Organic Chemistry

Alkynes

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Expected Outcomes

In the end of this chapter, student will have the ability to:

- Describe characteristics and physical properties of alkyne
- Draw and name alkyne using IUPAC nomenclature
- Write alkyne reaction mechanism

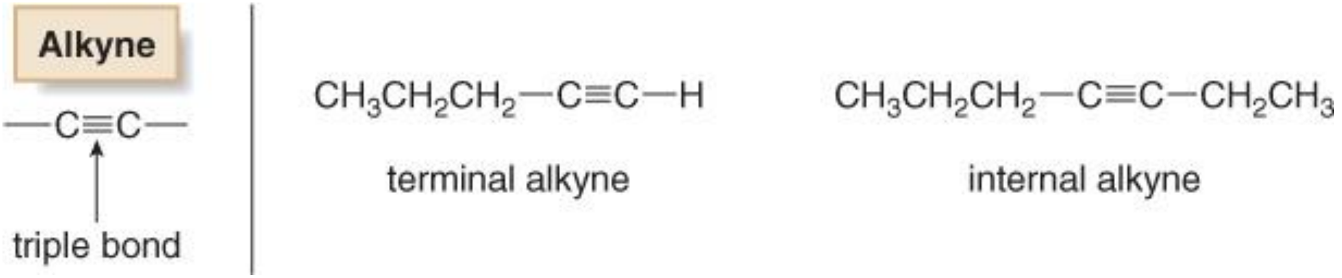
Contents

- Alkynes
- Physical properties
- Nomenclature
- Alkyne reaction mechanisms

Alkynes

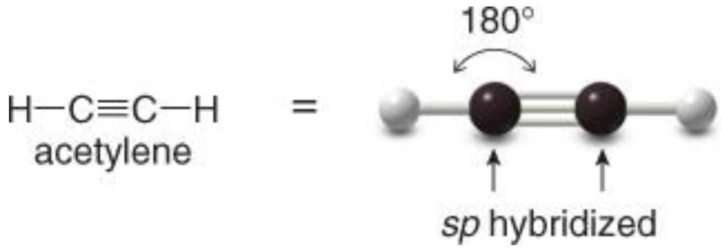
Introduction—Structure and Bonding

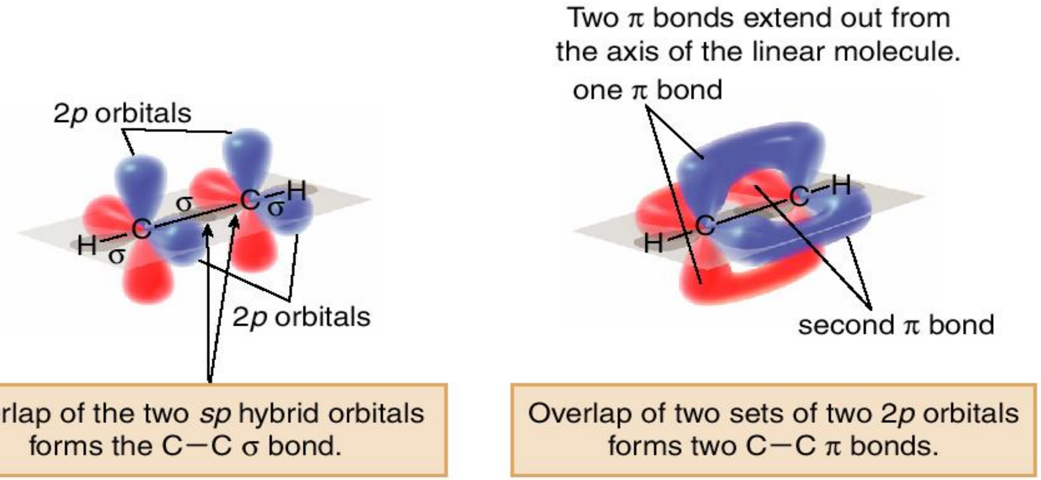
- Alkynes contain a carbon—carbon triple bond.
- **Terminal alkynes** have the triple bond at the end of the carbon chain so that a hydrogen atom is directly bonded to a carbon atom of the triple bond.
- **Internal alkynes** have a carbon atom bonded to each carbon atom of the triple bond.
- An alkyne has the **general molecular formula C_nH_{2n-2}**, giving it four fewer hydrogens than the maximum possible for the number of carbons present. Thus, **the triple bond introduces two degrees of unsaturation**.



Introduction—Structure and Bonding

- Recall that the triple bond consists of 2 π bonds and 1 σ bond.
- Each carbon is *sp* hybridized with a linear geometry and bond angles of 180^0.





Overlap of the two *sp* hybrid orbitals forms the C—C σ bond.

Overlap of two sets of two 2*p* orbitals forms two C—C π bonds.

- **The σ bond is formed by end-on overlap of the two *sp* hybrid orbitals.**
- **Each π bond is formed by side-by-side overlap of two 2*p* orbitals.**

Nomenclature

- Alkynes are named in the same general way that alkenes are named.
- In the IUPAC system, change the ***–ane*** ending of the parent alkane name to the suffix ***–yne***.
- Choose the **longest continuous chain that contains** both atoms of the triple bond and number the chain to give the triple bond the lower number.
- Compounds with two triple bonds are named as **diynes**, those with three are named as **triynes** and so forth.
- Compounds containing both a double and triple bond are named as **enynes**. The chain is numbered to give the **first** site of unsaturation (either $C=C$ or $C\equiv C$) the lower number.
- The simplest alkyne, $H\text{-}C\equiv C\text{-}H$, named in the IUPAC system as **ethyne**, is more often called **acetylene**, its common name.
- The two-carbon alkyl group derived from acetylene is called an **ethynyl** group.

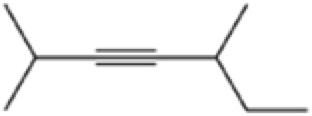
Naming Priority of functional groups

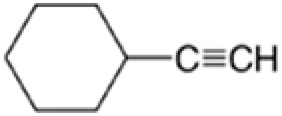
- Carboxylic acids
- Esters
- Aldehydes
- Ketones
- Alcohols

- Alkenes
- Alkynes
- Alkanes , Ethers , Halides

Nomenclature

Examples of Alkynes nomenclature



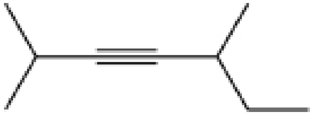


$CH_3CH_2{-}C{\equiv}C{-}C{\equiv}CH$

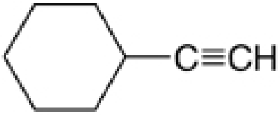
$HC{\equiv}C{-}CH_2CH{=}C(CH_3)_2$

Nomenclature

Examples of alkyne nomenclature



2,5-dimethyl-3-heptyne



ethynylcyclohexane

$CH_3CH_2-C\equiv C-C\equiv CH$

1,3-hexadiyne

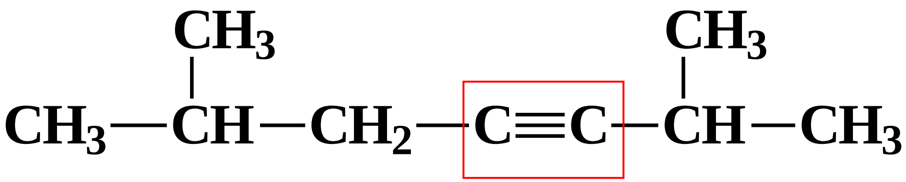
$HC\equiv C-CH_2CH=C(CH_3)_2$

5-methyl-4-hexen-1-yne

Common Names

Named as substituted acetylene.

$CH_3-\boxed{C\equiv C}H$ **methylacetylene**



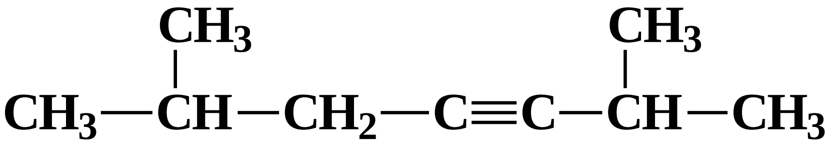
$$CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-\boxed{C\equiv C}-\overset{CH_3}{\overset{|}{C}H}-CH_3$$

isobutylisopropylacetylene

Name these:

$CH_3-C\equiv CH$

$CH_3-C\equiv C-CH_2-CH_2-Br$



$CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-C\equiv C-\overset{CH_3}{\overset{|}{C}H}-CH_3$

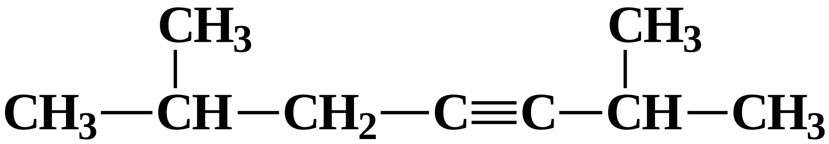
Name these:

$CH_3-C\equiv CH$

propyne or 1-propyne

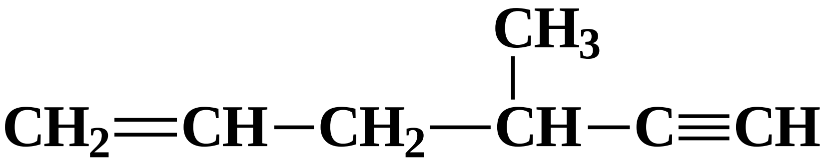
$CH_3-C\equiv C-CH_2-CH_2-Br$

5-bromo-2-pentyne

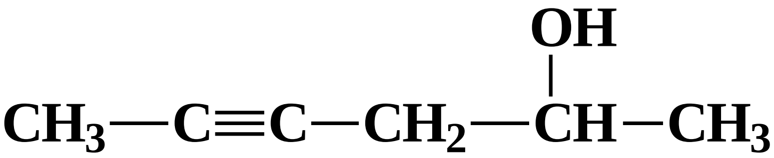


$$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-C\equiv C-\overset{\overset{CH_3}{|}}{C}H-CH_3$$

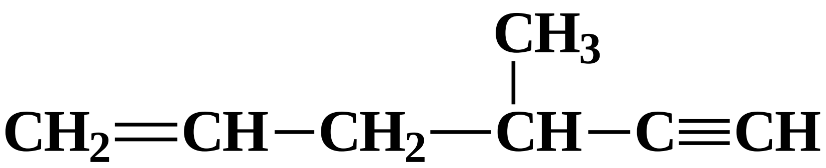
2,6-dimethyl-3-heptyne



$$\mathrm{CH_2{=}CH{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}H{-}C{\equiv}CH}$$

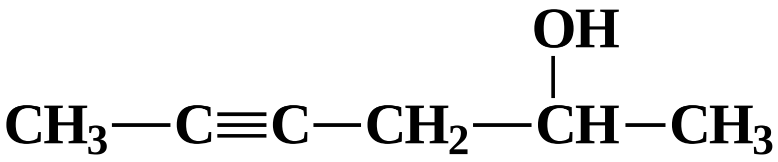


$$\mathrm{CH_3{-}C{\equiv}C{-}CH_2{-}\overset{\overset{OH}{|}}{C}H{-}CH_3}$$



$$\mathrm{CH_2{=}CH-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}H-C\equiv CH}$$

4-methyl-1-hexen-5-yne



$$\mathrm{CH_3-C\equiv C-CH_2-\overset{\displaystyle OH}{\overset{|}{C}}H-CH_3}$$

4-hexyn-2-ol

Physical Properties

- The physical properties of alkynes resemble those of hydrocarbons of similar shape and molecular weight.

- Alkynes have low melting points and boiling points.

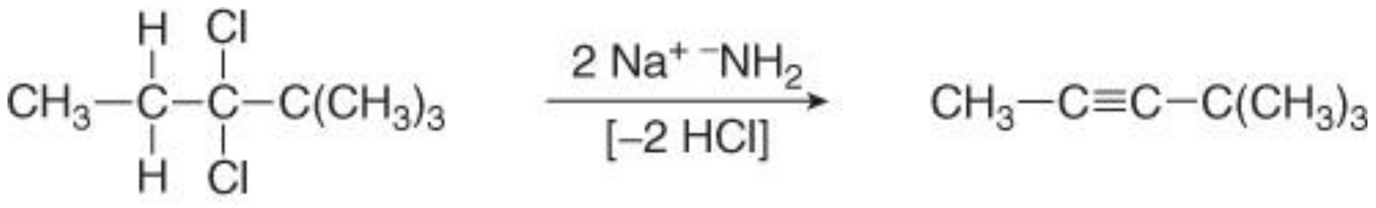
- Melting point and boiling point increase as the number of carbons increases.

- Alkynes are soluble in organic solvents and insoluble in water.

- Up to 4 carbons, gases at room temperature.

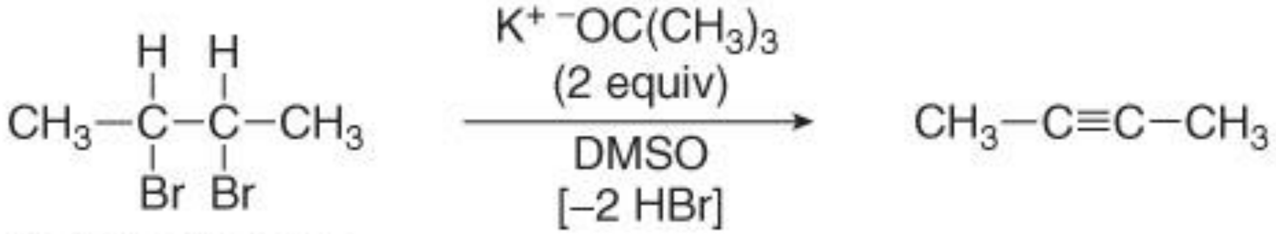
Preparation of Alkynes

- Recall that alkynes are prepared by elimination reactions. A strong base removes two equivalents of HX from a vicinal or geminal dihalide to yield an alkyne through two successive E2 elimination reactions.



geminal dichloride

$$CH_3-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}-C(CH_3)_3 \xrightarrow[\text{[-2 HCl]}]{2\ Na^+\ {}^-NH_2} CH_3-C{\equiv}C-C(CH_3)_3$$

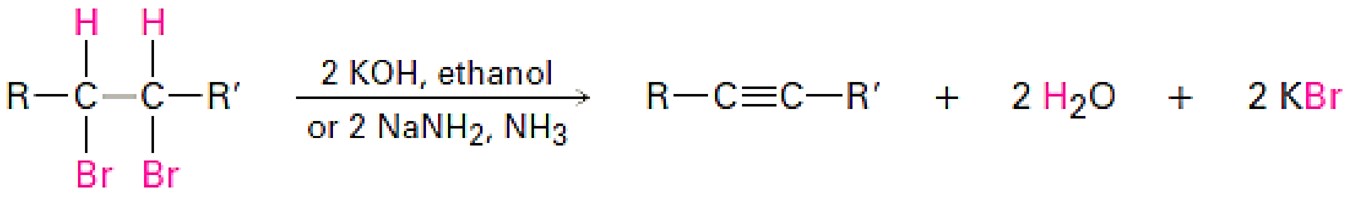


vicinal dibromide

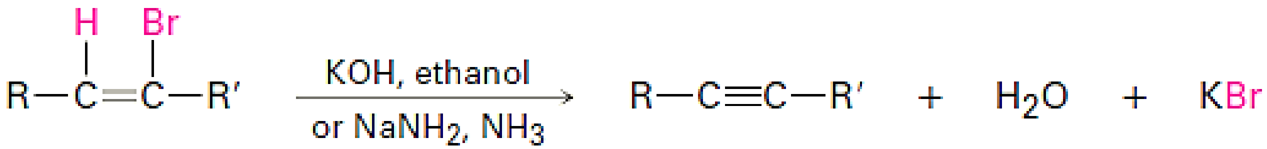
$$CH_3-\overset{\overset{H}{|}}{\underset{\underset{Br}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3 \xrightarrow[\substack{\text{DMSO} \\ \text{[-2 HBr]}}]{\substack{K^+\ {}^-OC(CH_3)_3 \\ \text{(2 equiv)}}} CH_3-C{\equiv}C-CH_3$$

1. Preparation of alkynes

(a) Dehydrohalogenation of vicinal dihalides



$$\mathrm{R{-}\underset{Br}{\overset{H}{C}}{-}\underset{Br}{\overset{H}{C}}{-}R'} \xrightarrow[\text{or 2 NaNH}_2\text{, NH}_3]{\text{2 KOH, ethanol}} \mathrm{R{-}C{\equiv}C{-}R'} + 2\,\mathrm{H_2O} + 2\,\mathrm{KBr}$$



$$\mathrm{R{-}\overset{H}{C}{=}\overset{Br}{C}{-}R'} \xrightarrow[\text{or NaNH}_2\text{, NH}_3]{\text{KOH, ethanol}} \mathrm{R{-}C{\equiv}C{-}R'} + \mathrm{H_2O} + \mathrm{KBr}$$

(b) Alkylation of acetylide anions

$$\mathrm{HC{\equiv}CH} \xrightarrow{\mathrm{NaNH_2}} \mathrm{HC{\equiv}C^-\ Na^+} \xrightarrow{\mathrm{RCH_2Br}} \mathrm{HC{\equiv}CCH_2R}$$

Acetylene **A terminal alkyne**

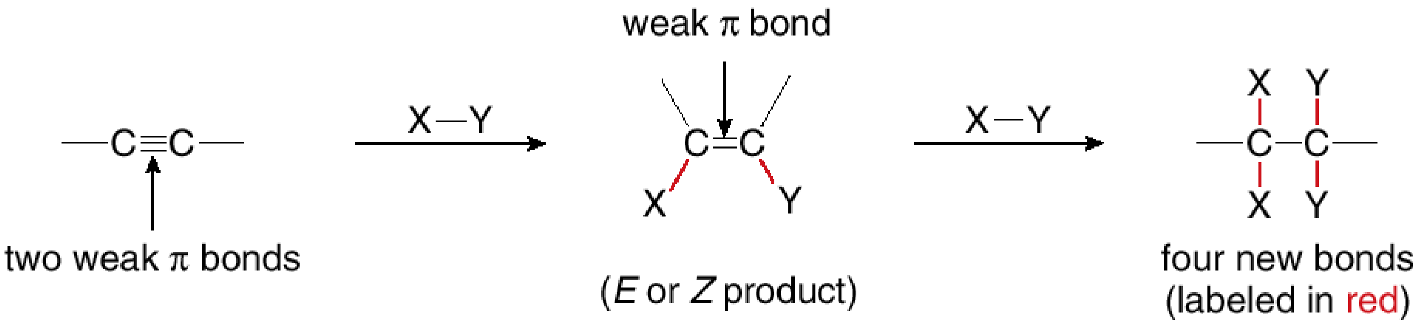
$$\mathrm{RC{\equiv}CH} \xrightarrow{\mathrm{NaNH_2}} \mathrm{RC{\equiv}C^-\ Na^+} \xrightarrow{\mathrm{R'CH_2Br}} \mathrm{RC{\equiv}CCH_2R'}$$

A terminal alkyne **An internal alkyne**

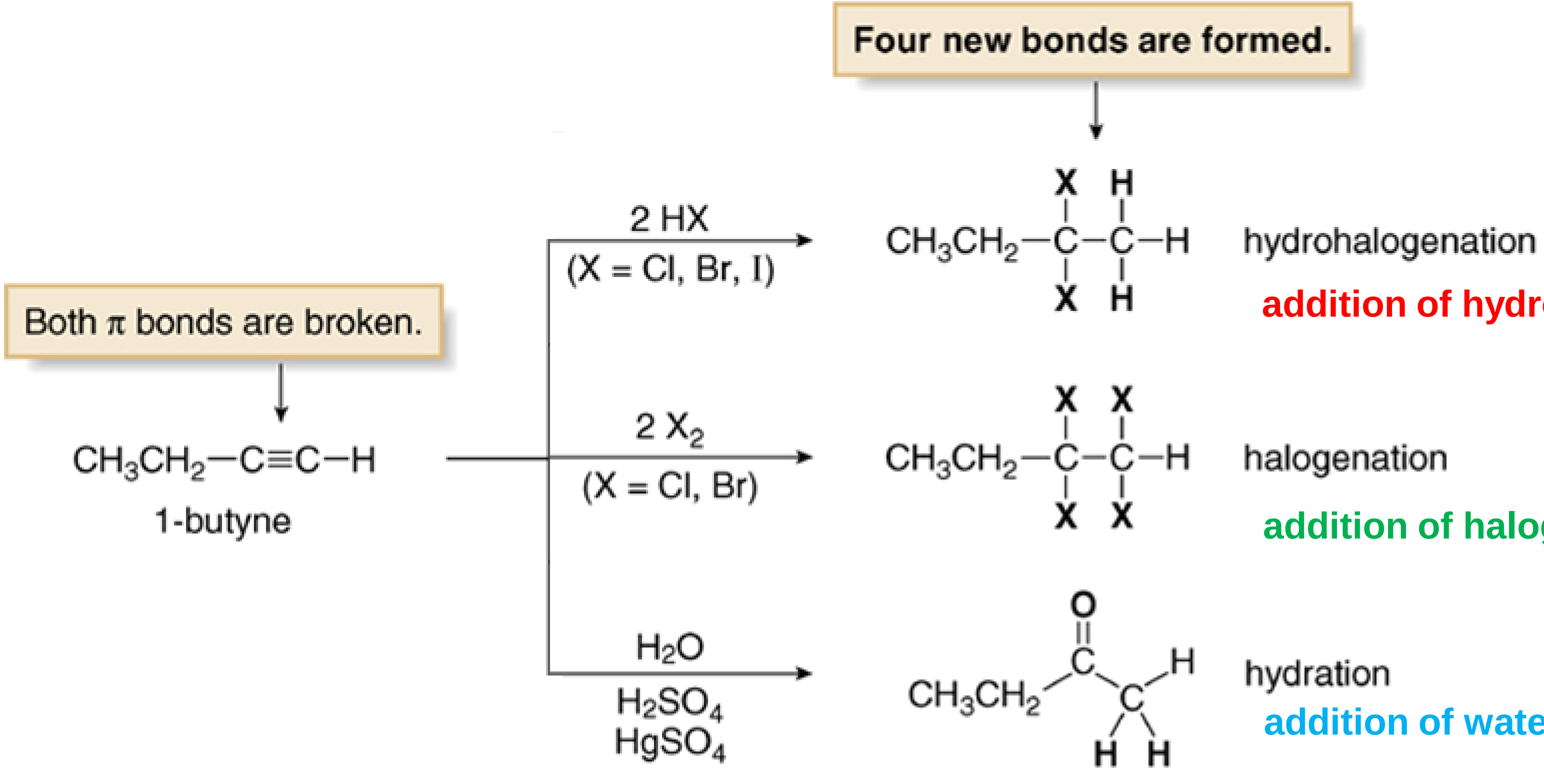
Introduction to Alkyne Reactions—Additions

- Like alkenes, alkynes undergo addition reactions because they contain relatively weak π bonds.
- Two sequential reactions can take place: addition of one equivalent of reagent forms an alkene, which can then add a second equivalent of reagent to yield a product having four new bonds.

Addition reaction



Introduction to Alkyne Reactions—Additions



Four new bonds are formed.

Both π bonds are broken.

$CH_3CH_2-C\equiv C-H$

1-butyne

2 HX

(X = Cl, Br, I)

$2\ X_2$

(X = Cl, Br)

H_2O

H_2SO_4

$HgSO_4$

hydrohalogenation

addition of hydrogen halides

halogenation

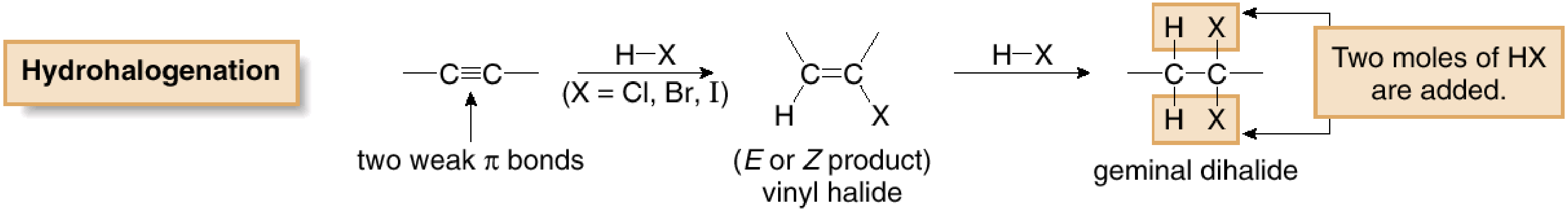
addition of halogens

hydration

addition of water

Hydrohalogenation—Electrophilic Addition of HX

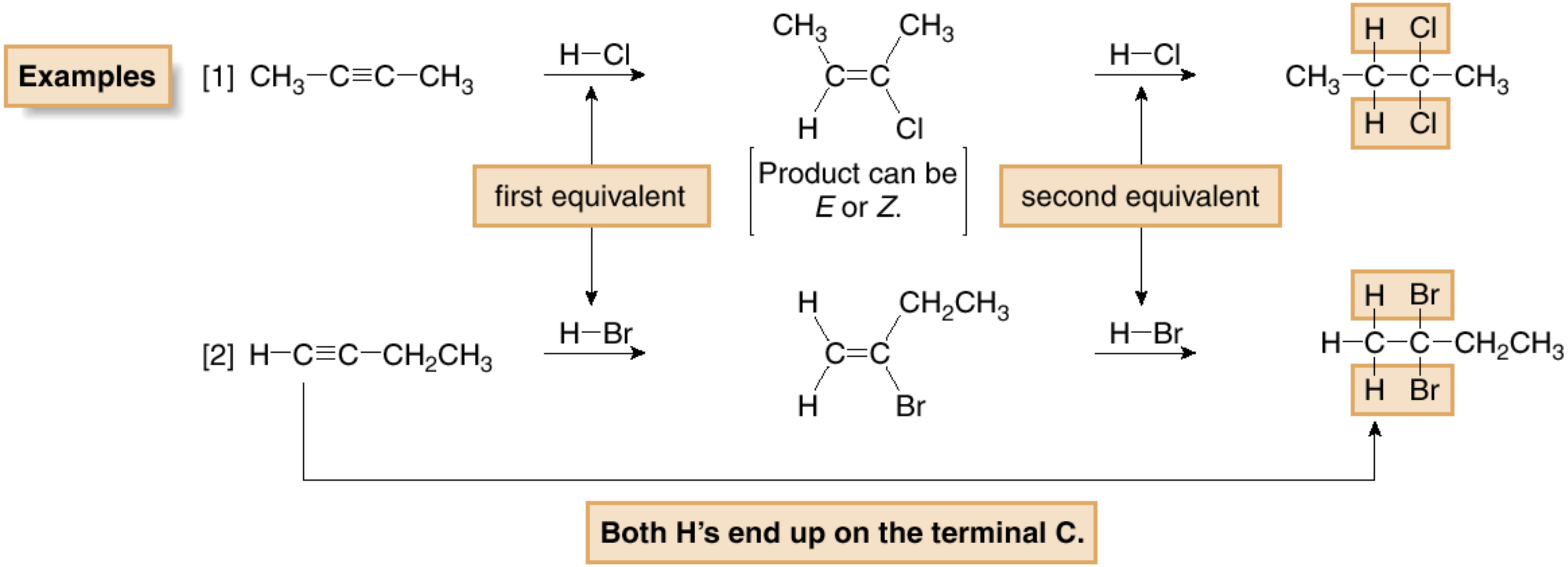
- Alkynes undergo Hydrohalogenation, i.e the addition of hydrogen halides, HX.



- Two equivalents of HX are usually used: addition of one mole forms a vinyl halide, which then reacts with a second mole of HX to form a **geminal dihalide**.

Hydrohalogenation—Electrophilic Addition of HX

- With two equivalents of HX, both H atoms bond to the *same* carbon.
- With a terminal alkyne, both H atoms bond to the *terminal* carbon; that is, the hydrohalogenation of alkynes follows Markovnikov's rule.



Examples

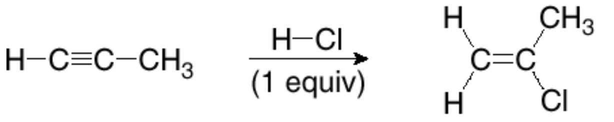
first equivalent

Product can be *E* or *Z*.

second equivalent

Both H's end up on the terminal C.

- With only one equivalent of HX, the reaction stops with formation of the vinyl halide.

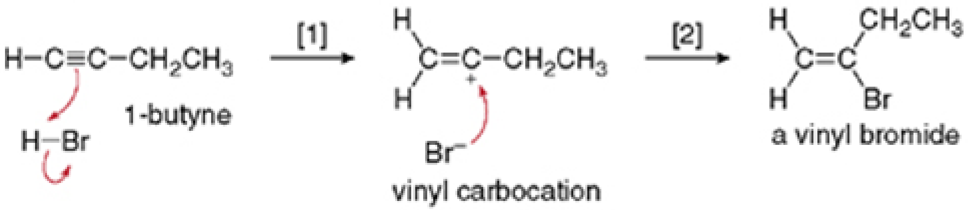


a vinyl chloride
(2-chloropropene)

Hydrohalogenation—Electrophilic Addition of HX

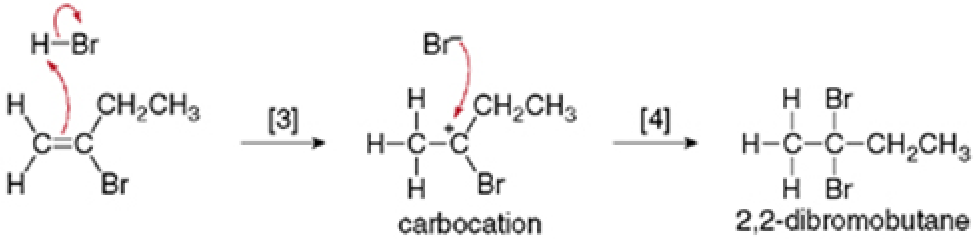
Electrophilic Addition of HX to an Alkyne

Part [1] Addition of HBr to form a vinyl halide



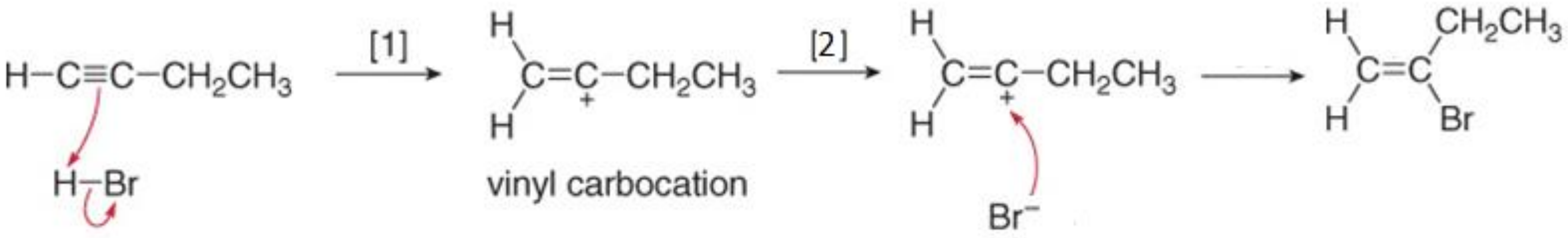
- The π bond attacks the H atom of HBr to form a new C−H bond, generating a **vinyl carbocation.** Addition follows Markovnikov's rule: H^+ adds to the less substituted carbon atom to form the **more substituted, more stable carbocation.** Nucleophilic attack of Br^- then forms a vinyl bromide; one mole of HBr has now been added.

Part [2] Addition of HBr to form a geminal dihalide

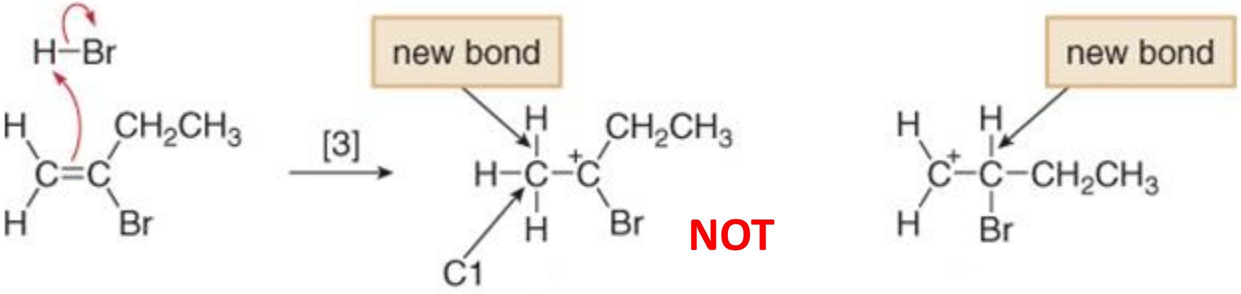


- **The second addition of HBr occurs in the same two-step manner.** Addition of H^+ to the π bond of the vinyl bromide generates a carbocation. Nucleophilic attack of Br^- then forms a geminal dibromide (2,2-dibromobutane), and two moles of HBr have now been added.

- Electrophilic addition of HX to alkynes is slower than electrophilic addition of HX to alkenes, even though alkynes are more polarizable and have more loosely held π electrons than alkenes.



- Markovnikov addition in step [3] places the H on the terminal carbon to form the more substituted carbocation A, rather than the less substituted carbocation B.



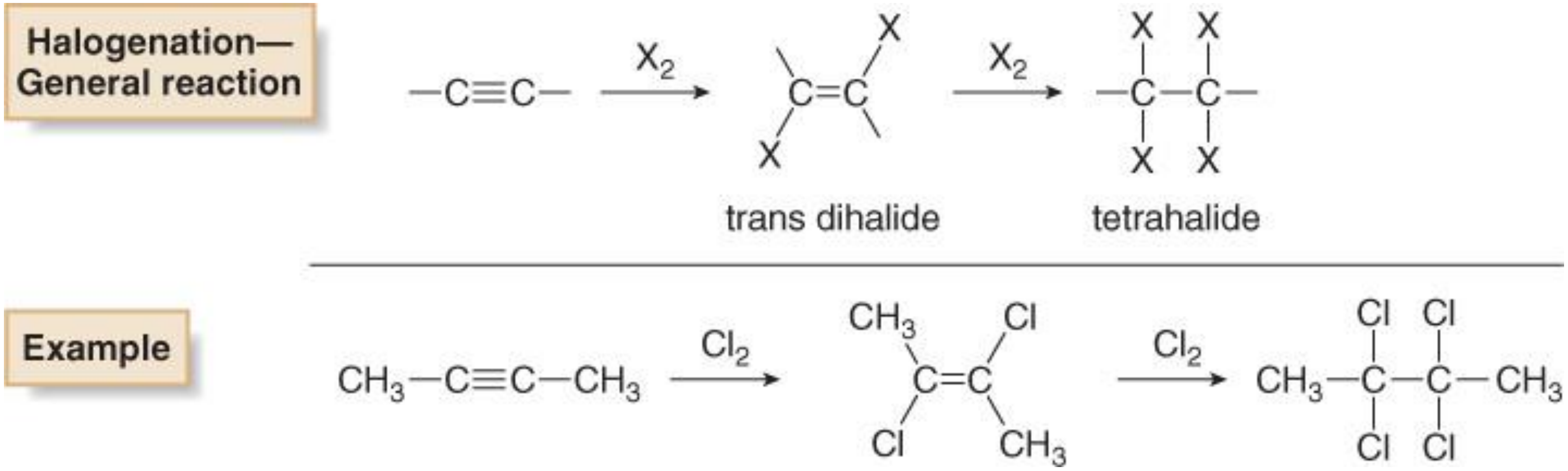
more stable carbocation

A

B

Halogenation—Addition of Halogen

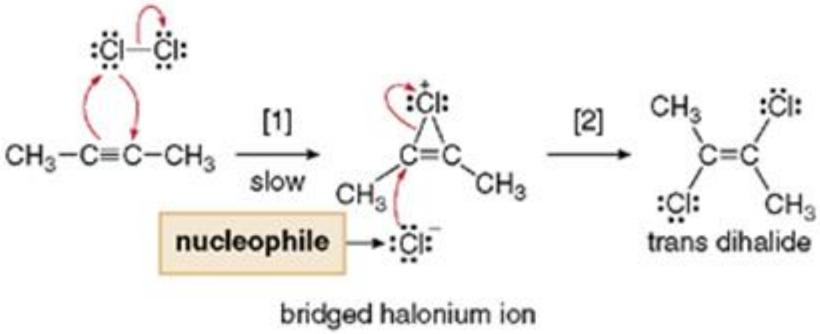
- Halogens X_2 (X = Cl or Br) add to alkynes just as they do to alkenes. Addition of one mole of X_2 forms a trans dihalide, which can then react with a second mole of X_2 to yield a tetrahalide.



Halogenation—Addition of Halogen

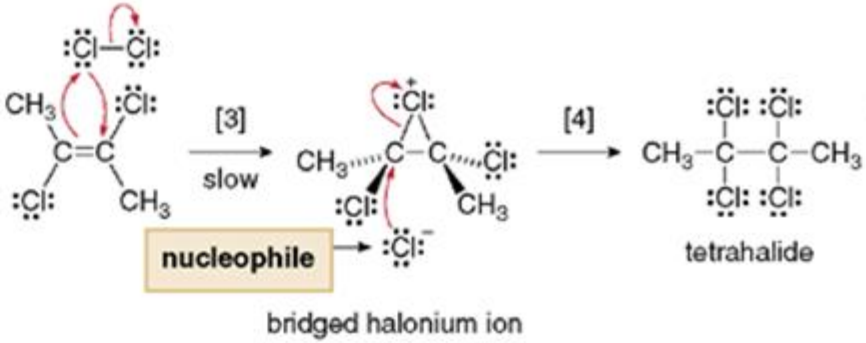
Addition of X_2 to an Alkyne—Halogenation

Part [1] Addition of X_2 to form a trans dihalide



- Two bonds are broken and two are formed in Step [1] to generate a **bridged halonium ion.** This strained three-membered ring is highly unstable, making it amenable to opening of the ring in the second step.
- Nucleophilic attack by Cl^- from the back side forms the trans dihalide in Step [2].

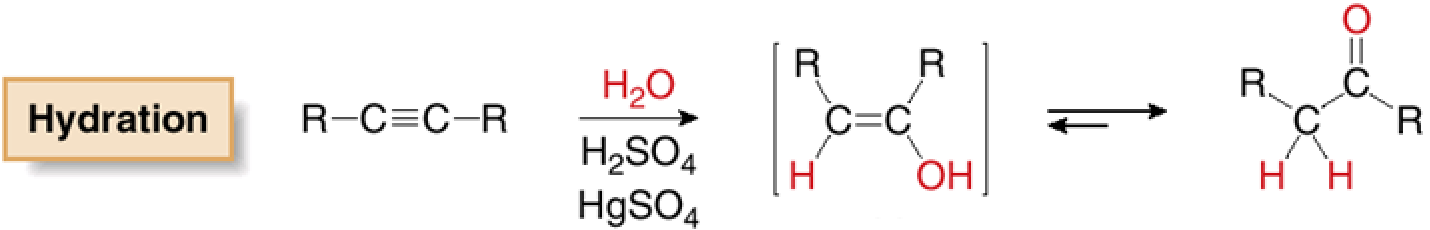
Part [2] Addition of X_2 to form a tetrahalide



- **Electrophilic addition** of Cl^+ in Step [3] forms the bridged halonium ion ring, which is opened with Cl^- to form the tetrahalide in Step [4].

Hydration—Electrophilic Addition of Water

- In the presence of strong acid or Hg^{2+} catalyst, the elements of H_2O add to the triple bond, but the initial addition product, an **enol**, is unstable and **rearranges** to a product containing a carbonyl group—that is, a C=O. A carbonyl compound having two alkyl groups bonded to the C=O carbon is called a **keto**ne.



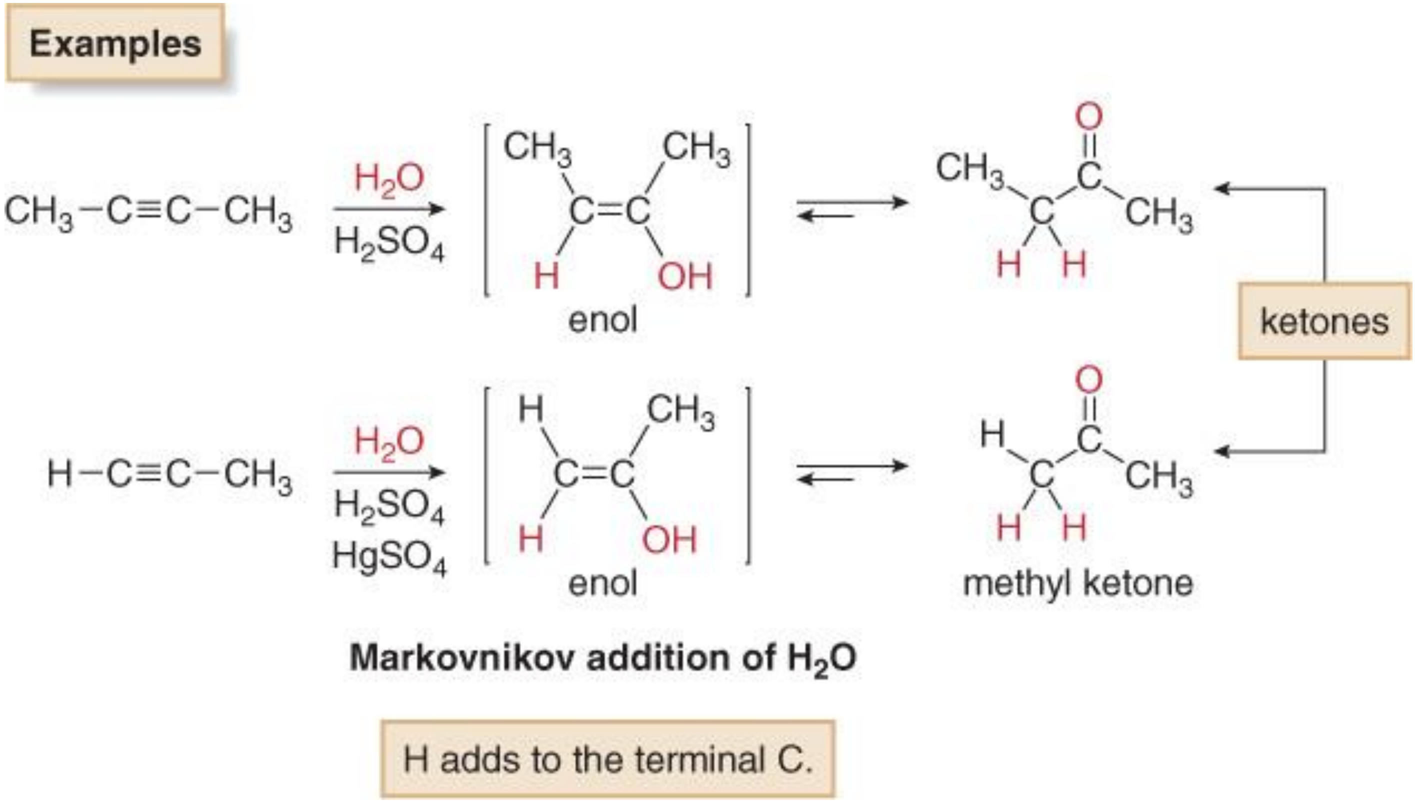
less stable enol

ketone

H_2O has been added

Hydration—Electrophilic Addition of Water

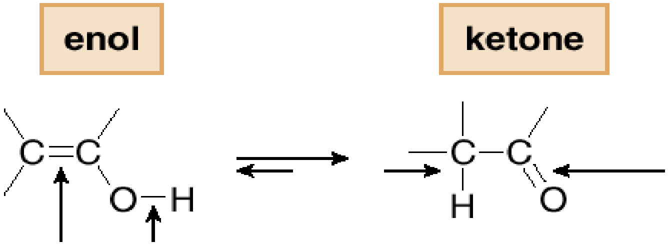
- **Internal alkynes undergo hydration with concentrated acid, whereas terminal alkynes require the presence of an additional Hg^{2+} catalyst—usually $HgSO_4$—to yield methyl ketones by Markovnikov addition of water.**



Hydration—Electrophilic Addition of Water

- Consider the conversion of a general enol A to the carbonyl compound B. A and B are **tautomer**: A is the **enol form** and B is the **keto form** of the tautomer.

- *Tautomers* are constitutional isomers that differ in the location of a double bond and a hydrogen atom. Two tautomers are in equilibrium with each other.



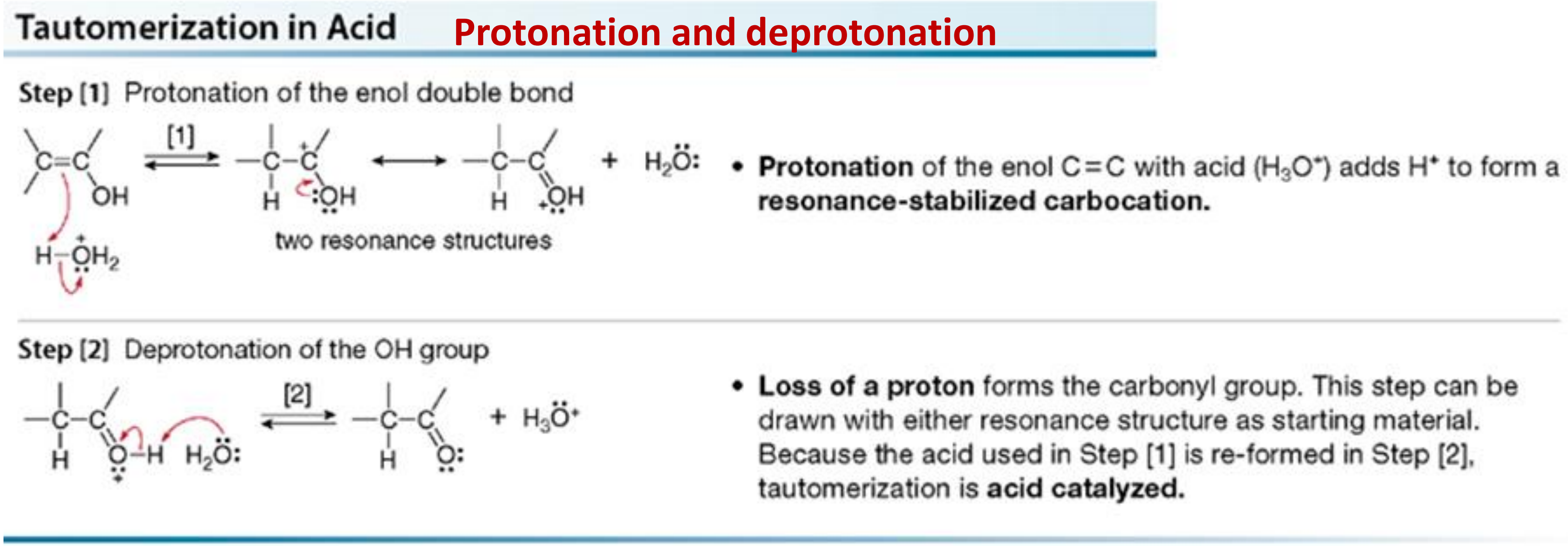
enol form
A

keto form
B

- An enol tautomer has an O–H group bonded to a C=C.
- A keto tautomer has a C=O and an additional C–H bond.

- Equilibrium favors the keto form largely because the C=O is much stronger than a C=C. **Tautomerization**, the process of converting one tautomer into another, is catalyzed by both acid and base.

Hydration—Electrophilic Addition of Water



Tautomerization in Acid

Protonation and deprotonation

Step [1] Protonation of the enol double bond

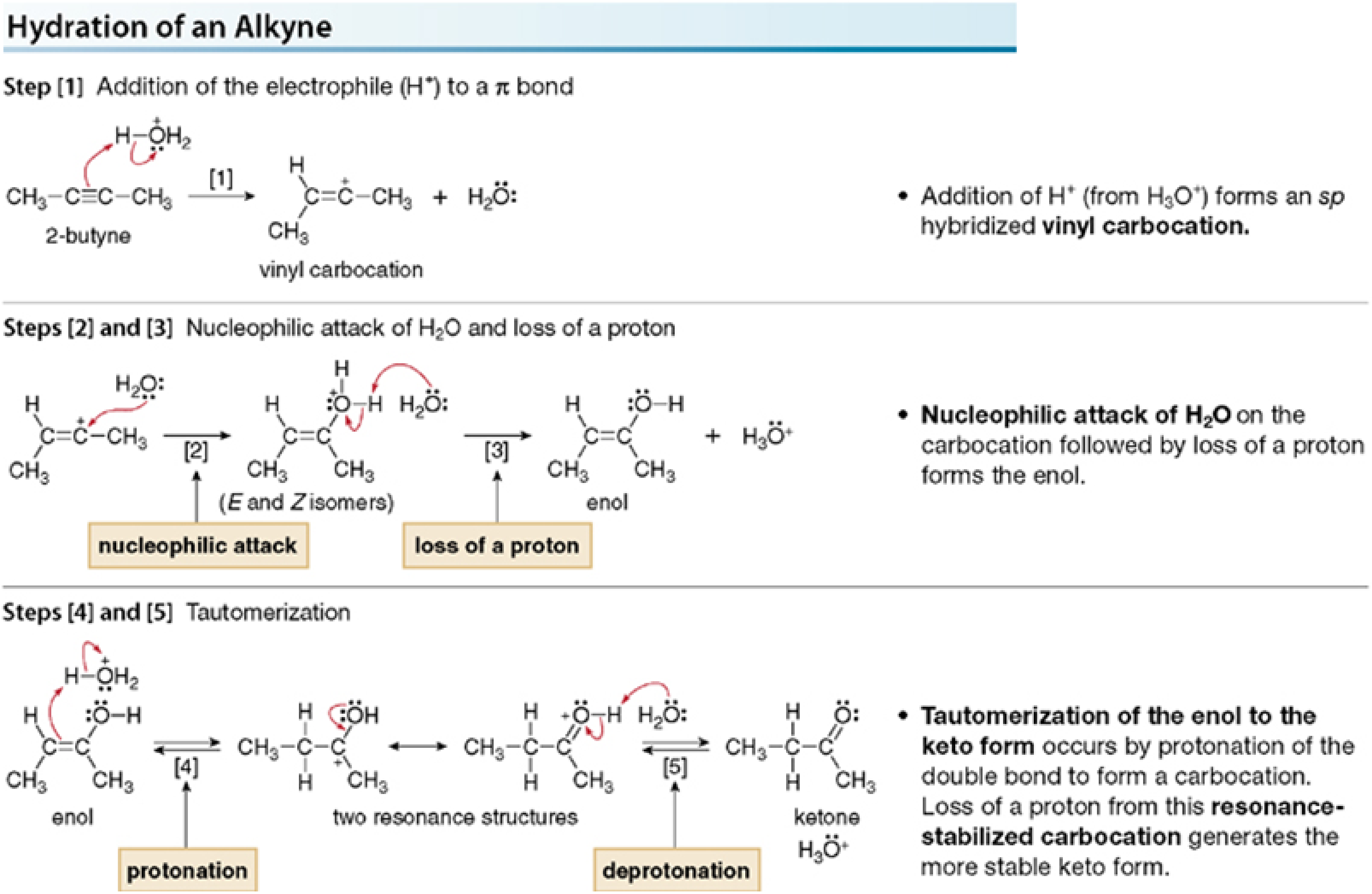
two resonance structures

- **Protonation** of the enol C=C with acid (H_3O^+) adds H^+ to form a **resonance-stabilized carbocation.**

Step [2] Deprotonation of the OH group

- **Loss of a proton** forms the carbonyl group. This step can be drawn with either resonance structure as starting material. Because the acid used in Step [1] is re-formed in Step [2], tautomerization is **acid catalyzed.**

Hydration—Electrophilic Addition of Water



Hydration of an Alkyne

Step [1] Addition of the electrophile (H^+) to a π bond

- Addition of H^+ (from H_3O^+) forms an *sp* hybridized **vinyl carbocation.**

Steps [2] and [3] Nucleophilic attack of H_2O and loss of a proton

- **Nucleophilic attack of H_2O** on the carbocation followed by loss of a proton forms the enol.

Steps [4] and [5] Tautomerization

- **Tautomerization of the enol to the keto form** occurs by protonation of the double bond to form a carbocation. Loss of a proton from this **resonance-stabilized carbocation** generates the more stable keto form.

CALCULATING DEGREE OF UNSATURATION

$$\boxed{DBU = C - H/2 + 1}$$

OR

$$C_cH_hN_nO_oX_x$$

$$DBU = \frac{(2c + 2) - (h - n + x)}{2}$$

- 1° unsaturation = 1 $C=C$ or 1 ring
- 2° unsaturation = 2 $C=C$, 2 rings, or $C\equiv C$, or combination of $C=C$ & rings
- 3° unsaturation = combination of double bonds, triple bonds, rings
- 4° unsaturation = typically indicates an aromatic ring

Summary

The degree of unsaturation can be calculated readily from the molecular formula of all compounds containing carbon, hydrogen, oxygen, nitrogen, sulphur, or the halogens, by applying the following rules:

Rule 1: Replace all halogens in the molecular formula by hydrogens.

Rule 2: Omit oxygen and sulphurs.

Rule 3: For each nitrogen, omit the nitrogen and one hydrogen.