Organic Chemistry, *Second Edition*

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Chapter 11
Alkynes

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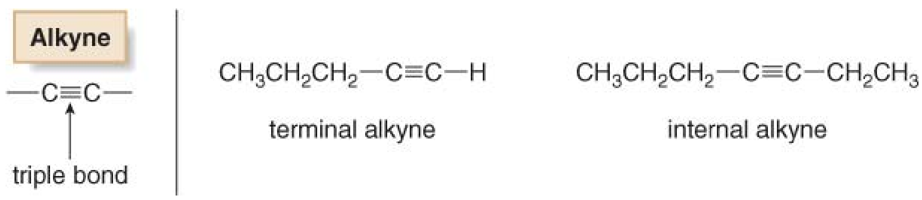
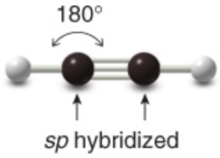
11.1 Introduction—Structure and Bonding

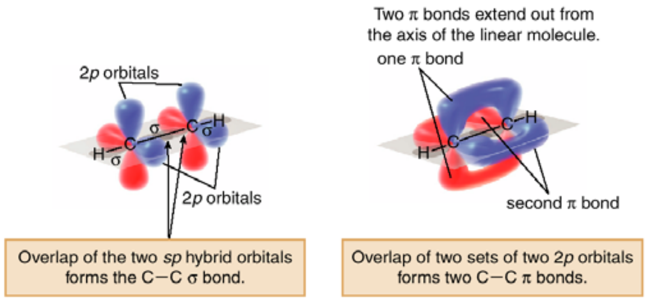
- **Alkynes contain a carbon—carbon triple bond.**
- **Terminal alkynes have the triple bond at the end of the carbon chain so that a hydrogen atom is directly bonded to a carbon atom of the triple bond.**
- **Internal alkynes have a carbon atom bonded to each carbon atom of the triple bond.**
- **An 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.**



- **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 180⁰.**

H–C≡C–H =
acetylene





- 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.

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- **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.**

HC≡CH		$CH_2{=}CH_2$		
200 kcal/mol	–	152 kcal/mol	=	48 kcal/mol
(σ + two π bonds)		(σ + π bond)		↑ **second π 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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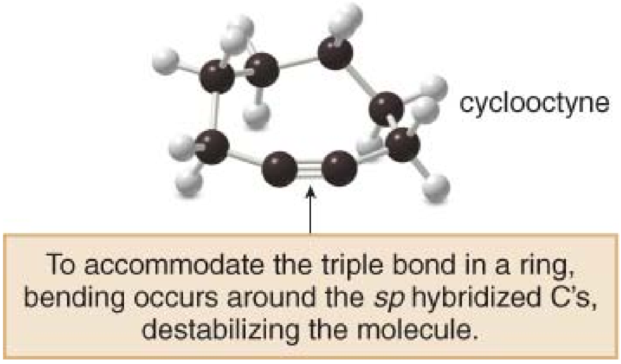
- Like trans cycloalkenes, cycloalkynes with small rings are unstable. The carbon chain must be long enough to connect the two ends of the triple bond without introducing too much strain.
- Cyclooctyne is the smallest isolable cycloalkyne, though it decomposes upon standing at room temperature after a short time.



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11.2 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 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≡C) the lower number.
- The simplest alkyne, H-C≡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.

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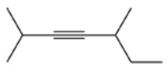
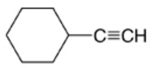
Figure 11.1 Examples of alkyne nomenclature



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

11.3 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.**

11.4 Interesting Alkynes

- **Acetylene (H-C≡C-H) is a colorless gas that burns in oxygen to form CO_2 and H_2O. The combustion of acetylene releases more energy per mole of product formed than any other hydrocarbons. It burns with a very hot flame and is an excellent fuel.**
- **Ethynylestradiol and norethindrone are two components of oral contraceptives that contain a carbon-carbon triple bond.**
  - **Both molecules are synthetic analogues of the naturally occurring female sex hormones estradiol and progesterone, but are more potent so they can be administered in lower doses.**
  - **Most oral contraceptives contain both of these synthetic hormones.**
  - **They act by artificially elevating hormone levels in a woman, thereby preventing pregnancy.**

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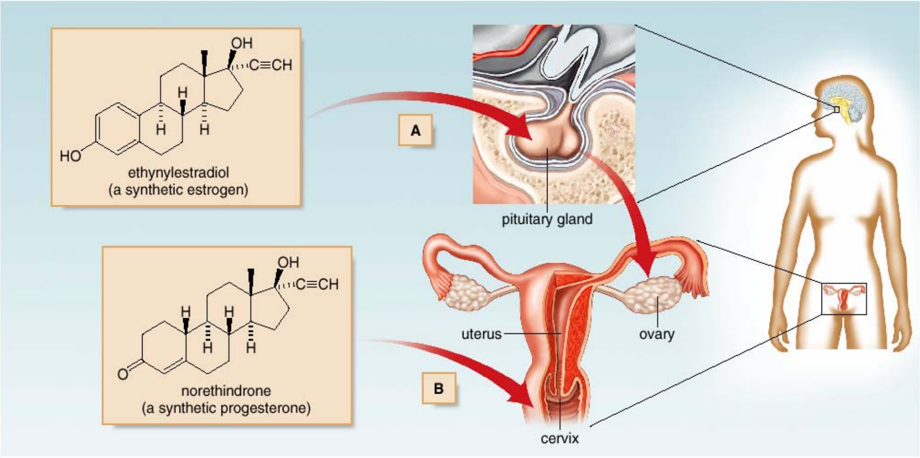
Figure 11.2 How oral contraceptives work

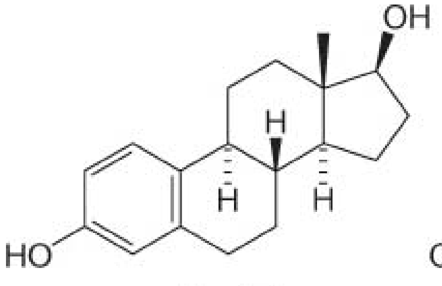


Monthly cycles of hormones from the pituitary gland cause ovulation, the release of an egg from an ovary. To prevent pregnancy, the two synthetic hormones in many oral contraceptives have different effects on the female reproductive system.

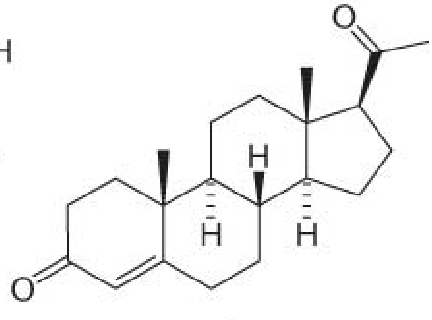
A: The elevated level of **ethynylestradiol,** a synthetic estrogen, “fools” the pituitary gland into thinking a woman is pregnant, so ovulation does not occur.

B: The elevated level of **norethindrone,** a synthetic progesterone, stimulates the formation of a thick layer of mucus in the cervix, making it difficult for sperm to reach the uterus.

Naturally occurring female sex hormones



estradiol



progesterone

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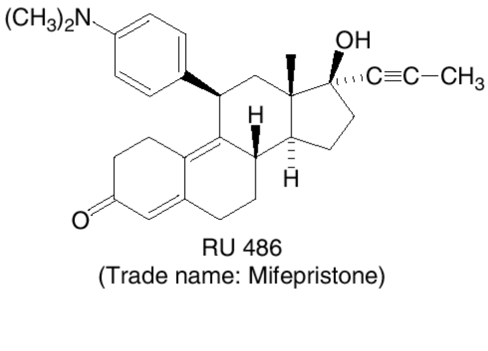
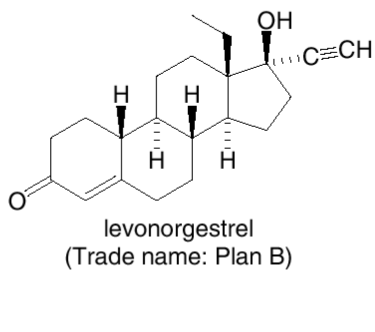
- **RU-486 and levonorgestrel are two other synthetic hormones. RU-486 blocks the effects of progesterone, thus preventing pregnancy. It is used to induce abortions within the first few weeks of pregnancy. Levonorgestrel interferes with ovulation, and so it prevents pregnancy if taken within a few days of unprotected sex.**



RU 486
(Trade name: Mifepristone)



levonorgestrel
(Trade name: Plan B)

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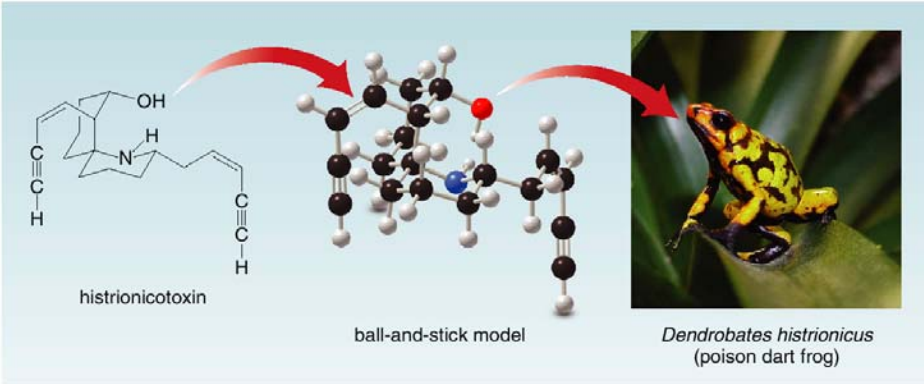
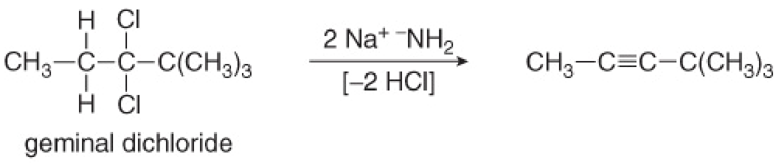
Figure 11.3 Histrionicotoxin

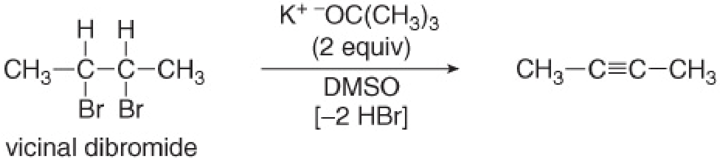


- Histrionicotoxin is a defensive toxin that protects *Dendrobates histrionicus* from potential predators. These small "poison dart" frogs inhabit the moist humid floor of tropical rainforests, and are commonly found in western Ecuador and Colombia. Histrionicotoxin acts by interfering with nerve transmission in mammals, resulting in prolonged muscle contraction.

11.5 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.**





11.6 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.

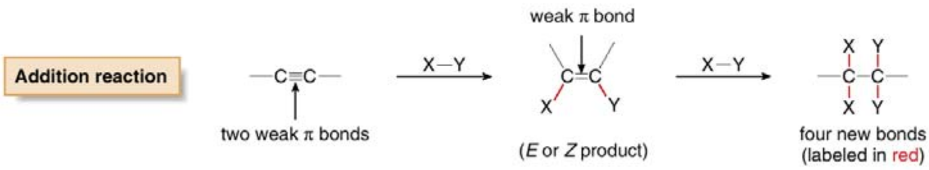


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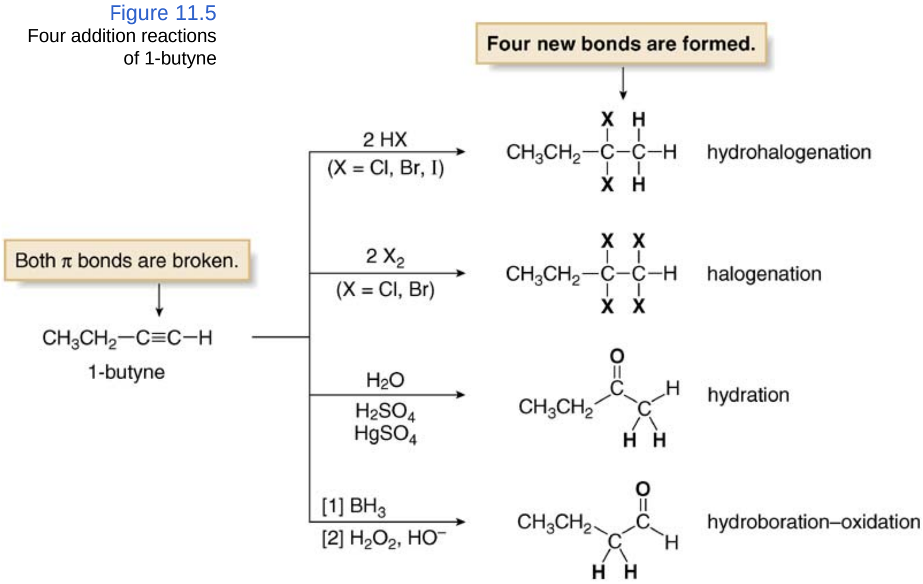
Figure 11.5
Four addition reactions of 1-butyne



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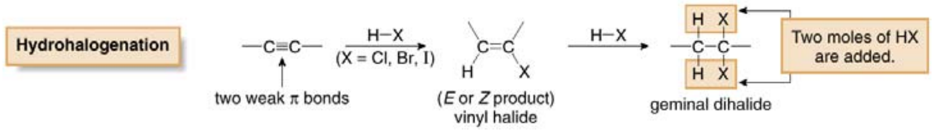
11.7 Addition of Hydrogen halides

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



- 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.

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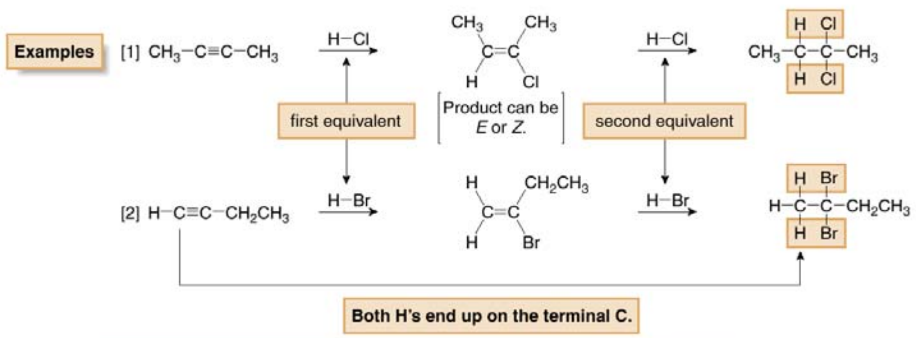
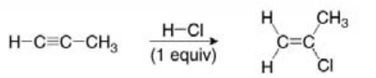
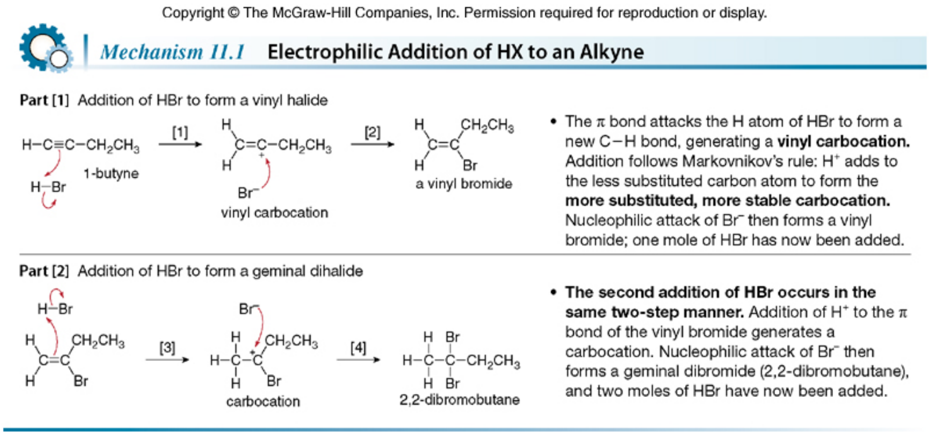
- With two equivalents of HX, both H atoms bond to the *same* carbon.
- With a terminal alkyne, both H atoms bond to the *terminal* carbon; that is, the hydrohalogenation of alkynes follows Markovnikov's rule.



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



a vinyl chloride
(2-chloropropene)



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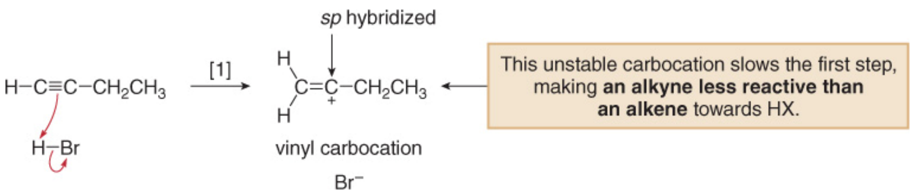
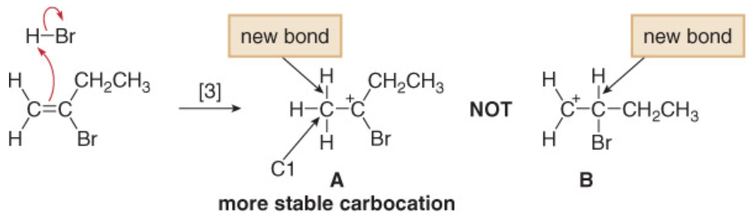
- **Electrophilic addition of HX to alkynes is slower than electrophilic addition of HX to alkenes, even though alkynes are more polarizable and have more loosely held π electrons than alkenes.**



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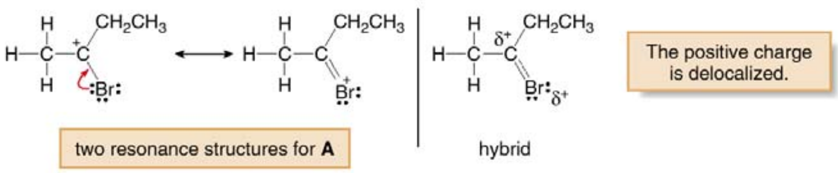
- **Carbocation A is stabilized by resonance, but B is not.**
- **Two resonance structures can be drawn for carbocation A, but only one Lewis structure can be drawn for carbocation B.**

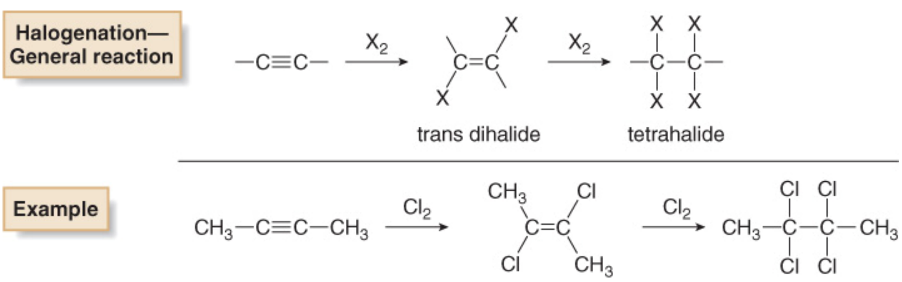


- Resonance stabilizes a molecule by delocalizing charge and electron density.
- Thus, halogens stabilize an adjacent positive charge by resonance.

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

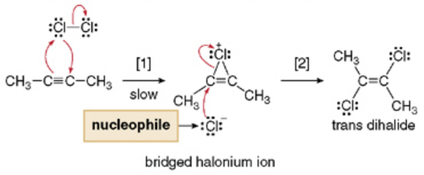
11.8 Addition of Halogen

- **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.**



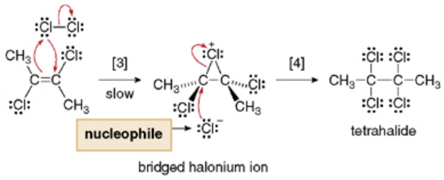
Mechanism 11.2 Addition of X_2 to an Alkyne—Halogenation

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 Cl^- from the back side forms the trans dihalide in Step [2].

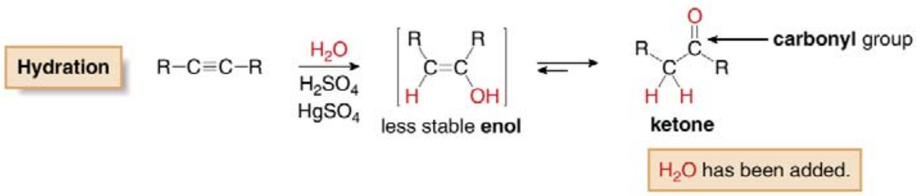
Part [2] Addition of X_2 to form a tetrahalide



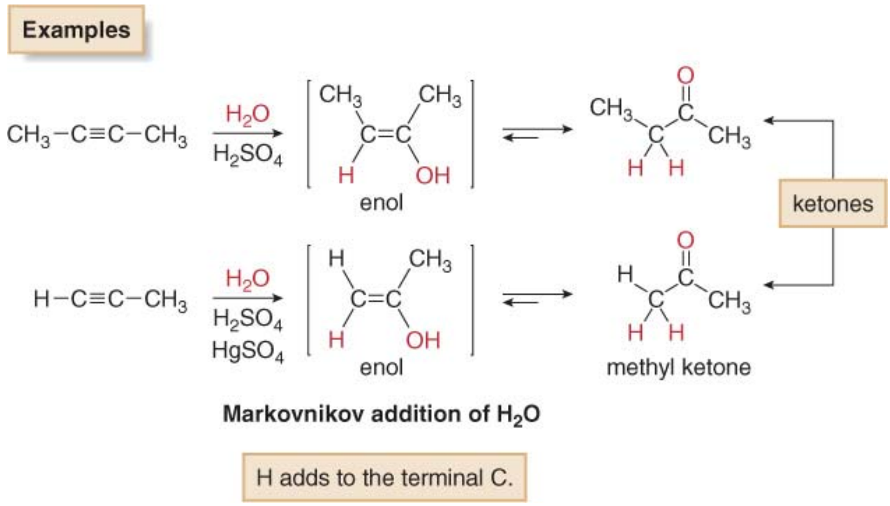
- **Electrophilic addition** of Cl^+ in Step [3] forms the bridged halonium ion ring, which is opened with Cl^- to form the tetrahalide in Step [4].

11.9 Addition of Water

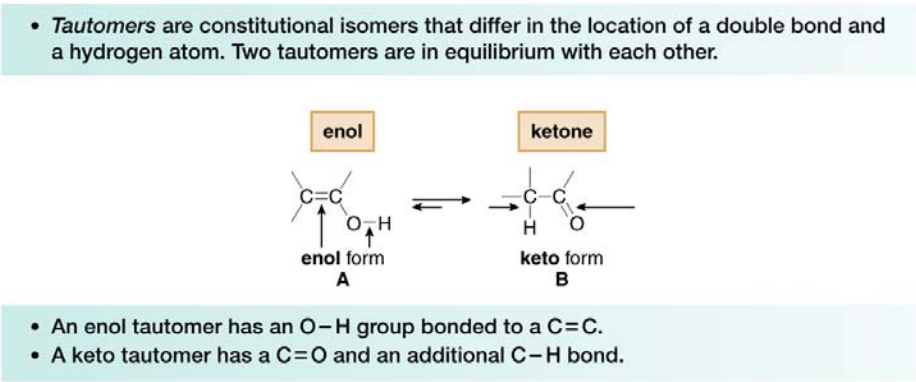
- **In the presence of strong acid or Hg^{2+} catalyst, the elements of H_2O add to the triple bond, but the initial addition product, an enol, is unstable and rearranges to a product containing a carbonyl group—that is, a C=O. A carbonyl compound having two alkyl groups bonded to the C=O carbon is called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



- **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.**



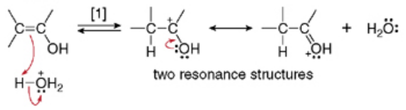
- **Consider the conversion of a general enol A to the carbonyl compound B. A and B are tautomers: A is the enol form and B is the keto form of the tautomer.**



- **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.**

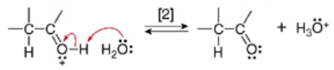
Mechanism 11.3 Tautomerization in Acid

Step [1] Protonation of the enol double bond



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

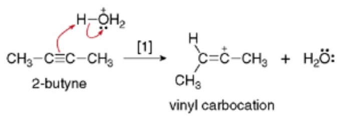
Step [2] Deprotonation of the OH group



- **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.**

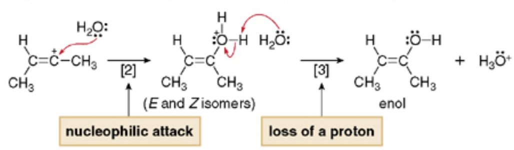
Mechanism 11.4 Hydration of an Alkyne

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



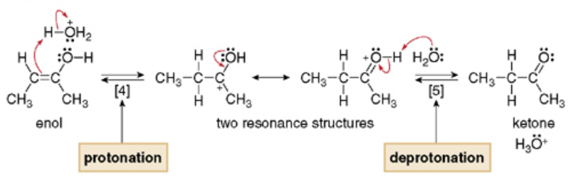
- Addition of H^+ (from H_3O^+) forms an *sp* hybridized **vinyl carbocation.**

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.

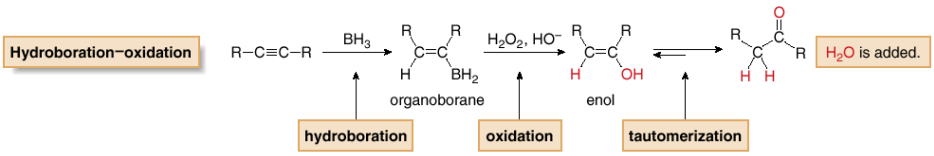
Steps [4] and [5] Tautomerization



- **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.

11.10 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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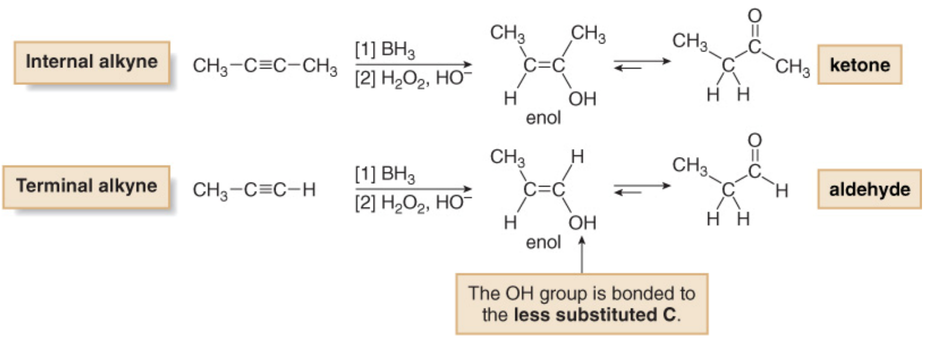
- **Hydroboration—oxidation of an internal alkyne forms a ketone.**
- **Hydroboration of a terminal alkyne adds BH_2 to the less substituted, terminal carbon. After oxidation to the enol, tautomerization yields an aldehyde, a carbonyl compound having a hydrogen atom bonded to the carbonyl carbon.**



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11.11 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.**

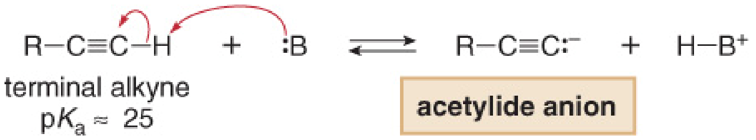
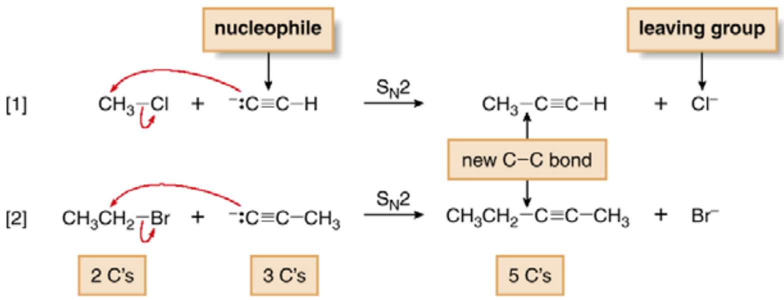


Table 11.1 A Comparison of Bases for Alkyne Deprotonation

	Base	pK_a of the conjugate acid
These bases are **strong** enough to deprotonate an alkyne.	$^-NH_2$	38
	H^-	35
These bases are ***not*** strong enough to deprotonate an alkyne.	^-OH	15.7
	^-OR	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 with CH_3X and 1⁰ alkyl halides.**



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

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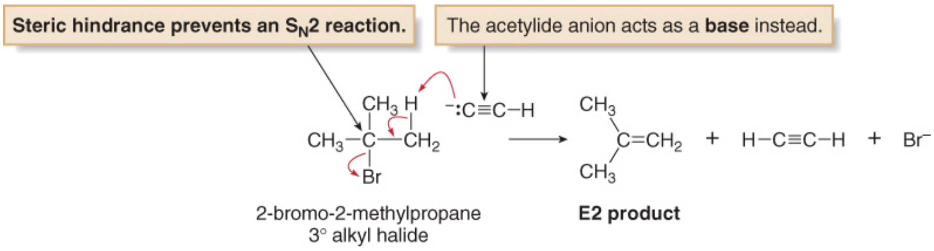
- **Steric hindrance around the leaving group causes 2° and 3 ° alkyl halides to undergo elimination by an E2 mechanism, as shown with 2-bromo-2-methylpropane.**
- **Thus, nucleophilic substitution with acetylide anions forms new carbon-carbon bonds in high yield only with unhindered CH_3X and 1° alkyl halides.**



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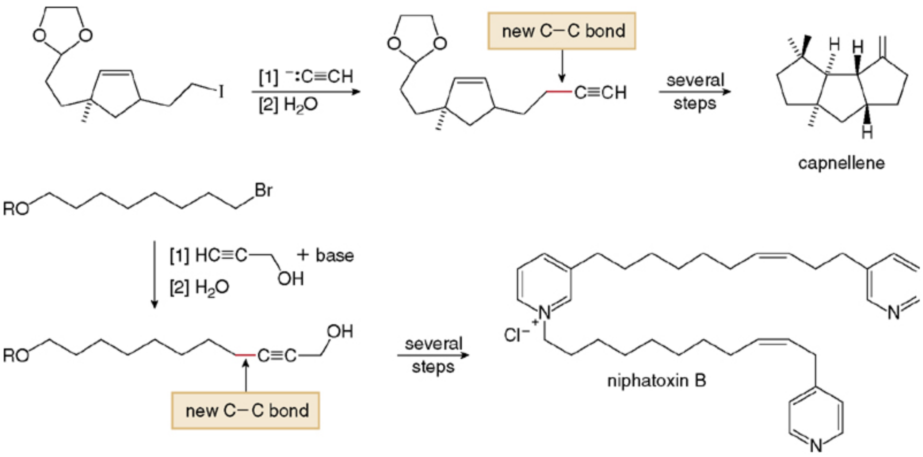
- **Carbon—carbon bond formation with acetylide anions is a valuable reaction used in the synthesis of numerous natural products.**

Figure 11.6 Use of acetylide anion reactions in the synthesis of two marine natural products



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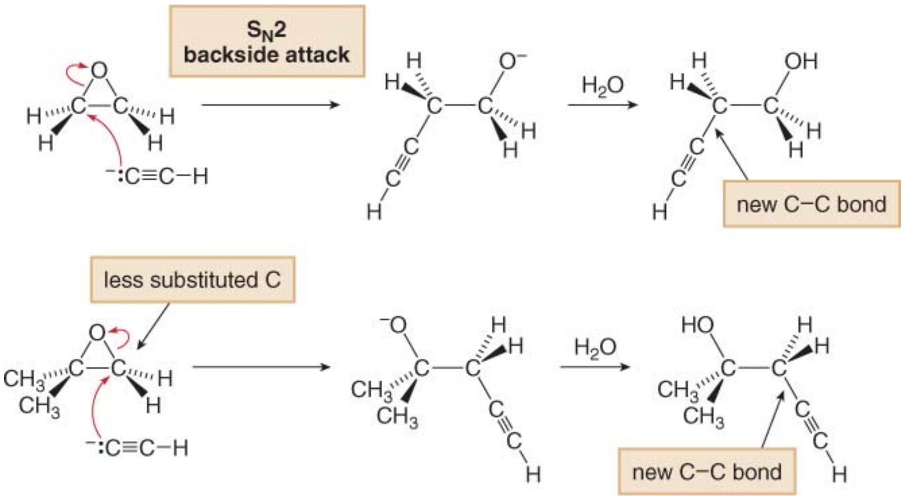
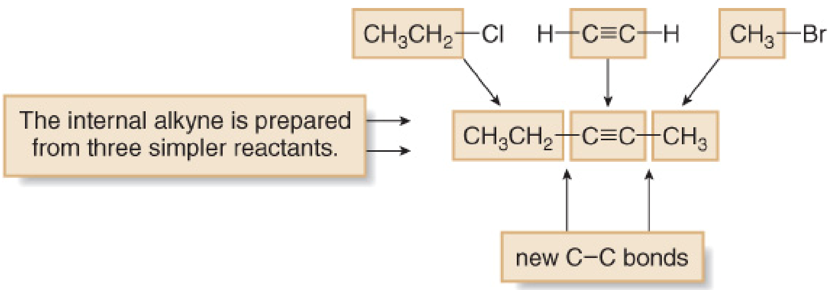
- **Acetylide anions are strong nucleophiles that open epoxide rings by an S_N2 mechanism.**
- **Backside attack occurs at the less substituted end of the epoxide.**



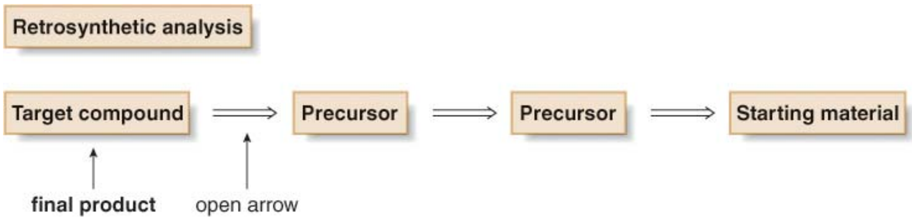
11.12 Synthesis

- **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.**

- To write a synthesis working backwards from the products to the starting materials, an open arrow (⇒) is used to indicate that the product is drawn on the left and the starting material on the right.
- The product of the synthesis is called the **target compound**.



- In designing a synthesis, reactions are often divided into two categories:
  1. Those that form new carbon-carbon bonds.
  2. Those that convert one functional group into another—that is, **functional group interconversions**.

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Synthesis

How To Develop a Retrosynthetic Analysis

Step [1] Compare the carbon skeletons of the starting material and product.

- If the product has more carbon–carbon σ bonds than the starting material, the synthesis must form one or more C–C bonds. If not, only functional group interconversion occurs.
- Match the carbons in the starting material with those in the product, to see where new C–C bonds must be added or where functional groups must be changed.

Step [2] Concentrate on the functional groups in the starting material and product and ask:

- What methods introduce the functional groups in the product?
- What kind of reactions does the starting material undergo?

Step [3] Work backwards from the product and forwards from the starting material.

- Ask: What is the immediate precursor of the product?
- Compare each precursor to the starting material to determine if there is a one-step reaction that converts one to the other. Continue this process until the starting material is reached.
- Always generate simpler precursors when working backwards.
- Use fewer steps when multiple routes are possible.
- Keep in mind that you may need to evaluate several different precursors for a given compound.

Step [4] Check the synthesis by writing it in the synthetic direction.

- To check a retrosynthetic analysis, write out the steps beginning with the starting material, indicating all necessary reagents.

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