

الكلية: كلية الطب العام

القسم او الفرع: فرع الكيمياء والكيمياء الحياتية

المرحلة: الاولى

استاذ المادة: مدمثال رياض ضبع اسم المادة باللغة العربية: الكيمياء العضوية

Organic Chemistry : اسم المادة باللغة الانكليزية

اسم المحاضرة الثالثة باللغة العربية: الالكاينات (الاستلينات)

اسم المحاضرة الثالثة باللغة الانكليزية :Alkyne



Organic chemistry Alkyne

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Alkyne

Hydrocarbons containing at least one triple bond are known as **alkynes**. The triple bond contains one σ bond and two π -bonds. The general formula for alkynes having only one triple bond is C_nH_{2n-2} . The first stable member of alkyne is **ethyne** which is also known as acetylene.

Isomers of alkynes

We have already discussed isomerism in general. We recommend you to read isomerism before reading this section.

The first two members of alkyne family — ethyne and propyne have only one structure but the higher members have more than one structure.

Example: Butyne has the following two structures:

Isomers of Butyne

$$CH \equiv C - CH_2 - CH_3$$
But-1-yne

$$CH_3$$
 — $C \equiv C - CH_3$
But-2-vne

Functional Isomerism

Alkynes are **functional isomers** with dienes.

Example: But-1-yne and buta-1,2-diene; but-1-yne and buta-1,3-diene are functional isomers.

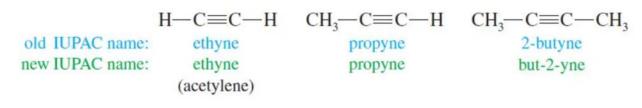
Ring-chain Isomerism

Alkynes are ring-chain isomers with cycloalkenes.

Ring chain isomerism

Propyne Cycloropene $CH_3 - C \equiv CH$

Naming Alkynes by IUPAC Nomenclature Rules



$$CH_3$$
 CH_3
 CH_3
 CH_3
 CH_3
 CH_4
 CH_5
 CH_5
 CH_5
 CH_6
 CH_6
 CH_7
 CH_7

1-penten-4-yne pent-1-en-4-yne

acetylenic hydrogen (no acetylenic hydrogen)
$$H - C = C - CH_2CH_3 \qquad CH_3 - C = C - CH_3$$
but-1-yne, a *terminal* alkyne but-2-yne, an *internal* alkyne

Preparation of Alkynes from Calcium Carbide

Ethyne is prepared by treating calcium carbide (CaC_2) with water.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

Calcium carbide needed for the preparation of ethyne can be prepared using the following steps :

Firstly, quicklime (CaO) is obtained by heating limestone (CaCO₃)

$$CaCO_3$$
 $\xrightarrow{\Delta}$ CaO + CO_2

Quicklime thus obtained is heated with coke to obtain calcium carbide.

$$CaO + 3C \xrightarrow{\Delta} CaC_2 + CO$$

Preparation of Alkynes from Vicinal Dihalides

Vicinal dihalides on heating with alcoholic solution of potassium hydroxide yield alkynes.

Alternatively, sodamide (NaNH₂) in liquid ammonia can be used instead of alcoholic KOH.

Physical State and Odour of Alkynes

The first three members of alkyne family — ethyne, propyne and butyne are colourless gases, the next eight members are liquids and the higher ones are solids. Except for ethyne, which has characteristic smell, all members are odourless.

Boiling Points of Alkynes

The boiling point of alkynes increases with molar mass. Among hydrocarbons, alkynes have higher boiling point than alkenes and alkanes because of the presence of triple bond in alkynes.

Solubility of Alkynes

Alkynes like alkanes and alkenes are non-polar; therefore, they are insoluble in water but readily dissolve in organic solvents such as ether, carbon tetrachloride and benzene.

Density of Alkynes

The density of alkynes increases with mass. All alkynes are lighter than water.

Reactions of Alkynes

Acidity of Alkynes

Alkynes react with strong bases such as sodium and sodamide to form sodium alkynide with the liberation of dihydrogen gas.

$$CH \equiv CH + Na \longrightarrow CH \equiv C^{-}Na^{+} + \frac{1}{2}H_{2}$$

$$Na^{+}C^{-} \equiv C^{-}Na^{+} + \frac{1}{2}H_{2}$$
Disodium ethynide

It may be noted that only the hydrogen atoms attached to the triply bonded carbon atoms are acidic.

$$CH_3 - C \equiv CH + NaNH_2 \longrightarrow CH_3 - C \equiv CNa + NH_3$$
Sodium propynide

Comparison of acidity between alkynes, alkenes and alkanes : Alkanes and alkenes do not undergo above reactions that suggests that alkynes are more acidic than alkanes and alkenes. Among hydrocarbons, acidity follows the order :

Addition of Dihydrogen to Alkynes

When dihydrogen (H_2) is added to alkynes in the presence of catalysts such as Pt, Pd or Ni, alkenes are first formed which react further with another molecule of dihydrogen to form alkanes.

$$CH \equiv CH + H_2 \xrightarrow{Pt/Pd/Ni} CH_2 = CH_2 \xrightarrow{H_1} CH_3 - CH_3$$

$$CH_3 - C \equiv CH + H_2 \xrightarrow{Pt/Pd/Ni} CH_3 - CH = CH_2 \xrightarrow{H_2} CH_3 - CH_2 - CH_3$$

Addition of Halogens to Alkynes

The addition of halogens (chlorine and bromine) to alkynes is as follows:

$$C \equiv CH + Br_2 \longrightarrow CH_3 - C = CH \xrightarrow{Br_2} CH_3 - C - CH$$

$$CH_3 \qquad Br \quad Br \qquad Br_2 \quad Br_2$$

$$1,2-Dibromopropene \qquad 1,1,2,2-Tetrabromopropane$$

Addition of Hydrogen Halides to Alkynes

Hydrogen halides, also known as halogen acids, add to alkyne to form first vinyl halides and then gem dihalides. Addition of halogen acids to unsymmetrical alkynes occur in accordance with markovnikov's rule.

Note: The general formula for vinyl halide is R-CH=CH-X. In gem dihalides, two halogens are attached to the same carbon atom.

Addition of Water to Alkynes

Alkynes resist to react with water. However, in the presence of HgSO₄ (mercury bisulphate) as catalyst, hydration occurs readily.

$$C \equiv CH + H - OH \xrightarrow{Hg^{2+}/H^{+}} CH_{3} - C = CH_{2} \xrightarrow{\text{Tautomerism}} CH_{3} - C - CH_{3}$$

$$CH_{3} \qquad OH \qquad O$$
Propanone

Polymerisation of Alkynes

Like alkenes, alkynes also undergo polymerisation reactions. For example, **linear polymerisation** of ethyne under suitable conditions produce polyacetylene (polyethyne) having formula $-(C_2H_2)_n$. It may be noted that the repeating units of polyethyne are $-(CH=CH-CH=CH)_n$.

Formation of benzene: Ethyne on passing through red hot iron tube at 873 K undergoes cyclic polymerisation leading to the formation of benzene.

