13. ORGANIC CHEMISTRY

III) ALKENES

SYNOPSIS

- Alkenes are unsaturated hydrocarbons. These contain a C =C. They contain two hydrogens less than corresponding alkanes.
- Double bonded carbon undergoes hybridisation.
- These are otherwise known as OLEFINS
- General formula of alkenes is C_nH_{2n}
- Bond angle is 120^o
- The C=C bond length in alkenes is which is less than the C-C single bond distance of in alkanes.
- In alkenes the double bond contains one sigma bond and a -bond. As Pi(π) electrons are easily available for reagents, they undergo electro philic addition reactions.
- Due to the presence of a double bond alkenes are more reactive than alkanes.
- The unsaturation (or) pi bond between carbon and carbon is identified by following reagents
  a) Br_2 water (reddish brown colour)
  b) Alkaline $KMnO_4$ (Pink colour of Baeyer's reagent)
- Unsaturated hydrocarbons decolourise above reagents.
- Alkenes exhibit chain, position, functional (ring chain isomerism) and cis-trans isomerism.

Nomenclature: Rules

a) The IUPAC name is derived from the IUPAC name of alkane by replacing ending "ane" by "ene"
   alongwith the position of double bonds.

b) The suffix used for alkene is - "ene"
   eg :- Alkane - ane+ene= Alkene
   CH_3-CH=CH-CH_3 But - 2 - ene.

c) In case of two double (or) three double bonds, the ending 'ene' of alkanes is suitably replaced by diene (or) triene.
   CH_3-CH_2-CH=C=CH_2, CH_2=CH-CH=CH_2
   Penta - 1, 2-diene Buta -1, 3-diene.

d) Residual part left after the removal of one H-atom from alkene is known as alkenyl group.
   According to nomenclature, these groups are named by replacing terminal 'e' of alkene by "yl"

Group	**Common**	**IUPAC**
CH_2=CH-	vinyl	ethenyl
CH_2=CH-CH_2-	allyl	prop-2-enyl

e) The longest continuous chain should include both the carbon atoms of the double bond.

f) The chain is numbered from the end that gives the lower number to the first carbon atom of the double bond.

eg:- CH_3-CH = CH_2,CH_3-CH_2-CH = CH_2

Propene But-1-ene

CH_3-CH = CH-CH_3

But-2-ene,

The compounds containing two double bonds are named as dienes.

CH_2=CH-CH=CH_2, Buta - 1,3-diene

Structure:

a) C = C contains one strong bond and one weak π bond

b) π bond contains loosely bonded electrons. These electrons attract electrophiles.

c) Alkenes are more reactive than alkanes due to loosely bonded electrons

	C = C	= C-H
	sp^2 - sp^2	sp^2 - s
Bond length	1.34 A^0	1.108A^0
Bond energy	143.1 k.cal/mol,	98.69 k.cal/mol.

Geometrical isomerism

a) Alkenes exihibit geometrical isomerism

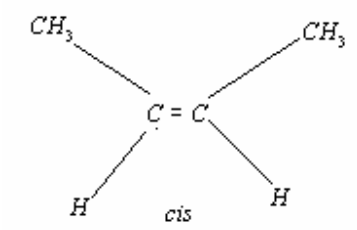
b) Alkenes with formula baC = Cab (or) daC = Cab exihibit geometrical isomerism

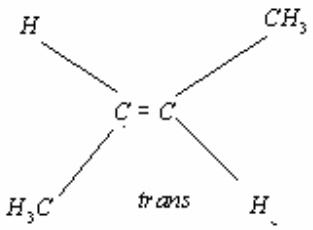
c) Trans isomers are more symmetrical than cis isomers

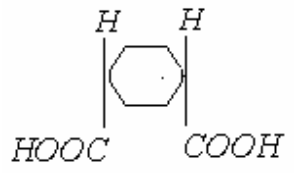
d) A cis - isomer - has lower melting point than trans isomer

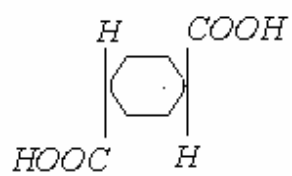
e) Physical properties like density, dipolemoment, refractive index and heat of combustion are more for cis isomer

f) Trans isomer is more stable than cis-isomer



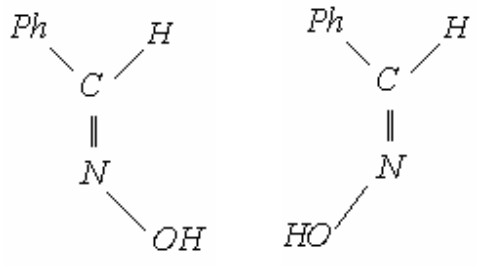






cis 1, 4-cyclohexane dicarboxylic acid Trans-1, 4 cyclohexanedicarboxylic acid

c)



Syn benzaldoxime Anti benzaldoxime

As geometrical isomers are not mirror images, they are called diastereomers and they have different properties.

PREPARATIONS

1. *Dehydration of ethyl alcohol*

$$CH_3-CH_2OH \xrightarrow[(or)\,Al_2O_3/350^0C]{con.H_2SO_4/170^0C} \underset{\text{Ethylene}}{CH_2=CH_2} + H_2O$$

2. *Dehydrohalogenation of alkyl halide*

$(R-X)\ X = Cl, Br, I$

$$CH_3-CH_2-Br \xrightarrow[\Delta]{Alc\,KOH} CH_2=CH_2 + HBr$$

Ethyl bromide

In this reaction H atom is eliminated from $\beta-$carbon atom

$\therefore$ it is known as $\beta-$ elimination reaction

3. *Dehalogenation*

$$\underset{\begin{matrix}|\\Br\end{matrix}}{\overset{\begin{matrix}|\\Br\end{matrix}}{CH_2-CH_2}} + Zn \xrightarrow[\Delta]{Alcohol} \underset{\text{Ethylene}}{CH_2=CH_2} + ZnBr_2$$

1, 2 dibromo ethane

4. *Controlled hydrogenation of acetylene*

(Lindlar's catalyst)

$$H-C\equiv C-H + H_2 \xrightarrow[Quinoline]{Pd-BaSO_4} \underset{\text{Ethylene}}{CH_2=CH_2}$$

5. *Industrial method*

$$CH_3-CH_3 \xrightarrow{\Delta} CH_2=CH_2 + H_2$$

(ethane obtained from natural gas)

PHYSICAL PROPERTIES

a) Ethylene is a colourless gas, and dissolves in non polar solvents like benzene, ether.

b) BP of ethylene - 150° C ,MP is -169°C

c) First three alkenes are gases, next fourteen alkenes are liquids and higher alkenes are solids

d) B.P. increases with the molecular weight

e) For every CH_2 group B.P. increases by 20-30K

f) Boilingpointsurfacearea

$$\propto \frac{1}{\text{No.of branched chains}}$$

CHEMICAL PROPERTIES

a) Ethene undergoes addition reactions.

b) In these addition reactions, the bond, which is weaker than the sigma bond, breaks.

c) In addition reaction 'Pi' bond cleavage takes place and as a result two new sigma bonds will be formed in the product.

CHEMICAL PROPERTIES

* ***Hydrogenation***:

$$CH_2 = CH_2 \xrightarrow[Ni/120^0C]{H_2/Pt,Pd\,(or)} CH_3 - CH_3$$

* ***Chlorination*** :

$$CH_2 = CH_2 \xrightarrow{Cl_2/CCl_4} \underset{\substack{| \\ Cl \\ 1,2\,dichloro\,ethane}}{CH_2 - CH_2} \quad \underset{| \\ Cl}{}$$

* ***Bromination***:

$$CH_2 = CH_2 \xrightarrow{Br_2/CCl_4} \underset{\substack{| \\ Br \\ 1,2\,dibromo\,ethane}}{CH_2 - CH_2} \quad \underset{| \\ Br}{}$$

* ***Addition of Hydrogen halide (HX):***

$$CH_2 = CH_2 \xrightarrow{HX} CH_3 - CH_2 - X, \text{ethyl halide}$$

$$(HX = HCl, HBr, HI)$$

Reactivity order HI>HBr>HCl>HF

Markovnikov's rule:- The negative part of the addendum (attacking molecule) attack the carbon atom which contains smaller number of hydrogen atoms.

$$CH_3 - CH = CH_2 + HBr \xrightarrow{H^+} \underset{\substack{2-Bromo\,Propane \\ (major)}}{CH_3 - \overset{\overset{Br}{|}}{CH} - CH_3}$$

$$+ \underset{\substack{1-Bromo\,Propane \\ (minor)}}{CH_3 - CH_2 - CH_2Br}$$

a) The mechanism proceeds through an achiral carbocation intermediate

b) The stability of carbocation is in the order tertiary > secondary > primary carbocation

* ***Anti Markownikoff's rule :-***

In the presence of peroxides during the addition of HBr to an unsymmetrical alkene the Br atom will join to the carbon carrying more hydrogen atoms while H-atom will go to the other carbon atom.

a) It is also known as Kharasch effect (or) Peroxide effect.

b) Anti Markownikoff's addition proceeds through since homolytic cleavage

c) 2^0 free radical is more stable than 1^0, so 1-bromopropane is major product

$$CH_3-CH=CH_2+HBr \xrightarrow{Peroxide} \underset{\substack{1-Bromopropane\\(major)}}{CH_3-CH_2-CH_2Br} + \underset{\substack{2-Bromopropane\\(minor)}}{CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3}$$

d) Only HBr follows peroxide effect, HF, HC*l*, HI do not exihibit peroxide effect even in presence of peroxide.

* **Addition of Hypochlorous Acid**

* $$CH_2=CH_2 \xrightarrow[or\,(Cl_2/H_2O)]{HOCl} \underset{\substack{\displaystyle OH\quad Cl\\ Ethylene\,chloro\\ hydrin}}{\underset{|\quad|}{CH_2-CH_2}}$$

* ***Addition of water***

$$CH_2=CH_2+H_2O \xrightarrow{H_2SO_4} CH_3CH_2OH$$

(ethyle hydrogen sulphate is formed as intermediate product)

$$CH_3-\underset{\displaystyle H}{\underset{|}{C}}=CH_2 \xrightarrow{H_3O^+} CH_3-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}-CH_3$$

* ***Addition of sulphuric acid***

$$CH_2=CH_2+H_2SO_4 \rightarrow \underset{\text{Ethyl hydrogen sulphate}}{CH_3CH_2HSO_4}$$

$$CH_3-CH=CH_2+H_2SO_4 \rightarrow CH_3-\underset{\displaystyle OSO_3H}{\underset{|}{CH}}-CH_3$$

Isopropyl hydrogen sulphate

The addition of cold conc. H_2SO_4 to alkene produces alkyl hydrogen sulphate by electrophilic addition following Markownikoff's rule

* ***Oxidation reaction :-***

a) Oxidation by Baeyer's reagent:-

Alkenes on passing through dilute alkaline 1% cold $KMnO_4$, form dihydroxy compounds (eg. glycols)

$$CH_2=CH_2 \xrightarrow{cold\ dil.\ alk.\ KMnO_4} \underset{\text{Ethylene glycol}}{CH_2OH-CH_2OH}$$

c) With air in the presence of Ag: In the presence of 'Ag' catalyst oxidises ethylene to ethylene oxide (epoxide)

$$CH_2=CH_2+\tfrac{1}{2}O_2 \xrightarrow[200-400^0C]{Ag} \underset{\displaystyle O}{CH_2-CH_2}$$

* ***Ozonolysis:-***

a) It is a test for unsaturation in molecules

b) The formation of Ozonide and its decomposition to give carbonyl compounds is known as ozonolysis

c) The total number of carbon atoms in two carbonyl compounds, is equal to total number of carbon atoms in alkene

d) Ozonolysis is used to detect the position and nature of unsaturation in a molecule

e) Symmetrical alkene gives rise to two molecules of same carbonyl compound

$$CH_2=CH_2+O_3 \rightarrow \underset{\text{Ozonide}}{C_2H_4(O_3)} \xrightarrow{Zn+H_2O} \underset{\text{Formaldehyde}}{2HCHO}+H_2O_2$$

$$\underset{\text{2-Methyl-1-Butene}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2} \xrightarrow[Zn+H_2O]{O_3} \underset{\text{Acetone}}{CH_3COCH_3}+HCHO$$

$$\underset{\text{2-Methyl-2-Butene}}{CH_3-CH=\overset{\overset{CH_3}{|}}{C}-CH_3} \xrightarrow[Zn+H_2O]{O_3} CH_3CHO+CH_3COCH_3$$

Polymerization reactions:- Alkenes form the basis of many important polymers.

a) Formation of polythene;

$$nCH_2=CH_2 \xrightarrow[O_2,\,200^0C]{1500-2000\,atm} \underset{\text{Polythene}}{\left[-CH_2-CH_2-\right]_n}$$

b) Several substituted ethylene compounds are used in polymerisation.

Ex: $CH_2=CH-X$

$CH_2=CH-Cl$ Vinyl chloride

$CH_2=CH-CN$ Vinyl cyanide

$CH_2=CH-COO-CH_3$ Vinyl methylester

* ***Combustion reaction :-***

a) The combustion of alkenes is also exothermic, used for welding purposes in oxy-ethylene welding.

$CH_2=CH_2+3O_2 \rightarrow 2CO_2+2H_2O;\ \Delta H=-Ve$

* **With S_2Cl_2:-**

$$2CH_2=CH_2+S_2Cl_2 \rightarrow \underset{\textit{Mustard gas}}{\left(ClCH_2CH_2\right)_2 S}$$

It is poisonous gas. It is used as war gas

USES:

a) Ethylene is used in the manufacture of ethyl alcohol, polythene etc.

b) It is used in the preparation of ethylene glycol which is used as an antifreeze

c) Ethylene is used in the preparation of mustard gas.