



Chem 145

Unsaturated hydrocarbons

Alkynes

Chapter 4

1434-1435

2013-2014

2st semester

Dr. Seham ALTERARY

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



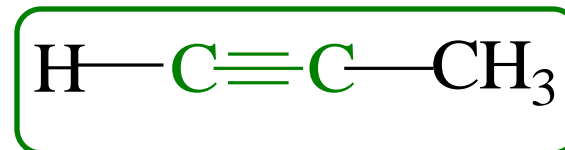
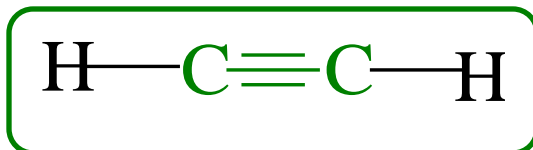
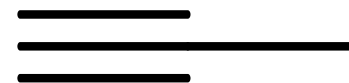
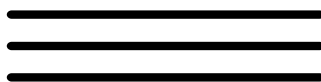
Nomenclature

The simplest members of the **alkynes** series (**C₂** and **C₃**) are usually called by their common Names.

Chemical formula:



Chemical structure:



Common Name:

Acetylene

Allylene

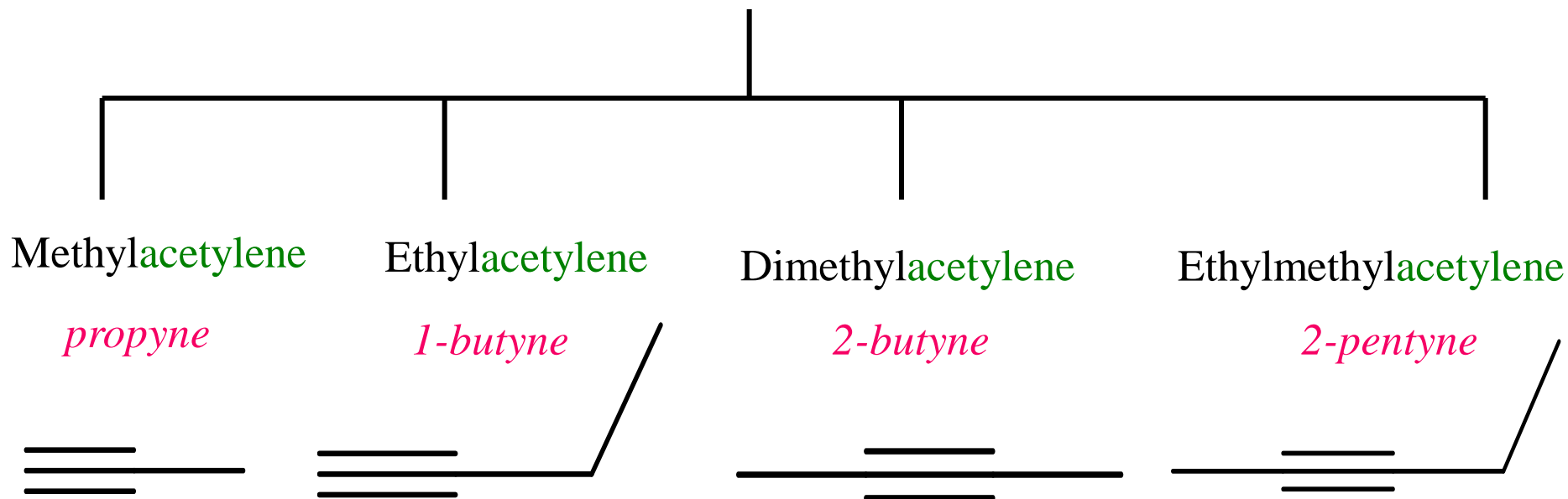
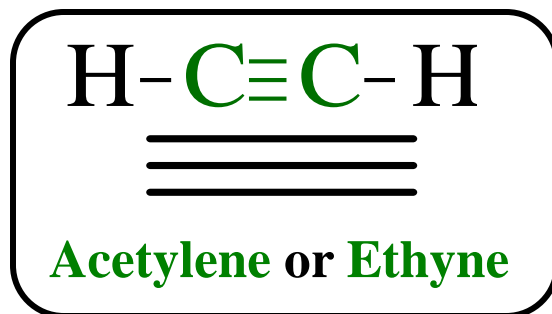
IUPAC Name:

Ethyne

Propyne

Naming Alkynes: a) Common system

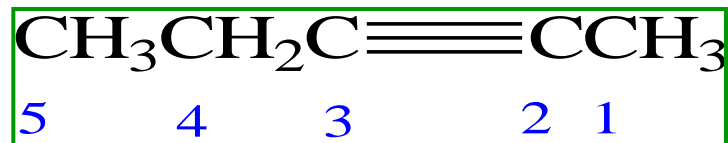
- ❑ The **alkynes** are sometimes referred to as the **acetylene series**.
- ❑ The **higher members** of the series being **named as** derivatives of acetylene.



b) IUPAC Naming of Alkynes.

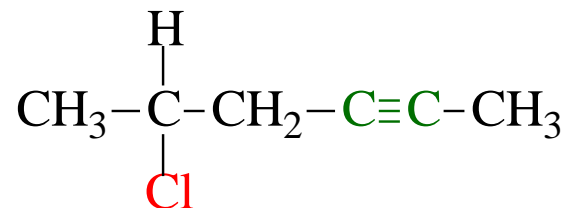
The rules for naming **alkynes** in the **IUPAC system** are identical with those for **alkenes**, except for the ending.

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.



is **5-chloro-2-hexyne**.

Q: If double and triple are exist in the same molecule ?

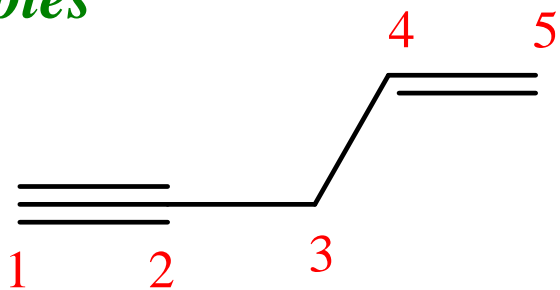
If both a **double bond** and a **triple bond** are present, the compound is an **alkenyne** .

Note that,

An “e” is dropped from “ene” as resion of being followed by vowel “y” in “yne”.

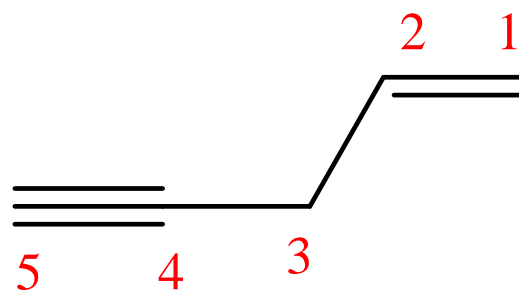
- ✓ The numbering starts from **the end** containing **the lower** numbered **multiple bond**.
- ✓ If the **double bond** and the **triple bond** will **have the same numbers** from either end of the chain, **the numbering of the double bonds takes locational priority**; that is the **double bond** assigned **the lower number**.

Examples



Not

~~Pent-4-en-1-yne~~



Pent-1-en-4-yne

Problem 4.7 Write the condensed structural formula for

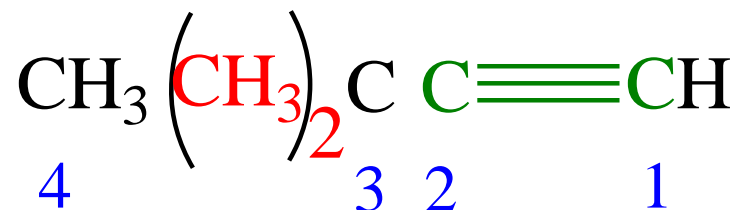
(a) 1-Pentyne



(b) 3-Hexyne



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

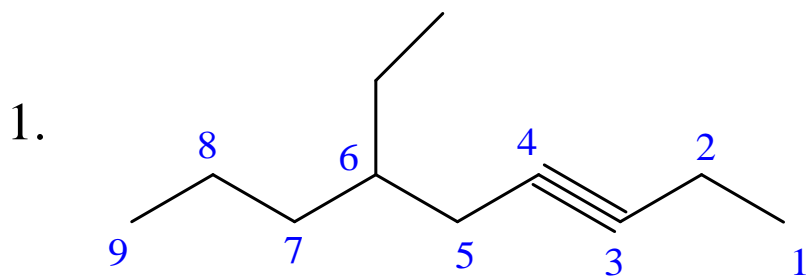


(d) 1-Cyclohexyl-2-butyne

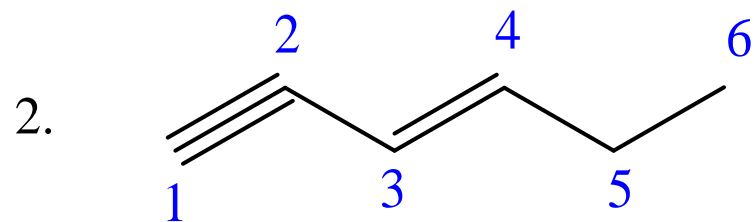


Examples

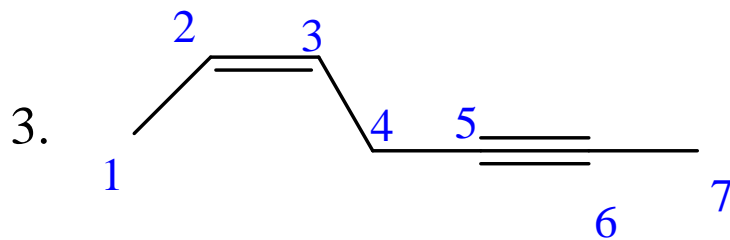
Give the name of the following



6-Ethyl-3-nonyne



Hex-3-en-1-yne



Hept-2-en-5-yne

Excercise

Draw the structure of the following

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

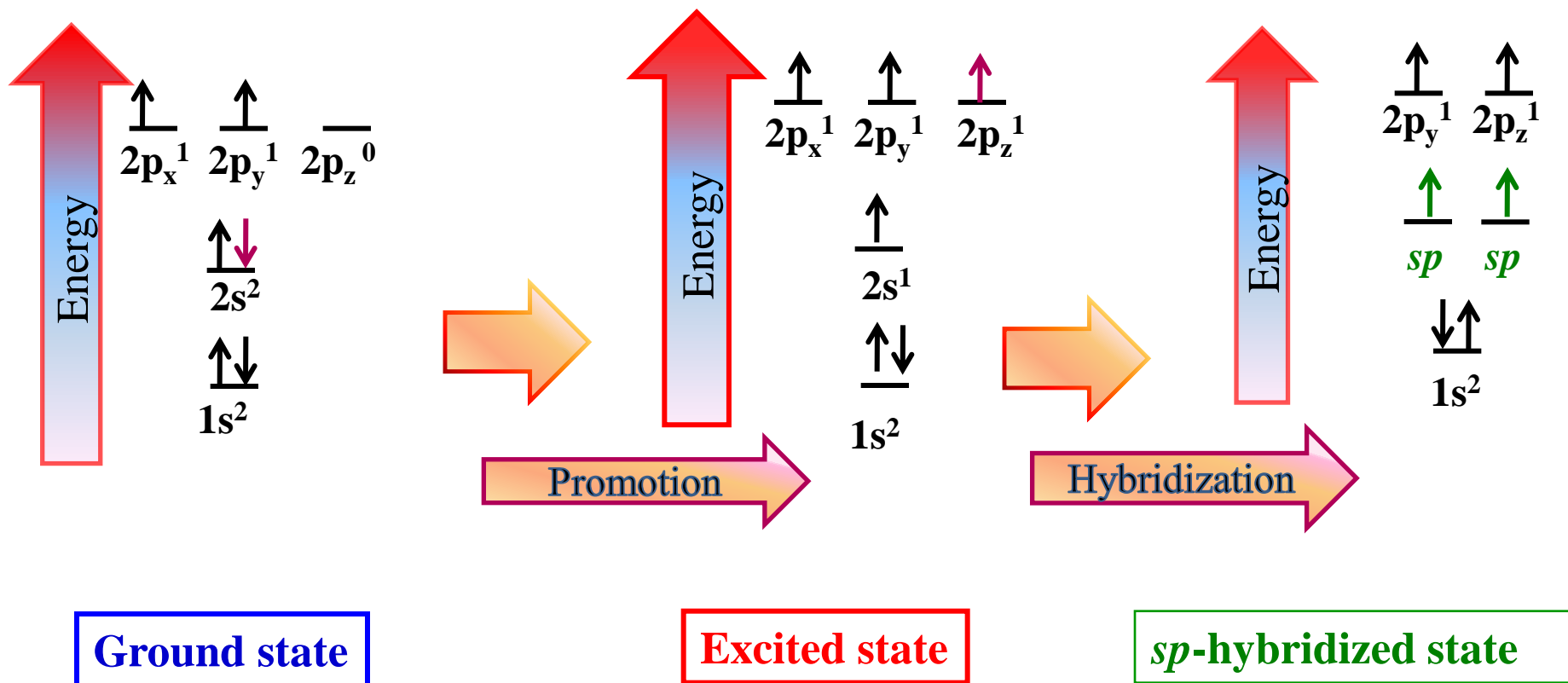
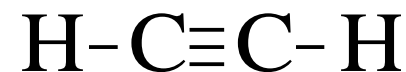
(2) 5-Isopropyloctyne

(3) 1-Cyclobutyl-3-methyl-1-butyne

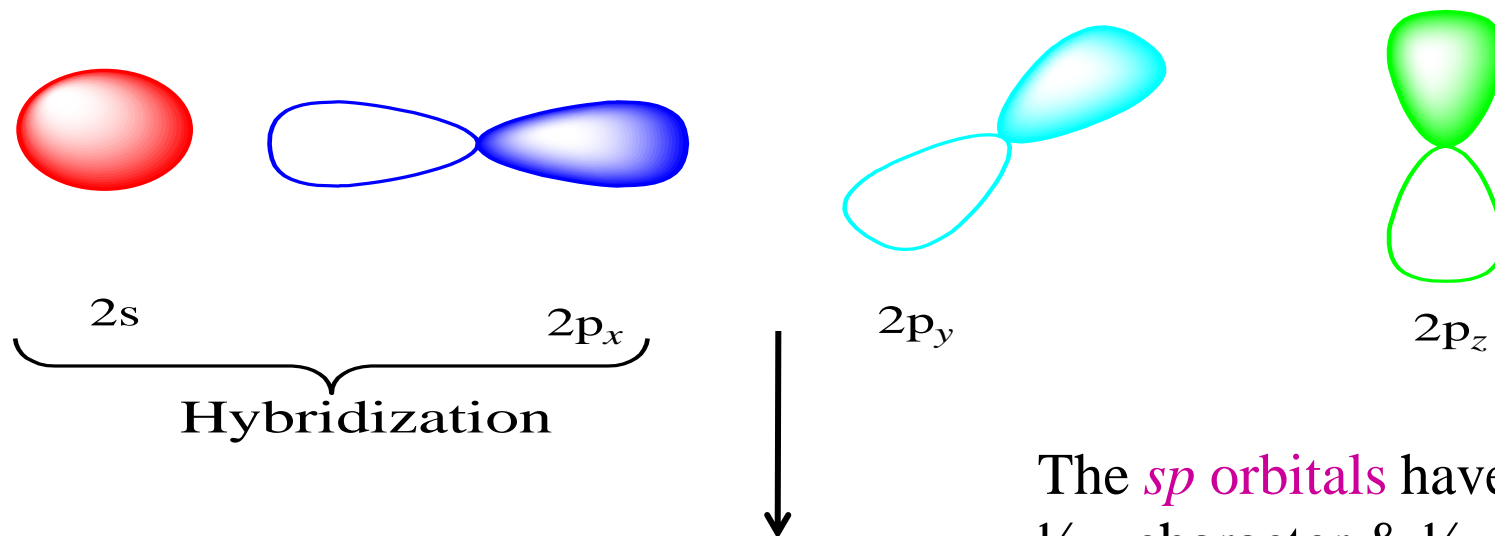
The Hybridization of Alkynes.

Example

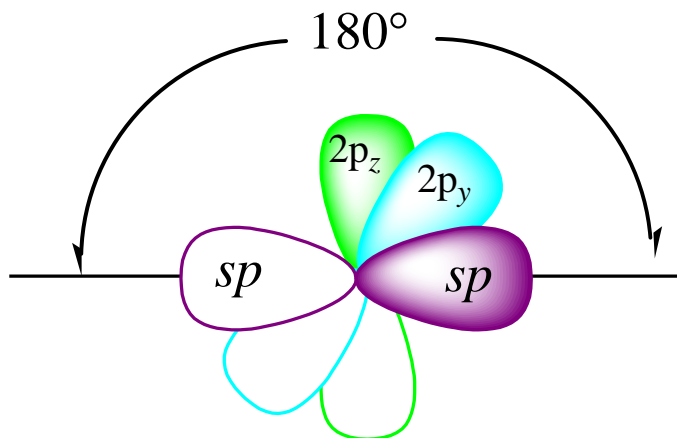
For the simplest alkyne, Ethyne, or Acetylene



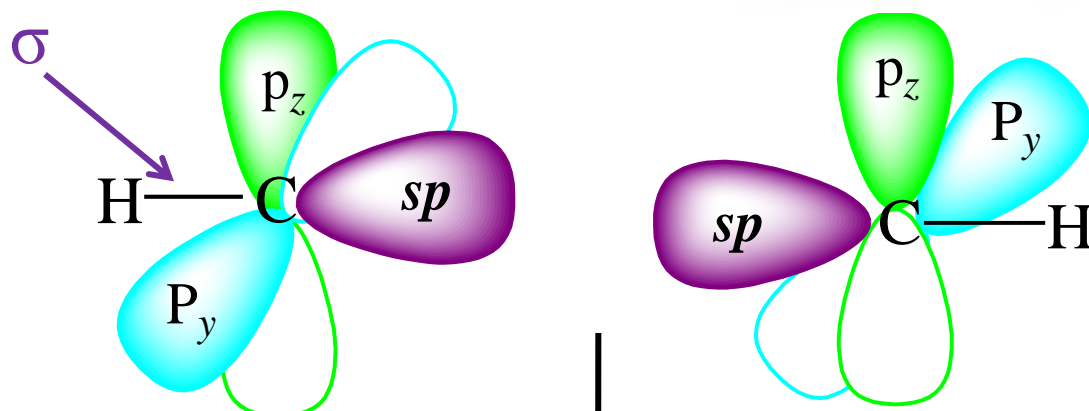
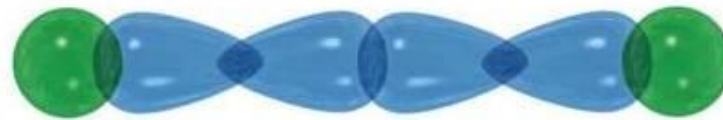
The hybridization of a $2s$ orbital and $2p$ orbital to form two linear sp -hybridized orbitals with bond angle 180° and two unhybridized p orbitals perpendicularly oriented to each other and to the plan of the hybrid sp orbitals.



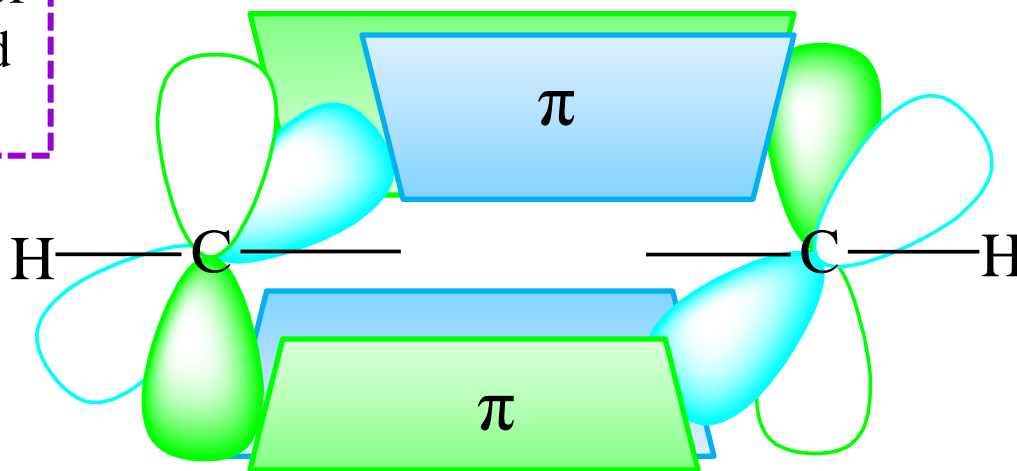
The sp orbitals have $\frac{1}{2} s$ character & $\frac{1}{2} p$ character



a) Bond Formation in Acetylene



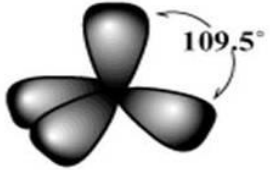
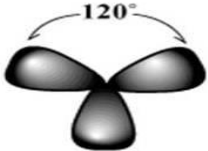
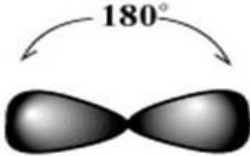
$sp-sp$
 p_y-p_y , and p_z-p_z



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.

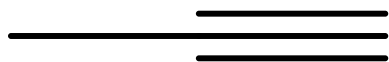
The comparative chart of **bond length** of **alkane**, **alkene** and **alkyne** is given below:

Class	Bond	Hybridized bond orbital	Bond Length	Structure
Alkane	C-C	sp^3-sp^3	1.54 Å	
	C-H	sp^3-1s	1.112 Å	
				Tetrahedral
Alkene	C=C	sp^2-sp^2	1.34 Å	
	C-H	sp^2-1s	1.108 Å	
				Trigonal planar
Alkyne	C≡C	$sp-sp$	1.20 Å	
	C-H	$sp-1s$	1.08 Å	
				Linear

Terminal and Internal Alkynes

1- Terminal alkynes

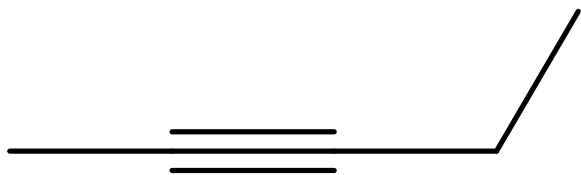
Have a **hydrogen atom** bonded to at least one of the **sp hybridized** carbons (those involved in **the triple bond**). An example would be **methylacetylene** (**1-propyne** using IUPAC nomenclature).



1-propyne

2- Internal alkynes

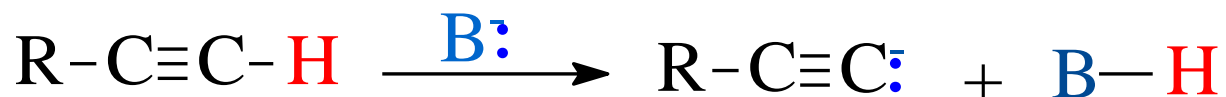
Have something other than hydrogen attached to the **sp hybridized** carbons, usually another carbon atom, but could be a heteroatom. A good example is **2-pentyne**, in which there is a methyl group on one side of the **triple bond** and **an ethyl** group on the other side.



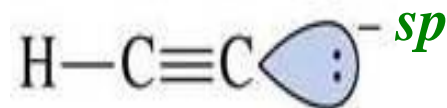
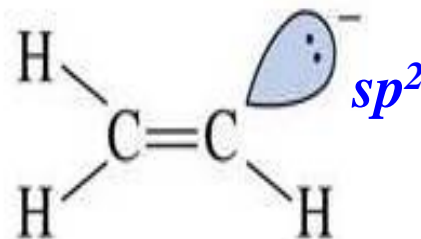
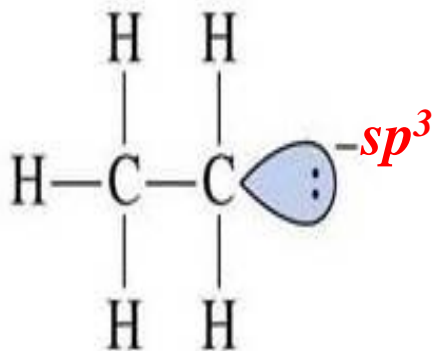
2-pentyne

The Acidity of terminal Alkynes

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



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

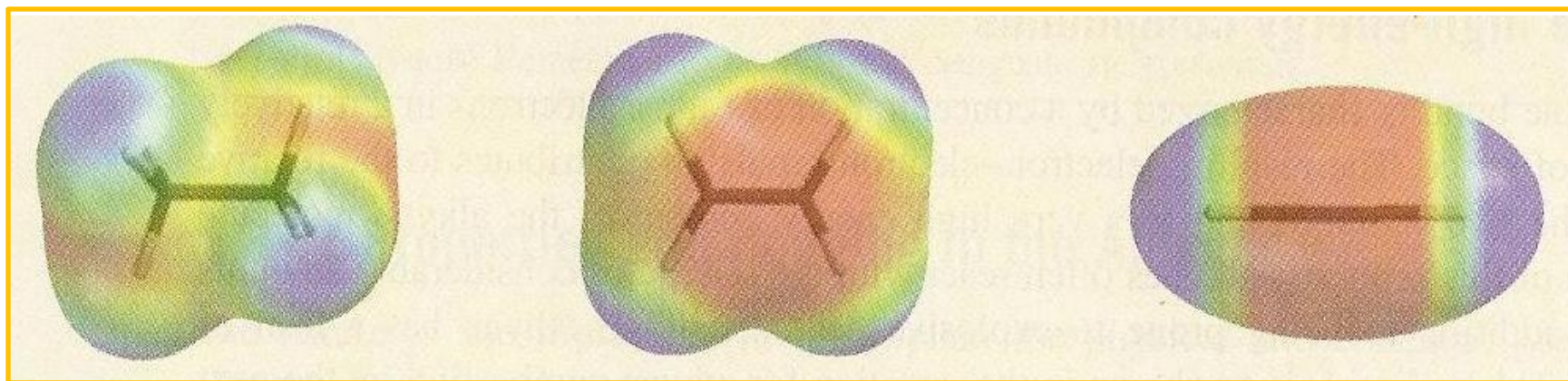


The **acidic character** is due to the fact that in acetylene or **triple bonded C atom**, an increase in **s** character (**sp hybridization**) give rise to **higher electronegativity** to C atom and thus **H atom** in **C—H** (i.e. **sp —1s**) bond acquires more **polarity** to show **acidic nature**.

Relative acidities of Alkanes, 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.

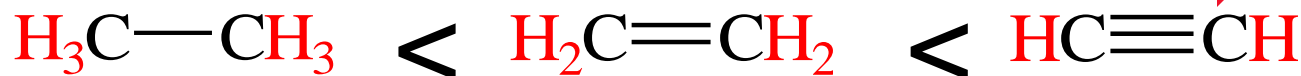


Ethane

Ethene

Ethyne

Increasing acidity



pK_a

62

45

26

Hybridization of C

sp^3

sp^2

sp

% s Character

25%

33%

50%

Physical Properties of Alkynes.

The physical properties of **alkyne** 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 .

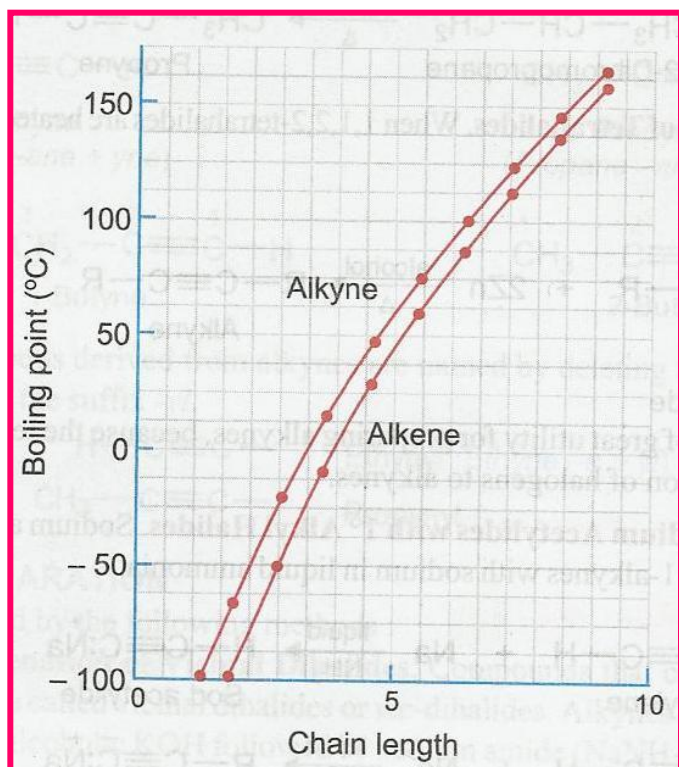
• *Boiling point*

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**.



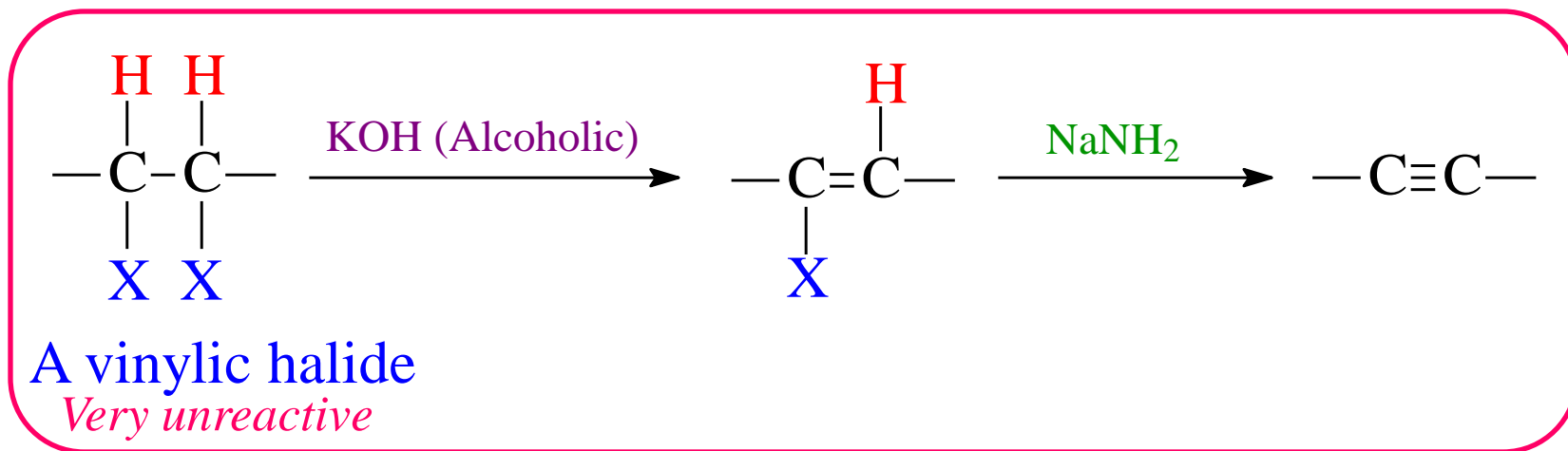
Name	m.p. °C
Ethane	-88.6 °C
Ethene	-103.7 °C
Ethyne	-84.0 °C

General Methods for The Preparation of Alkynes.

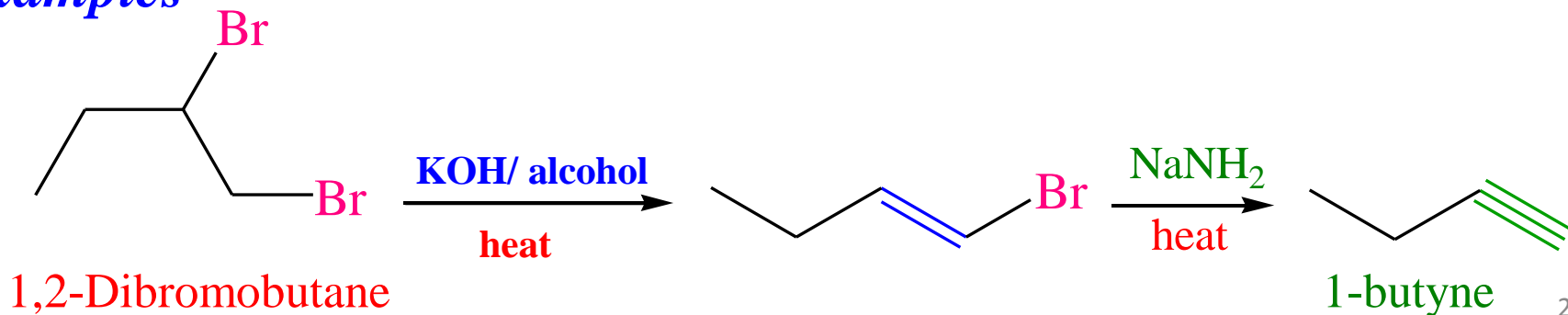
(A) Dehydrohalogenation of alkyl halides using a strong base

The General Reaction

By treating **vicinal dihalides** with **strong base** (alcoholic KOH), followed by **sodium amide** (NaNH_2), results in the formation of **Alkyne**.



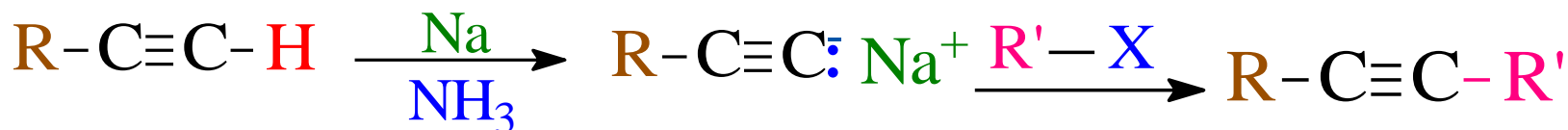
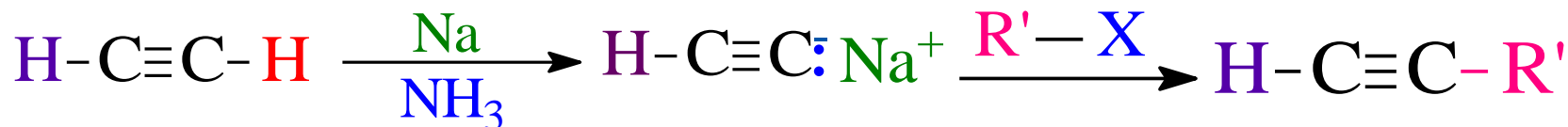
Examples



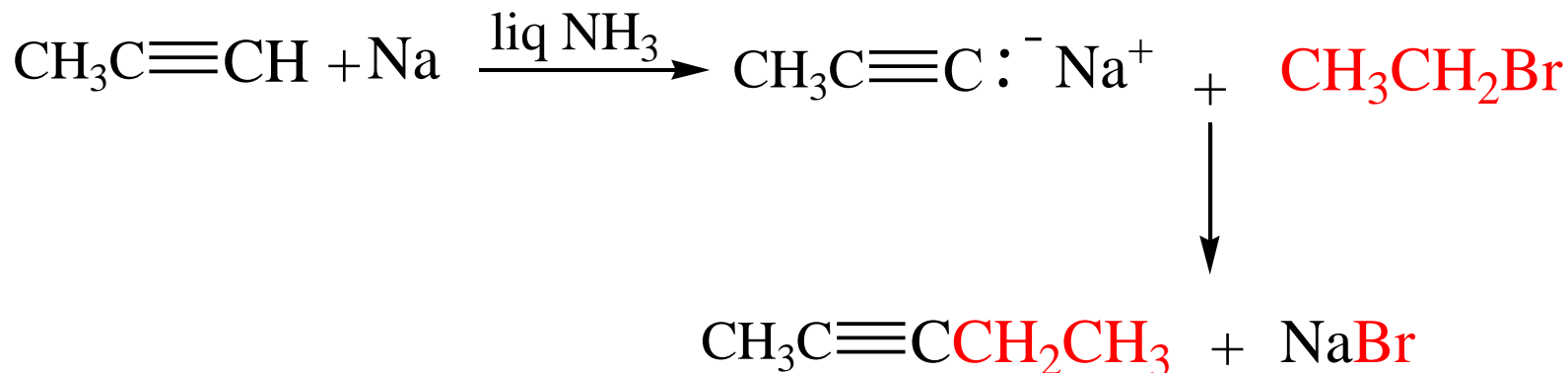
(B) Reaction of sodium Acetylide with Primary Alkyl Halides

- ❑ 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



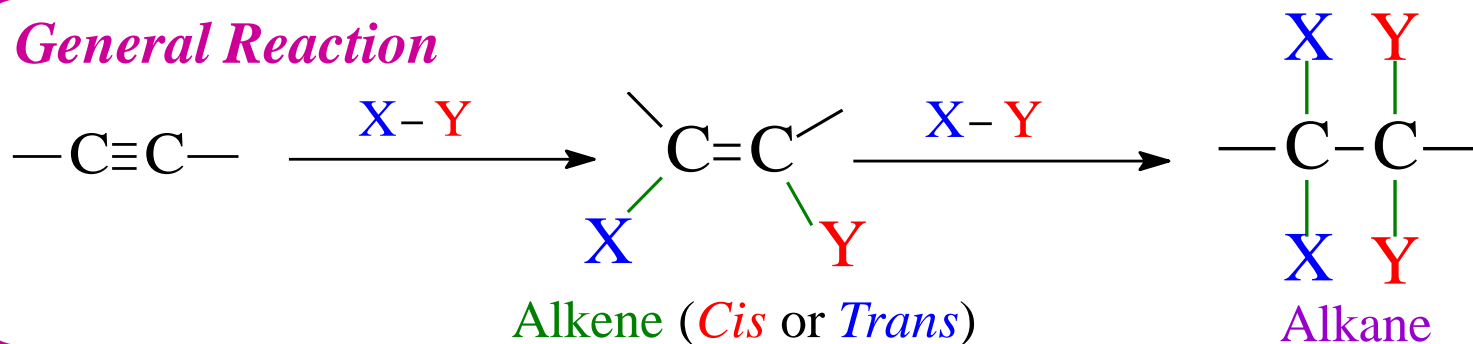
Example



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



Addition Reaction for Alkynes



Addition of Hydrogen

Addition of Halogen

Addition of Hydrogen halide

Addition of water: Hydration

1

Addition of Hydrogen

1. Complete Addition

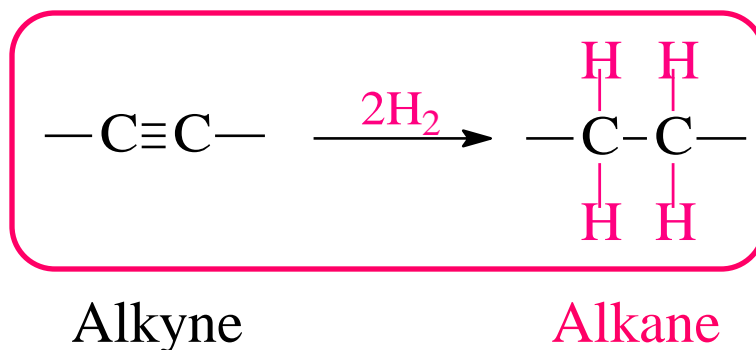
Controlled Addition
2. *Cis*-Alkene

Controlled Addition
3. *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**.

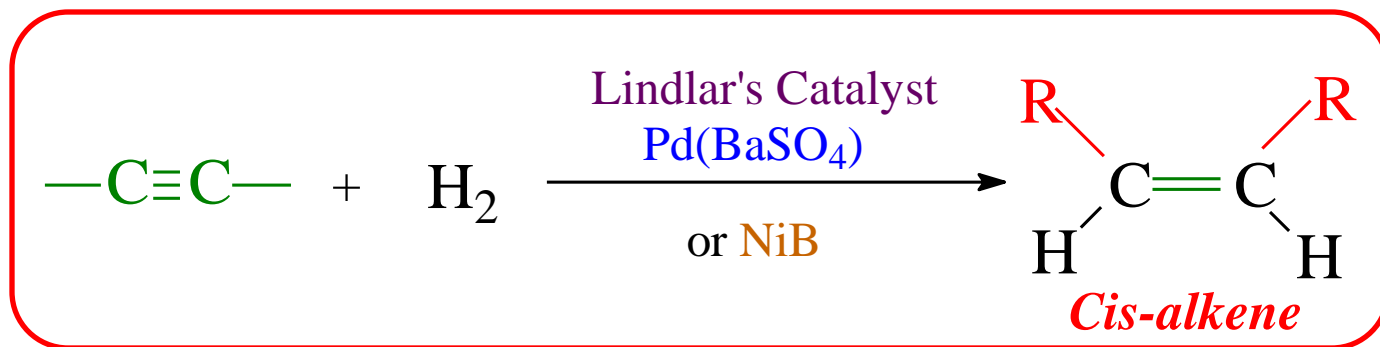
General equation



Case "2"

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**.

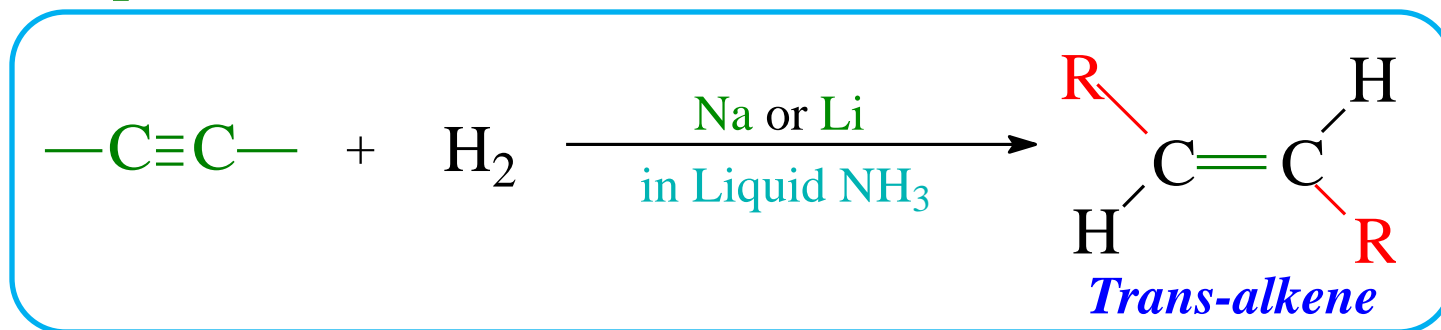
General equation



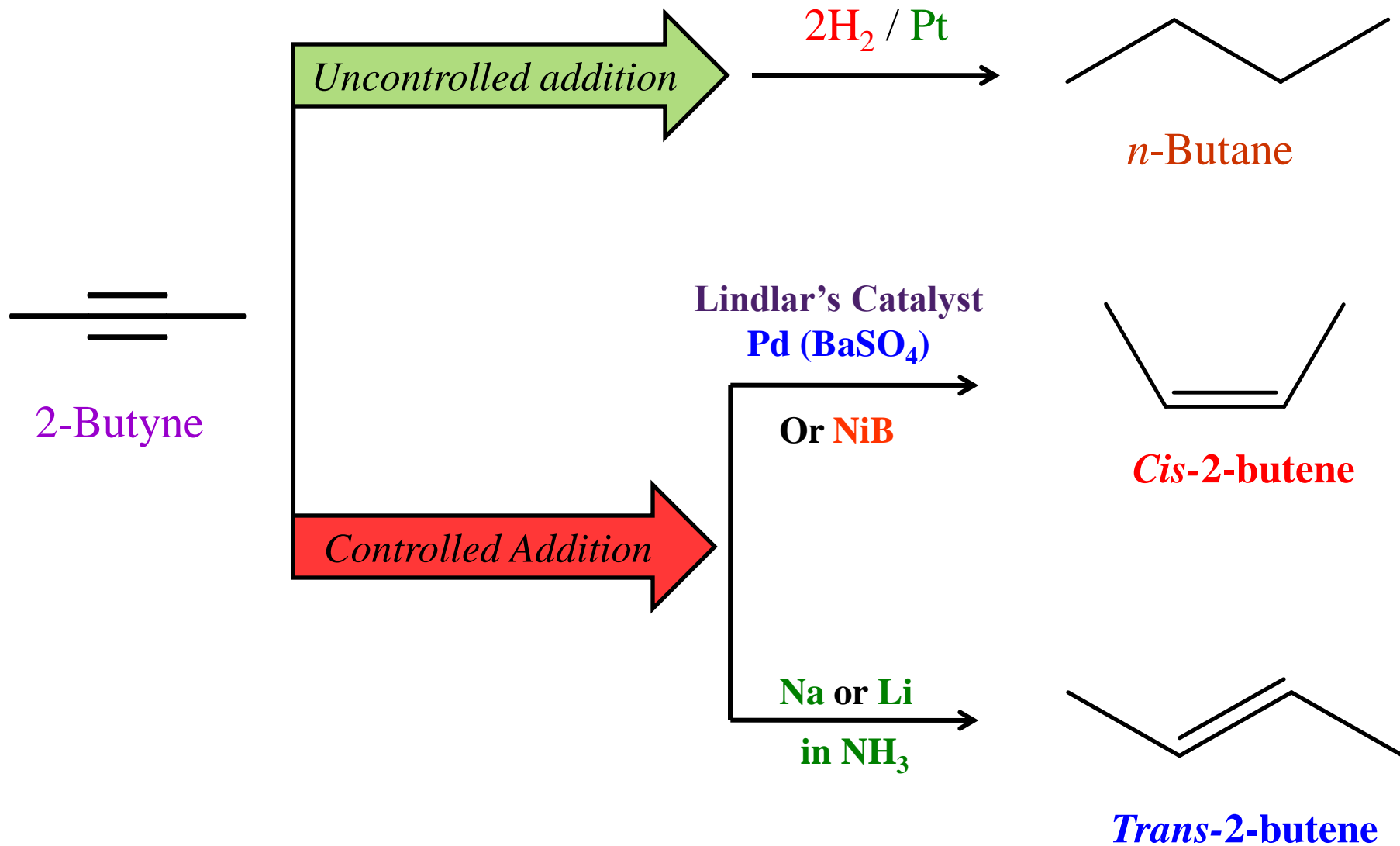
Case "3"

When we use **Na; Sodium** or **Li; Lithium** metal dissolved in **NH₃; liquid ammonia**, we obtain **trans alkene** as product.

General equation



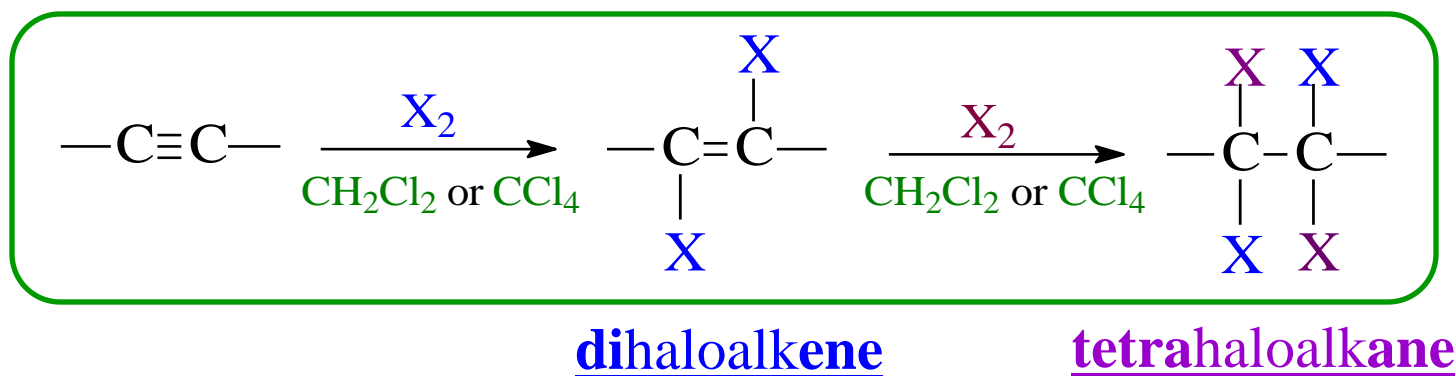
Examples



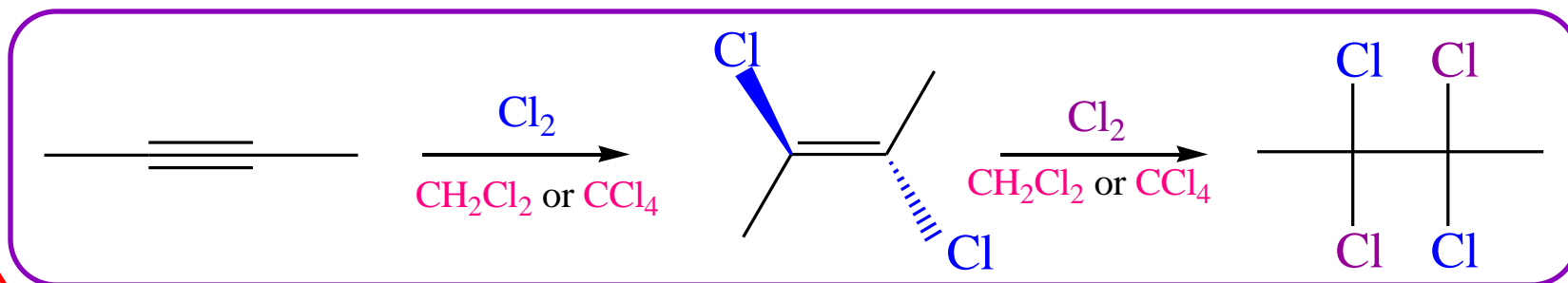
Addition of Halogen

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



Example



Initial addition of halogen X_2 usually gives *trans* dihalide intermediate.

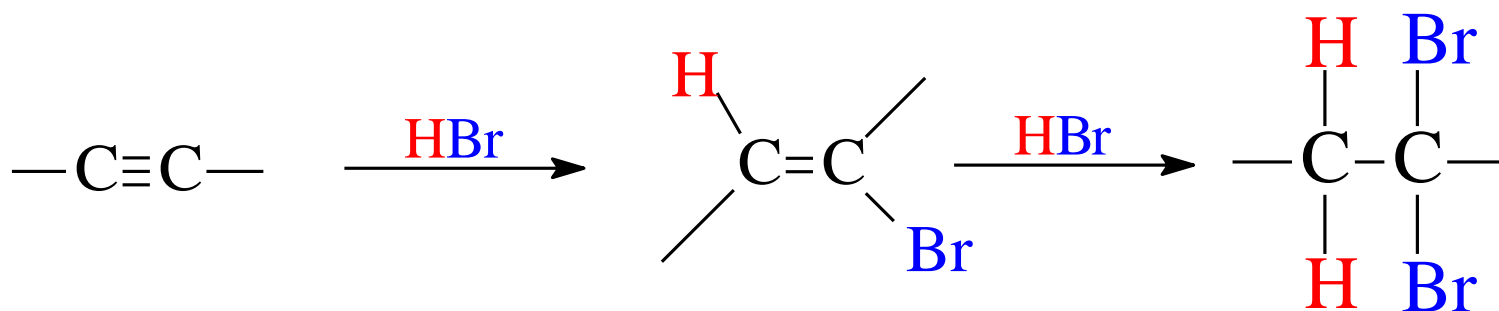
Addition of Hydrogen halide

The addition of **hydrogen chloride HCl**, **bromide HBr**, or **iodide 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

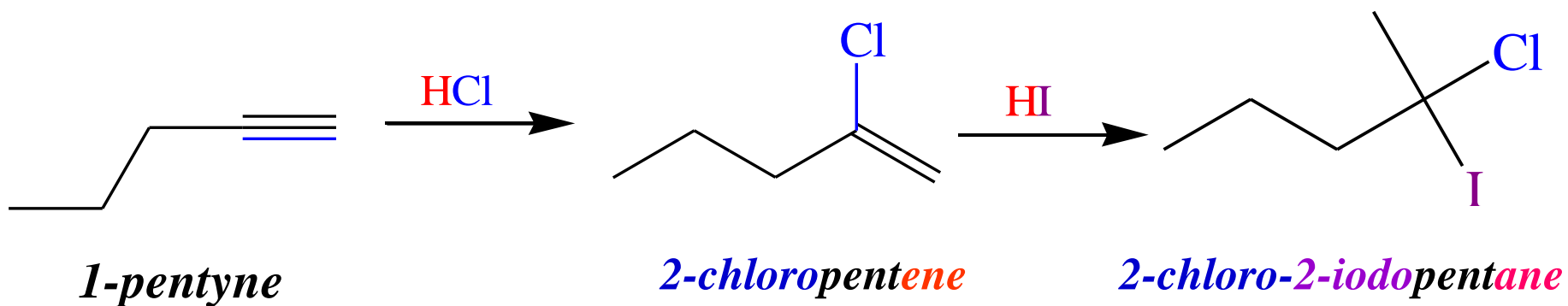
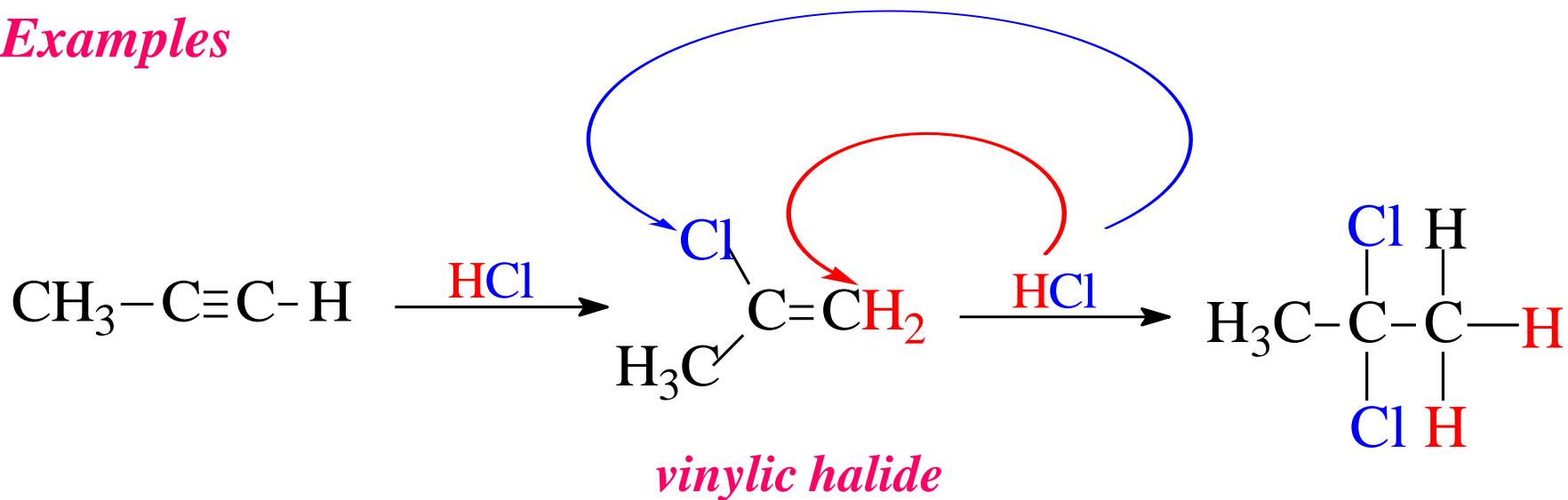


Halo alkene

geminal dihalide

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

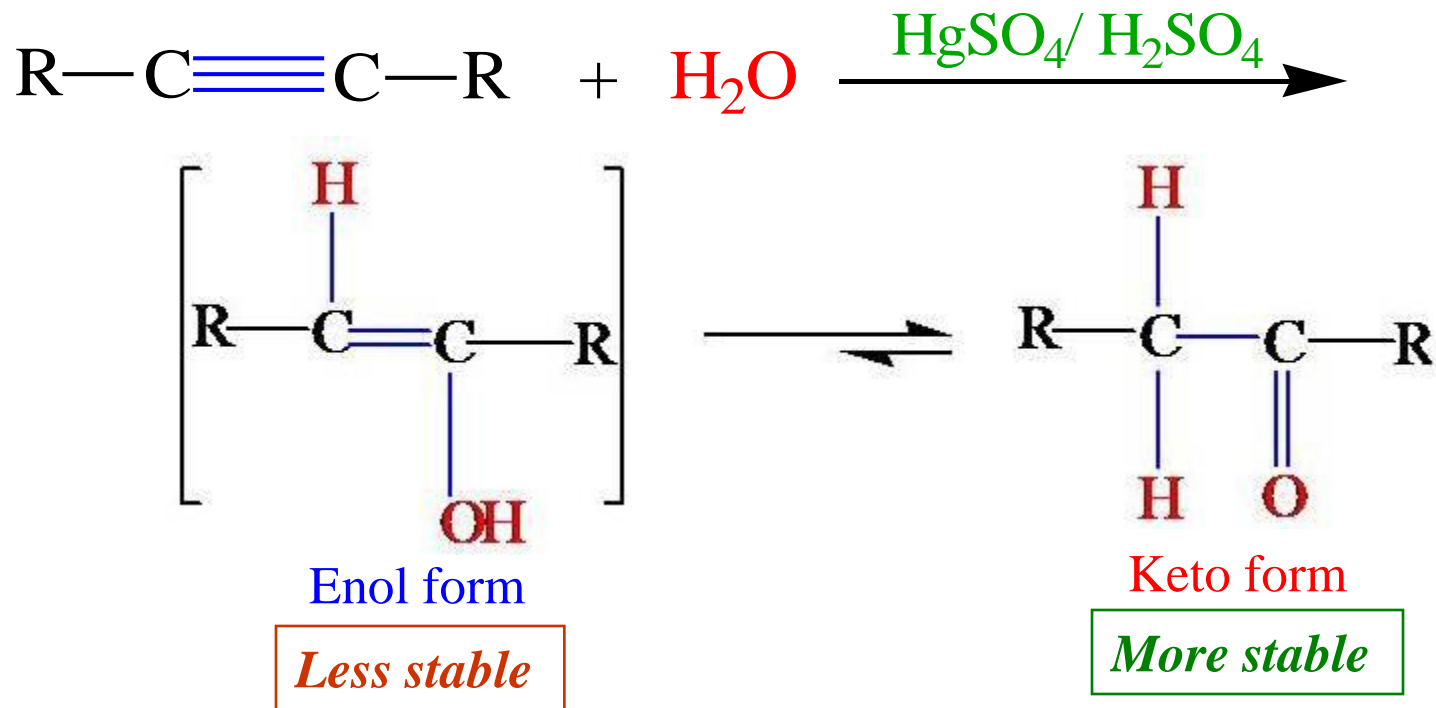
Examples




Addition of Water : Hydration

Water adds to alkynes in the presence of dilute sulfuric acid and mercuric sulfate catalyst, to yield an enol. However the initially formed enol reacts further to produce a ketone.

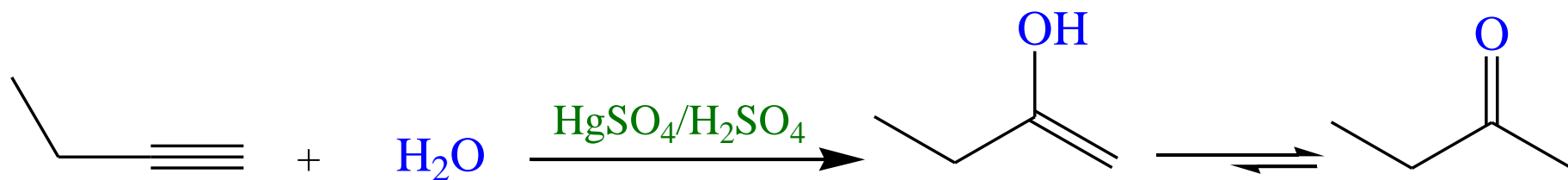
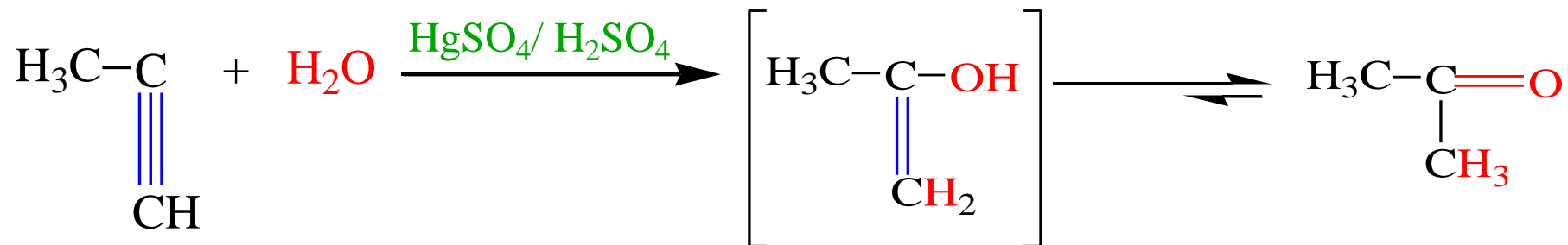
General equation



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



Thank you

