Synthesis of Alkenes

(Via Elimination reactions)

1 - Dehydrohalogenation of alkyl halides: (by the action of alcoholic KOH).

The ease of Dehydrohalogenation of alkyl halides is in the order: 3° > 2° > 1° > CH3X (Why?)

The rate of elimination depends on the halogen, reactivity of alkyl halides increasing with decreasing strength of the C-X bond.

ZAITSEV'S RULE:

In Dehydrohalogenation (-HX) of alkyl halides or dehydration (- H_2O) of alcohol the hydrogen atom will be eliminated easily from the carbon atom which is attached to the lower number of hydrogen atoms.

CH₃CH₂CHCH₃
$$\xrightarrow{\text{KOH}}$$
 CH₃CH=CHCH₃ + CH₃CH=CH₂

Cl
2-butene
2-chlorobutane

20%

Mechanism:

The Dehydrohalogenation of alkyl halides is an elimination reaction that called 1,2-elimination and take place either by \mathbf{E}_1 (unimolecular) or \mathbf{E}_2 (bimolecular) mechanism depending on the structure of alkyl halide.

a) E1 (unimolecular) mechanism:

Where C-X bond is broken first and a carbonium ion as intermediate will be formed.

The stability of the carbonium ion:

3° carbonium ion > 2° carbonium ion > 1° carbonium ion > CH₃+

This can be interrelated in the term of hyberconjugation and the inductive effect, where the alkyl groups have (+I)

[electrons-donor] which increase the electron cloud and so decrease the +ve charge on Carbonium ion [decreasing the charge on ion \implies more stable].

a) E2 (bimolecular) mechanism:

Where the reaction take place in one step by forming transition state. This transition state is more stable; when the free energy of activation for the reaction is lower and the product is formed faster [that has the more highly substituted double bond].

2-Dehydration of Alcohol (R-OH) (by Al_2O_3 at $300^{\circ}C$ or heat with Conc. H_2SO_4).

The ease of dehydration: $3^{\circ} > 2^{\circ} > 1^{\circ} > CH_3OH$

$$-\stackrel{|}{C} - \stackrel{|}{C} - \stackrel{|}{C} - \stackrel{|}{\Delta} - \stackrel{|}{C} - \stackrel{|$$

1°Alcohol
$$CH_3CH_2CH_2OH$$
n-propanol Al_2O_3
 $CH_3CH=CH_2 + H_2O$
Propene

2°Alcohol CH_3CH_2
 CH_3
 $CH_3CH=CH_2 + H_2O$
 $CH_3CH=CH_3 + H_2O$
 $CH_3CH=CHCH_3 + H_3C$
 $CH_3CH=CHC$

3°Alcohol
$$H_3C$$
— CH_3 $Conc.H_2SO_4$ CH_3 $CH_$

The Mechanism for Dehydration of Alcohol:

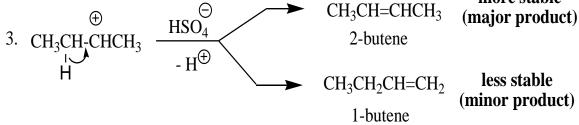
1º Alcohol

1.
$$H_2SO_4$$
 $\xrightarrow{\oplus}$ H + HSO_4

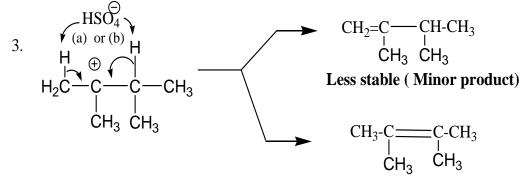
2. CH_3CH_2 - O - H + H $\xrightarrow{\oplus}$ CH_3CH_2 - O - H $\xrightarrow{\oplus}$ CH_3CH_2 + H_2O

3. H - CH_2 - CH_2 $\xrightarrow{\oplus}$ CH_2 = CH_2

2º Alcohol



Rearrangement during Dehydration of Secondary Alcohols:



More stable (Major product)

3- Dehalogenation of Vicinal Dihalides (by Zn dust. Or NaI).

Avic-dihalide

A gem-dihalide

4- Hydrogenation of Alkynes: (by H2 / Pd).

H₃C-C
$$\equiv$$
C-CH₃ $\xrightarrow{\text{H}_2}$ H₃C-C $=$ C-CH₃ $\xrightarrow{\text{H}_2}$ CH₃CH₂CH₂CH₃

2-Butyne Butane

Syn Addition of hydrogen:

Synthesis of cis-Alkenes (or Z-Alkene).

(In the presence of P-2 catalyst)

Ni(OCCH₃)₂
$$\xrightarrow{\text{NaBH}_4}$$
 Ni₂B

P-2

H₃C-CH₂-C \equiv C-CH₂-CH₃ $\xrightarrow{\text{H}_2/\text{Ni}_2\text{B}}$ (Syn addition)

3-Hexyne

(Z)-3-Hexene (cis-3-Hexene)

Anti-addition of hydrogen:

Synthesis of trans-Alkenes (or E-Alkene).

(In the presence of sodium or lithium metal in ammonia or ethylamine)

H₃C-CH₂-C
$$\equiv$$
C-CH₂-CH₃ $\xrightarrow{1) \text{LiC}_2\text{H}_5\text{NH}_2}$

$$\xrightarrow{-78 \text{ °C}}$$
2) NH4Cl
(Anti addition)
(Anti addition)
(E)-3-Hexene (trans-3-Hexene)

5- Kolb's Synthesis:

Electrolysis of the potassium salt of saturated dicarboxylic acids.

$$\begin{array}{c} \text{CH}_2\text{COOK} \\ \text{CH}_2\text{COOK} \end{array} \xrightarrow{\text{electrolysis}} \qquad \qquad \\ \text{H}_2\text{C} = \text{CH}_2 + 2\text{CO}_2 + 2\text{KOH} + \text{H}_2 \\ \text{Pot.succinate} \end{array}$$