

Organic Chemistry

Alkynes

by

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<http://ocw.ump.edu.my/course/view.php?id=491>

Chapter Description

- Aims
 - The students should **understand** the fundamental of organic chemistry in terms of alkynes
 - The students should be able to **explain** the fundamental of organic chemistry in terms of alkynes
- Expected Outcomes
 - Explain the basic knowledge in alkynes
 - Describe the chemical reactions and conditions for alkynes reactions
 - Describe the synthesis reactions involving alkynes in certain industrial application
- References
 - Janice Gorzynski Smith (2008), Organic chemistry, Mc Graw-Hill
 - T. W. Graham Solomons. (2008). Organic chemistry, 9th ed, Mc Graw-Hill
 - K. Peter C. Vollhardt, Neil E. Schore, (2009). Organic chemistry, Fourth Edition: Structure and Function, Pub Chem



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Alkynes



Alkynes

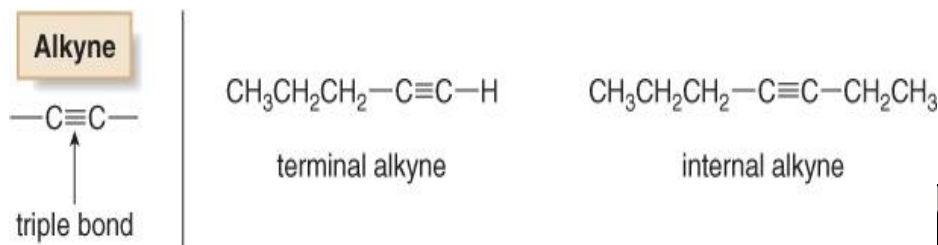
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Alkynes

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.**



Alkynes

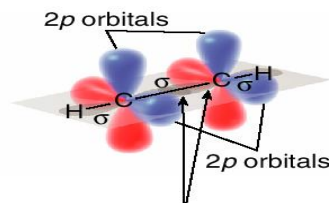
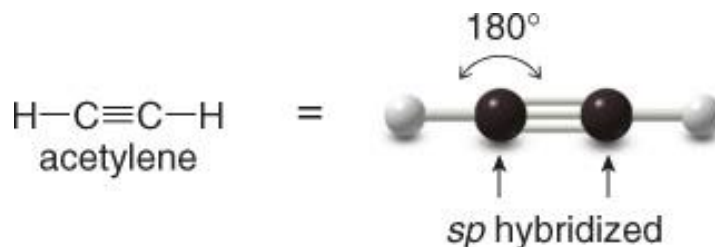
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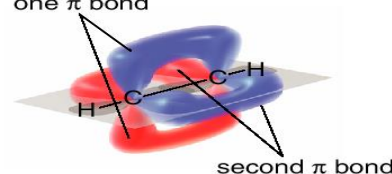
Introduction—Structure and Bonding

- 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° .



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

Two π bonds extend out from the axis of the linear molecule.
one π bond



Overlap of two sets of two $2p$ 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 $2p$ orbitals.



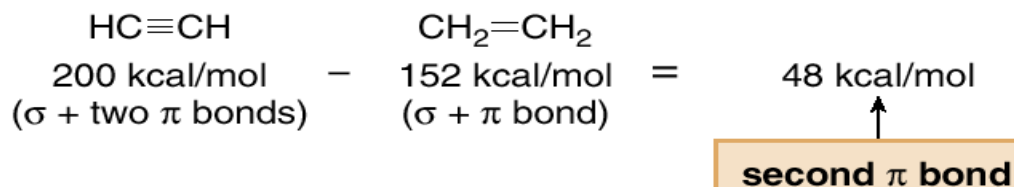
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Introduction—Structure and Bonding

- Bond dissociation energies of the C—C bonds in ethylene (one σ and one π bond) and acetylene (one σ and two π bonds) can be used to estimate the strength of the second π bond of the triple bond.



- Both π bonds of a C—C triple bond are weaker than a C—C σ bond, making them much more easily broken. As a result, alkynes undergo many addition reactions.
- Alkynes are more polarizable than alkenes because the electrons in their π bonds are more loosely held.



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Alkynes

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 *triyne*s and so forth.
- ❑ Compounds 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, $H-C\equiv C-H$, 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*.



Alkynes

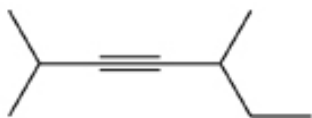
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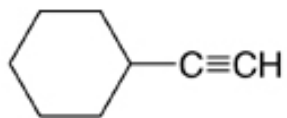
Alkynes

Nomenclature

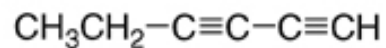
Examples of alkyne nomenclature



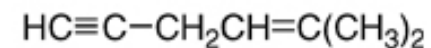
2,5-dimethyl-3-heptyne



ethynylcyclohexane



1,3-hexadiyne



5-methyl-4-hexen-1-yne



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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.



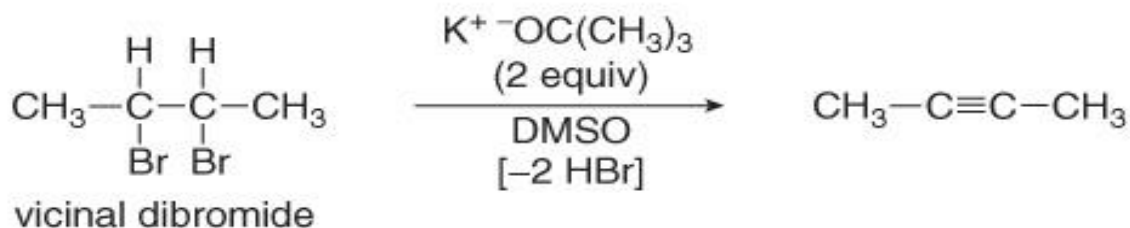
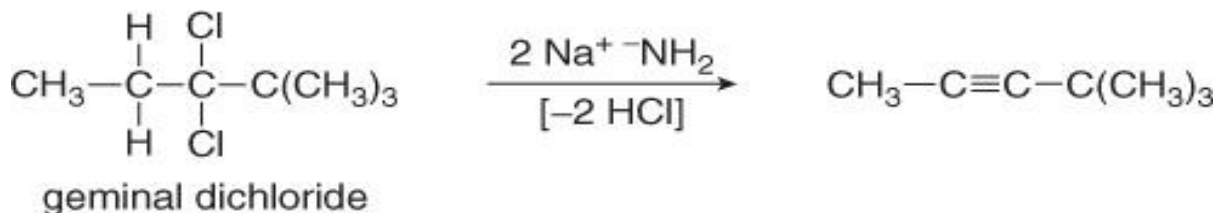
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Preparation of Alkynes

- 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.



Alkynes

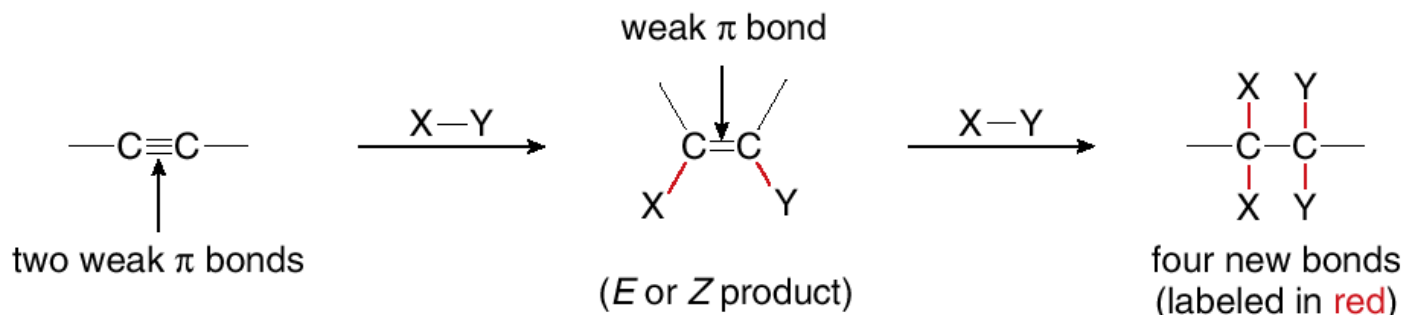
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Introduction to Alkyne Reactions—Additions

- 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



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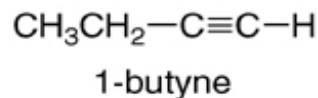
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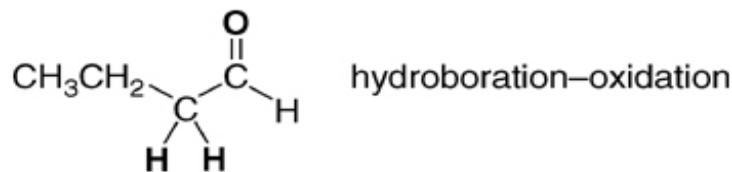
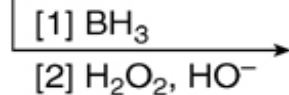
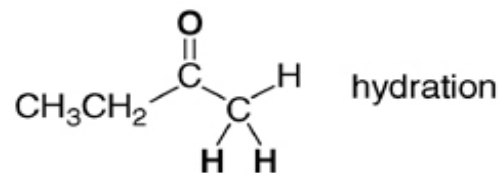
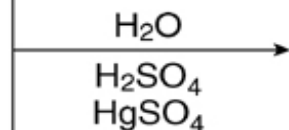
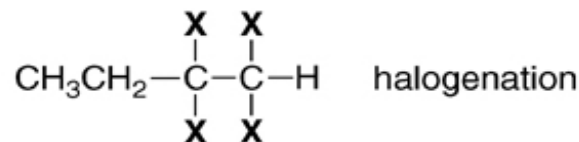
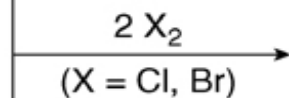
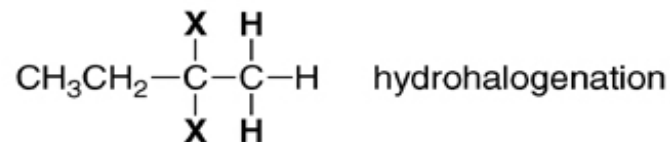
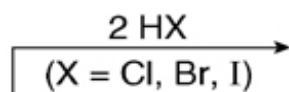
Introduction to Alkyne Reactions

Four addition reactions
of 1-butyne

Both π bonds are broken.



Four new bonds are formed.



Alkynes

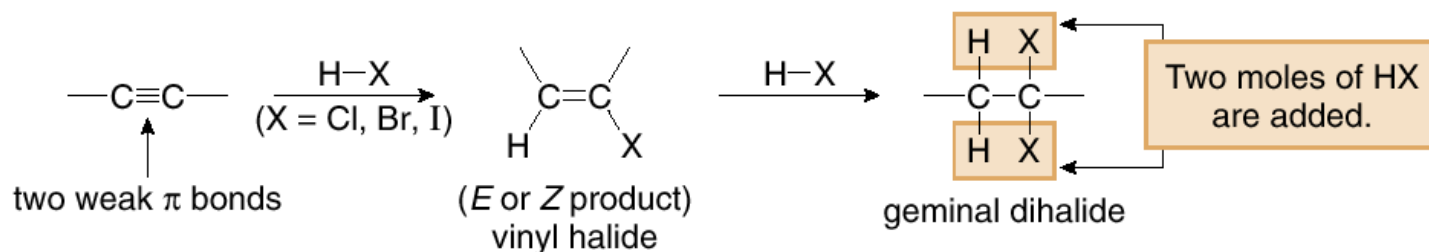
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Hydrohalogenation—Electrophilic Addition of HX

- Alkynes undergo hydrohalogenation, i.e. the, addition of hydrogen halides, HX (X = Cl, Br, I).

Hydrohalogenation



- 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.



Alkynes

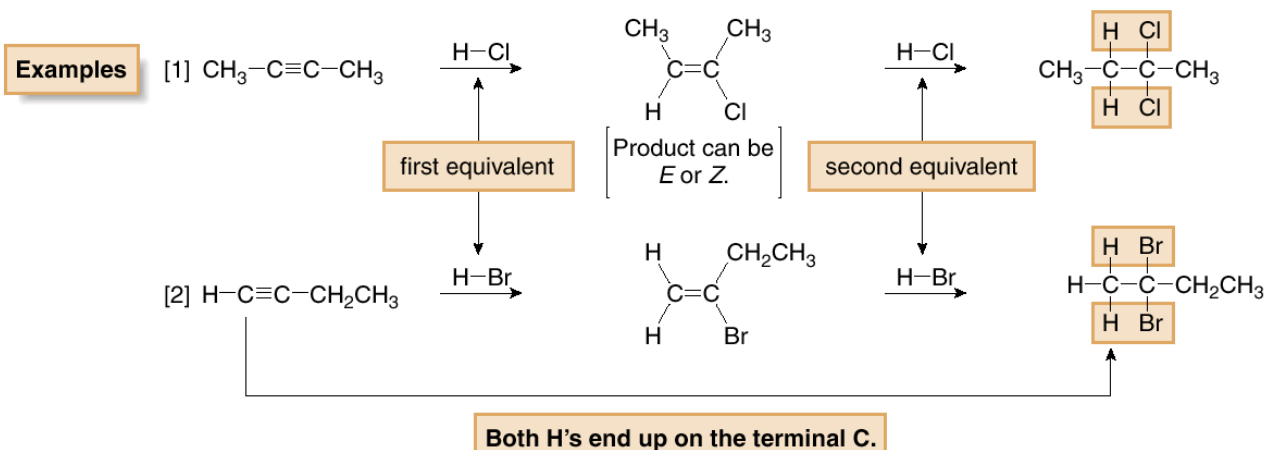
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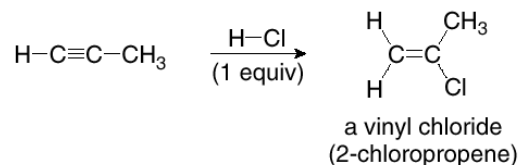
Alkynes

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.



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



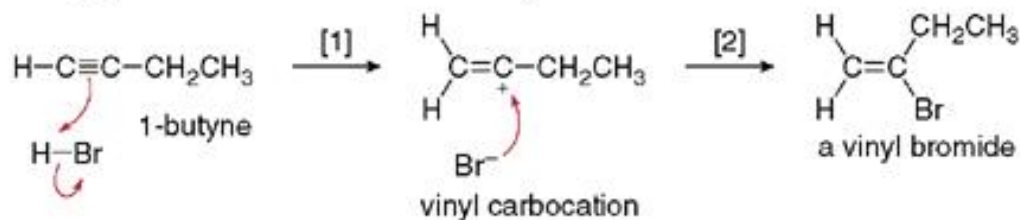
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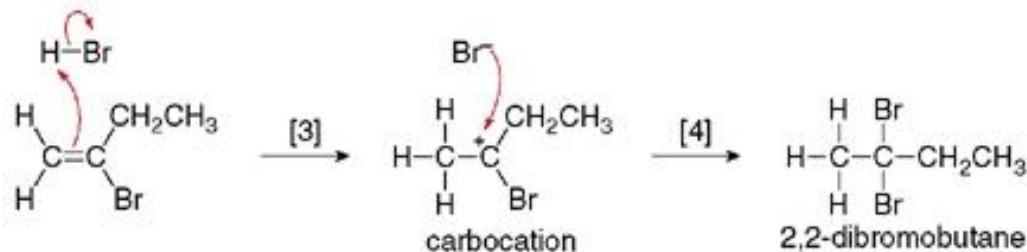
Hydrohalogenation—Electrophilic Addition of HX

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.



Alkynes

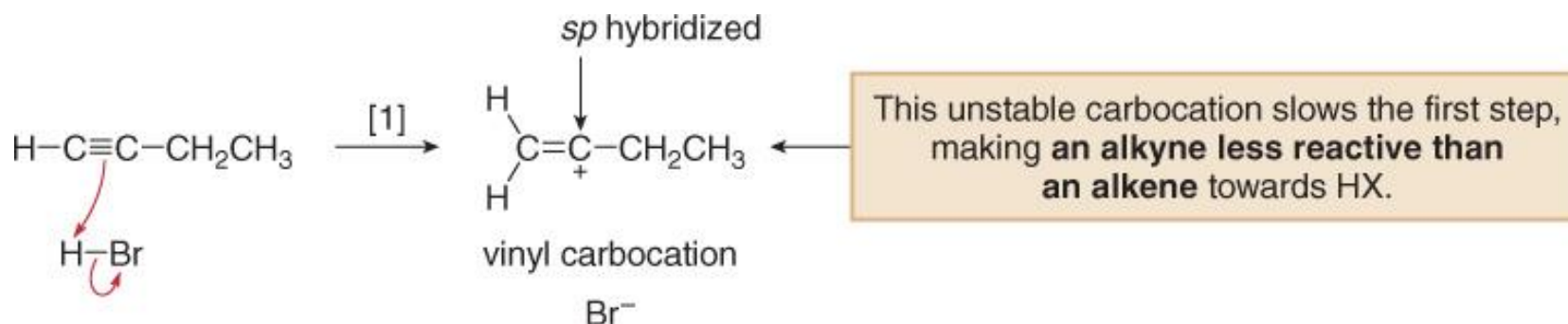
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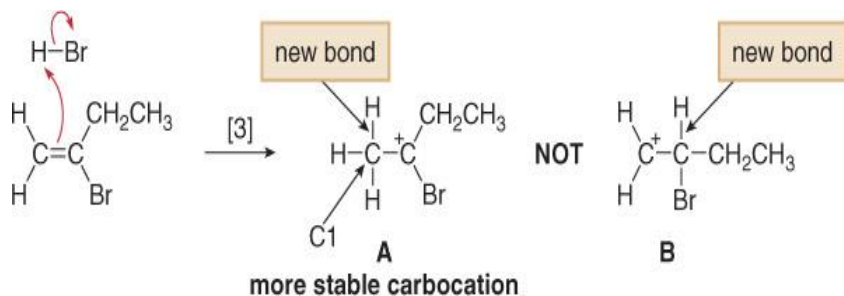
Alkynes

Introduction to Alkyne Reactions

- 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.



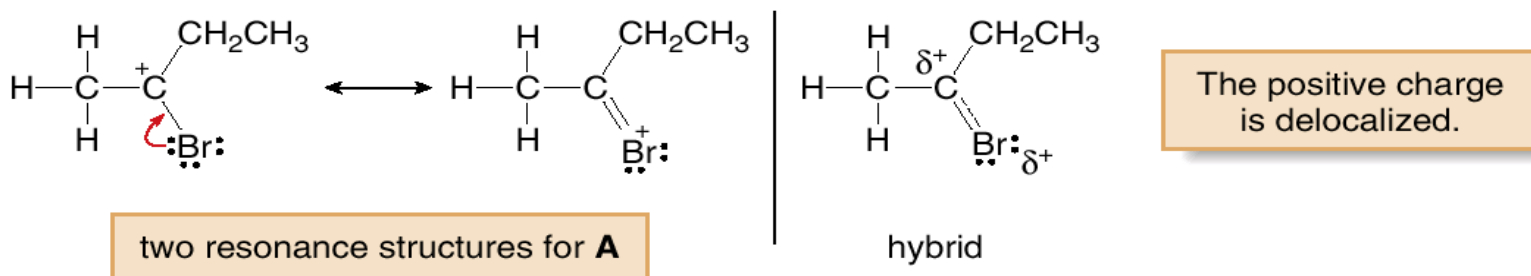
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Introduction to Alkyne Reactions

- 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.



Alkynes

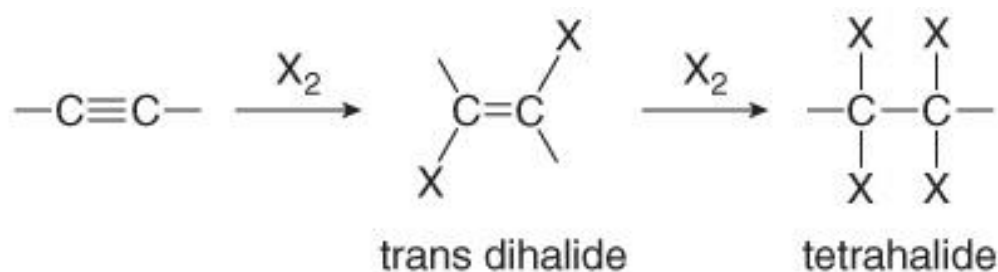
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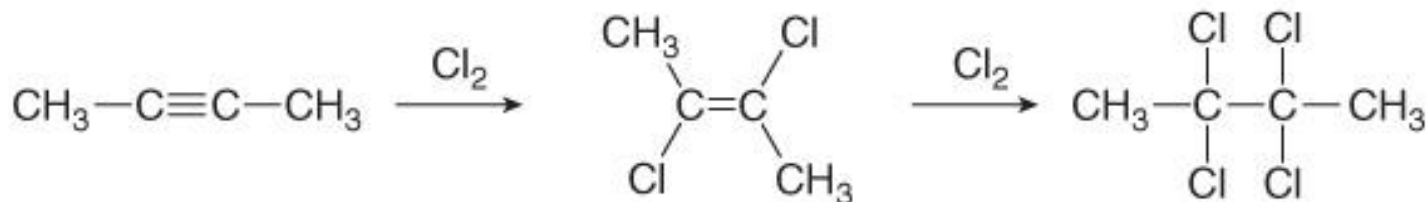
Halogenation—Addition of Halogen

- Halogens X_2 ($X = \text{Cl}$ 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— General reaction



Example



Alkynes

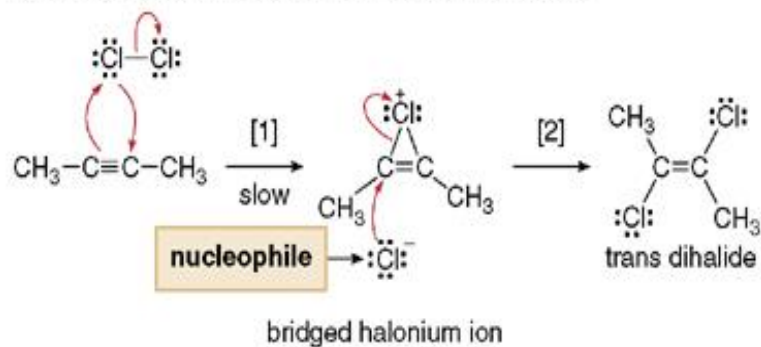
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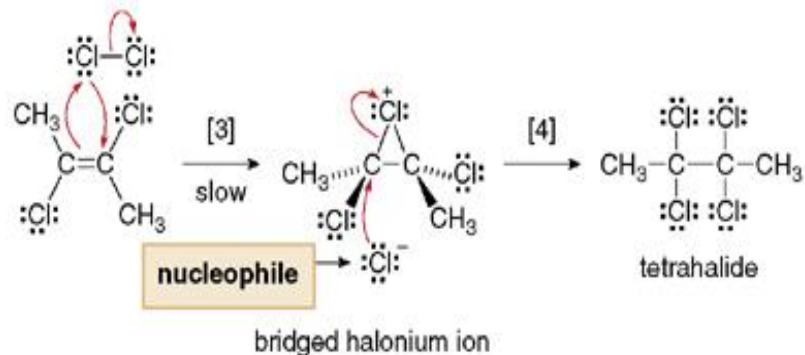
Halogenation—Addition of Halogen

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].



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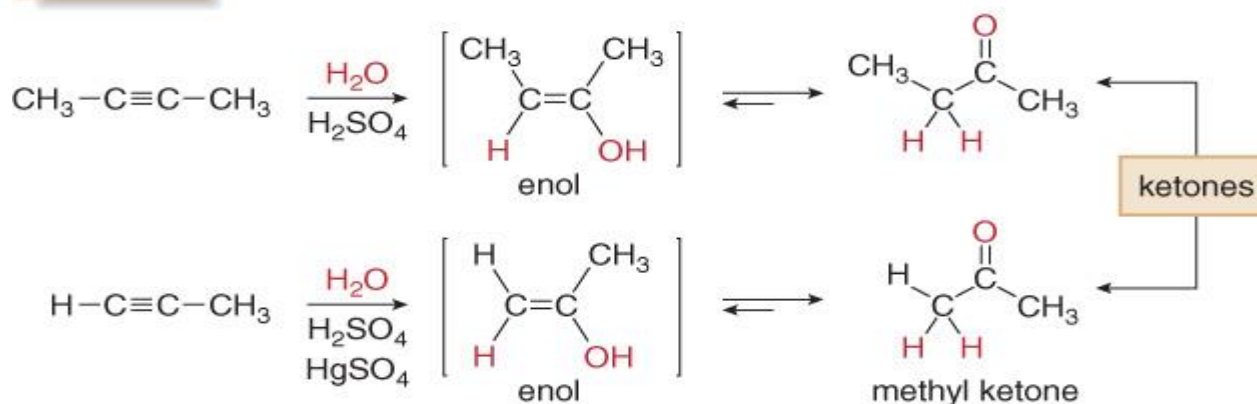
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Alkynes

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.

Examples



Markovnikov addition of H_2O

H adds to the terminal C.



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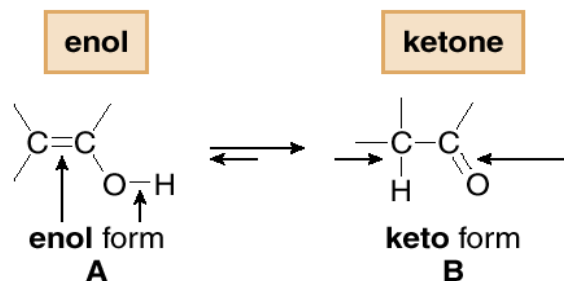
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Alkynes

Hydration—Electrophilic Addition of Water

- 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.



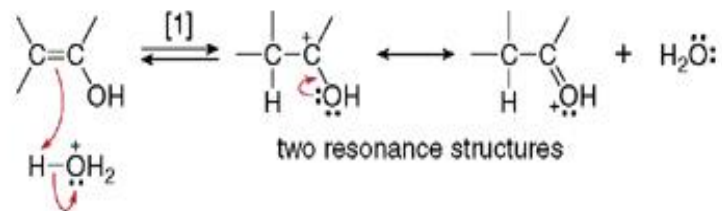
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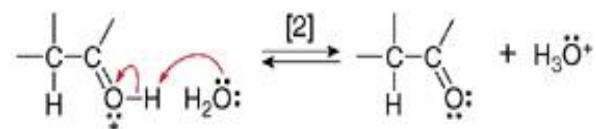
Hydration—Electrophilic Addition of Water

Step [1] Protonation of the enol double bond



- **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**.



Alkynes

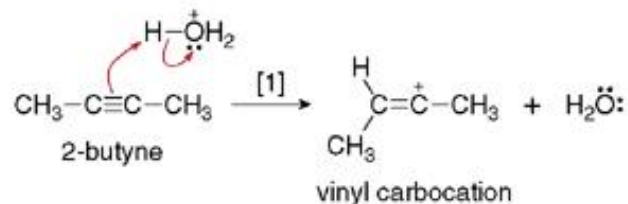
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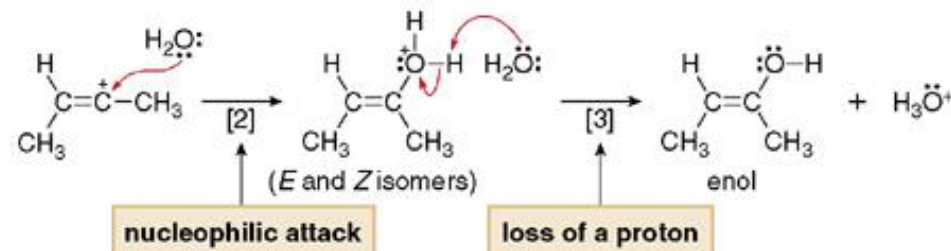
Hydration—Electrophilic Addition of Water

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



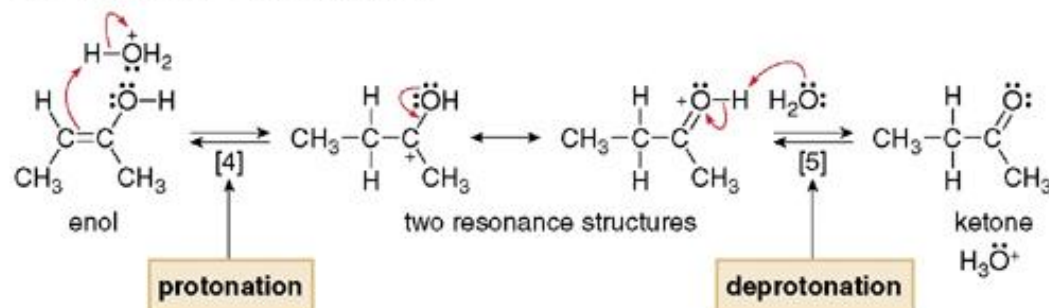
- Addition of H^+ (from H_3O^+) forms an sp hybridized **vinyl carbocation**.

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.



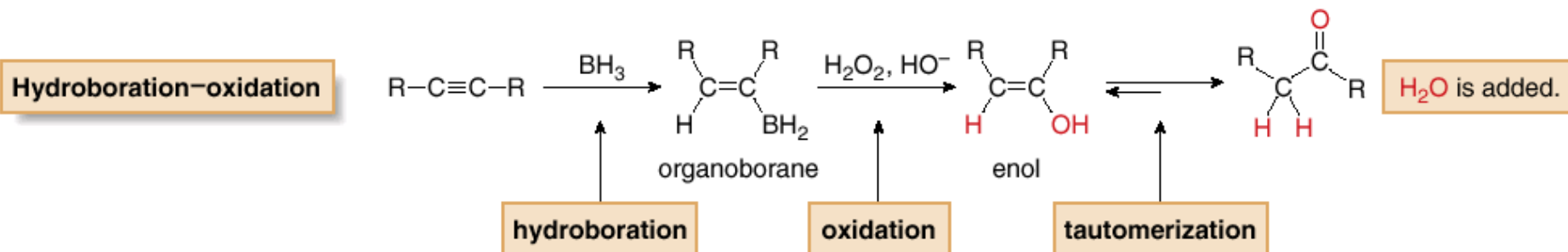
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Hydroboration—Oxidation

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.



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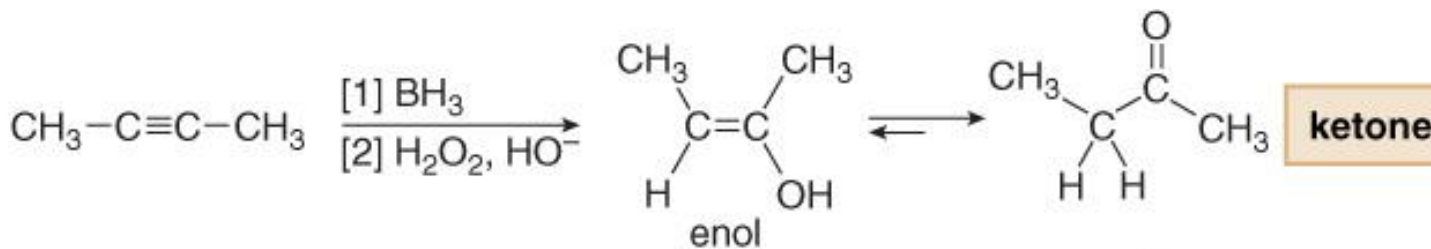
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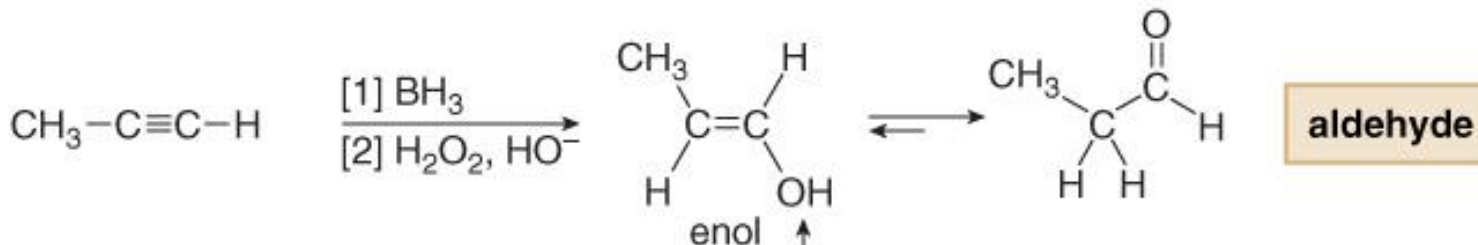
Hydroboration—Oxidation

- Hydroboration—oxidation of an internal alkyne forms a ketone.
- Hydroboration of a terminal alkyne adds 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.

Internal alkyne



Terminal alkyne



The OH group is bonded to the less substituted C.

Alkynes

Introduction to Alkyne Reactions—Acetylide anions

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



	Base	pK_a of the conjugate acid
These bases are strong enough to deprotonate an alkyne.	{ NH_2^- H^-	38 35
These bases are not strong enough to deprotonate an alkyne.	{ OH^- OR^-	15.7 15.5–18



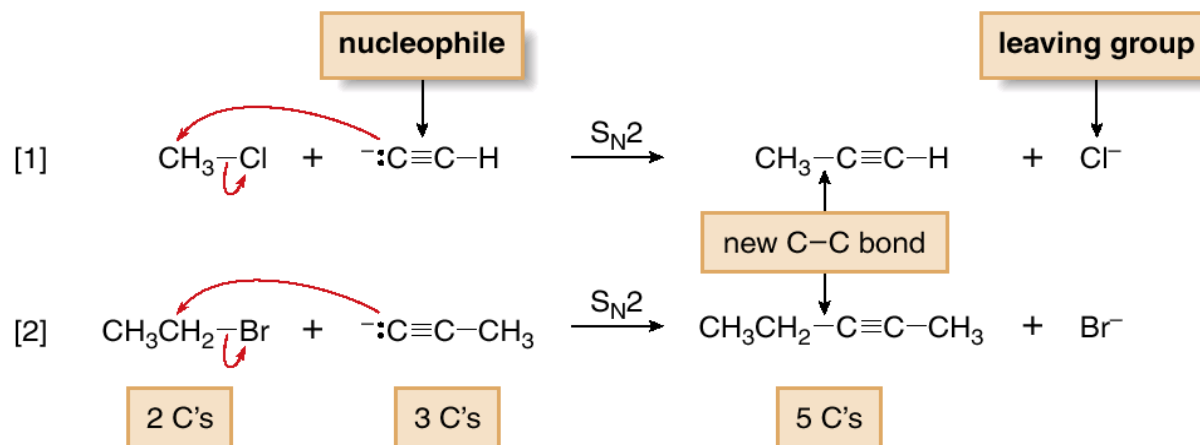
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Reactions of Acetylide Anions

- 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 with CH_3X and 1° alkyl halides.



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



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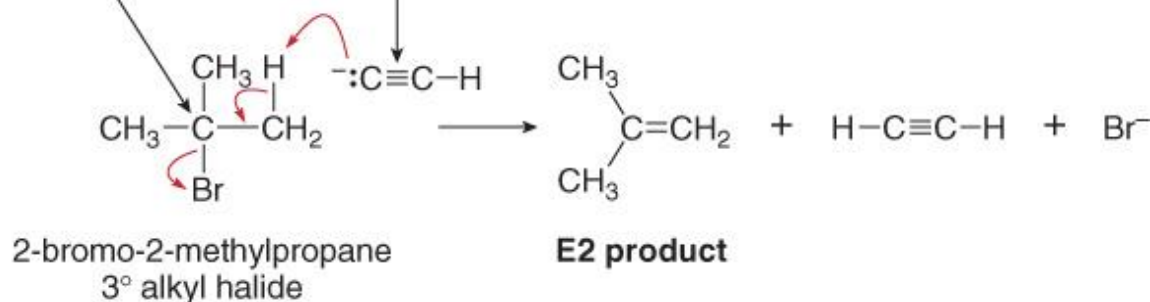
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Reactions of Acetylide Anions

- 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 CH₃X and 1° alkyl halides.

Steric hindrance prevents an S_N2 reaction.

The acetylide anion acts as a base instead.



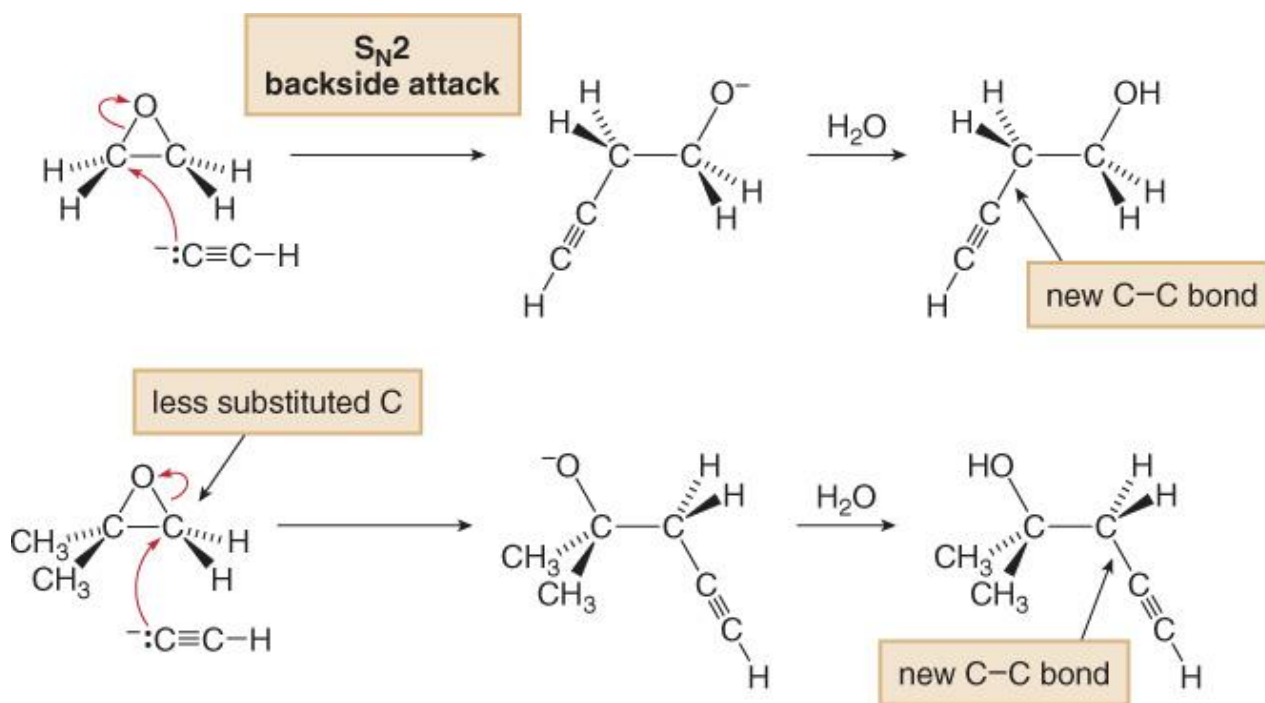
Alkynes

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<http://ocw.ump.edu.my/course/view.php?id=491>

Reactions of Acetylide Anions

- 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.



Alkynes

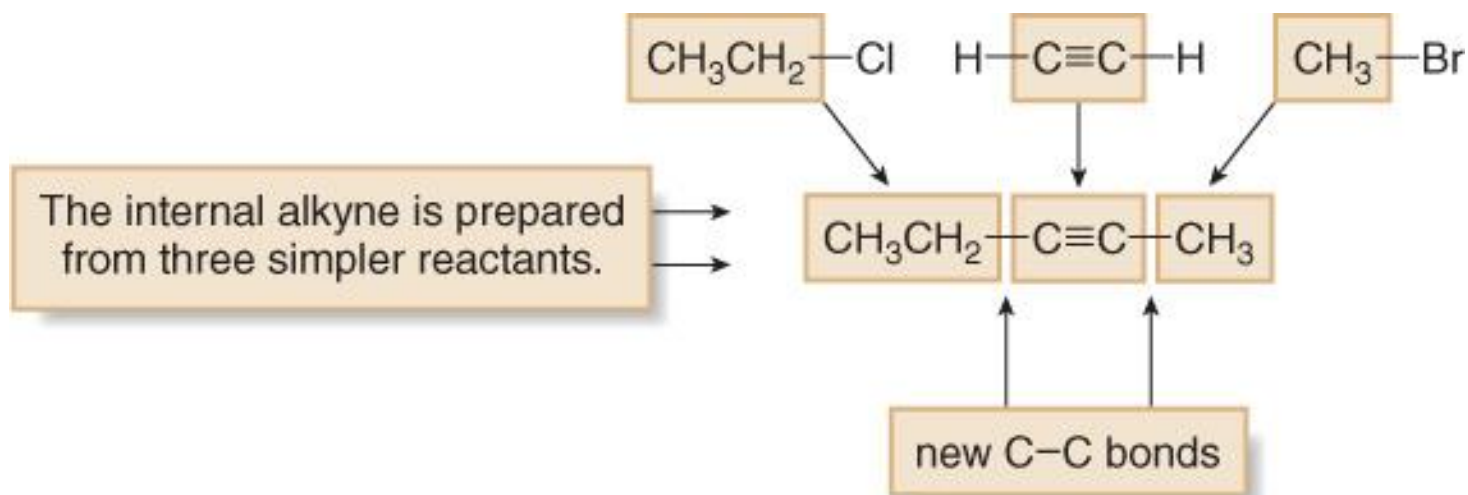
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Synthesis

- You can now begin to consider (for example) how to prepare a five-carbon product from three smaller precursor molecules using the reactions you have learned.



- To plan a synthesis of more than one step, we use the process of **retrosynthetic analysis**—that is, working backwards from a desired product to determine the starting materials from which it is made.

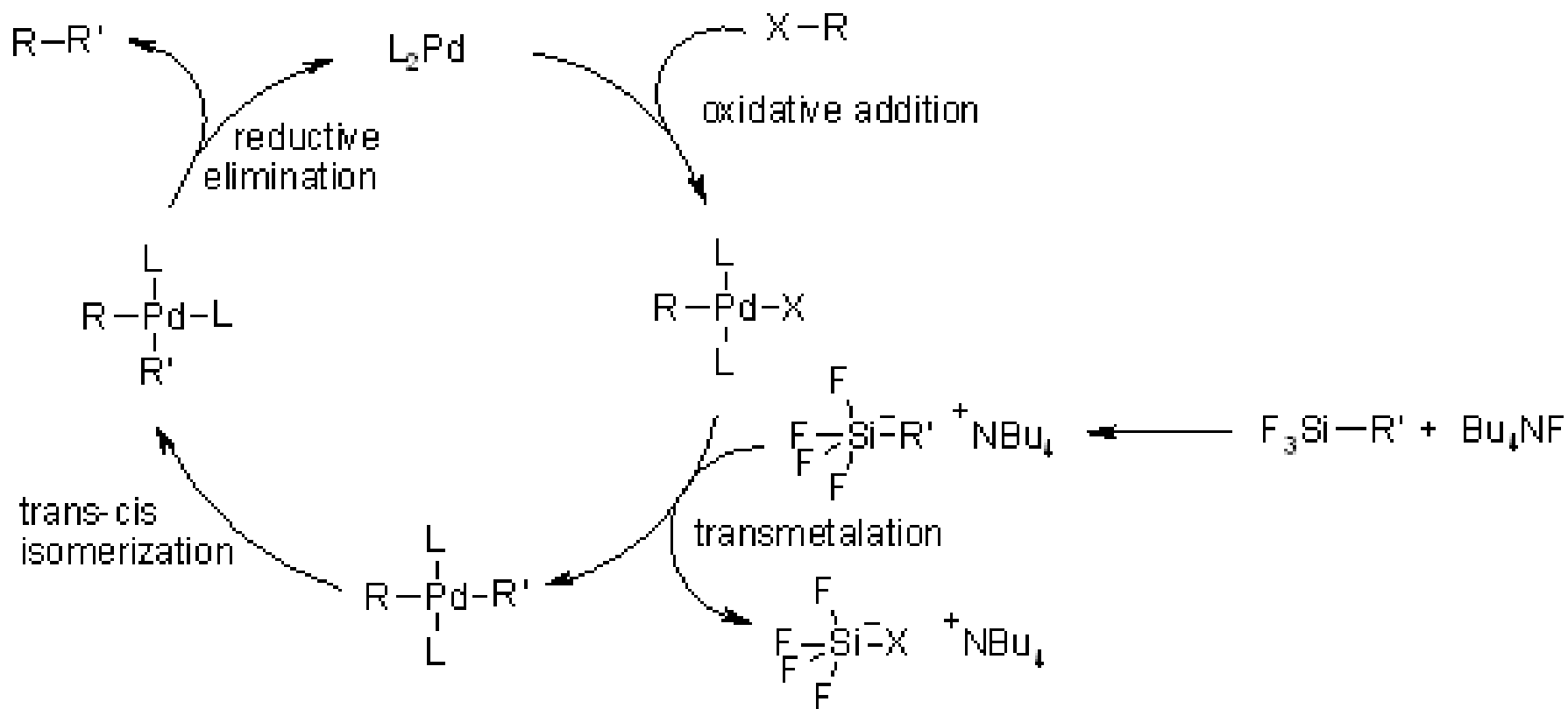


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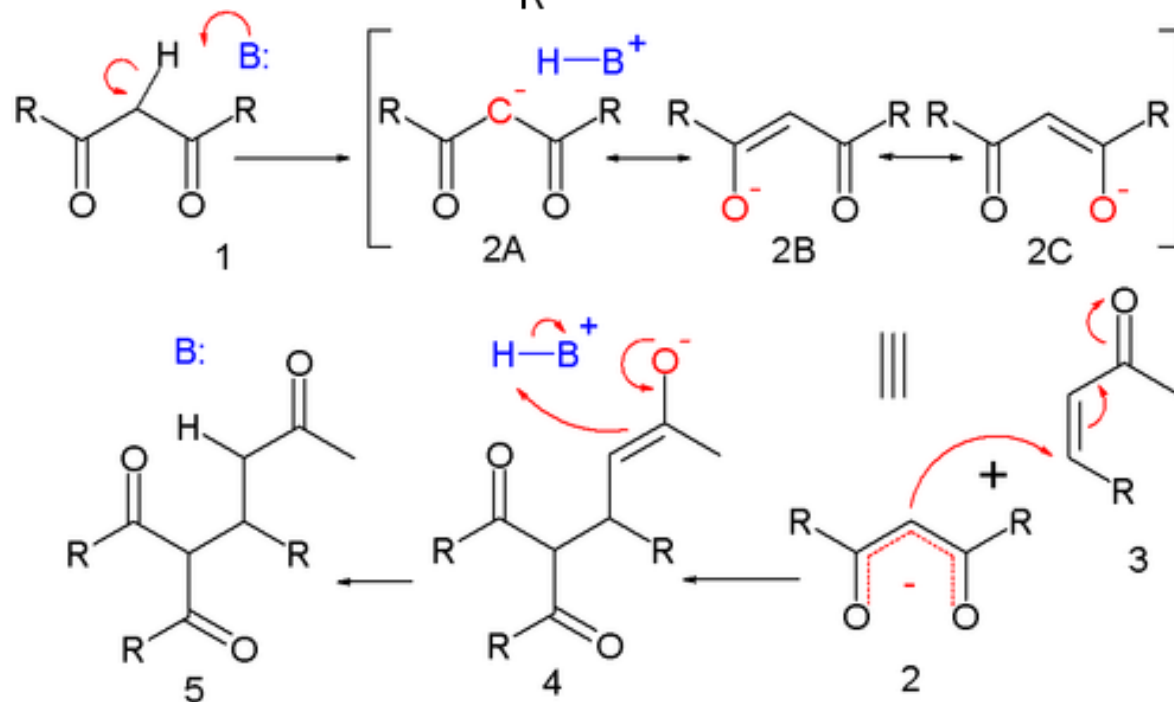
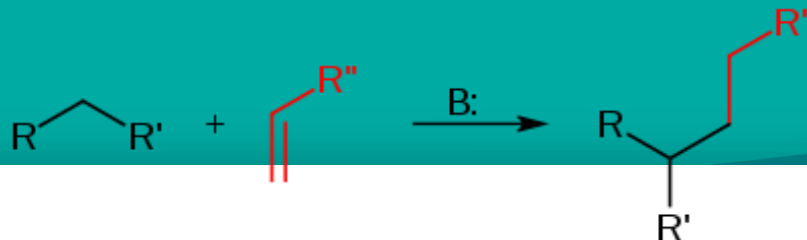
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Hiyama Coupling



Michael reaction



The [reaction mechanism](#) is 1 (with R an [alkoxy](#) group) as the nucleophile: [Deprotonation](#) of 1 by base leads to [carbanion](#) 2 stabilized by its electron-withdrawing groups. Structures 2a to 2c are three [resonance structures](#) that can be drawn for this species, two of which have [enolate](#) ions. This nucleophile reacts with the electrophilic alkene 3 to form 4 in a [conjugate addition reaction](#). Proton abstraction from protonated base (or solvent) by the enolate 4 to 5 is the final step.



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Conclusion of The Chapter



- Conclusion #1
 - The fundamental of alkynes with its nomenclature were understandable.
- Conclusion #2
 - The fundamental of alkynes included its reactions involves were practically explained.
- Conclusion #3
 - The synthesis of alkynes was understandable.



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