

# Alkenes and Alkynes

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# ALKENES

- ❖ Organic compounds containing at least one carbon-carbon double bond(C=C)in their chemical structure.
- ❖ They are interchangeably known as olefins.
- ❖ Alkenes are class of unsaturated hydrocarbons.
- ❖ General formula,  $C_nH_{2n}$  (n=2,3,...)
- ❖ Carbon is **sp<sup>2</sup>-hybridized**
- ❖ For example:  
 $C_2H_4$  – ethylene,  $CH_2=CH_2$

# PHYSICAL PROPERTIES OF ALKENES

## *Boiling points and densities:*

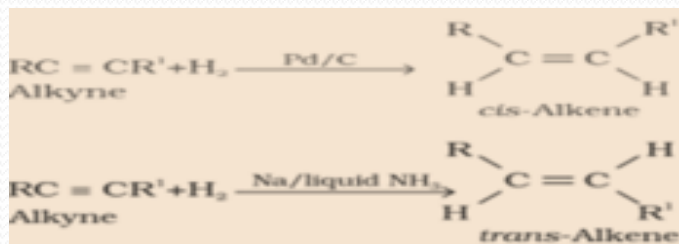
- Most physical properties of alkenes are similar to those alkanes.
- Example: the boiling points of 1-butene, *cis*-2-butene, *trans*-2-butene and *n*-butane are close to 0°C.
- Densities of alkenes: around 0.6 or 0.7 g/cm<sup>3</sup>.
- Boiling points of alkenes increase smoothly with molecular weight.
- Increased branching leads to greater volatility and lower boiling points.

# *Polarity*

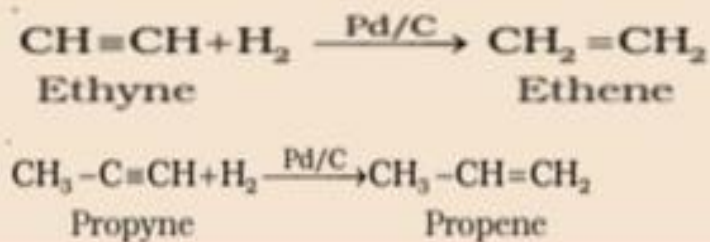
- Relatively nonpolar.
- Insoluble in water but soluble in non-polar solvents such as hexane, gasoline, halogenated solvents and ethers.
- Slightly more polar than alkanes because:
  - i) electrons in the pi bond is more polarizable (contributing to instantaneous dipole moments).
  - ii) the vinylic bonds tend to be slightly polar (contributing to a permanent dipole moment).

## Partial Hydrogenation of Alkynes

Alkynes undergo partial reduction to produce alkenes. The reaction takes place in the presence of palladised charcoal that has been deactivated with poisonous compounds such as quinolone or sulfur compounds, also known as **Lindlar's catalyst**. The reaction leads to the formation of compounds having **cis-alkenes**. However, if the same alkynes reduction takes place with sodium present in liquid ammonia, the resultant product will be **trans alkenes**.



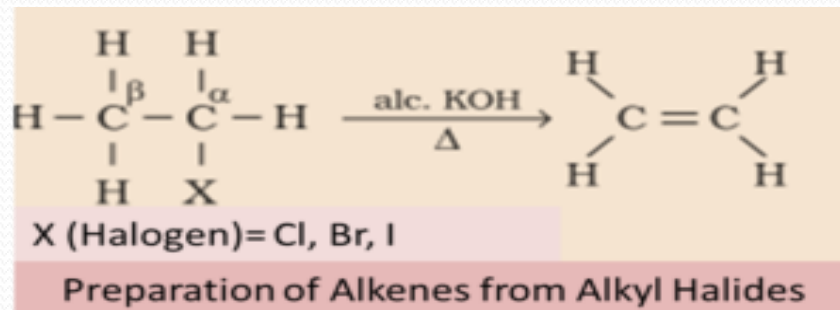
Method of Alkenes Preparation from Alkynes



Example of Alkenes from Alkynes

## Dehydrohalogenation of Alkyl Halides

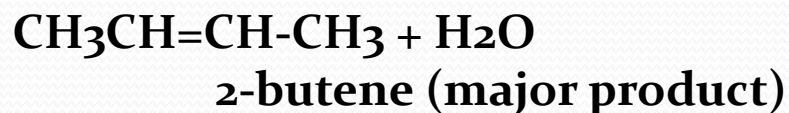
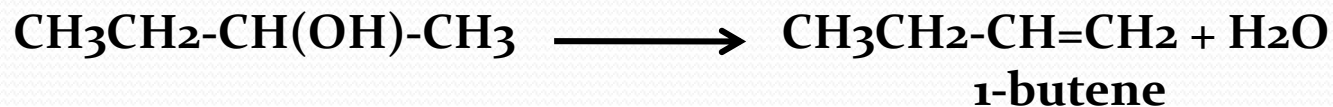
R-X or Alkyl Halides undergo heating with alcoholic potash to form alkenes. Dissolving potassium hydroxide in an alcohol such as ethanol leads to the formation of alcoholic potash. In this reaction, the heating of alkyl halides with alcoholic potash will remove one molecule from halogen acid leading to the formation of alkenes. Thus, it is a  $\beta$ -elimination reaction example because removal of hydrogen atom takes place from the  $\beta$  carbon atom.



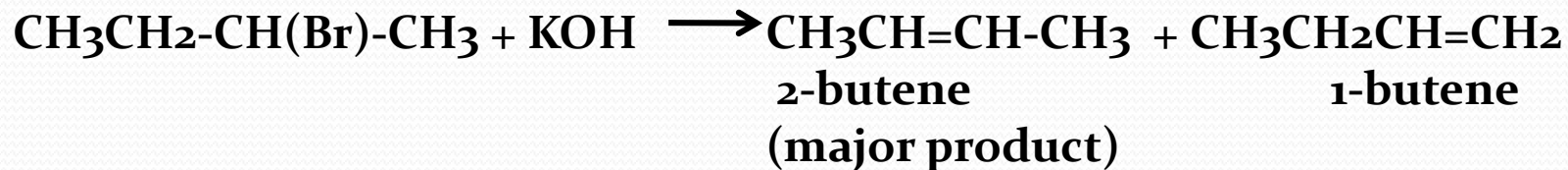
## ***Saytzeff rule:***

A reaction that produces an alkene would favour the formation of an alkene that has the greatest number of substituents attached to the C=C group.

### **Dehydration of alcohols**

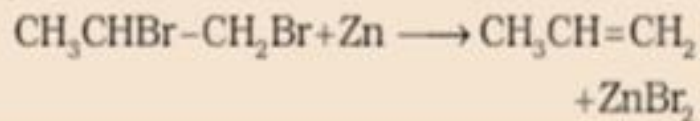
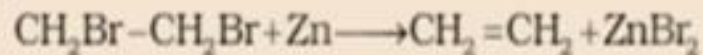


### **Dehydrohalogenation of haloalkanes**



# Dehalogenation of Vicinal Dihalides

Vicinal halides are compounds containing two halogen atoms present on two adjacent carbon atoms. Vicinal dihalides undergo treatment with zinc metal to form an alkene. The treatment of vicinal dihalides with zinc metal will help in removal of a molecule from  $ZnX_2$  thereby resulting in the formation of the alkene.

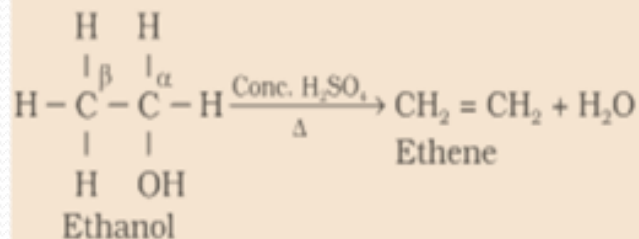


Examples of Preparation of Alkenes from Vicinal Dihalides



# Dehydration of Alcohols

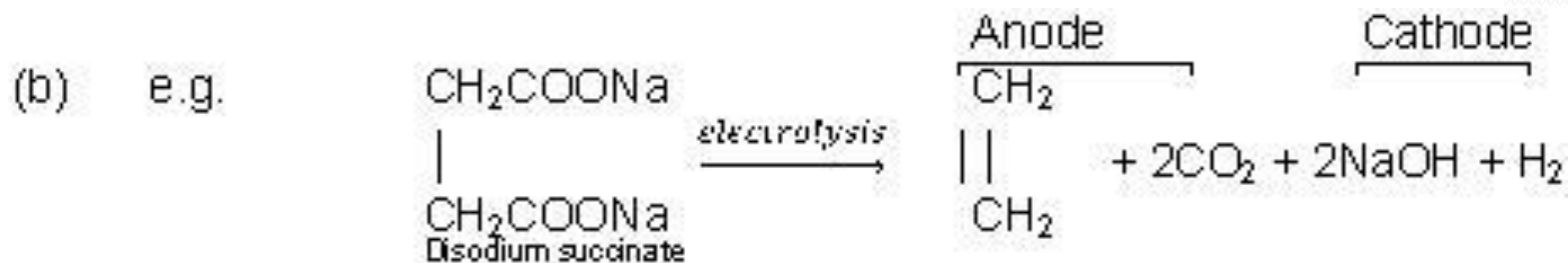
Alcohol reacts with the concentrated sulphuric acid upon heating to form alkenes. The reaction is an example of acidic dehydration of alcohols because the reaction results in the elimination of a water molecule in the presence of an acid. The reaction is also a  $\beta$ -elimination reaction because the functional group of alcohol (-OH) eliminates extracts one hydrogen atom from  $\beta$ -carbon atom.



Alkenes Preparation from Acidic Dehydration

# Kolbe's Electrolysis

Electrolysis of aqueous solutions of sodium or potassium salts of saturated dicarboxylic acids gives alkene.



# Chemical Properties of Alkenes

Alkenes are unsaturated compounds, which makes them highly reactive. Most of these chemical reactions occur at the Carbon-Carbon double bonds. This makes alkenes far more reactive than alkanes. Alkenes undergo three types of main reactions, which are as follows

## Addition Reactions

**Addition of Hydrogen:** In the presence of nickel or platinum alkenes will react to add to its molecular chain one diatomic molecule hydrogen to form alkanes. This reaction is called Hydrogenation.

## **Addition of Halogens:**

Halogens will react with alkenes to form vicinal dihalides. Iodine will not react with alkenes. But Bromine reacts with alkenes and will attach at the unsaturated site. In fact, the reaction is used to as proof of unsaturation.



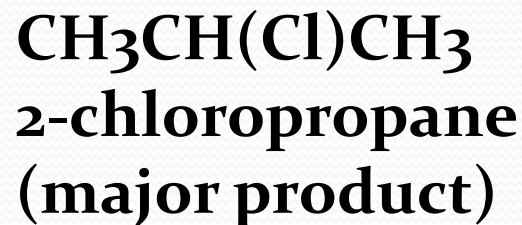
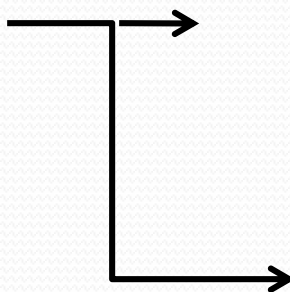
## **Addition of Water:**

According to the Markovnikov rule, water will react with an alkene to form alcohols. This happens in the presence of sulphuric acid.

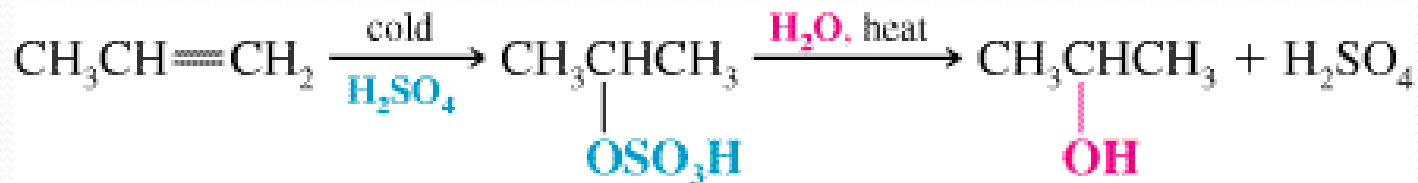
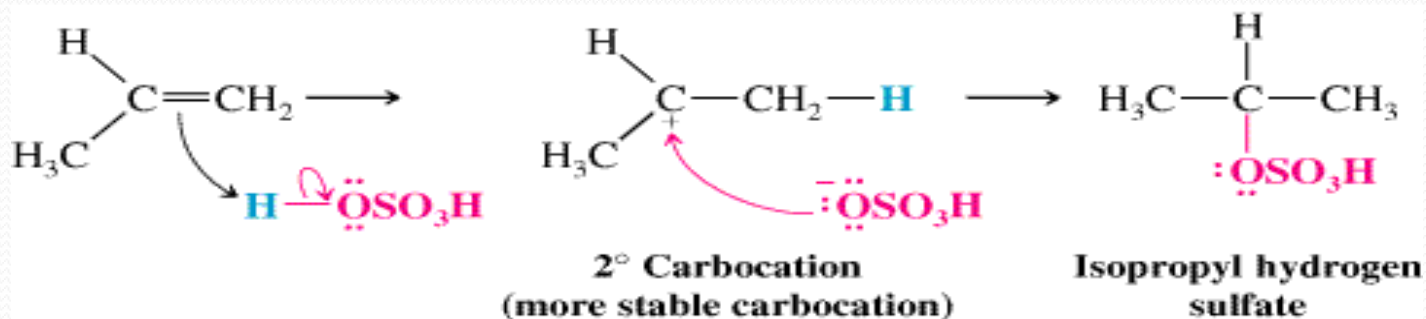
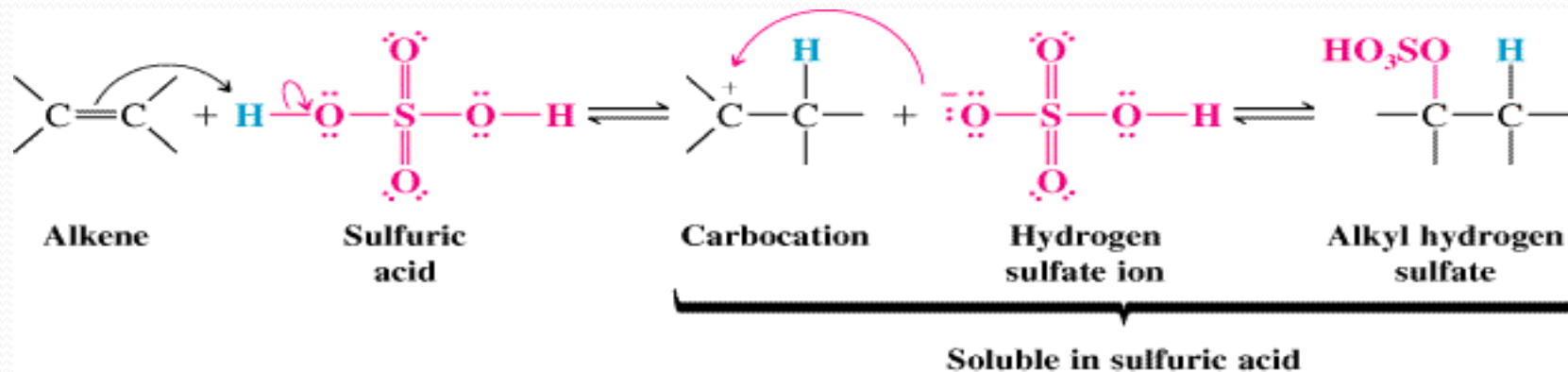


## ADDITION OF HYDROGEN HALIDES TO UN-SYMMETRICAL ALKENES & MARKOVNIKOV'S RULE

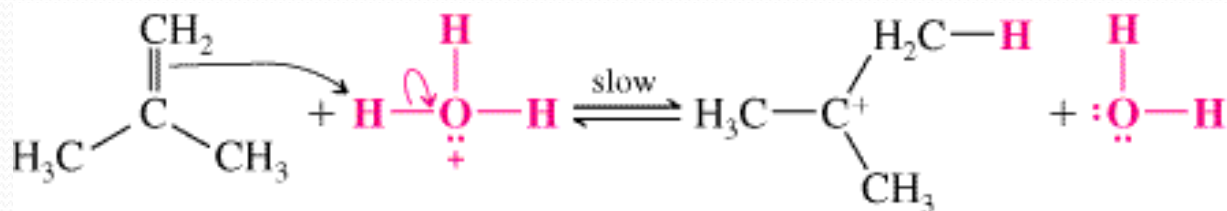
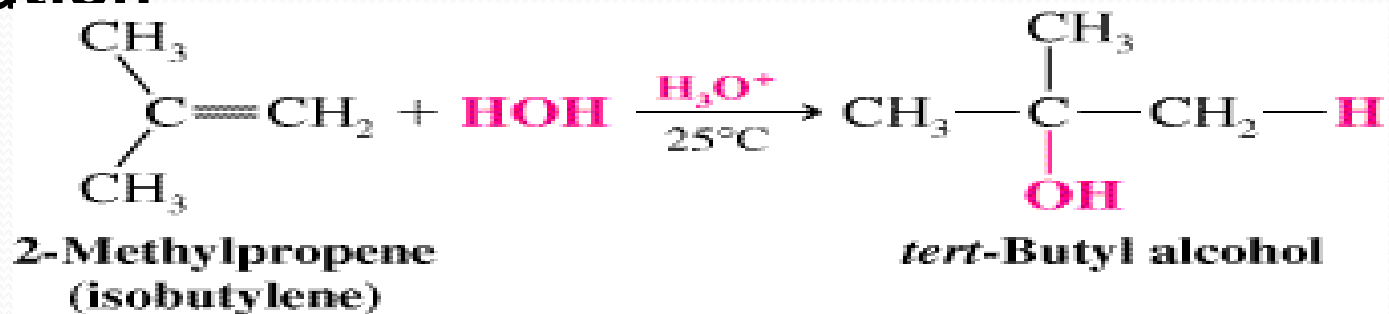
The addition of HX to an unsymmetrical alkene, the hydrogen atom attaches itself to the carbon atom (of the double bond) with the larger number of hydrogen atoms.



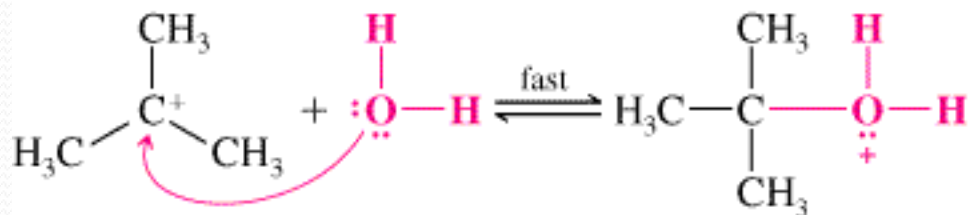
# Addition of Sulfuric Acid to Alkenes



# Addition of Water to Alkenes: Acid-Catalyzed Hydration

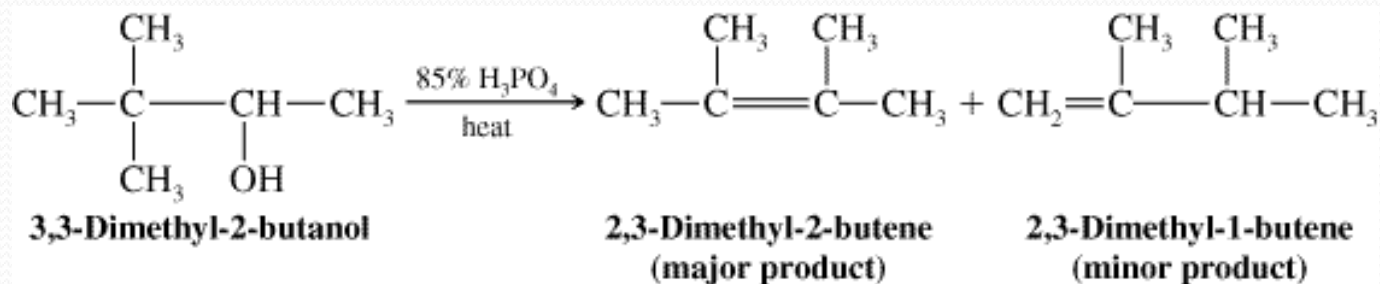
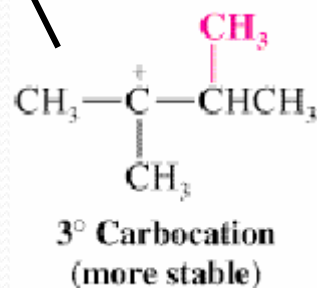
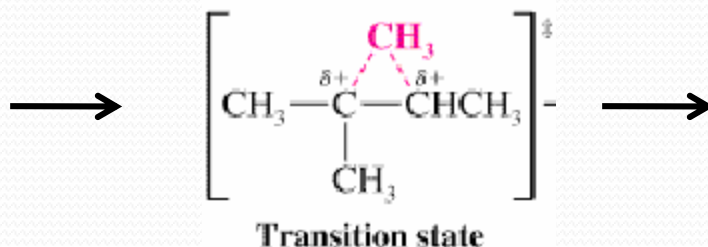
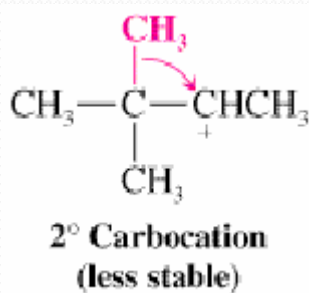
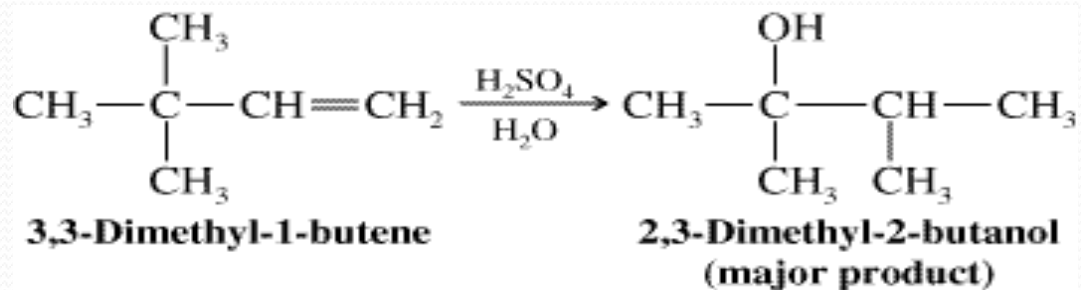


The alkene donates an electron pair to a proton to form the more stable 3° carbocation.



The carbocation reacts with a molecule of water to form a protonated alcohol.

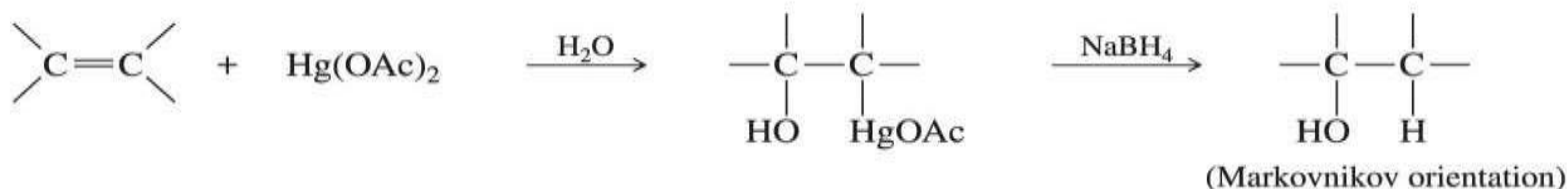
# Addition of Water to Alkenes: Rearrangement



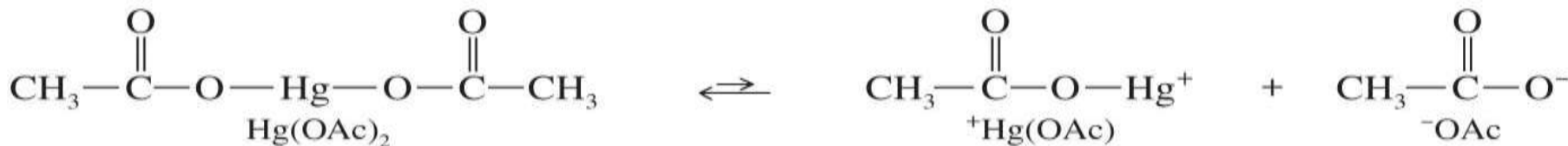


# Oxymercuration-Demercuration

This is another alternative for converting alkenes to alcohols with Markovnikov orientation. This method has the advantage of not involving free carbocationic species, and thus removes the possibility of rearrangements.

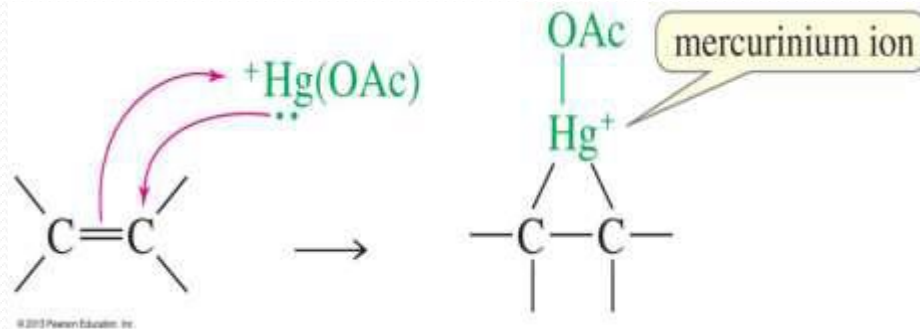


The reagent is called mercuric acetate, and is usually abbreviated to  $\text{Hg}(\text{OAc})_2$ . In solution it ionizes into acetate ion and a positively charged mercury species which is very electrophilic.



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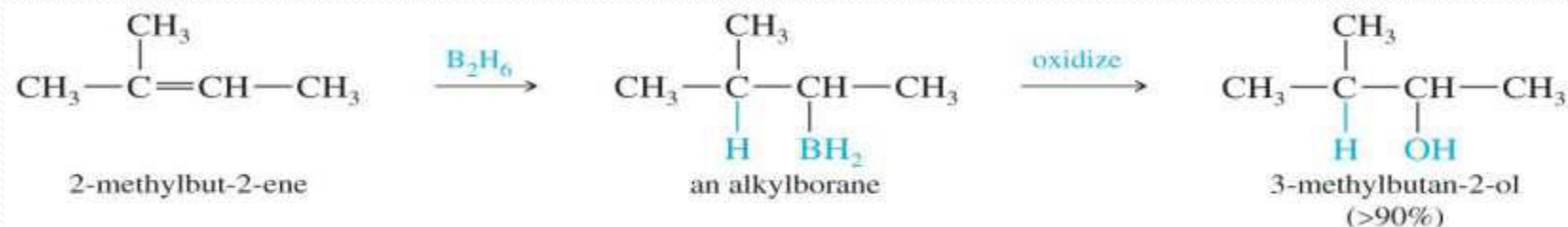
*Oxymercuration is the electrophilic attack of this species on a double bond, giving a 3 membered ring compound called a mercurinium ion. Oxymercuration-demercuration also gives Markovnikov orientation of the alcohol.*



# Hydroboration of Alkenes

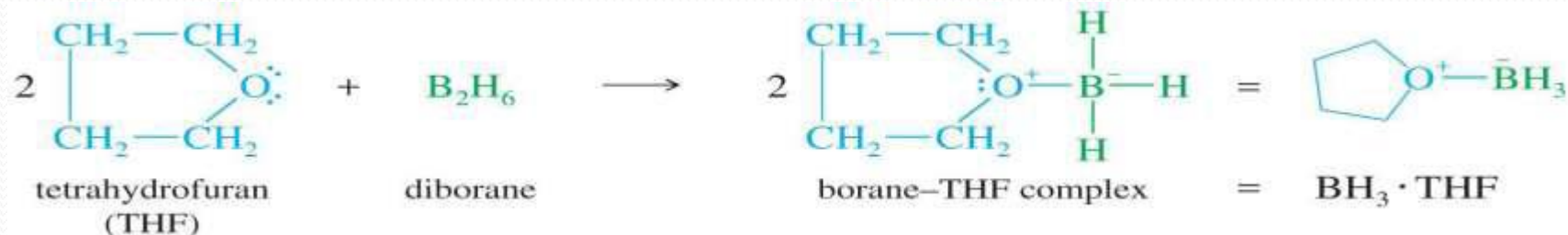
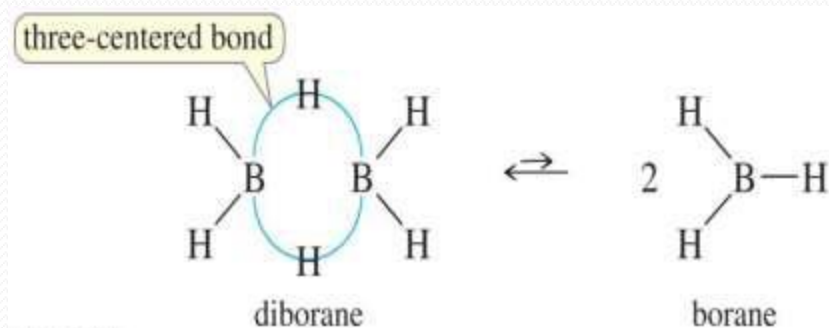
We have studied three ways of hydrating alkenes to give Markovnikov orientated alcohols.

There is also a way to obtain anti-Markovnikov oriented alcohols:



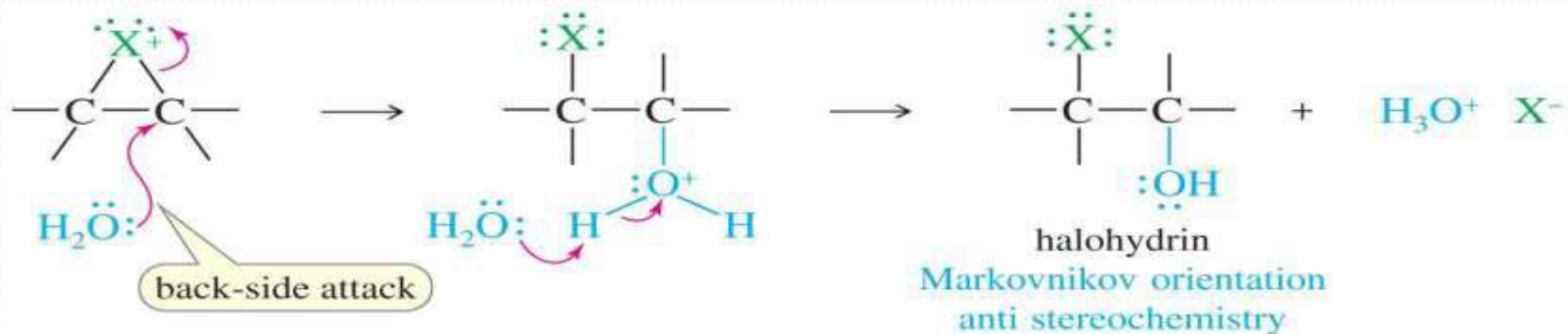
Borane adds to alkenes with anti-Markovnikov orientation, and these alkyl boranes can then be oxidized to alcohols.

Borane (BH<sub>3</sub>) itself is unstable, and exists either as a dimer or as a complex with THF.

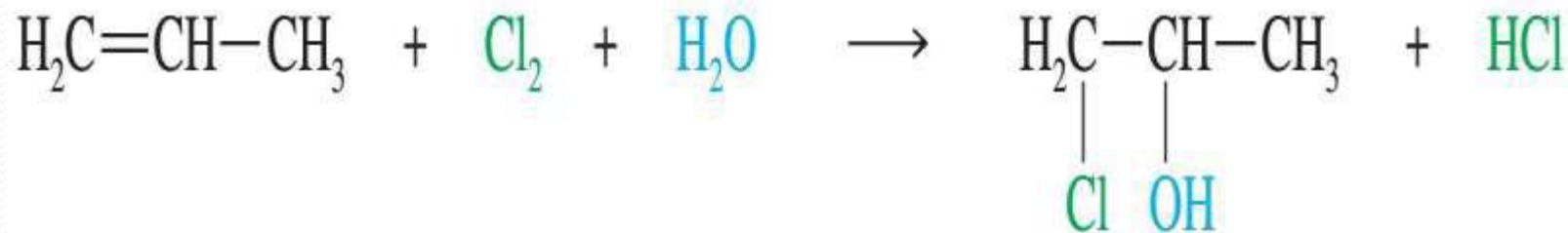


# Halohydrin Formation

When the halogenation reaction takes place in the presence of a nucleophilic solvent, a nucleophile **different from the halide** can open the halonium ring.

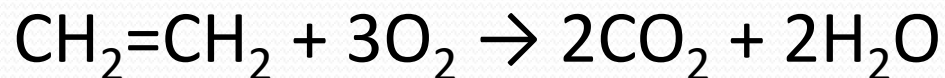


If the reaction is performed in the presence of water, **Halohydrins are produced**. The stereochemistry of the intermediate bromonium ring determines that the final product must be of **anti addition, since ring opening must occur via backside attack**. When propene reacts with chlorine water, the major product has the Cl bound to the less highly substituted carbon, and hydroxyl to the most highly substituted carbon



## Oxidation Reactions

- **Combustion Reaction:** The combustion of alkenes is very exothermic, it will give out huge amounts of thermal energy. A practical example of this reaction is seen in welding of metals. It is known as oxy-ethylene welding.



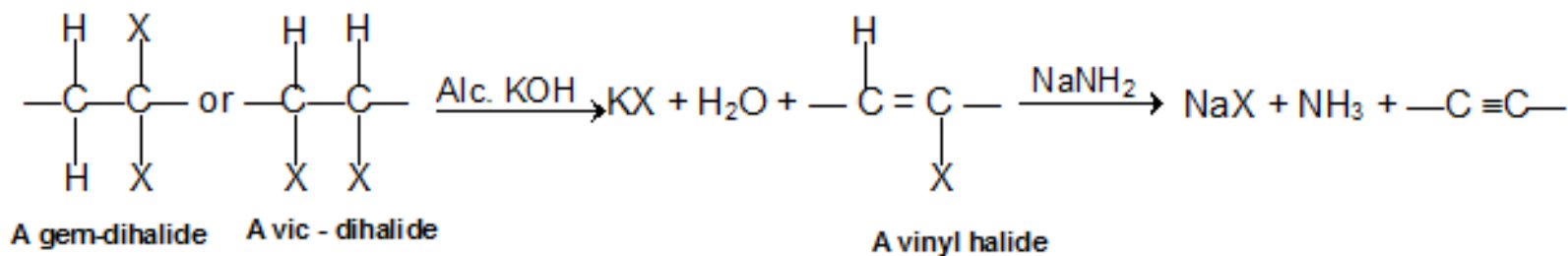
- **Oxidation by Pottasium Permanganate:** When alkenes are reacted with cold dilute  $\text{KMnO}_4$  also known as Baeyer's reagent, it forms vicinal glycols. It will also decolourize the pink colour of  $\text{KMnO}_4$ . So it is used for testing unsaturation in compounds.

# • Preparation of Alkynes:

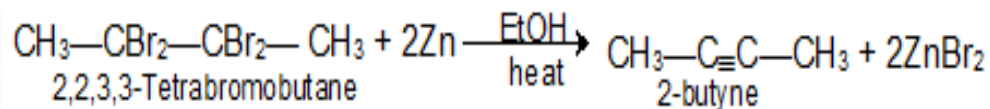
## Laboratory Methods

### Dehydrohalogenation of vic-Dihalides or gem-Dihalides

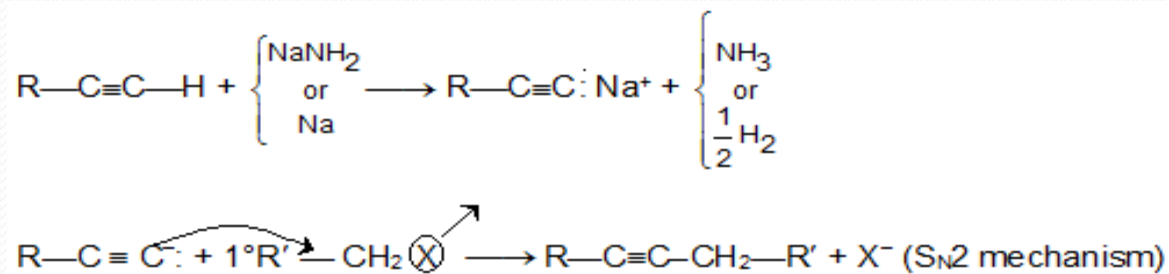
Alkynes are prepared by elimination reactions. A strong base removes two equivalents of HX from a vicinal or geminal dihalide to yield an alkyne through two successive E<sub>2</sub> elimination reactions.



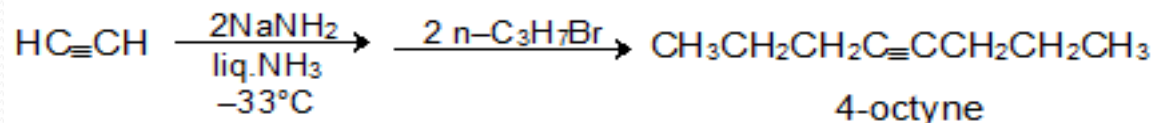
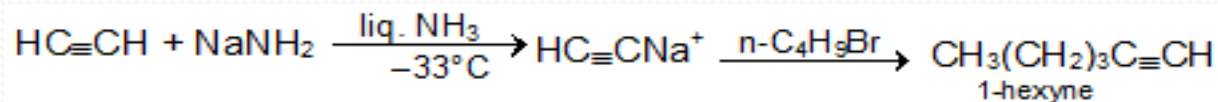
### Dehalogenation of vic-Tetrahalogen Compounds



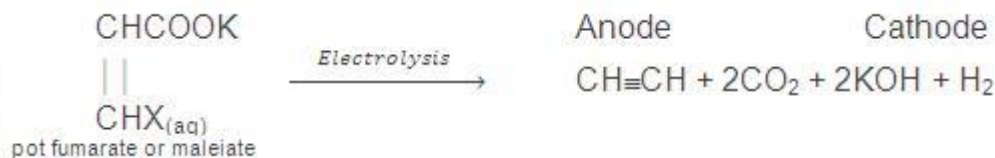
## Alkyl Substitution in Acetylene



There is a fair amount of variety possible using this method. Acetylene itself may be alkylated either once to make a terminal alkyne or twice to make an internal alkyne.



## By Kolbe's electrolytic method

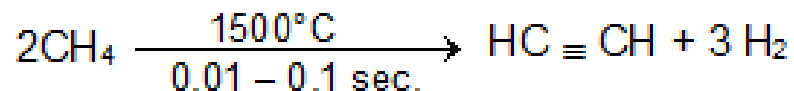


### Industrial Preparation

Acetylene itself is formed from the reaction of the inorganic compound calcium carbide with water.



The reaction is endothermic at room temperatures, but is favored at high temperatures. This method was once an important industrial process. However, the method has now been replaced by a process in which  $\text{CH}_4$  is pyrolyzed in a flow system with short contact time.



# Physical Properties of Alkynes

The properties of alkynes pretty much follow the same pattern of those of alkanes and alkenes.

Alkynes are unsaturated hydrocarbon with a triple bond.

All alkynes are odourless and colourless with the exception of ethylene which has a slight distinctive odour.

The first three alkynes are gases, and the next eight are liquids. All alkynes higher than these eleven are solids

Alkynes are slightly polar in nature.

The B.P and M.P of alkynes increases as their molecular structure grows bigger. The B.P increases with increase in their molecular mass

B.P of alkynes are slightly higher than those of their corresponding alkenes, due to the one extra bond at the carbon site.

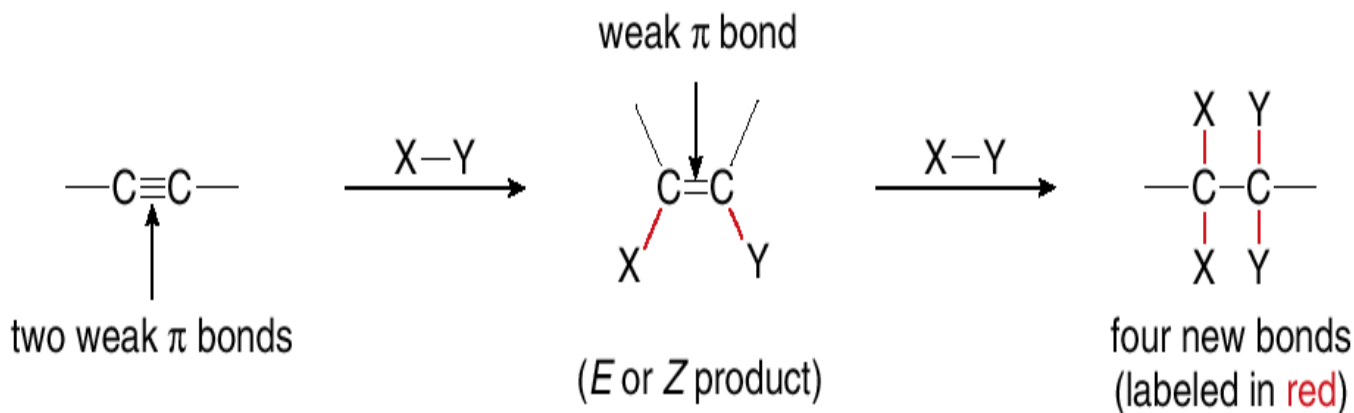


# Addition Reactions

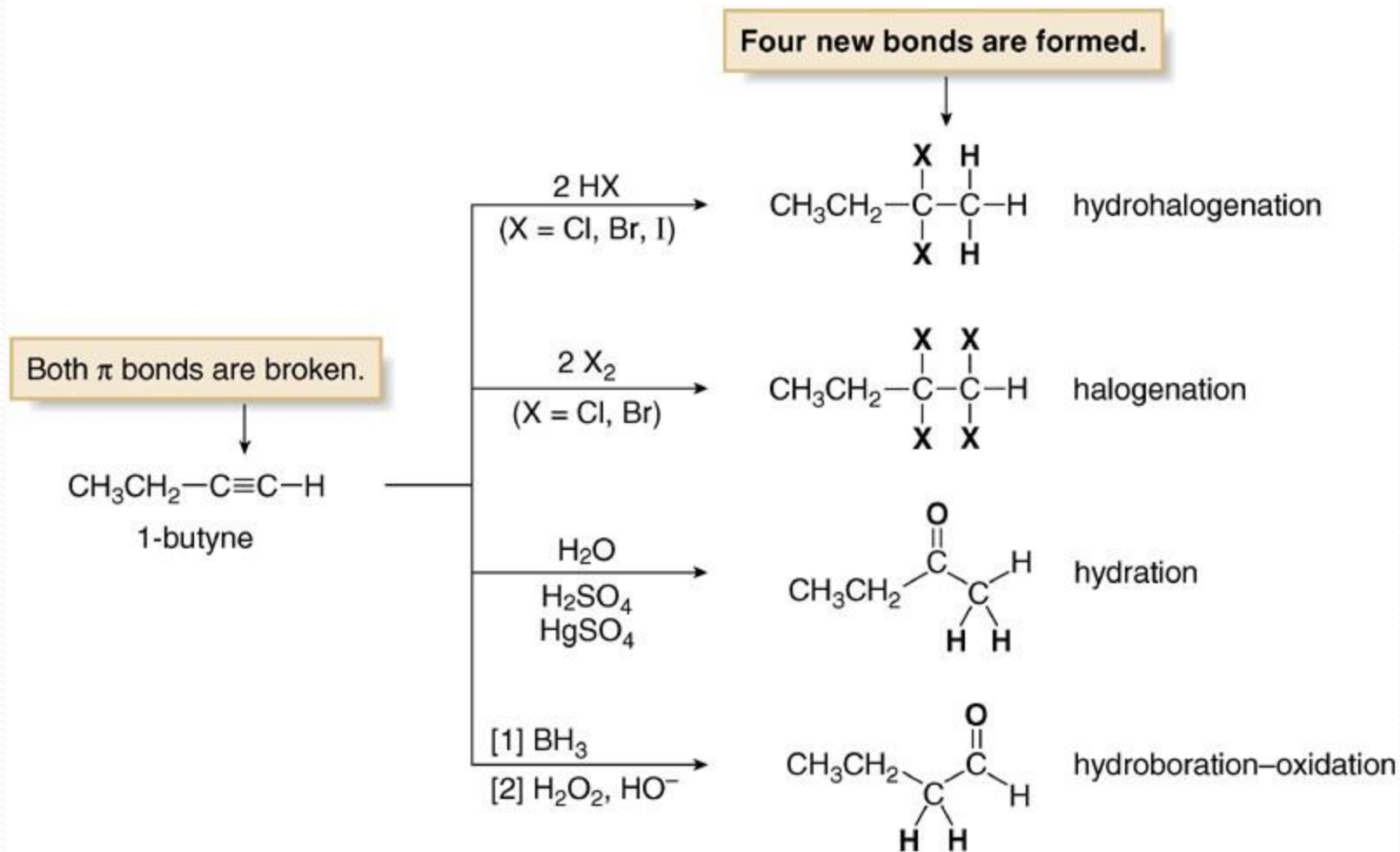
Like alkenes, alkynes undergo addition reactions because they contain relatively weak pi bonds.

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



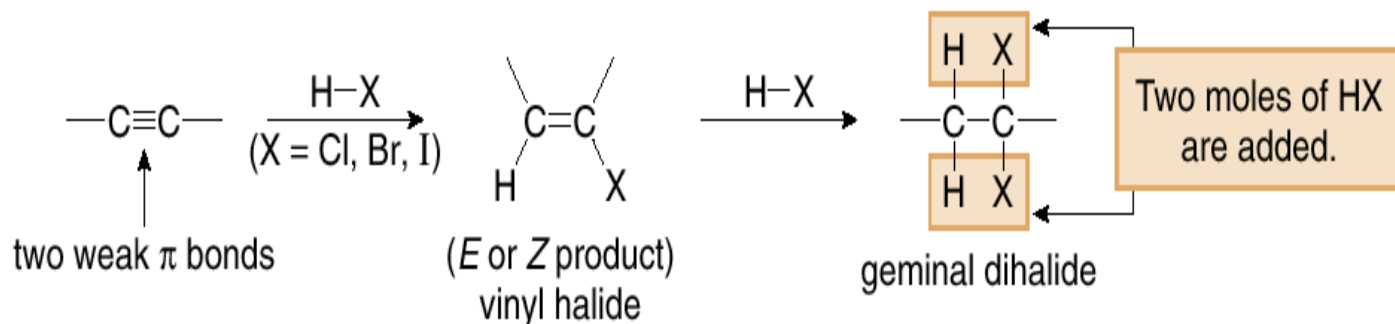
# Four addition reactions of 1-butyne



# Hydrohalogenation Electrophilic Addition of HX

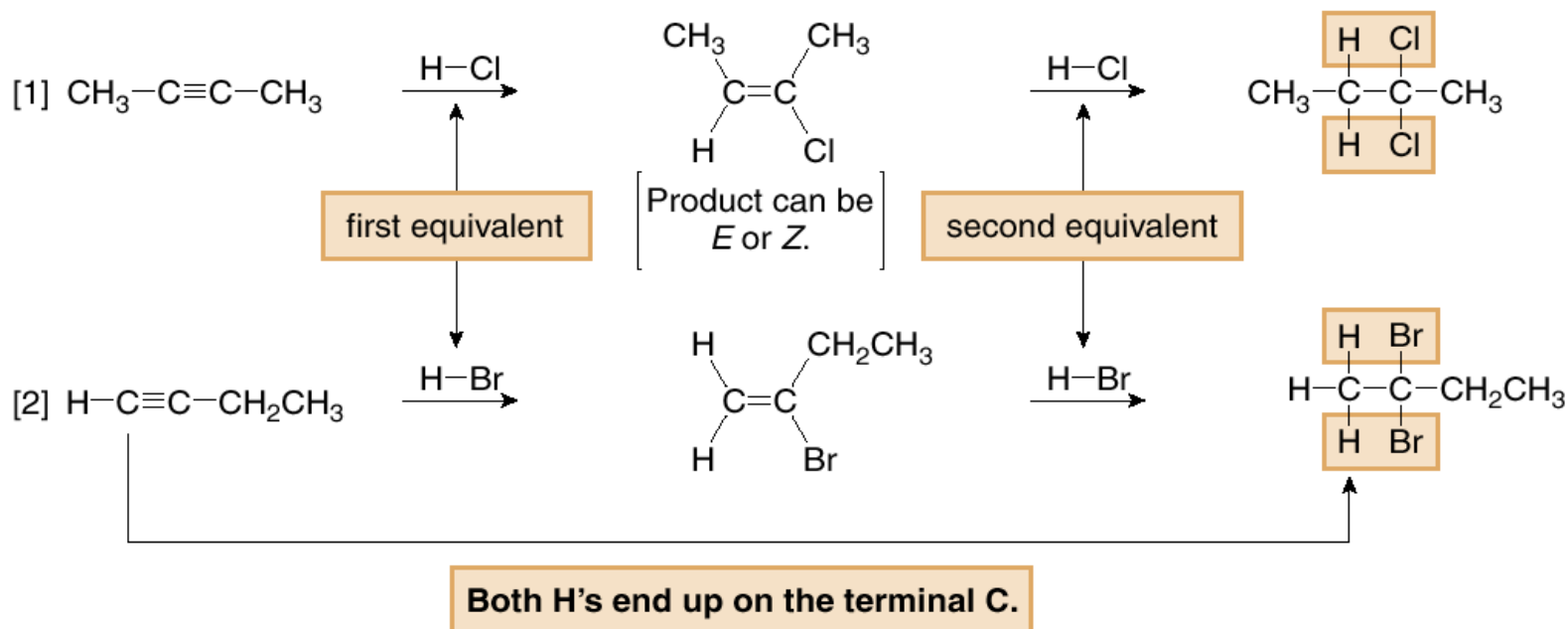
Two equivalents of HX are usually used: addition of one mole forms a vinyl halide, which then reacts with a second mole of HX to form a geminal dihalide.

## Hydrohalogenation

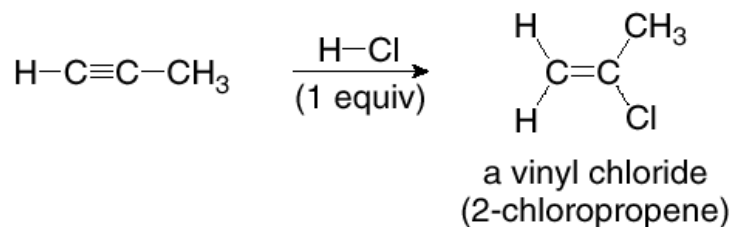


- With two equivalents of HX, both H atoms bond to the *same* carbon.
- With a terminal alkyne, both H atoms bond to the *terminal* carbon; that is, the hydrohalogenation of alkynes follows Markovnikov's rule.

**Examples**



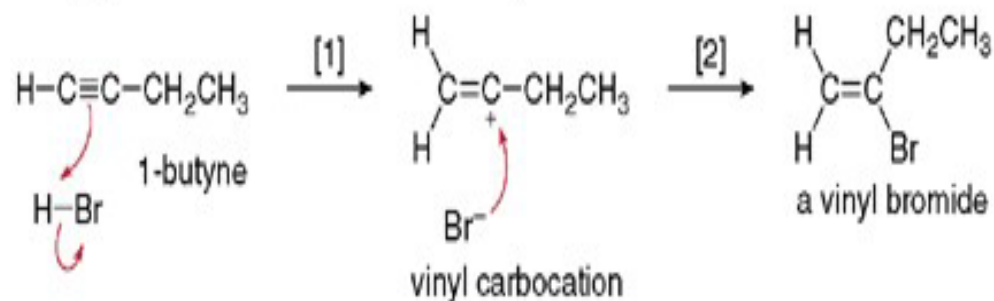
- With only one equivalent of HX, the reaction stops with formation of the vinyl halide.





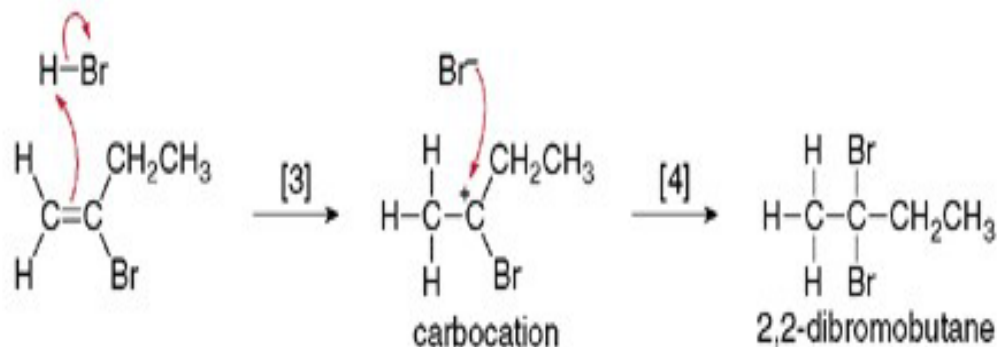
## Mechanism 11.1 Electrophilic Addition of HX to an Alkyne

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



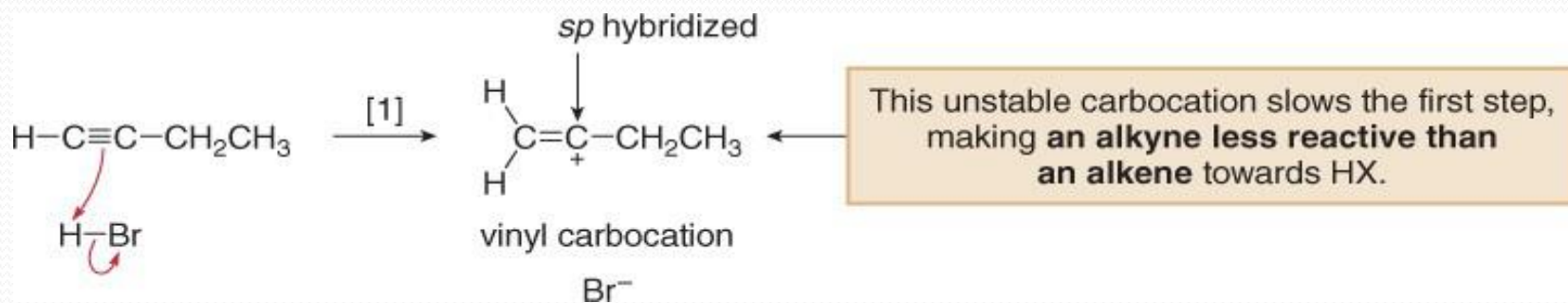
- The  $\pi$  bond attacks the H atom of HBr to form a new C-H bond, generating a **vinyl carbocation**. Addition follows Markovnikov's rule:  $\text{H}^+$  adds to the less substituted carbon atom to form the **more substituted, more stable carbocation**. Nucleophilic attack of  $\text{Br}^-$  then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

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

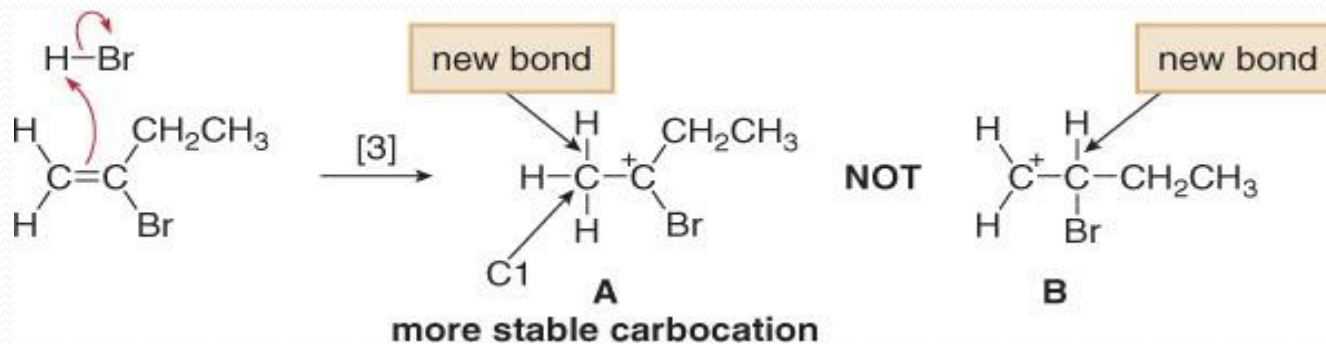


- The **second addition of HBr occurs in the same two-step manner**. Addition of  $\text{H}^+$  to the  $\pi$  bond of the vinyl bromide generates a carbocation. Nucleophilic attack of  $\text{Br}^-$  then forms a geminal dibromide (2,2-dibromobutane), and two moles of HBr have now been added.

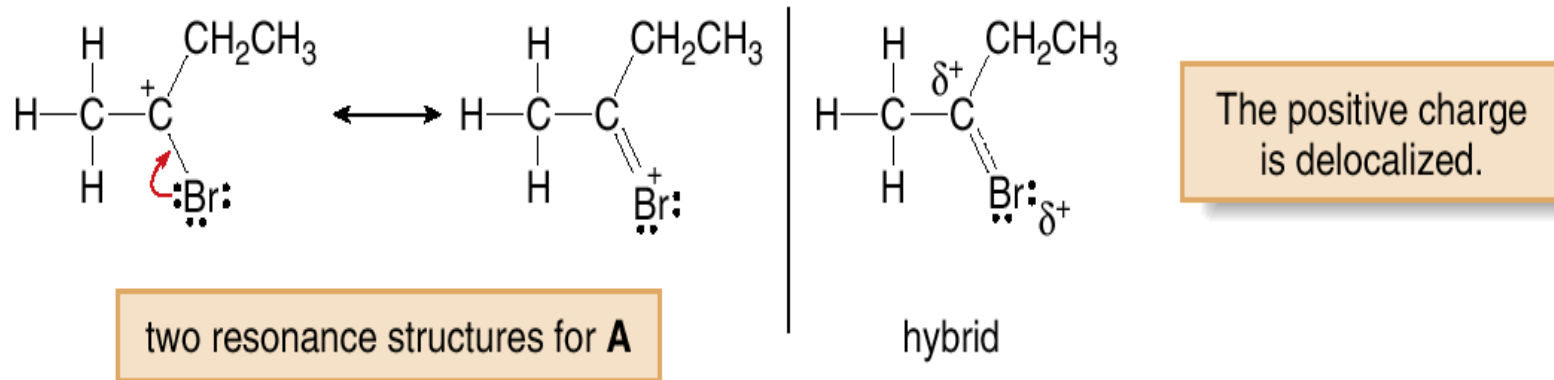
Electrophilic addition of HX to alkynes is slower than electrophilic addition of HX to alkenes, even though alkynes are more polarizable and have more loosely held p electrons than alkenes.



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.



Carbocation A is stabilized by resonance, but B is not. Two resonance structures can be drawn for carbocation A, but only one Lewis structure can be drawn for carbocation B.



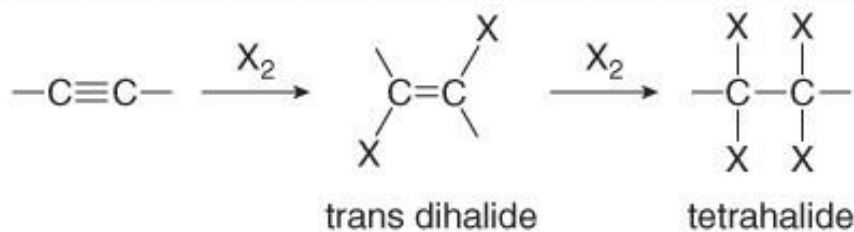
- Resonance stabilizes a molecule by delocalizing charge and electron density.
- Thus, halogens stabilize an adjacent positive charge by resonance.

Markovnikov's rule applies to the addition of HX to vinyl halides because addition of  $H^+$  forms a resonance stabilized carbocation.

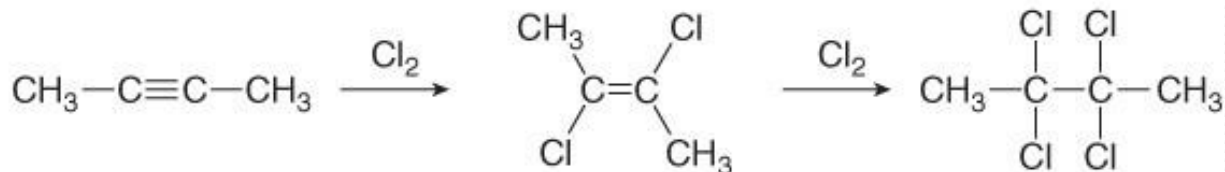
# Halogenation—Addition of Halogen

Halogens  $X_2$  ( $X = \text{Cl}$  or  $\text{Br}$ ) 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—  
General reaction



Example

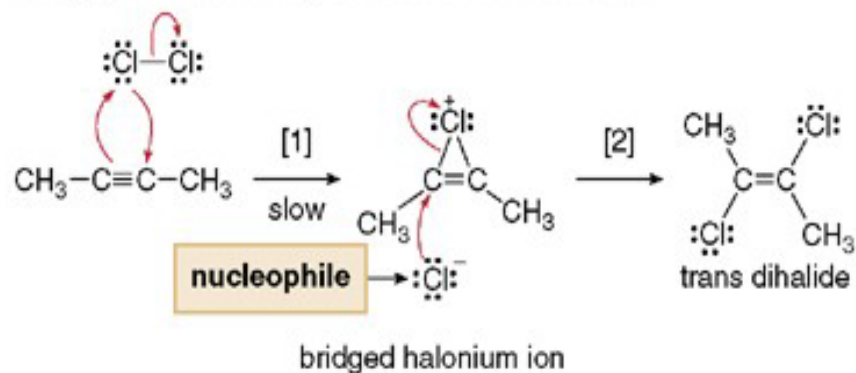






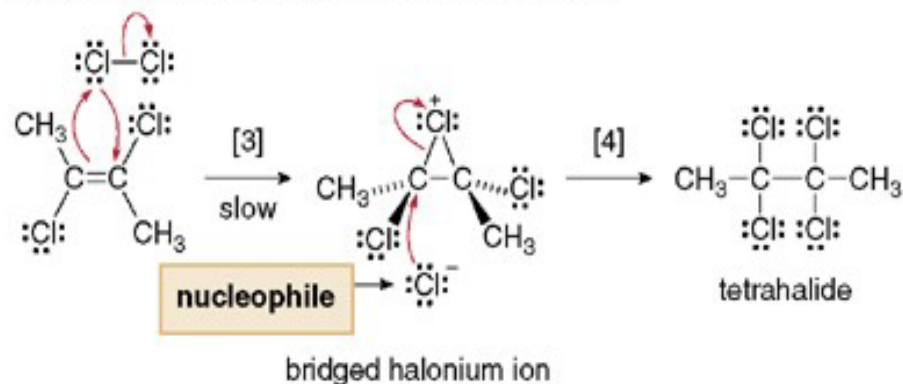
## Mechanism 11.2 Addition of $X_2$ to an Alkyne—Halogenation

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  $\text{Cl}^-$  from the back side forms the trans dihalide in Step [2].

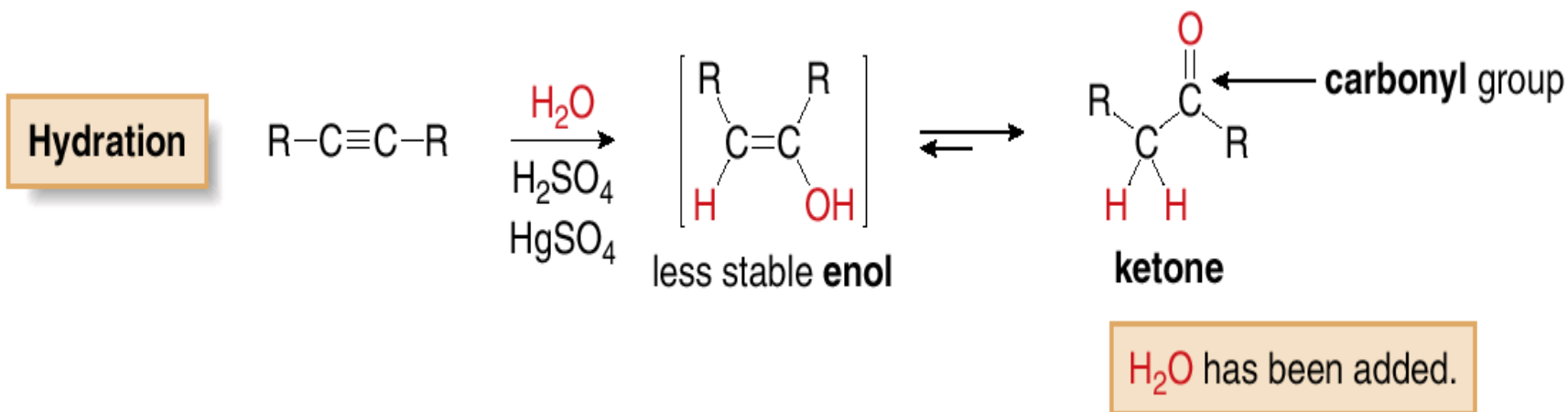
Part [2] Addition of  $X_2$  to form a tetrahalide



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

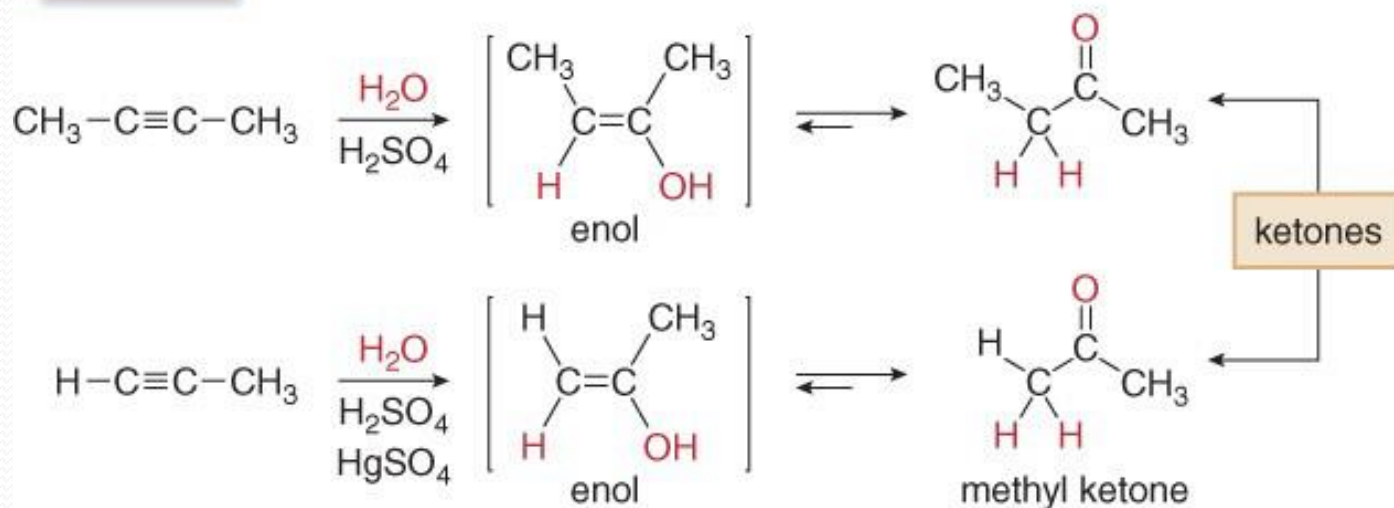
# Hydration—Electrophilic Addition of Water

In the presence of strong acid or  $\text{Hg}^{2+}$  catalyst, the elements of  $\text{H}_2\text{O}$  add to the triple bond, but the initial addition product, an enol, is unstable and rearranges to a product containing a carbonyl group i.e, a  $\text{C}=\text{O}$ . A carbonyl compound having two alkyl groups bonded to the  $\text{C}=\text{O}$  carbon is called a ketone.



Internal alkynes undergo hydration with concentrated acid, whereas terminal alkynes require the presence of an additional  $\text{Hg}^{2+}$  catalyst—usually  $\text{HgSO}_4$ —to yield methyl ketones by Markovnikov addition of water.

### Examples

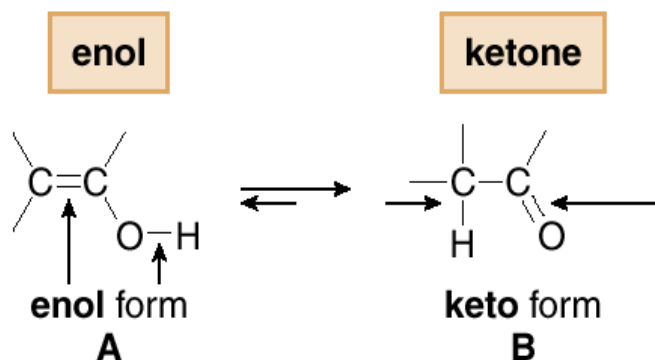


Markovnikov addition of  $\text{H}_2\text{O}$

H adds to the terminal C.

Consider the conversion of a general enol A to the carbonyl compound B. A and B are tautomers: 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.



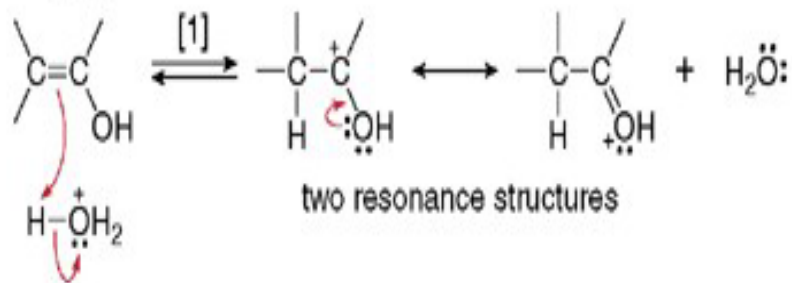
- An enol tautomer has an O-H group bonded to a C=C.
- A keto tautomer has a C=O and an additional C-H bond.

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.



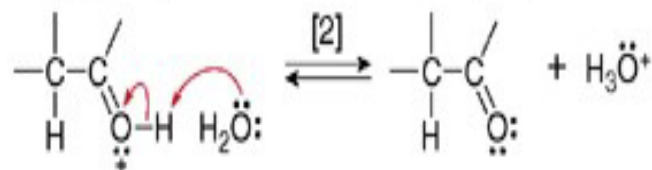
## Mechanism 11.3 Tautomerization in Acid

Step [1] Protonation of the enol double bond



- **Protonation** of the enol C=C with acid ( $\text{H}_3\text{O}^+$ ) adds  $\text{H}^+$  to form a **resonance-stabilized carbocation**.

Step [2] Deprotonation of the OH group

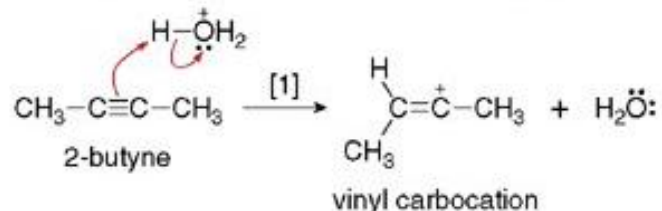


- **Loss of a proton** forms the carbonyl group. This step can be drawn with either resonance structure as starting material. Because the acid used in Step [1] is re-formed in Step [2], tautomerization is **acid catalyzed**.



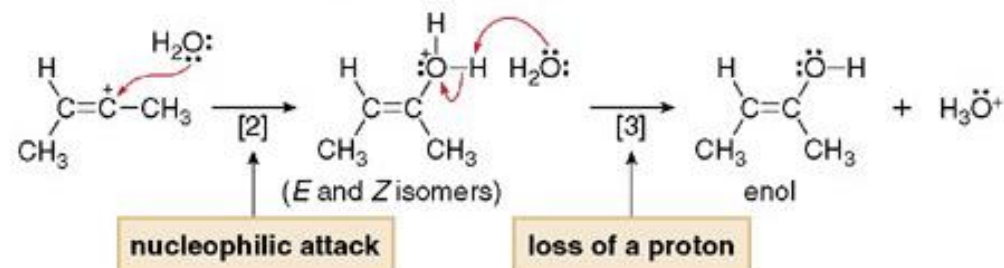
## Mechanism 11.4 Hydration of an Alkyne

Step [1] Addition of the electrophile ( $\text{H}^+$ ) to a  $\pi$  bond



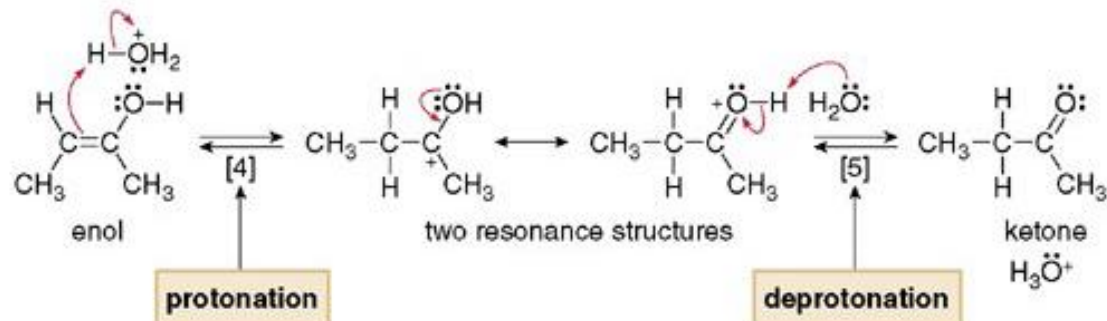
- Addition of  $\text{H}^+$  (from  $\text{H}_3\text{O}^+$ ) forms an  $sp$  hybridized **vinyl carbocation**.

Steps [2] and [3] Nucleophilic attack of  $\text{H}_2\text{O}$  and loss of a proton



- **Nucleophilic attack of  $\text{H}_2\text{O}$**  on the carbocation followed by loss of a proton forms the enol.

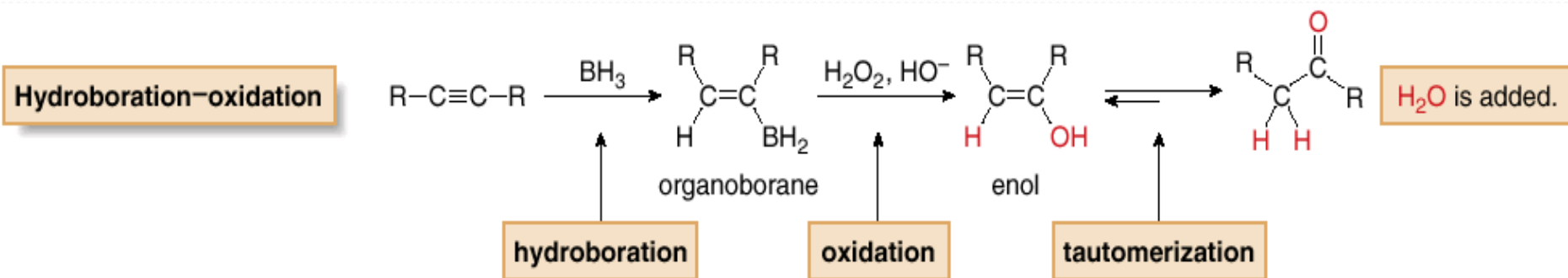
Steps [4] and [5] Tautomerization



- **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.

# Hydroboration—Oxidation

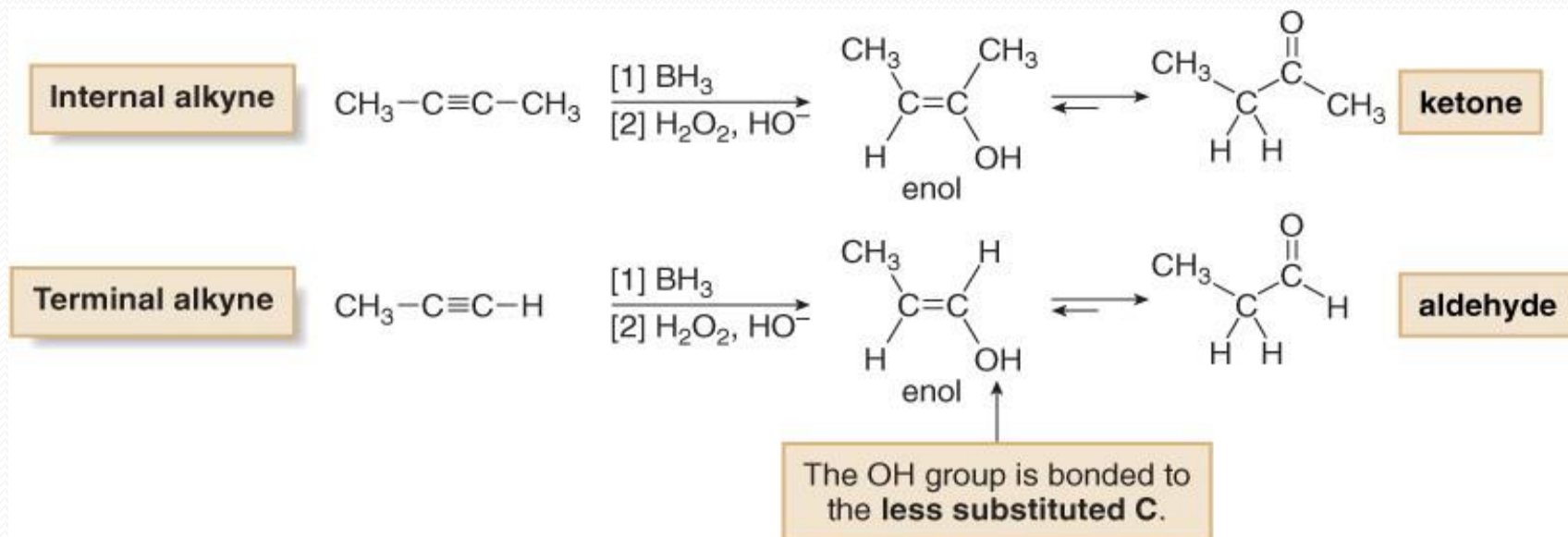
Hydroboration—oxidation is a two step reaction sequence that converts an alkyne to a carbonyl compound.



- Addition of borane forms an organoborane.
- Oxidation with basic  $H_2O_2$  forms an enol.
- Tautomerization of the enol forms a carbonyl compound.
- The overall result is addition of  $H_2O$  to a triple bond.

**Hydroboration—oxidation of an internal alkyne forms a ketone.**

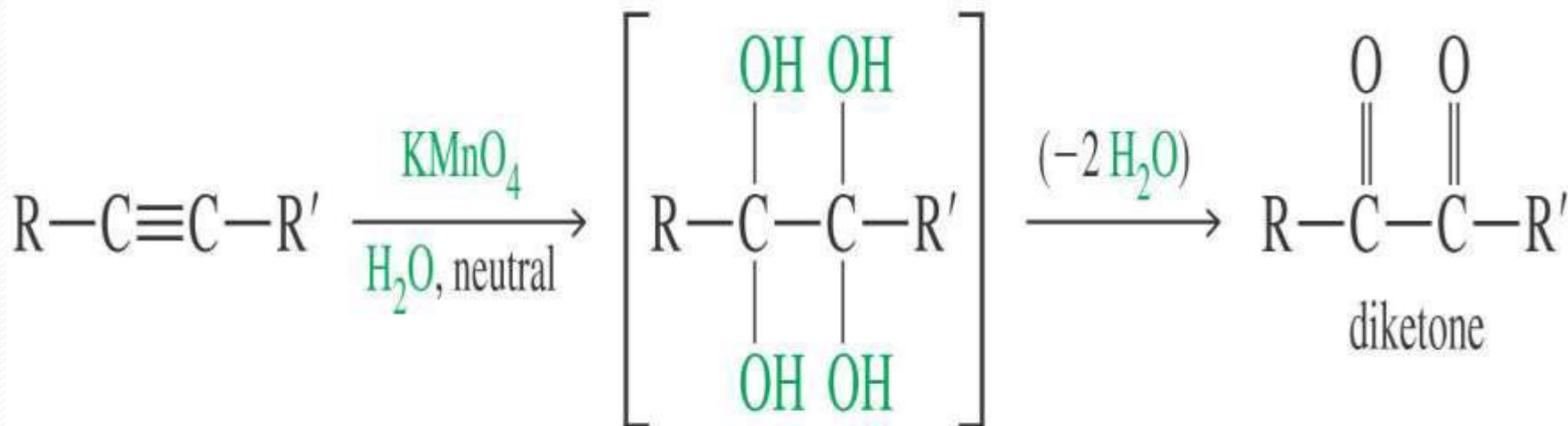
- **Hydroboration of a terminal alkyne adds  $\text{BH}_2$  to the less substituted, terminal carbon. After oxidation to the enol, tautomerization yields an aldehyde, a carbonyl compound having a hydrogen atom bonded to the carbonyl carbon.**





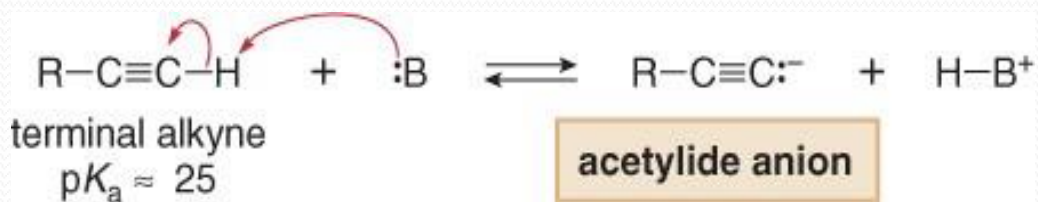
# Oxidation

*The same reagents that oxidized alkenes can oxidize alkynes in a similar way. Using  $\text{KMnO}_4$  under neutral conditions, vicinal diketones are obtained with internal alkynes.*



# Acidic nature

Because *sp* hybridized C—H bonds are more acidic than *sp*<sup>2</sup> and *sp*<sup>3</sup> hybridized C—H bonds, terminal alkynes are readily deprotonated with strong base in a Bronsted-Lowry acid-base reaction. The resulting ion is called the acetylide ion.



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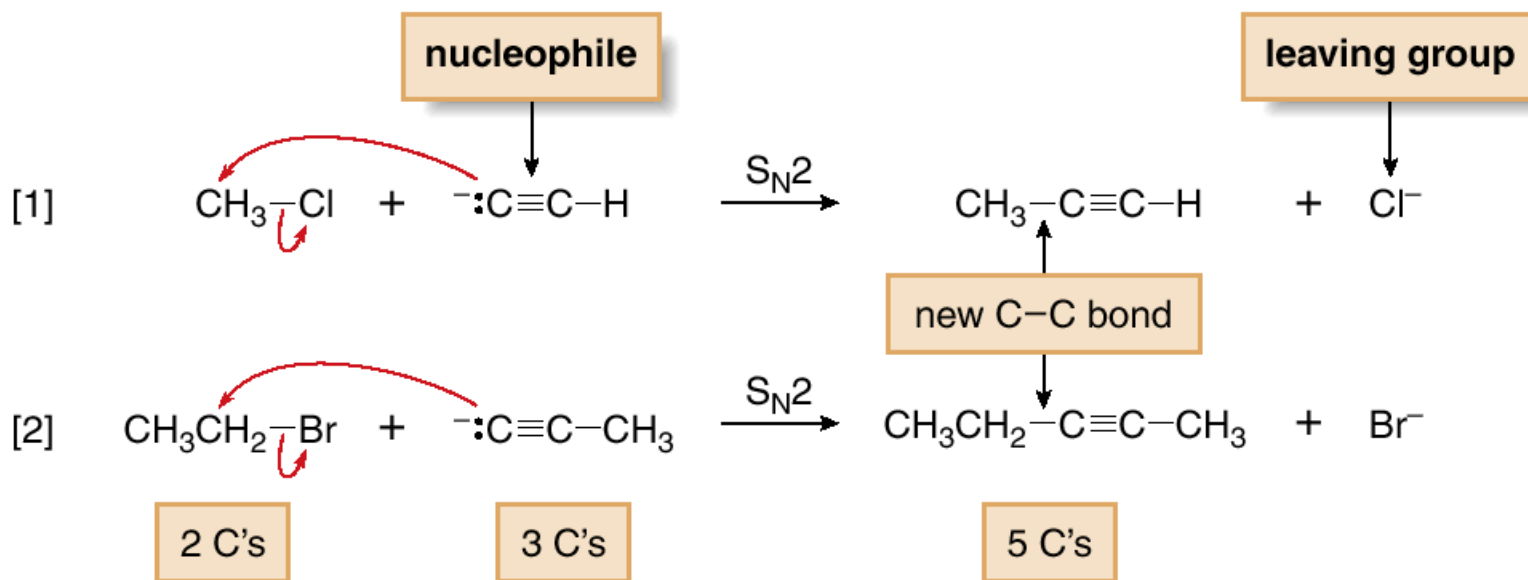
**Table 11.1**

**A Comparison of Bases for Alkyne Deprotonation**

	Base	$pK_a$ of the conjugate acid
These bases are <b>strong</b> enough to deprotonate an alkyne.	{ $\text{NH}_2^-$ $\text{H}^-$	38 35
These bases are <b>not</b> strong enough to deprotonate an alkyne.	{ $\text{OH}^-$ $\text{OR}^-$	15.7 15.5–18

Acetylide anions react with unhindered alkyl halides to yield products of nucleophilic substitution.

• Because acetylides are strong nucleophiles, the mechanism of substitution is  $S_N2$ , and thus the reaction is fastest 10 times with  $CH_3X$  than other alkyl halides.



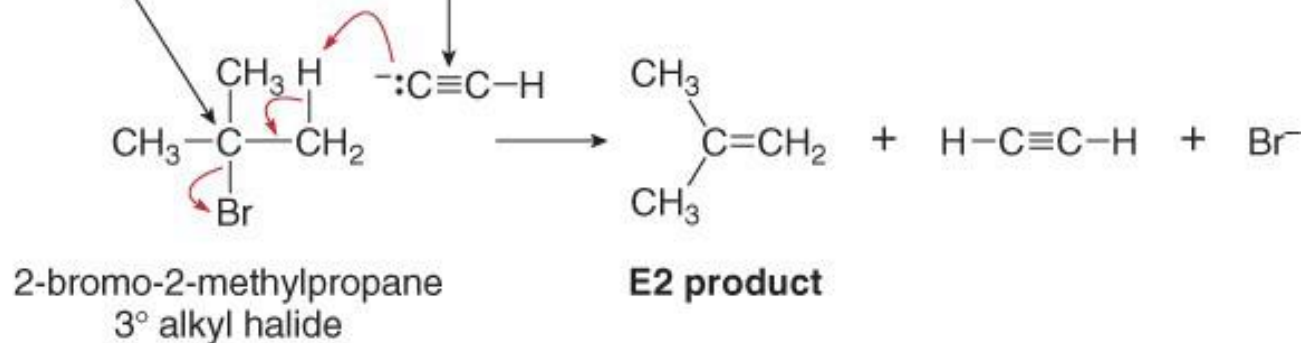
• Nucleophilic substitution with acetylide anions forms new carbon-carbon bonds.

Steric hindrance around the leaving group causes 2° and 3° alkyl halides to undergo elimination by an E2 mechanism, as shown with 2-bromo-2-methylpropane.

- Thus, nucleophilic substitution with acetylide anions forms new carbon-carbon bonds in high yield only with unhindered CH<sub>3</sub>X and 1° alkyl halides.

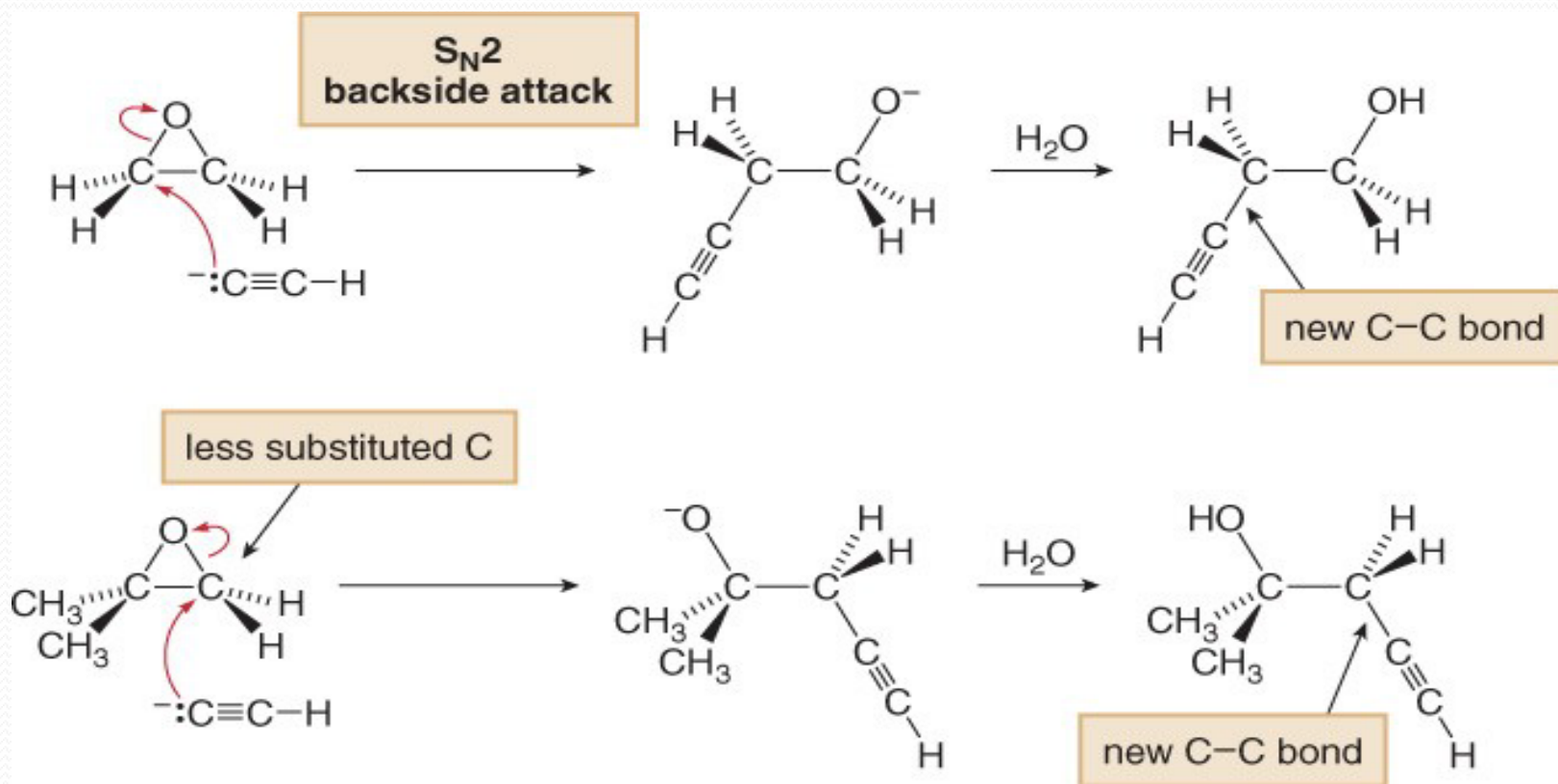
Steric hindrance prevents an S<sub>N</sub>2 reaction.

The acetylide anion acts as a **base** instead.



Acetylide anions are strong nucleophiles that open epoxide rings by an  $S_N2$  mechanism.

- Backside attack occurs at the less substituted end of the epoxide.



## Polymerization

Alkynes can undergo linear and cyclic polymerization under suitable conditions. They polymerize to give compounds that have a higher molecular weight than the original alkyne. e.g.,

- ❑ Ethyne will polymerize to give polyacetylene or polyethene (of higher molecular weight), This is an example of linear polymerization.
- ❑ For cyclic polymerization passing ethyne through a red-hot iron tube at a minimum of 877K will give benzene.



**Just a note to say...**

*Thank You!*