenclature of Freons :

Freon is expressed as : **Freon-cba** Where, a – [Number of

 $\begin{array}{cccc} \text{Where,} & a - & [\text{Number of F-atoms}] \\ b - & [1 + \text{Number of H-atoms}] \\ c - & [\text{Number of C-atoms} -1] \\ \text{Example}: C_2Cl_4F_2 \text{ is expressed as Freon-112} \\ a = 2 \ ; \ b = 1 + 0 \ ; \qquad c = 2 - 1 \\ \end{array}$ 

cba = 112

• Freon is odourless, non-corrosive, non-toxic gas. It can easily be liquefied hence widely used as refrigerant.

# (d) Ethylene glycol :

• It is colourless, hygroscopic, toxic, sweet and viscous liquid. It has boiling point 197° due to intramolecular H-bonding.

• It is used as antifreezer for car radiator and also used as de-icing fluid for aeroplane wings

• It is one of the monomer of terylene or dacron and glyptal.

### Preparation and reactions of glycol :



Dioxane (industrial solv

# (e) Glycerol :

It is trihydroxy alcohols having one 2° alcohol and two1° alcohol groups. It is colourless odourless, viscous hygroscopic, non-toxic liquid with boiling point 290° C.

### **Preparation :**

(i) Alkali hydrolysis of fats and oils which are ester of fattyacid. This reaction is saponification and irreversible in nature.



(ii) From elements

$$C + H \xrightarrow{\text{electric arc}} H - C = C - H \xrightarrow{\text{NaNH}/\text{NH}_3(\ell)} H - C = C - \text{Na} \xrightarrow{\text{CH}_3\text{I}} H - C = C - C\text{H}_3$$

$$\downarrow H_3^{++}/H_2\text{SO}_4$$

$$C\text{H}_3 - C\text{H} = O \xrightarrow{(i) C\text{H}_3 - MgBr} C\text{H}_3 - C\text{H} - C\text{H}_3 \xrightarrow{\text{Cu}/\Lambda} C\text{H}_3 - C\text{H}_3$$

$$C\text{H}_3 - C\text{H} = O \xrightarrow{(i) H_3^0} C\text{H}_3 - C\text{H} - C\text{H}_3 \xrightarrow{\text{Cu}/\Lambda} C\text{H}_3 - C\text{H}_3$$

$$C\text{H}_2 - C\text{H} = C\text{H}_2 \xleftarrow{\text{Cl}_2/500^{\circ}\text{C}} C\text{H}_3 - C\text{H} = C\text{H}_2 \xleftarrow{\text{Al}_2\text{O}_2/\Lambda}$$

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$$C\text{H}_2 - C\text{H} - C\text{H}_2 \xrightarrow{\text{Cl}_2/\Lambda}$$

$$C\text{H}_2 - C\text{H} - C\text{H}_2 \xrightarrow{\text{Cl}_2/\Lambda}$$

$$C\text{H}_2 - C\text{H} - C\text{H}_2 \xrightarrow{\text{Cl}_2/\Lambda}$$

$$C\text{H}_2 -$$

### **Reactions of glycerol :**



- Dunston Test is a test for glycerol in which pink colour (obtained on addition of a drop of phenolphthalein to nearly 5 ml of borax solution) disappears with additional few drops of glycerol. The pink colour further appears on heating and reappear on cooling.
- Nitroglycerine is a poisonous yellow oily liquid. It becomes safer explosive when absorbed over **kieselguhr** (It is a kind of mineral).
- A mixture of gun cotton (cellulose nitrate) and nitroglycerine is blasting material.
- Cordite is a mixture of gun powder, vaseline and nitroglycerine, also it is said to be smokeless explosive.