Chem 145
Unsaturated hydrocarbons
Alkynes
Chapter 4
1434-1435
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2nd semester
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By the end of this chapter you should be familiar with:

- Definition for Alkynes.
- Nomenclature of Alkynes.
  - Common System
  - IUPAC Naming
- The Hybridization of Alkynes.
  - Bond Formation in Acetylene
  - The comparative chart of bond length in aliphatic hydrocarbons
- Terminal and Internal Alkynes.
  - Acidity of terminal Alkynes.
- Physical Properties of Alkynes.
- General Methods of Preparation of Alkynes.
- Reactions of Alkynes.
Alkynes

Are **the third class** of **simple hydrocarbons** that contain at least one **triple-bond** between **two carbon atoms**.

The **general chemical formula** of alkynes is

$$C_nH_{2n-2}$$
The simplest members of the **alkynes** series ($\text{C}_2$ and $\text{C}_3$) are usually called by their common Names.

- **Chemical formula:** $\text{C}_2\text{H}_2$ \quad $\text{C}_3\text{H}_4$
- **Chemical structure:**
  - Acetylene: \[ \text{H} \equiv \text{C} \equiv \text{C} \equiv \text{H} \]
  - Allylene: \[ \text{H} \equiv \text{C} \equiv \text{C} \equiv \text{CH}_3 \]
- **Common Name:** Acetylene \quad Allylene
- **IUPAC Name:** Ethyne \quad Propyne
Naming Alkynes:  

a) Common system

- The alkynes are sometimes referred to as the acetylene series.

- The higher members of the series being named as derivatives of acetylene.

\[
\text{H} - \text{C}≡\text{C} - \text{H}
\]

Acetylene or Ethyne

- Methylacetylene
  - propyne

- Ethylacetylene
  - 1-butyne

- Dimethylacetylene
  - 2-butyne

- Ethylmethylacetylene
  - 2-pentyne
b) IUPAC Naming of Alkynes.

The rules for naming alkynes in the IUPAC system are identical with those for alkenes, except for the ending.

1. Find the longest chain that contains the triple bond, then apply with "-yne" as a suffix indicating an alkyne.

2. Number the carbon atoms of the longest continuous chain, starting at the end closest to the triple bond. Thus,

3. The position of the triple bond is indicated by placing the lower of the pair of numbers assigned to the triple-bonded carbon atoms in front of the name of the alkyne. Thus the compound shown in above is 2-pentyne.

4. The location and name of any substituent atom or group is indicated. For example, the compound.

   \[
   \text{H} \\
   \text{CH}_3-\text{C-CH}_2-\text{C}\equiv\text{C-CH}_3 \\
   \text{Cl}
   \]

   is \textbf{5-chloro-2-hexyne}.
Q: If double and triple are exist in the same molecule?

If both a double bond and a triple bond are present, the compound is an *alkenyne*.

**Note that,**
An “e” is dropped from “ene” as reason of being followed by vowel “y” in “yne”.

✔ The numbering starts from the end containing the lower numbered multiple bond.

✔ If the double bond and the triple bond will have the same numbers from either end of the chain, the numbering of the double bonds takes *locational priority*; that is the double bond assigned the lower number.

**Examples**

![Diagram of examples](image)

*Not* Pent-4-en-1-yne

Pent-1-en-4-yne
Problem 4.7 Write the condensed structural formula for

(a) 1-Pentyne

$$\text{CH}_3\text{CH}_2\text{C} \equiv \text{CCH}_2\text{CH}_2\text{CH}_3$$

(b) 3-Hexyne

$$\text{CH}_3\text{CH}_2\text{C} \equiv \text{CCH}_2\text{CH}_2\text{CH}_3$$

(c) 3,3-dimethyl-1-butyne

$$\text{CH}_3\left(\text{CH}_3\right)_2\text{C} \equiv \text{CCH}_2\text{CH}_3$$

(d) 1-Cyclohexyl-2-butyne

$$\text{CH}_2\text{C} \equiv \text{CCH}_3$$
Examples

Give the name of the following

1. 6-Ethyl-3-nonyne

2. Hex-3-en-1-yne

3. Hept-2-en-5-yne
Excercise

Draw the structure of the following

(1) 4-methyl-1-hexen-5-yne

(2) 5-Isopropyloctyne

(3) 1-Cyclobutyl-3-methyl-1-butyne
The Hybridization of Alkynes.

Example

For the simplest alkyne, Ethyne, or Actelyne \( \text{H-} \text{C} \equiv \text{C} \text{-} \text{H} \)

Ground state

Excited state

\( sp \)-hybridized state
The hybridization of a 2s orbital and 2p orbital to form two linear sp-hybridized orbitals with bond angle 180° and two unhybridized p orbitals perpendicularly oriented to each other and to the plan of the hybrid sp orbitals.

The sp orbitals have $\frac{1}{2}$ s character & $\frac{1}{2}$ p character.
a) Bond Formation in Acetylene

The C(triple bond)C bond is composed of one sigma bond and two pi bonds.

Head-to-head overlap between two *sp*-hybrid orbitals to form *σ* bond between 2 carbons of acetylene and side-side overlap of the *p_y* orbitals and *p_z* to form two *π* bonds.
The comparative chart of bond length of alkane, alkene and alkyne is given below:

<table>
<thead>
<tr>
<th>Class</th>
<th>Bond</th>
<th>Hybridized bond orbital</th>
<th>Bond Length</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkane</td>
<td>C–C</td>
<td>(sp^3–sp^3)</td>
<td>1.54 Å</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td></td>
<td>C–H</td>
<td>(sp^3–1s)</td>
<td>1.112 Å</td>
<td></td>
</tr>
<tr>
<td>Alkene</td>
<td>C=CC</td>
<td>(sp^2–sp^2)</td>
<td>1.34 Å</td>
<td>Trigonal planar</td>
</tr>
<tr>
<td></td>
<td>C–H</td>
<td>(sp^2–1s)</td>
<td>1.108 Å</td>
<td></td>
</tr>
<tr>
<td>Alkyne</td>
<td>C≡C</td>
<td>(sp–sp)</td>
<td>1.20 Å</td>
<td>Linear</td>
</tr>
<tr>
<td></td>
<td>C–H</td>
<td>(sp–1s)</td>
<td>1.08 Å</td>
<td></td>
</tr>
</tbody>
</table>
Terminal and Internal Alkynes

1- Terminal alkynes

Have a hydrogen atom bonded to at least one of the \( sp \) hybridized carbons (those involved in the triple bond. An example would be methylacetylene (1-propyne using IUPAC nomenclature).

\[
\text{CH}_3\text{C≡CH}
\]

1-propyne

2- Internal alkynes

Have something other than hydrogen attached to the \( sp \) hybridized carbons, usually another carbon atom, but could be a heteroatom. A good example is 2-pentyne, in which there is a methyl group on one side of the triple bond and an ethyl group on the other side.

\[
\text{CH}_3\text{C≡CCH}_2\text{CH}_3
\]

2-pentyne
The Acidity of terminal Alkynes

The *acidity of a terminal alkyne* means the ability for simple hydrocarbon to be deprotonated.

\[ R-\text{C}≡\text{C}-\text{H} \xrightarrow[\text{B}^+]{\text{B}^-} R-\text{C}≡\text{C}^- + \text{B}^-\text{H} \]

*Acetylene* and all terminal alkynes are acidic in nature i.e. H atom attached on triple bonded C atom behaves as acidic.

The acidic character is due to the fact that in acetylene or triply bonded C atom, an increase in s character (*sp* hybridization) give rise to higher electronegativity to C atom and thus H atom in C—H (i.e. *sp*—1s) bond acquires more polarity to show acidic nature.
Relative acidities of Akanes, Alkenes, and Alkynes:

Electrostatic Potential Maps of Ethane, Ethene, and Ethyne

The increasingly positive polarization of the hydrogen atoms is reflected in their increasingly blue shadings, whereas the carbon atoms become more electron rich (red) along the series.

Ethane  |  Ethene  |  Ethyne
-------|----------|--------
H3C—CH3 | H2C═CH2  | HC≡CH  
Increasing acidity

pK<sub>a</sub>  
62  <  45  <  26

Hybridization of C
sp<sup>3</sup>  <  sp<sup>2</sup>  <  sp

% s Character
25%  <  33%  <  50%
Physical Properties of Alkynes.

The physical properties of alkynes are similar to those of alkenes & alkanes.

• **Physical State:**
  - The first lower member of unbranched alkynes starting from $C_2$ until $C_4$ are gases.
  - The next eight members of alkynes ($C_5$ to $C_8$ carbon atoms) are liquids.
  - and higher members ($C_9>$) are solids under normal conditions of temperature and pressure.

• **Solubility**
Alkynes are insoluble in water, but are fairly soluble in organic solvents such as, benzene $C_6H_6$ & carbon tetrachlorid $CCl_4$.

• **Boiling point**
Their boiling points show the usual increase with increasing carbon number, and the usual effects of chain-branching (lower melting and boiling points due to increased surface area).
✓ Compared to alkanes and alkenes, alkynes have a slightly higher boiling point. 

Why??

This observation is in accord with London force, because the alkyne is linear (180° C) and the alkene has bent shape (120°C). i.e the alkyne is easier to stack next to one another.

<table>
<thead>
<tr>
<th>Name</th>
<th>m.p. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>-88.6 °C</td>
</tr>
<tr>
<td>Ethene</td>
<td>-103.7 °C</td>
</tr>
<tr>
<td>Ethyne</td>
<td>-84.0 °C</td>
</tr>
</tbody>
</table>
General Methods for The Preparation of Alkynes.

(A) Dehydrohalogenation of alkyl halids using a strong base

The General Reaction

By treating vicinal dihalides with strong base (alcoholic KOH), followed by sodium amide (NaNH₂), results in the formation of Alkyne.

A vinylic halide

Very unreactive

Examples

1,2-Dibromobutane

KOH/ alcohol

heat

Br

KOH/ alcohol

heat

Br

1-butyn
(B) Reaction of sodium Acetylide with Primary Alkyl Halides

- The acidic acetylenic hydrogens in acetylene or 1-alkynes can be replaced by certain metals to form **salts** Known as; **metal acetylides**.

- The reaction takes place with sodium; Na in liquid ammonia; NH₃ or sodium amide (NaNH₂) to form sodium acetylides.

- Sodium acetylides react with **primary** alkyl halides to yield higher alkynes.

**The General Reaction**

\[
\begin{align*}
\text{H-C≡C-H} \quad &\xrightarrow{\text{Na, NH₃}} \quad \text{H-C≡C:Na}^+ \quad &\xrightarrow{R'-X} \quad \text{H-C≡C-R'} \\
\text{R-C≡C-H} \quad &\xrightarrow{\text{Na, NH₃}} \quad \text{R-C≡C:Na}^+ \quad &\xrightarrow{R'-X} \quad \text{R-C≡C-R'}
\end{align*}
\]

**Example**

\[
\text{CH₃C≡CH} + \text{Na} \quad \xrightarrow{\text{liq NH₃}} \quad \text{CH₃C≡C:}^- \text{Na}^+ \quad + \quad \text{CH₃CH₂Br}
\]

\[
\text{CH₃C≡CCH₂CH₃} + \text{NaBr}
\]
Reactions of Alkynes.

Alkynes undergo reactions that are similar to those of alkenes, except that they are capable of adding two molecules of a reagent for each triple bond present.

**General Reaction**

\[
\begin{align*}
-C≡C- & \xrightarrow{X-Y} \quad C=C- \quad \xrightarrow{X-Y} \quad C-C-
\end{align*}
\]

Alkene (*Cis* or *Trans*)

Alkane

**Addition Reaction for Alkynes**

1. Addition of Hydrogen
2. Addition of Halogen
3. Addition of Hydrogen halide
4. Addition of water: Hydration
Addition of Hydrogen

1. Complete Addition
2. Controlled Addition
   2.1. Cis-Alkene
   2.2. Trans-Alkene

Case “1”

Alkyne may add hydrogen in the presence of suitable catalyst (pd, Pt, or Ni) similar to the case in alkenes. However, the hydrogenation cannot be stopped at alkene stage, and the final product is always an alkane.

General equation

\[
\begin{align*}
\text{C≡C} & \quad \xrightarrow{2\text{H}_2} \quad \text{C–C} \\
\text{Alkyne} & \quad \text{Alkane}
\end{align*}
\]
Hydrogenation can be stopped at the intermediate alkene stage by the use of modified catalyst such as Lindlar Catalyst. As a result this method affords a stereoselective synthesis of cis alkene from alkyne.

**General equation**

\[
\text{C} \equiv \text{C} + \text{H}_2 \xrightarrow{\text{Lindlar's Catalyst} \quad \text{Pd(BaSO}_4)} \quad \text{C} = \text{C} \\
\text{H} \quad \text{H} \quad \text{R} \quad \text{R}
\]

**Cis-alkene**

When we use Na; Sodium or Li; Lithium metal dissolved in NH\(_3\); liquid ammonia, we obtain trans alkene as product.

**General equation**

\[
\text{C} \equiv \text{C} + \text{H}_2 \xrightarrow{\text{Na or Li} \quad \text{in Liquid NH}_3} \quad \text{C} = \text{C} \\
\text{H} \quad \text{H} \quad \text{R} \quad \text{R}
\]

**Trans-alkene**
Examples

Uncontrolled addition

2H₂ / Pt

n-Butane

Lindlar’s Catalyst
Pd (BaSO₄)

Or NiB

Cis-2-butene

Na or Li
in NH₃

Trans-2-butene

2-Butyne

Controlled Addition
Addition of Halogen

Alkynes react with halogens to yield tetrahaloalkanes. Two molecules of the halogen (chlorine or bromine) add to the triple bond as follows:

The General Reaction

\[
\text{C\equiv C} \xrightarrow{X_2} \text{C} = \text{C} \xrightarrow{X_2} \text{C} - \text{C} \\
\text{CH}_2\text{Cl}_2 \text{ or } \text{CCl}_4 \quad \text{CH}_2\text{Cl}_2 \text{ or } \text{CCl}_4
\]

**Example**

Initial addition of halogen $X_2$ usually gives *trans* dihalide intermediate.
The addition of hydrogen chloride $\text{HCl}$, bromide $\text{HBr}$, or iodide $\text{HI}$ to alkynes follows Markovnikov’s rule.

**If two moles of HX is added:**

- **First halogen** follows alkene hydrohalogenation regioselectivity rules, i.e.; obeys Markovnikov’s rule.
- **Second halogen** goes on same carbon as first halogen; geminal dihalide.

**The General Reaction**

\[ \text{C≡C} \rightarrow \text{C=Br} \rightarrow \text{C=C} \rightarrow \text{C=HBr} \rightarrow \text{C=C} \]

*Halo alkene*  
*geminal dihalide*
Although the reaction can usually be stopped after addition of 1 equivalent of HX to yield a *vinylic halide*, an excess of HX leads to formation of a dihalide product.

**Examples**

\[
\text{CH}_3-\text{C}≡\text{C}-\text{H} \xrightarrow{\text{HCl}} \text{C}=\text{CH}_2 \xrightarrow{\text{HCl}} \text{H}_3\text{C}-\text{C}≡\text{C}-\text{H}
\]

*vinylic halide*

\[
\text{HCl} \quad \text{HCl}
\]

\[
\text{Cl} \quad \text{Cl}
\]

\[
\text{Cl} \quad \text{I}
\]

1-pentyne 2-chloropentene 2-chloro-2-iodopentane
Water adds to alkynes in the presence of dilute sulfuric acid and murcuric sulfate catalyst to yield an enol. However the initially formed enol reacts further to produce a ketone.

**General equation**

\[ R-\overset{\cdots}{C=C}C-R + H_2O \xrightarrow{\text{HgSO}_4/\text{H}_2\text{SO}_4} \]

\[
\begin{array}{c}
\text{Enol form} \\
\begin{array}{c}
\text{Less stable} \\
\end{array}
\end{array}
\quad \iff \quad \begin{array}{c}
\text{Keto form} \\
\begin{array}{c}
\text{More stable} \\
\end{array}
\end{array}
\]

Such isomers, differing only in the placement of a hydrogen atom, are called tautomers.
To hydrate an alkyne a **mercury catalyst** is added (in contrast to alkene reactions when acidic water alone is sufficient)

**Examples**

\[
H_3C\equiv C\quad +\quad H_2O \quad \xrightarrow{HgSO_4/\ H_2SO_4} \quad [H_3C\equiv C-OH] \quad \xrightarrow{} \quad H_3C\equiv C\equiv O
\]

\[
\text{Propyne} \quad +\quad H_2O \quad \xrightarrow{HgSO_4/\ H_2SO_4} \quad \text{Propenal} \quad \xrightarrow{} \quad \text{Propanal}
\]
Thank you