Alkenes.

These are the acyclic hydrocarbon in which carbon-carbon contain double bond. These are also known as olefins, because lower alkene react with halogens to form oily substances. General formula is $C_n H_{2n}$.

Ex: Ethene C_2H_4 , Propene C_3H_6 , Butene C_4H_8

(1) Structure

- (i) Hybridization of unsaturated 'C' atom is sp^2
- (ii) Geometry of unsaturated 'c' atom is trigonal planer
- (iii) C H Bond length is 1.34 Å
- (iv) C = C Bond energy is 143.1 K cal/mol
- (v) C H Bond length is 1.10 Å
- (vi) C = C Bond energy is 108 Kcal/mol



(2) Isomerism

- (i) Chain Isomerism: $CH_3 CH_2 CH = CH_2$ and $(CH_3)_2 C = CH_2$
- (Ii) Position Isomerism: $CH_2 = CH CH_2 CH_3$ and $CH_3 CH = CH CH_3$
- (iii) **Functional Isomerism:** [Ring chain] $CH_3 CH_2 CH = CH_2$ and $CH_2 CH_2$ | |

$$CH_2 - CH_2$$

Cyclo butene

(iv) GeometricalIsomerism: $CH_3 - C - H$ and $CH_3 - C - H$ || || || $CH_3 - C - H$ $H - C - CH_3$ cis-2-butene Trans-2-butene(v) Optical Isomerism: $H - C - CH_3$ | CH_2CH_3

Note: Cumulated polythene having even no. of double bonds. Which has = C

a system at the both end b

can exhibit optical isomerism but cannot exhibit geometrical isomerism.

Cumulated polythene having odd no. of double bonds which have = C system at both end can b

exhibit geometrical isomerism but cannot exhibit optical isomerism.

(3) **Preparation methods**

(i) From Alkynes: $R - C \equiv C - H + H_2 \xrightarrow{\text{Lindlar's Catalyst}}_{Pd. BaSO_4} R - \stackrel{H}{C} = \stackrel{C}{C} - H$

Note: Poison's catalyst such as $BaSO_4$, $CaCO_3$ are used to stop the reaction after the formation of alkene.

(ii) From mono halides:
$$R - \stackrel{H}{C} - \stackrel{H}{C} - H + Alc. KOH \xrightarrow{-HX} R - C = \stackrel{H}{C} - H$$

 $H X \qquad H$

Note: If we use alc. *NaOH* in place of *KOH* then trans product is formed in majority because of its stability. According to saytzeff rule.

(iii) From dihalides

(a) From Gem dihalides

Note: If we take two different types of gemdihalides then we get three different types of alkenes. Above reaction is used in the formation of symmetrical alkenes only.

(b) From vicinal dihalides:
$$R - \stackrel{H}{\underset{|}{C-C-C-H}} H + Zn dust \xrightarrow{\Delta} R - \stackrel{H}{\underset{|}{C-H}} R - \stackrel{H}{\underset{|}{C-H}} H = \stackrel{H}{\underset{|}{Z-H}} H = \stackrel{H}{\underset{|}{Z-H}} R - \stackrel{H}{\underset{|}{Z-H}} R - \stackrel{H}{\underset{|}{Z-H}} R = \stackrel{H}{\underset{|}{Z-H}} R - \stackrel{H}{\underset{|}{Z-H}} R = \stackrel{H}{\underset{|}{Z-H}} R - \stackrel{H}{\underset{|}{Z-H}} R - \stackrel{H}{\underset{|}{Z-H}} R = \stackrel{H}{\underset{|}{Z-H}} R - \stackrel{H}{\underset{|}{Z-H}} R = \stackrel{H}{\underset{|}{Z-H}} R - \stackrel{H}{\underset{|}{Z$$

Note: Alkene is not formed from 1, 3 dihalides. Cycloalkanes are formed by dehalogenation of it.

$$\begin{array}{c} CH_2 - CH_2 - CH_2 \xrightarrow{Zn \text{ dust}} & CH_2 \\ | & | \\ X & X & H_2C \xrightarrow{CH_2} \end{array}$$

(iv) By action of *NaI* on vicdihalide:
$$C - C \xrightarrow[acetone]{NaI} C \xrightarrow{C} C \xrightarrow{C} C$$
 unstable

(v) From alcohols [Laboratory method]: $CH_3CH_2OH \xrightarrow{H_2SO_4 \text{ or } H_3PO_4}{443 \text{ K}} CH_2 = CH_2 + H_2O$ Ethyl alcohol

(vi) Kolbe's reaction: | + 2 H_2O $\xrightarrow{Electrolysis}$ || + 2 CO_2 + H_2 + 2KOH CH_2COOK CH_2 Potassium succinate CH_2 Ethene

(vii) From esters [Pyrolysis of ester]: $CH_3 - CO - O$ $H_{Glass wool 450^\circ}$ $| \cdots | \cdots | \lim_{liq.N_2} H_2 - CH_2 \xrightarrow{CH_3 - COOH} H_{CH_2 - CH_2}$



(ix) Action of copper alkyl on vinyl chloride: $H_2C = CHCl \xrightarrow{CuR_2} H_2C = CHR$ Vinyl chloride

(x) By Grignard reagents: $Mg \xrightarrow{R} + X \xrightarrow{CH} = CH_2 \xrightarrow{MgX_2 + R - CH} = CH_2$

$$O \\ || \\ (Ph)_3 P = CH - R + CH - R \longrightarrow (Ph)_3 P = O + R - CH = CH - R$$

(xii) **From β** bromo ether [Boord synthesis]

$$Br \quad O - C_2 H_5$$

$$| \qquad | \qquad R - CH - CH$$

$$| \qquad | \qquad C_4 H_g OH$$

$$R - CH = CH - R' + Zn < O - C_2 H_5$$

$$O - C_2 H_5$$

(4) Physical Properties

(i) Alkenes are colorless and odorless.

(ii) These are insoluble in water and soluble in organic solvents.

(iii) Physical state

 $C_1 - C_4 \longrightarrow Gas$ $C_5 - C_{16} \longrightarrow Liquid$ $> C_{16} \longrightarrow Solid wax$

(iv) B.P. and M.P. decreases with increasing branches in alkene.

(v) The melting points of cis isomers are lower than trans isomers because cis isomer is less symmetrical than trans. Thus trans packs more tightly in the crystal lattice and hence has a higher melting point.

(vi) The boiling points of cis isomers are higher than trans isomers because cis-alkenes has greater polarity (Dipole moment) than trans one.

(vii) These are lighter than water.

(viii) **Dipole moment:** Alkenes are weakly polar. The, π -electrons of the double bond. Can be easily polarized. Therefore, their dipole moments are higher than those of alkanes.

The symmetrical trans alkenes are non-polar and hence have zero dipole moments in these alkene the dipole moment of individual bonds are equal in opposite direction. Therefore these get cancelled resulting zero dipole moment for the molecule.



Thus symmetrical and unsymmetrical cis alkene are polar and hence have finite dipole moments



(5) Chemical properties

(i) **Francis experiment:** According to Francis electrophile first attacks on olefinic bond.

(ii) Reaction with hydrogen:
$$R - C = C - R + H_2 - \frac{Ni}{H} + \frac{R}{H} + \frac{CCl_4}{H} + CH_2 - CH_2$$

$$(ii) Reaction with hydrogen: R - C = C - R + H_2 - \frac{Ni}{H} + \frac{R}{H} + \frac{CCl_4}{H} + \frac{CCl_4}{$$

(iii) **Reduction of alkene via hydroboration:** Alkene can be converted into alkane by protolysis $RCH = CH_2 \xrightarrow{H-BH_2} (R - CH_2 - CH_2)_3 B \xrightarrow{H^+/H_2O} R - CH_2 - CH_3$

Hydroboration: Alkene give addition reaction with diborane which called hydroboration. In this reaction formed trialkylborane, which is very important and used for synthesis of different organic compound



The overall result of the above reaction appears to be antimarkownikoff's addition of water to a double bond.

(iv) By treatment with AgNO₃ + NaOH: This reaction gives coupling

$$6CH_{3} - CH_{2} -$$

(v) **Birch reduction:**This reaction is believed to proceed via anionic free radical mechanism.

$$R - CH = CH_2 \xrightarrow[+e^-]{Na} R - CH - CH_2 \xrightarrow[+e^-]{Et-O-H} R - CH - CH_3 \xrightarrow[+e^-]{Na} R - CH_2 - CH_3 \xrightarrow[+e^-]{Na} R - CH_3 \xrightarrow[+e^-]{Na} R$$

(vi) Halogenation

$$CH_{3}CH = CH_{2} + Cl_{2} \xrightarrow{500^{\circ}C} ClCH_{2} - CH = CH_{2} + HCl$$
Allylchloride
or 3-Chloro -1-propene

Note: If NBS [N-bromo succinimide] is a reagent used for the specific purpose of brominating alkenes at the allylic position.



In presence of polar medium alkene form vicinal dihalide with halogen.



Reactivity of halogen is $F_2 > Cl_2 > Br_2 > I_2$

(vii) Reaction with HX [Hydrohalogenation]



According to markownikoff's rule and kharasch effect.

$$CH_3 - CH = CH_2 + HBr \longrightarrow CH_3 - CH_3 - CH_2 - H$$
 Markownikoff rule
Br H

(Based on F.R.M.) $CH_3 - CH = CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3 - \begin{array}{c}H & H & H & H \\ | & | & | & | & | \\ -C - C - H + CH_3 & -C - C - H \\ | & | & | & | \\ Br & H & H & Br \\ (\text{minor}) & (\text{major}) \end{array}$

(viii) Reaction with hypohalous acids: $CH_2 = CH_2 + H \stackrel{-}{O} \stackrel{+}{Cl} \longrightarrow CH_2OH.CH_2Cl_{Ethylene}$

Note: In case of unsymmetrical alkenes markownikoff rule is followed.

(ix) Reaction with sulphuric acid: $CH_2 = CH_2 + H^+ HSO_4 \longrightarrow CH_3 CH_2 HSO_4$ Ethylene $CH_3 CH_2 HSO_4 \longrightarrow CH_2 = CH_2 + H_2 SO_4$

Note: This reaction is used in the separation of alkene from a gaseous mixture of alkanes and alkenes.

(x) Reaction with nitrosyl chloride



Note: If hydrogen is attached to the carbon atom of product, the product changes to more stable oxime.



(Blue color)

(xi) Oxidation: With alkaline KMnO₄ [Bayer's reagent]: This reaction is used as a test of unsaturation.

$$H H H$$

$$R - C = C - H + [O] + H - OH \xrightarrow{Alk KMnO_4} R - C - C - H$$

$$H H H$$

$$H O OH$$

$$H H H$$

$$H O OH$$

$$H O OH$$

$$H H H$$

$$H O OH$$

(xii) Hydroxylation



Note: If per benzoic acid or peroxy acetic acid is used then oxirane are formed.

(xiii) Combustion: $C_n H_{2n} + \frac{3n}{2}O_2 \longrightarrow nCO_2 + nH_2O$

They burn with luminous flame and form explosive mixture with air or oxygen. (xiv) Ozonolysis



Application of Ozonolysis: This process is quite useful to locate the position of double bond in an alkene molecule. The double bond is obtained by joining the carbon atoms. of the two carbonyl compounds.

Ex.

(xv) **Oxy – mercuration demercuration**: With mercuric acetate (in THF), followed by reduction with $NaBH_4 / NaOH$ is also an example of hydration of alkene according to markownikoff's rule.

Ex.



(xvi) Epoxidation



(xvii) Hydroboration

 $3R - CH = CH_2 + BH_3 \longrightarrow (R - CH_2 - CH_2)_3 B \xrightarrow{H_2O_2/OH^-} R - CH_2 - CH_2 - OH + B(OH)_3$ Trialkyl bora ne

(Anti markownikoff's rule)

(xviii) Hydroformylation:
$$R - CH = CH_2 + CO + H_2 \xrightarrow{CoH(CO)_4} R - \begin{array}{c} H & H \\ | & | \\ C - C - C - H \\ | & | \\ H & C = O \\ | \\ H \end{array}$$

Note: If $CO + H_2O$ is taken then respective acid is formed.

$$R - CH = CH_{2} + CO + H_{2}O \xrightarrow{CoH(CO)_{4}} R - CH_{2} - CH_{2}$$
$$|$$
$$COOH$$

(xix) Addition of formaldehyde

$$H_{2}C = O + \overset{\oplus}{H} \longrightarrow [H_{2}C = \overset{\oplus}{O}H \longleftrightarrow H_{2}\overset{\oplus}{C} - OH]_{H_{2}}\overset{R-CH=CH_{2}}{\longrightarrow} R - \overset{\oplus}{C}H - CH_{2} - CH_{2} - OH \xrightarrow{HOH}_{-H^{+}}$$

$$R - CH \longrightarrow CH_{2} \\ O \longrightarrow O \\ CH_{2} \\ Cyclic acetal } \xleftarrow{HCHO/\overset{\oplus}{H}} R - CH - CH_{2} - CH_{2} \\ OH \\ OH \\ OH \\ I,3-diol$$

(xx) **Polymerization**

$$\begin{array}{c|c} H & H \\ | & | \\ C = C & \xrightarrow{Trace O_2 + Catalyst} \\ | & | \\ H & H \end{array} \end{array} \left[\begin{array}{c|c} H & H & H \\ | & | & | \\ - C - C - C - C \\ | & | & | \\ H & H & H \end{array} \right]_{n}$$

Note: If in polymerization zeigler- natta catalyst $[(R)_3 Al + TiCl_4]$ is used then polymerization is known as zeigler-natta polymerization.

(xxi) **Isomerization**: $CH_3 - CH_2 - CH_2 - CH = CH_2$ The mechanism proceeds via carbocation. (xxii) **Addition of HNO_3**: $CH_2 = CH_2 + HO - NO_2 \longrightarrow CH_2OH.CH_2NO_2$ Ethene (xxiii) **Addition of Acetyl chloride**: $CH_2 = CH_2 + CH_3COCl \longrightarrow CH_2ClCH_2COCH_3$ Ethene

(6) **Uses**

(i) For the manufacture of polythene – a plastic material; (ii) For artificial ripening of fruits; (iii) As a general anesthetic; (iv) As a starting material for a large number of compounds such as glycol, ethyl halides, ethyl alcohol, ethylene oxide, etc.; (v) For making poisonous mustard gas (War gas); (vi) For making ethylene-oxygen flame.