Alkenes and their preparation





Alkenes

- Alkenes are unsaturated hydrocarbons containing carbon-carbon double bond (C=C)in their molecules.
- They have the general formula C_nH_{2n} . The simplest member of alkene family is ethene, C_2H_4 . The alkenes are also called olefins (Greek olefiant meaning oil forming) because the larger member of the series (such as ethylene, propylene, etc react with chlorine to form oily products.

Preparation of Alkenes



From Alkynes

Alkynes can be reduced to alkenes using palladium charcoal (palladised charcoal) catalyst partially deactivated with poison like sulphur compounds or quioline. Partially deactivated palladised charcoal is known as Lindlar's catalyst. Alkynes can also be reduced to alkenes with sodium in liquid ammonia which is called Birch reduction.

For eg: $CH_3-C\equiv C-CH_3 \xrightarrow{Pd-C, H_2} CH_3CH=CHCH_3$ But-2-yne But-2-ene $CH_3-C\equiv CH+H_2 \longrightarrow CH_3-CH=CH_2$ Propone Propene $CH\equiv CH+H2 \xrightarrow{Pd/C} CH2=CH2$ Ethyne Ethene

From Alkyl Halides

Alkene can be prepared from alkyl halides(usually bromides or iodides) by treating with alcoholic potash(potassium hydroxide dissolved in ethanol). This reaction removes a molecule of HX and therefore, the reaction is called dehydrohalogenation. In this reaction, the hydrogen atom is eliminated from β carbon atom (carbon atom next to the carbon to which halogen is attached). Therefore, the reaction is also called β -

elimination real H H $H = \frac{H}{C} + \frac{H}{C} + \frac{H}{C} + \frac{H}{\Delta} + \frac{H}{\Delta} + \frac{H}{C} = C$ $H = \frac{H}{H} + \frac{H}{X} + \frac{H}{\Delta} + \frac{H}{H} +$

Nature of halogen atom and the alkyl group determine rate of the reaction. It is observed that for halogens, the rate is: Iodine>Bromine>Chlorine while for alkyl group it is Tertiary> Secondary>Primary.

From Vicinal Dihalides

Dihalogen derivatives of alkanes in which two halogens atoms are attached to adjacent carbon atoms (called vicinal dihalogen derivatives) are converted to alkenes by heating with zinc dust in ethyl alcohol. For eg:

 $CH_{3}CHBr-CH_{2}Br+Zn \longrightarrow CH_{3}CH=CH_{2}+ZnBr$

From Alcohols

Alkenes are prepared from alcohols by heating with protonic acids such as sulphuric acid at about 443K. This reaction is called dehydration of alcohols CH₃CH₂OH H2SO4 or H3PO4 CH₂=CH₂+H₂O

This reaction is also an example of β -elimination reaction because –OH group takes out one hydrogen atom from the β - ci H H

Chemical Properties of alkenes

Addition of dihydrogen

Alkenes add up on molecule of dihydrogen gas in the presence of finally divided nickle, palladium or platinum to form alkanes.

Addition of Halogens

Halogens like bromine or chlorine add up to alkene to form vicinal dihalides. The reddish orange colour of bromine solution in carbon tetrachloride is discharged when bromine adds up to an unsaturation site. This reaction is used as a test for unsaturation. Addition of halogen to alkene is an example of electrophilic addition reaction.

Addition of Hydrogen Halides

Hydrogen halides (HCI, HBr, HI) add up to alkenes to form alkyl halides. The order of reactivity of the hydrogen halides is HI>HBr>HCI. Like addition of halogens to alkenes, addition of hydrogen halides is also an example of electrophilic addition reaction

Effect of Addition of halogens

- (i) $CH_2 = CH_2 + Br Br \xrightarrow{CCl_4} CH_2 CH_2$ Ethene | | |Br Br 1,2 Dibromoethane (13.38)
- (11) $CH_3 CH = CH_2 + CI CI \longrightarrow CH_3 CH CH_2$ $I \qquad I \qquad I$ $CI \qquad CI$ $I \qquad I$ $I \qquad$
 - (13.39)

Addition of HBr to symmetrical alkenes

• Addition reactions of HBr to symmetrical alkenes take place by electrophilic addition reactions where similar groups are attached to the double bond.

CH₂=CH₂ +H−Br
$$\longrightarrow$$
CH₃-CH₂ -Br
CH₃ -CH=CH-CH₃ +HBr \rightarrow CH₃ -CH₂ -CH₂CH₃
 $|$
Br

Addition of HBr to symmetrical alkenes

 When HBr is added to propene then it yields 1-bromopropane and 2-bromopropane



The markovnikov's rule

Markovnikov, a Russian chemist made a generalisation in 1869. these generalisation led Markovnikov to frame a rule call Markovnikov rule. The rule stated that:

"During the addition across unsymmetrical multiple bond, the negative part of the addendum (attacking molecule)joins with the carbon atom which carries smaller number of hydrogen atoms while the positive part goes to the carbon atom with more hydrogen atom."



Vladimir markovnikov

Mechanism of markovnikov's rule



The secondary carbocation is more stable than the primary carbocation , therefore, the former predominates because it is formed at a faster rate.

 The secondary carbocation is attacked by Br⁻ion to form the product as follows :

$$H_3C - CH - CH_3 + Br \rightarrow CH_3 - CH - CH_3$$

Br
2 - Bromopropane

Kharash's effect or peroxide effect or anti markovnikov's rule

- In the presence of peroxide, addition of HBr to unsymmetrical alkenes like propene takes place contrary to the Markovnikov rule. This happens only with HBr but not with HCI and HI.
- This reaction is known as
 peroxide or Kharash effect or



MORRIS SELIG

REACTION OF ANTI MARKOVNIKOV'S RULE

The reaction for anti markovnikov's rule is as follows:-



MECHANISM FOR ANTIMARKOVNIKOV'S RULE

• Step 1:-



• Step 2 :-





• Step 4 :-

- The last step shows that 2-bromopropane is obtained as the minor product.
- The peroxide effect is not observed in addition of HCl and HI. This may be due to the fact that the H–Cl bond being stronger than H–Br bond is not cleaved by the free radical, whereas the H–I bond is weaker and iodine free radicals combine to form iodine molecules instead of adding to the double bond.

Addition of sulphuric acid

 Cold concentrated sulphuric acid adds to alkenes in accordance with Markovnikov rule to form alkyl hydrogen sulphate by the electroph

$$CH_2 = CH_2 + H - O - S - O - H$$

 \downarrow
 $CH_3 - CH_2 - O SO_2 - OH or C_2H_5HSO_4$
Ethyl hydrogen sulphate

Addition of water

 In the presence of a few drops of concentrated sulphuric acid alkenes react with water to form alcohols, in accordance with the Markovnikov

$$\begin{array}{ccc} & & & & & & & \\ \mathrm{CH}_{3}-\mathrm{C}=\mathrm{CH}_{2}+\mathrm{H}_{2}\mathrm{O} & \xrightarrow{\mathrm{H}^{+}} & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ \mathrm{CH}_{3} & & & & & & \\ & & & & & & & \\ \mathrm{2-Methylpropene} & & & & & & & \\ \end{array}$$

rule.

Oxidation

Alkenes react with cold dilute aqueous or alkaline potassium permanganate solution to form 1,2-diols called glycols. The glycols contain two –OH groups on adjacent carbon atoms This reaction of addition of two hydroxyl groups to each end of double bond is called hydroxylation of the double bond.

ozonolysis

Alkenes are oxidised with ozone to form ozonides which are unstable compounds. These are reduced with zinc and water forming aldehydes and ketones. The reaction is called ozonolysis.

$$\begin{array}{cccc} CH_{3}CH=CH_{2}+O_{3}\longrightarrow CH_{3}-CH & CH_{2} \\ Propene & & & & & \\ O & - & O \\ Propene & ozonide \\ & & & & \\ & & & \\ & & & \\ & & & \\ CH_{3}CHO & + & HCHO \\ Ethanal & & Methana \end{array}$$

Polymerisation

Polymerisation is a process in which a large number of simple (same or different) molecules combine to form a bigger molecule of higher molecular mass. The small molecule are called monomers while the bigger molecule are called macromolecules or polymers.

$$n(CH_2=CH_2) \xrightarrow{High temp./pressure} (CH_2=CH_2) \xrightarrow{High temp./pressure} (CH_2=CH_2) \xrightarrow{High temp./pressure} (CH_2=CH_2)$$