

Al-Mustaqbal University College

Department of Medical Laboratory Techniques

Subject :- General Chemistry (1) Part (B) lecture (3)

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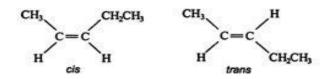
ALKENES AND ALKÝNE

Molecular and Structural Formulas

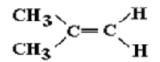
The alkenes are hydrocarbons that composed of carbon and hydrogen atoms with at least one double bond in the carbon chain. Alkenes with only one double bond have the general formula of C $_n$ H $_{2n}$. where n equals any integer greater than one. The simplest alkene, ethene, has two carbon atoms and a molecular formula of C $_2$ H $_4$. The structural formula for ethene is CH $_2$ =CH $_2$. In longer alkene chains, the additional carbon atoms are attached to each other by single covalent bonds. Each carbon atom is also attached to sufficient hydrogen atoms to produce a total of four single covalent bonds about itself. In chains with four or more carbon atoms, the double bond can be located in different positions, leading to the formation of **structural isomers.** For example, the alkene of molecular formula C $_4$ H $_8$ has three isomers.

$CH_3-CH_2-CH=CH_2$ $CH_3-CH=CH-CH_3$ and $(CH_3)_2 C=CH_2$.

In addition to structural isomers, alkenes also form geometric isomers (cistrans isomers). Because rotation around a multiple bond is impossible without breaking it, groups attached to the double bonded carbon atoms always remain in the same relative positions. The *cis-trans* isomers differ from each other by the position of attached groups relative to double bond, one having similar groups on the same side is called *cis* and one having similar groups on opposite side called *trans*. An example of geometric isomerism is 2-pentene



The prefix *cis*- means on the same side and the prefix *trans* means across or on the opposite side .. The two groups attached to each carbon must be different for *cis*- *trans* isomerism to occur. If either carbon of the double bond of an alkene is bonded to identical atoms or groups, *cis*-*trance* isomers cannot exist. For example the following alkene has not optical isomerism.



IUPAC System of naming alkenes:-

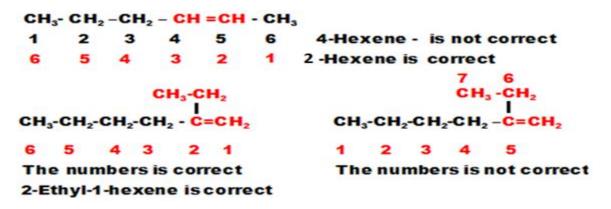
Alkenes are normally named using the IUPAC system. The rules for alkenes are similar to those used for alkanes. <u>The following rules summarize alkenes</u> <u>naming</u>.

1-The ene suffix (ending) indicates an alkene or cycloalkene.

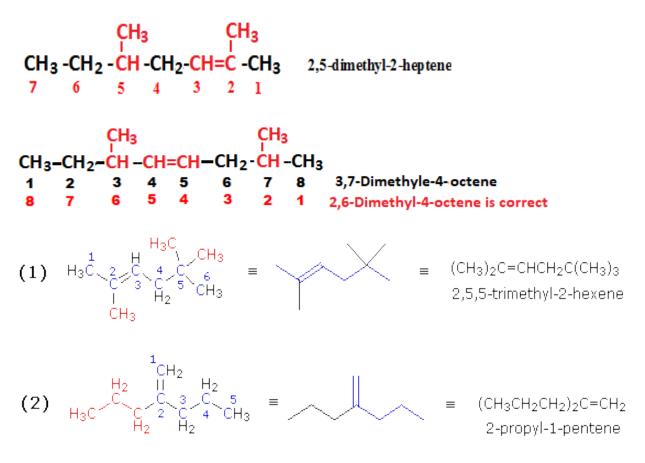
2- Number the carbon atoms of the longest continuous chain, starting at the end closest to the double bond

$\begin{array}{rrrr} \text{CH}_3\text{-}\text{CH}_2\text{-}\text{CH}_2\text{-}\text{CH}_2\text{-}\text{CH}_2\text{-}\text{CH}_2\text{-}\text{CH}_2\text{-}\text{CH}_2\text{-}\text{CH}_3\text{-}2\text{-}\text{pentene} \\ 5 & 4 & 3 & 2 & 1 & 1 & 2 & 3 & 4 & 5 \end{array}$

3- The position of double bond (C=C) is indicated by placing the lower of the pair of numbers assigned to the double bonded carbon atoms in the front of the name of alkene. The longest chain chosen for the root name must include both carbon atoms of the double bond



4. The location and name of any substituent molecule or group is indicated. For example, If the double bond is in the center of the chain, the nearest substituent rule is used to determine the end where numbering starts.



Preparation of Alkenes :-

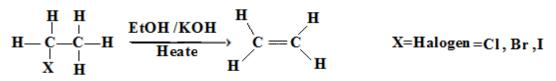
1-Preparation of Alkenes from Alkynes

Alkynes undergo partial reduction with a particular quantity of dihydrogen to produce alkenes. The reaction takes place in the presence of palladised charcoal that has been deactivated with poisonous compounds such as quinolone or sulfur compounds, also known as Lindlar's catalyst. The reaction leads to the formation of compounds having cis-geometric conformation. However, if the same alkynes reduction takes placed with sodium present in liquid ammonia, the resultant product will be trans alkenes

$$\begin{array}{cccc} R-C \equiv C-R'+H_2 & \xrightarrow{Pd/C} & R-CH=CH-R' \\ CH_3C \equiv CCH_2CH_3+H_2 & \xrightarrow{Pd/C} & CH_3CH=CHCH_2CH_3 \\ CH_3-CH_2-C \equiv CCH_2CH_3+H_2 & \xrightarrow{Pd/C} & CH_3-CH_2-CH=CHCH_2CH_3 \end{array}$$

2-Preparation of Alkenes from Alkyl Halides :-

R-X or Alkyl Halides undergo heating with alcoholic potash to form alkenes. Dissolving potassium hydroxide in an alcohol such as ethanol leads to the formation of alcoholic potash. In this reaction, the heating of alkyl halides with alcoholic potash will remove one molecule from halogen acid leading to the formation of alkenes. Thus, it is a β -elimination reaction example because removal of hydrogen atom takes place from the β carbon atom.



The rate of reaction is dependent on the alkyl group and nature of halogen atom. The order, in this case, is iodine > bromine > chlorine. The rate of reaction according to the alkyl group is tertiary > secondary > primary.

$CH_3 - CH_2 - CH_2 - CH_2 - Br$, $CH_3 - CH_2 - CH_2 - CH_3$, $CH_3 - CH_3 -$

3- Preparation of Alkenes from Vicinal Dihalides :-

Vicinal halides are compounds containing two halogen atoms present on two adjacent carbon atoms. Vicinal dihalides undergo treatment zinc metal to form an alkene. The treatment of vicinal dihalides with zinc metal will help in removal of a molecule from ZnX_2 thereby resulting in the formation of the alkene. The reaction is an example dehalogenation.

 $\begin{array}{ccc} CH_2Br\text{-}CH_2Br+Zn & \longrightarrow & CH_2=CH_2+ZnBr_2\\ CH_3CHBr\text{-}CH_2Br+Zn & \longrightarrow & CH_3CH=CH_2+ZnBr_2 \end{array}$

4- Dehydration from alcohol :-

The reaction is an example of acidic dehydration of alcohols because the reaction results in the elimination of a water molecule in the presence of an acid, in this case, sulphuric acid. Furthermore, the reaction is also an example of β -elimination reaction because the functional group of alcohol (-OH) eliminates extracts one hydrogen atom from β -carbon atom.

$$H \stackrel{H}{\underset{OH}{\overset{I}{\xrightarrow{}}}} H \stackrel{H}{\underset{H}{\overset{Onc.H_2SO_4}{\xrightarrow{}}}} \stackrel{H}{\underset{Heate}{\xrightarrow{}}} C = C \stackrel{H}{\underset{H}{\overset{H}{\xrightarrow{}}}} H_2O$$

Reaction of alkenes:-

Alkenes are relatively stable compounds, but are more reactive than alkanes due to the presence of a carbon–carbon double bond. The majority of the reactions of alkenes involve the rupture of this double bond, forming new single bonds.

1-Hydrogenation:-

Hydrogenation of alkenes produces the corresponding alkanes. The reaction is carried out under pressure at a temperature of 200 °C in the presence of a metallic catalyst Common industrial catalysts are based on Pt, Ni or Pd. The simplest example of this reaction is the catalytic hydrogenation of ethylene (ethane) to yield ethane:

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

2-Hydration :-

Hydration, the addition of water across the double bond of alkenes, yields alcohol. The reaction is catalyzed by strong acids such as sulfuric acid. This reaction is carried out on an industrial scale to make ethanol.

$$\mathbf{CH}_2 = \mathbf{CH}_2 + \mathbf{H}_2\mathbf{O} \xrightarrow{\mathbf{H}_2\mathbf{SO}_4} \mathbf{CH}_3 - \mathbf{CH}_2\mathbf{OH}$$

1- 3- Halogenation:-

In halogenation, the addition of elemental Br_2 or Cl_2 to alkenes yields vicinal dibromo- and dichloroalkanes (1,2-dihalides), respectively.

$CH_{3}CH = CH_{2} + Br_{2} \longrightarrow CH_{3}-CHBr-CH_{2}Br$ $CH_{2} = CH_{2} + Cl_{2} \longrightarrow ClCH_{2}-CH_{2}Cl.$ 4- Hydrohalogenation:-

Hydrohalogenation is the addition of hydrohalic such as HCl or HI to alkenes to yield the corresponding alkanhalides.

$\mathbf{CH}_{3}\text{-}\mathbf{CH} = \mathbf{CH}_{2} + \mathbf{HI} \longrightarrow \mathbf{CH}_{3}\text{-}\mathbf{CHI}\text{-}\mathbf{CH}_{3}$

If the two carbon atoms at the double bond are linked to a different number of hydrogen atoms, the halogen is found preferentially at the carbon with fewer hydrogen substituents (or the acid hydrogen (H) gets attached to the carbon with more hydrogen substituents, and the <u>halide</u> (X) group gets attached to the carbon with more alkyl substituents) (Markovnikov's Rule).

 $\mathbf{CH}_3\mathbf{-}\mathbf{CH} = \mathbf{CH}_2 + \mathbf{HBr} \longrightarrow \mathbf{CH}_3\mathbf{-}\mathbf{CHBr}\mathbf{-}\mathbf{CH}_3$

CH₃

CH₃

$CH_3 - C = CH CH_2CH_3 + HBr \longrightarrow CH_3 CBrCH_2CH_2CH_3$ <u>5- Oxidation:-</u>

Alkenes are oxidized with a large number of oxidizing agents. In the presence of oxygen, alkenes burn with a bright flame to produce CO_2 and water:

$CH_2 = CH_2 + 3O_2 \xrightarrow{KMnO_4} 2CO_2 + 2H_2O$

Alkynes

Alkynes are unsaturated hydrocarbons that have at least one triple covalent bond between two carbon atoms. The general formula of the alkynes with one triple carbon-carbon bond is C_nH_{2n-2} . The simplest alkyne is acetylene (ethyne) H-C=C-H. the alkynes have sp¹ hybridization in the (C=C)so the structure of ethyne (CH=CH) is linear

Classification of alkyne: -

Alkyne are further classified as terminal or non-terminal alkynes according as the triple bond is present at the carbon chain or within the carbon chain. Terminal alkynes $CH_3 C \equiv CH (Propyne) C H_3 CH_2 C \equiv CH (1-Butyne)$ Non-Terminal alkynes $CH_3 C \equiv C CH_3 (2-Butyne) , CH_3 C \equiv CCH_2 CH_3 (2-Pentyne)$

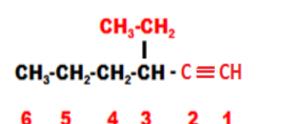
IUPAC Rules for Alkyne Nomenclature: -

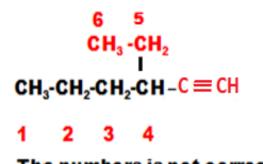
The IUPAC rules for naming alkynes are

1) - The same as those for alkanes except that the ending is -yne.

2) - The yne suffix (ending) indicates an alkyne or cycloalkyne.

3) - The longest chain chosen for the root name must include both carbon atoms of the triple bond.





The numbers is correct 3-Ethyl-1-hexyne is correct

The numbers is not correct

4)- The root chain must be numbered <u>from the end nearest a triple bond</u> <u>carbon atom</u>. If the triple bond is in the center of the chain, the nearest substituent rule is used to determine the end where numbering starts.

5) - The smaller of the two numbers designating the carbon atoms of the triple bond is used as the triple bond locator.

6) - If several multiple bonds are present, each must be assigned a locator number.

The following examples illustrate the rules:

$H-C \equiv C-C_2H_5$	CH₃—C≡=C—C	H₃
1-butyne	2- butyne	
$CH_3 - C \equiv C - C - CH_3$ $I \qquad 2 \qquad 3 \qquad \qquad 5$ $CH_3 = C - C - CH_3$	4,4-dimethy 1-2-pentyne	
CH₃ CH₃		
CH ₃ -ĊHĊH -CH ₂ -C	≡C-CH₃	
7 6 5 4 3 1 2 3 4 5	2 1 5,6-Dimethyl-2-	heptyne is correct
1 2 3 4 5	6 7 2 ,3-Dimethyl-5	heptyne is not correct

Reaction of alkynes :-

Most of the reactions of alkynes are similar to those of alkenes. The same reagents that add to carbon-carbon double bond also add to carbon-carbon triple bond . But it is possible to add two molecules of reagent to each alkyne.

1- Halogenation: -

The addition of X_2 X Halogen =F, Cl , Br and I molecules to alkynes is obtain as CH₃-CH₂- C=C H+Br₂ \longrightarrow CH₃-CH₂-CBr = CHBr

 $CH_3-CH_2- CBr = CHBr + Br_2 \longrightarrow CH_3-CH_2-CBr_2-CHBr_2$ $1-butyne \longrightarrow 1,2-dibromo-1-butene \longrightarrow 1,1,2,2-tetrabromobutane$ 2- Hydrogenation

$$\begin{array}{cccc} \mathbf{CH}_{3}\text{-}\mathbf{C} \equiv \mathbf{CH} & \stackrel{\mathbf{H}_{2}}{\longrightarrow} & \mathbf{CH}_{3}\text{-} & \mathbf{CH} & = \mathbf{CH}_{2} & \stackrel{\mathbf{H}_{2}}{\longrightarrow} & \mathbf{CH}_{3}\text{-} & \mathbf{CH}_{2}\text{-} & \mathbf{CH}_{3} \\ propyne & \stackrel{}{\longrightarrow} & propene & \stackrel{}{\longrightarrow} & propane \end{array}$$

3- Hydrohalogenation :-

The addition of HX is obtain according to Markovnikov Rule the acid <u>hydrogen</u> (H) gets attached to the carbon with more hydrogen substituents, and the <u>halide</u> (X) group gets attached to the carbon with more alkyl substituents) (Markovnikov's Rule)

 $CH_3-C \equiv CH + HCl \rightarrow CH_3-CCl = CH_2 + HCl \rightarrow CH_3-CCl_2-CH_3$

4- Hydration: -

One difference between the acid catalyzed hydration of alkenes and that of alkynes. Alkynes form alcohol (se above). Alkynes form compounds containing C=O bond.

 $\begin{array}{c} OH \\ CH_3\text{-}C \equiv CH + H_2O \end{array} \xrightarrow[]{H_2SO_4} CH_3\text{-} C = CH_2 \end{array} \xrightarrow[]{rearrangement} CH_3\text{-} C + CH_3 \\ \end{array} \xrightarrow[]{OH} O \\ (H_2SO_4) \xrightarrow[]{(H_2SO_4)} CH_3 + CH_3 +$

Methods of preparation of alkyne

1-By the reacton of water on calcium carbide:-

Ethyne (acetylene is prepared in the laboratory as well as commercial scale by the action of water with calcium carbide

 $CaC_2 + 2H_2O \rightarrow HC \equiv CH + Ca(OH)_2$

2- Preparation by dehydrohalogenation of dihaloalkanes:-:-

Alkyne are prepared by dehydrohalogenation of Vicinal dihaloalkanes by heating them with an alcholic solution of potasium hydroxide .The reaction is ocure in two steps and each step involves the loss of a molcule HBr .

 $\begin{aligned} & BrCH_2CHBrCH_2CH_3 + KOH \ (alc.) \rightarrow CH_2 = CBrCH_2CH_3 + KBr + H_2O \\ & CH_2 = CBr \ CH_2CH_3 + KOH \ (alc.) \rightarrow CH \equiv C \ CH_2CH_3 + KBr + H_2O \\ & \underline{3-By \ dehalogenation \ of \ alkyle \ tetrahalides} :- \end{aligned}$

Tetrahaloalkanes when heated with zinc dust in methanol undergo dehalogenation to yield alkynes.

 $CH_3 - CBr_2 - CBr_2 - CH_2 CH_3 + 2 Zn \rightarrow CH_3 - C \equiv C - CH_2 CH_3 + 2 ZnBr_2$

4- By dehalogenation of haloforms :-

Chloroform and iodoform on heating with silver powder undergo dehalogenation to form ethyne

 $HC-Cl_3 + 6 Ag + Cl_3-CH \rightarrow H C \equiv C H + 6 AgCl$ $HC-I_3 + 6 Ag + I_3-CH \rightarrow H C \equiv C H + 6 AgI$ 5- Synthesis of higher alkyene from actylene:-

Actylene is first terated with sodium metal at 475 K ith sodamide in liquid ammonia at 196 K to form so dium acetylide. This upon tretaments with alkylehalides gives higher alkynes,

$$\begin{split} H & - \mathbb{C} \equiv \mathbb{C} - \mathbb{H} + \mathbb{N}a\mathbb{N}H_2 \longrightarrow \mathbb{H} \mathbb{C} \equiv \mathbb{C}^{-1}\mathbb{N}a^+ + \mathbb{N}H_3 \\ H & - \mathbb{C} \equiv \mathbb{C}^{-1}\mathbb{N}a^+ + \mathbb{C}H_3\mathbb{B}r \longrightarrow \mathbb{H} \mathbb{C} \equiv \mathbb{C}\mathbb{C}\mathbb{H}_3 + \mathbb{N}a\mathbb{B}r \\ H & - \mathbb{C} \equiv \mathbb{C}^{-1}\mathbb{N}a^+ + \mathbb{C}H_3\mathbb{C}H_2\mathbb{C}H_2\mathbb{I} \longrightarrow \mathbb{H} \mathbb{C} \equiv \mathbb{C}\mathbb{C}\mathbb{H}_2\mathbb{C}H_2\mathbb{C}H_3 + \mathbb{N}a\mathbb{I} \\ H & - \mathbb{C} \equiv \mathbb{C}^{-1}\mathbb{H} + \mathbb{N}a\mathbb{N}H_2 \longrightarrow \mathbb{H} \mathbb{C} \equiv \mathbb{C}^{-1}\mathbb{N}a^+ + \mathbb{N}H_3 \\ H & - \mathbb{C} \equiv \mathbb{C}^{-1}\mathbb{N}a^+ + \mathbb{C}H_3\mathbb{B}r \longrightarrow \mathbb{H} \mathbb{C} \equiv \mathbb{C}\mathbb{C}\mathbb{H}_3 + \mathbb{N}a\mathbb{B}r \\ H & - \mathbb{C} \equiv \mathbb{C}\mathbb{C}\mathbb{H}_3 + \mathbb{N}a\mathbb{N}H_2 \longrightarrow \mathbb{N}a\mathbb{C} \equiv \mathbb{C}\mathbb{C}\mathbb{H}_3 + \mathbb{N}H_3 \\ \mathbb{N}a & - \mathbb{C} \equiv \mathbb{C}\mathbb{C}\mathbb{H}_3 + \mathbb{C}H_3\mathbb{C}H_2\mathbb{B}r \longrightarrow \mathbb{C}H_3\mathbb{C}H_2\mathbb{C} \equiv \mathbb{C}\mathbb{C}\mathbb{H}_3 + \mathbb{N}a\mathbb{B}r \end{split}$$