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# CHM 103: Organic Chemistry I

Presented by:

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# CHEMISTRY OF ALKYNES

- there is at least **one triple-bond** between the atoms in the molecules.
- are unsaturated because of the existence of a multiple bond in the molecule.
- general molecular formula of the alkene series of hydrocarbons is **C<sub>n</sub>H<sub>2n-2</sub>**.
- The first member is **ethyne** (previously called acetylene).
- all alkynes end in "**-yne**".

## Types of alkyne

- ❑ terminal alkyne: A terminal alkyne is an alkyne in whose molecule there is at least one hydrogen atom bonded to a triply bonded carbon atom.



- ❑ internal alkyne: An internal alkyne is an alkyne in whose molecule there are no hydrogen atoms bonded to triply bonded carbon atoms.

## Alkynes Physical Properties



1. insoluble in water.
2. soluble in the usual organic solvents of low polarity (e.g. ligroin, ether, benzene, carbon tetrachloride, etc.).
3. less dense than water.
4. boiling points show the usual increase with increasing carbon number.



**Table of the physical properties of Alkynes**

Name	Formula	MP degC	BP degC	Density(20C)
=====	=====	=====	=====	=====
Acetylene	HCCH	-82	-75	
Propyne	HCCCH <sub>3</sub>	-101.5	-23	
1-Butyne	HCCCH <sub>2</sub> CH <sub>3</sub>	-122	91	
1-Pentyne	HCC(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	-98	40	0.695
1-Hexyne	HCC(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	-124	72	0.719
1-Heptyne	HCC(CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	-80	100	0.733
1-Octyne	HCC(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	-70	126	0.747
1-Nonyne	HCC(CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	-65	151	0.763
1-Decyne	HCC(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	-35	182	0.770
2-Butyne	CH <sub>3</sub> CCCH <sub>3</sub>	-24	27	0.694
2-Pentyne	CH <sub>3</sub> CCCH <sub>2</sub> CH <sub>3</sub>	-101	55	0.714

**Alkynes: Acidity**

Alkynes of the general structure



referred to as terminal alkynes. These types of alkynes are weakly acidic. Exposure to a strong base, such as sodium amide, produces an acid-base reaction.

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### ➤ Alkynes: Acidity

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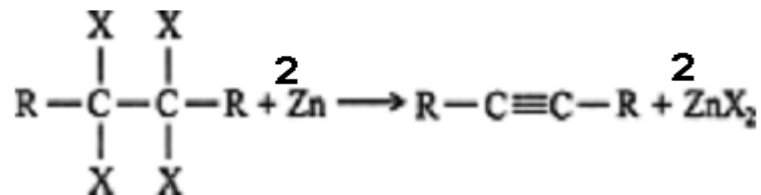
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□ are weakly acidic. And produces an acid-base reaction.



# Alkynes: Preparations

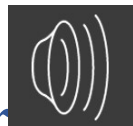
- **Dehydrohalogenation.** The loss of a hydrogen atom and a halogen atom from adjacent alkane carbon atoms leads to the formation of an alkyne. The halogen atoms may be located on the same carbon (a **geminal dihalide**) or on adjacent carbons (a **vicinal dihalide**). Vicinal tetrahaloalkanes can be dehalogenated with zinc metal in an organometallic reaction to form alkynes



- **Substitution.** Larger alkynes can be generated by reacting an alkyl halide with an acetylide ion, which is generated from a shorter alkyne.



- **Ethyne (acetylene) preparation.** Ethyne, which is commonly called acetylene, is the simplest alkyne. Historically, it was prepared by reacting calcium carbide with water.



# Reactions of Alkynes

❑ **Hydrogenation.** Alkynes undergo catalytic hydrogenation with the same catalysts used in alkene hydrogenation: **platinum, palladium, nickel, and rhodium.**

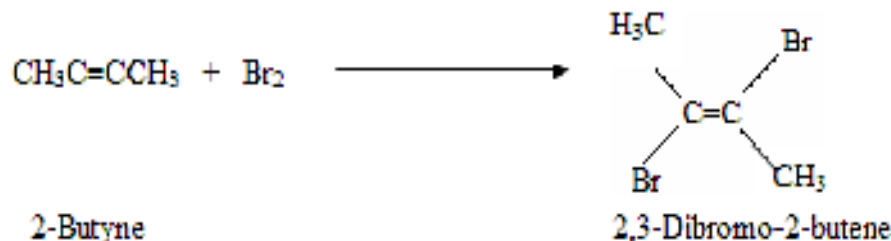
Greater yields of alkenes are possible with the use of poisoned catalysts. One such catalyst, the

1. **Lindlar catalyst:** finely divided palladium coated with quinoline and absorbed on calcium carbonate.

2. **Sodium in liquid ammonia at low temperatures.** This reaction is a chemical reduction rather than a surface reaction. The hydrogen atoms are not attached to a surface, but are added to the alkene from different directions, leading to the **trans** isomer.

$$\text{R}-\text{C}\equiv\text{C}-\text{R} \xrightarrow[2. \text{NH}_4\text{OH}]{1. \text{Na}, \text{NH}_3} \text{trans-RCH=CHR}$$

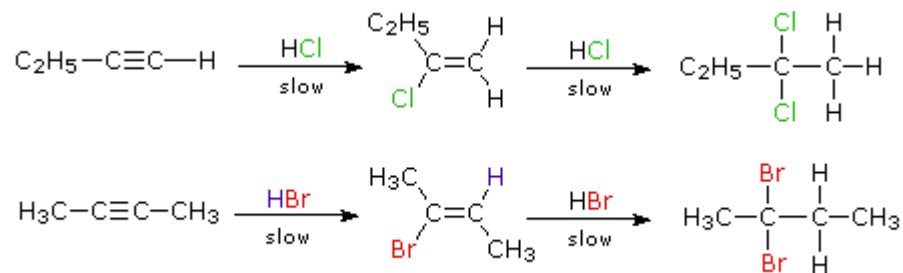
- ❑ **Halogenation.** 7  
manner as halogen



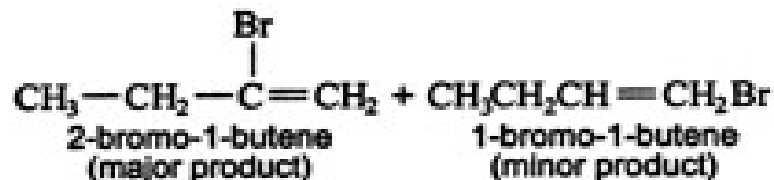
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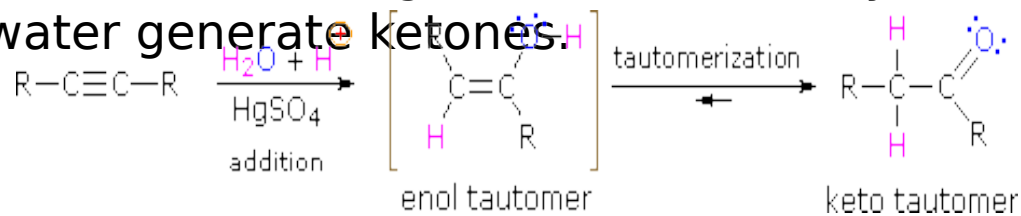
□ **Hydrohalogenation.** Hydrogen halides react with alkynes in the same manner as they do with alkenes



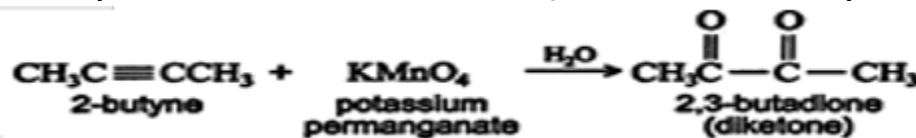
Both steps in the above addition follow the Markovnikov rule. Thus, the addition of hydrogen bromide to 1-butyne gives 2-bromo-1-butene as the major product of the first step.



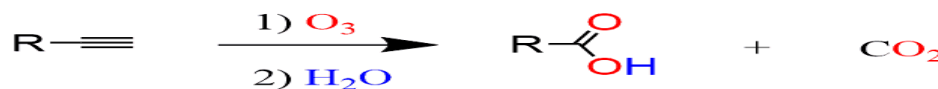
□ **Hydration.** The addition of the elements of water across the triple bond of an alkyne leads to the formation of aldehydes and ketones. Water addition to terminal alkynes leads to the generation of aldehydes, while nonterminal alkynes and water generate ketones.



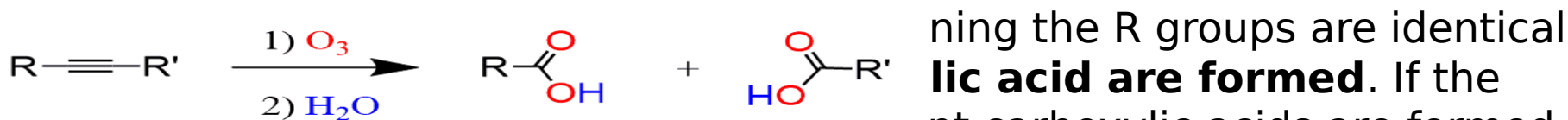
- Oxidation.** Alkynes are oxidized by the same reagents that oxidize alkenes. Disubstituted alkynes react with potassium permanganate to yield vicinal diketones (Vic-diketones or 1,2-diketones) or, under more vigorous conditions, carboxylic acids.



- Ozonolysis.** It is an **Oxidative Cleavage** reaction where both the  $\pi$  and  $\sigma$  bonds of the double or a triple bond are broken to form two carbonyl groups. **Ozonolysis of internal alkynes, terminal alkynes, and carbon dioxide:**



- carboxylic acids:** on the other hand, produces two carboxylic acids:



- If the R groups are identical, **one carboxylic acid is formed**. If the R groups are different, **two different carboxylic acids are formed**.

- Polymerization.** Alkynes can be polymerized by both cationic and free radical methods. The reactions and mechanisms are identical with those of alkenes.

