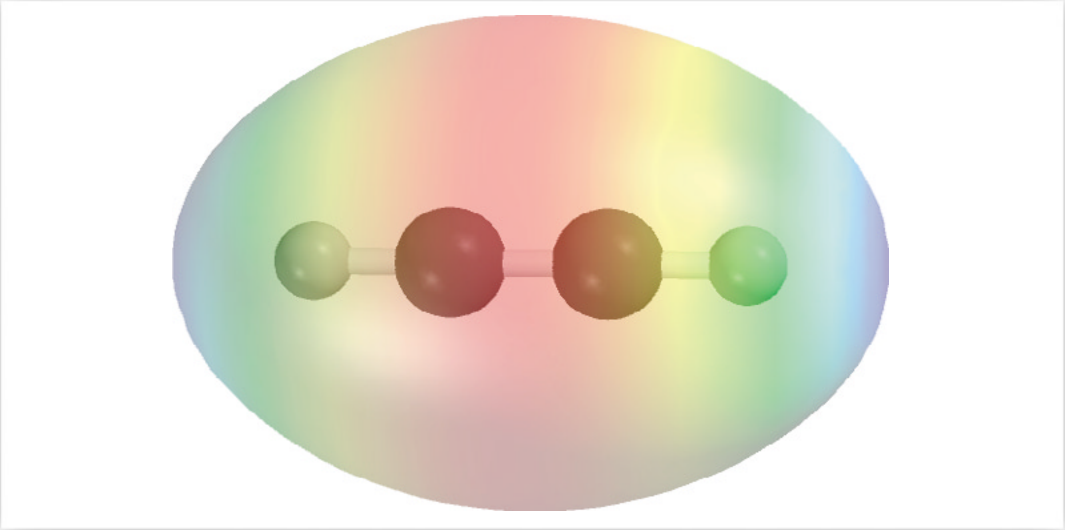


CHAPTER 9

ALKYNES

Hydrocarbons that contain a carbon–carbon triple bond are called **alkynes.** Noncyclic alkynes have the molecular formula C_nH_{2n-2}. *Acetylene* ($HC\equiv CH$) is the simplest alkyne. We call compounds that have their triple bond at the end of a carbon chain ($RC\equiv CH$) *monosubstituted,* or *terminal, alkynes.* Disubstituted alkynes ($RC\equiv CR'$) are said to have *internal* triple bonds. You will see in this chapter that a carbon–carbon triple bond is a functional group, reacting with many of the same reagents that react with the double bonds of alkenes.

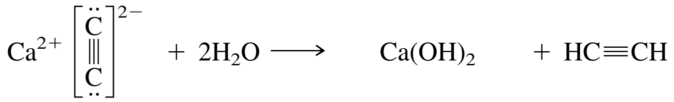
The most distinctive aspect of the chemistry of acetylene and terminal alkynes is their acidity. As a class, compounds of the type $RC\equiv CH$ are the most acidic of all simple hydrocarbons. The structural reasons for this property, as well as the ways in which it is used to advantage in chemical synthesis, are important elements of this chapter.

9.1 SOURCES OF ALKYNES

Acetylene was first characterized by the French chemist P. E. M. Berthelot in 1862 and did not command much attention until its large-scale preparation from calcium carbide in the last decade of the nineteenth century stimulated interest in industrial applications. In the first stage of that synthesis, limestone and coke, a material rich in elemental carbon obtained from coal, are heated in an electric furnace to form calcium carbide.

$$\underset{\substack{\text{Calcium oxide}\\ \text{(from limestone)}}}{CaO} + \underset{\substack{\text{Carbon}\\ \text{(from coke)}}}{3C} \xrightarrow{1800\text{–}2100°C} \underset{\text{Calcium carbide}}{CaC_2} + \underset{\text{Carbon monoxide}}{CO}$$

Calcium carbide is the calcium salt of the doubly negative carbide ion ($:\overset{-}{C}\equiv\overset{-}{C}:$). Carbide dianion is strongly basic and reacts with water to form acetylene:



$$Ca^{2+}\left[:C\equiv C:\right]^{2-} + 2H_2O \longrightarrow Ca(OH)_2 + HC\equiv CH$$

Calcium carbide Water Calcium hydroxide Acetylene

PROBLEM 9.1 Use curved arrows to show how calcium carbide reacts with water to give acetylene.

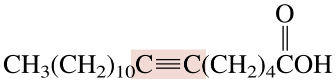
Beginning in the middle of the twentieth century, alternative methods of acetylene production became practical. One of these is based on the dehydrogenation of ethylene.

$$CH_2{=}CH_2 \xrightleftharpoons{\text{heat}} HC\equiv CH + H_2$$

Ethylene Acetylene Hydrogen

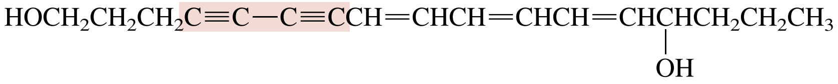
The reaction is endothermic, and the equilibrium favors ethylene at low temperatures but shifts to favor acetylene above 1150°C. Indeed, at very high temperatures most hydrocarbons, even methane, are converted to acetylene. Acetylene has value not only by itself but is also the starting material from which higher alkynes are prepared.

Natural products that contain carbon–carbon triple bonds are numerous. Two examples are *tariric acid,* from the seed fat of a Guatemalan plant, and *cicutoxin,* a poisonous substance isolated from water hemlock.



$$CH_3(CH_2)_{10}C\equiv C(CH_2)_4\overset{O}{\overset{\|}{C}}OH$$

Tariric acid



$$HOCH_2CH_2CH_2C\equiv C{-}C\equiv CCH{=}CHCH{=}CHCH{=}CH\underset{OH}{\underset{|}{C}}HCH_2CH_2CH_3$$

Cicutoxin

Diacetylene (HC≡C—C≡CH) has been identified as a component of the hydrocarbon-rich atmospheres of Uranus, Neptune, and Pluto. It is also present in the atmospheres of Titan and Triton, satellites of Saturn and Neptune, respectively.

9.2 NOMENCLATURE

In naming alkynes the usual IUPAC rules for hydrocarbons are followed, and the suffix *-ane* is replaced by *-yne*. Both acetylene and ethyne are acceptable IUPAC names for HC≡CH. The position of the triple bond along the chain is specified by number in a manner analogous to alkene nomenclature.

$HC\equiv CCH_3$	$HC\equiv CCH_2CH_3$	$CH_3C\equiv CCH_3$	$(CH_3)_3CC\equiv CCH_3$
Propyne	1-Butyne	2-Butyne	4,4-Dimethyl-2-pentyne

PROBLEM 9.2 Write structural formulas and give the IUPAC names for all the alkynes of molecular formula C_5H_8.

When the —C≡CH group is named as a substituent, it is designated as an *ethynyl* group.

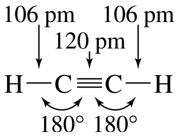
9.3 PHYSICAL PROPERTIES OF ALKYNES

Alkynes resemble alkanes and alkenes in their physical properties. They share with these other hydrocarbons the properties of low density and low water-solubility. They are slightly more polar and generally have slightly higher boiling points than the corresponding alkanes and alkenes.

Examples of physical properties of alkynes are given in Appendix 1.

9.4 STRUCTURE AND BONDING IN ALKYNES: *sp* HYBRIDIZATION

Acetylene is linear, with a carbon–carbon bond distance of 120 pm and carbon–hydrogen bond distances of 106 pm.



Linear geometries characterize the H—C≡C—C and C—C≡C—C units of terminal and internal triple bonds, respectively as well. This linear geometry is responsible for the relatively small number of known *cycloalkynes.* Figure 9.1 shows a molecular model for cyclononyne in which the bending of the C—C≡C—C unit is clearly evident. Angle strain destabilizes cycloalkynes to the extent that cyclononyne is the smallest one that is stable enough to be stored for long periods. The next smaller one, cyclooctyne, has been isolated, but is relatively reactive and polymerizes on standing.

In spite of the fact that few cycloalkynes occur naturally, they gained recent attention when it was discovered that some of them hold promise as anticancer drugs. (See the boxed essay *Natural and "Designed" Enediyne Antibiotics* following this section.)

An *sp* hybridization model for the carbon–carbon triple bond was developed in Section 1.18 and is reviewed for acetylene in Figure 9.2. Figure 9.3 maps the electrostatic potential in ethylene and acetylene and shows how the second π bond in acetylene causes a band of high electron density to encircle the molecule.

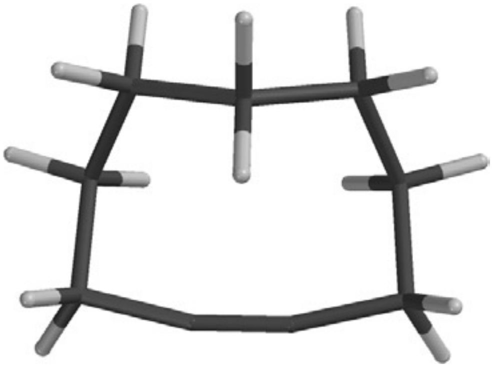


FIGURE 9.1 Molecular model of cyclononyne, showing bending of bond angles associated with triply bonded carbons. This model represents the structure obtained when the strain energy is minimized according to molecular mechanics and closely matches the structure determined experimentally. Notice too the degree to which the staggering of bonds on adjacent atoms governs the overall shape of the ring.

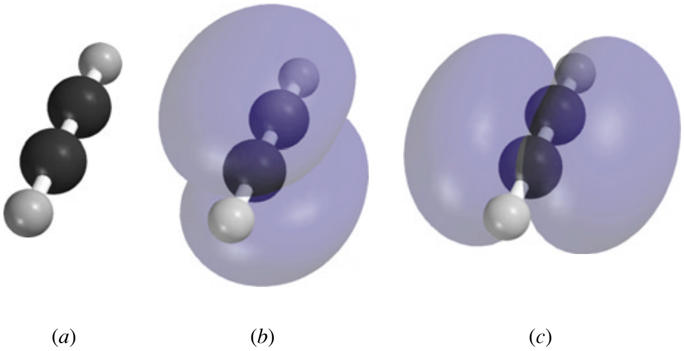


FIGURE 9.2 The carbon atoms of acetylene are connected by a $\sigma + \pi + \pi$ triple bond. Both carbon atoms are *sp*-hybridized, and each is bonded to a hydrogen by an *sp*–1*s* σ bond. The σ component of the triple bond arises by *sp*–*sp* overlap. Each carbon has two *p* orbitals, the axes of which are perpendicular to each other. One π bond is formed by overlap of the *p* orbitals shown in (*b*), the other by overlap of the *p* orbitals shown in (*c*). Each π bond contains two electrons.

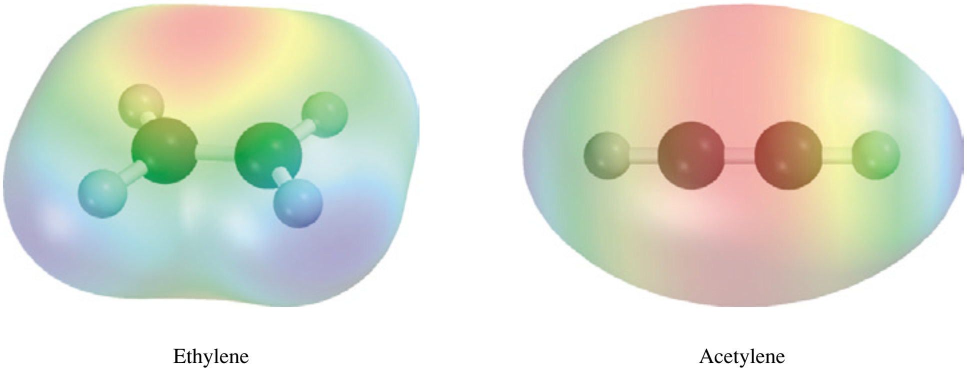


FIGURE 9.3 Electrostatic potential maps of ethylene and acetylene. The region of highest negative charge (red) is associated with the π bonds and lies between the two carbons in both. This electron-rich region is above and below the plane of the molecule in ethylene. Because acetylene has two π bonds, its band of high electron density encircles the molecule.

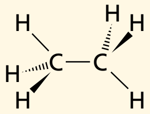
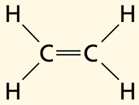
At this point, it's useful to compare some structural features of alkanes, alkenes, and alkynes. Table 9.1 gives some of the most fundamental ones. To summarize, as we progress through the series in the order ethane → ethylene → acetylene:

1. The geometry at carbon changes from tetrahedral → trigonal planar → linear.
2. The C—C and C—H bonds become shorter and stronger.
3. The acidity of the C—H bonds increases.

All of these trends can be accommodated by the orbital hybridization model. The bond angles are characteristic for the sp^3, sp^2, and *sp* hybridization states of carbon and don't require additional comment. The bond distances, bond strengths, and acidities are related to the *s* character in the orbitals used for bonding. *s* Character is a simple concept, being nothing more than the percentage of the hybrid orbital contributed by an *s* orbital. Thus, an sp^3 orbital has one quarter *s* character and three quarters *p,* an sp^2 orbital has one third *s* and two thirds *p,* and an *sp* orbital one half *s* and one half *p.* We then use this information to analyze how various qualities of the hybrid orbital reflect those of its *s* and *p* contributors.

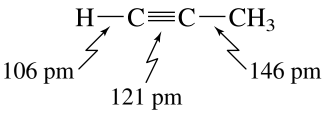
Take C—H bond distance and bond strength, for example. Recalling that an electron in a 2*s* orbital is, on average, closer to the nucleus and more strongly held than an

TABLE 9.1 Structural Features of Ethane, Ethylene, and Acetylene

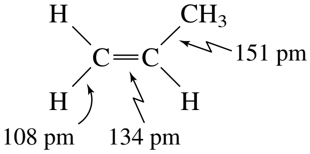
Feature	Ethane	Ethylene	Acetylene
Systematic name	Ethane	Ethene	Ethyne
Molecular formula	C_2H_6	C_2H_4	C_2H_2
Structural formula			H—C≡C—H
C—C bond distance, pm	153	134	120
C—H bond distance, pm	111	110	106
H—C—C bond angles	111.0°	121.4°	180°
C—C bond dissociation energy, kJ/mol (kcal/mol)	368 (88)	611 (146)	820 (196)
C—H bond dissociation energy, kJ/mol (kcal/mol)	410 (98)	452 (108)	536 (128)
Hybridization of carbon	sp^3	sp^2	sp
s character in C—H bonds	25%	33%	50%
Approximate acidity as measured by K_a (pK_a)	10^{-62} (62)	10^{-45} (45)	10^{-26} (26)

electron in a 2*p* orbital, it follows that an electron in an orbital with more *s* character will be closer to the nucleus and more strongly held than an electron in an orbital with less *s* character. Thus, when an *sp* orbital of carbon overlaps with a hydrogen 1*s* orbital to give a C—H σ bond, the electrons are held more strongly and the bond is stronger and shorter than electrons in a bond between hydrogen and sp^2-hybridized carbon. Similar reasoning holds for the shorter C—C bond distance of acetylene compared to ethylene, although here the additional π bond in acetylene is also a factor.

The pattern is repeated in higher alkynes as shown when comparing propyne and propene. The bonds to the *sp*-hybridized carbons of propyne are shorter than the corresponding bonds to the sp^2 hybridized carbons of propene.



Propyne



Propene

How do the bond distances of molecular models of propene and propyne compare with the experimental values?

An easy way to keep track of the effect of the *s* character of carbon is to associate it with electronegativity. As the *s* character of carbon increases, so does that carbon's apparent electronegativity (the electrons in the bond involving that orbital are closer to carbon). The hydrogens in C—H bonds behave as if they are attached to an increasingly more electronegative carbon in the series ethane → ethylene → acetylene.

PROBLEM 9.3 How do bond distances and bond strengths change with electronegativity in the series NH_3, H_2O, and HF?

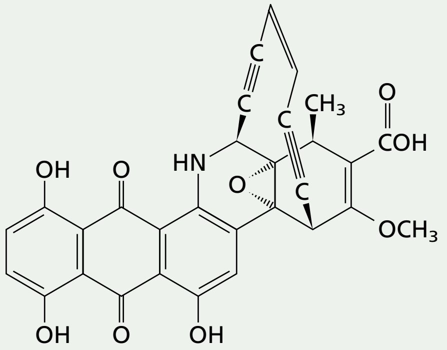
The property that most separates acetylene from ethane and ethylene is its acidity. It, too, can be explained on the basis of the greater electronegativity of *sp*-hybridized carbon compared with sp^3 *and* sp^2.

NATURAL AND “DESIGNED” ENEDIYNE ANTIBIOTICS

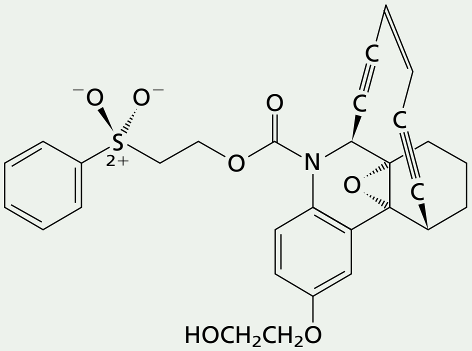
Beginning in the 1980s, research directed toward the isolation of new drugs derived from natural sources identified a family of tumor-inhibitory antibiotic substances characterized by novel structures containing a $C\equiv C{-}C{=}C{-}C\equiv C$ unit as part of a 9- or 10-membered ring. With one double bond and two triple bonds (*-ene* + *di-* + *-yne*), these compounds soon became known as *enediyne* antibiotics. The simplest member of the class is *dynemicin A*;* most of the other enediynes have even more complicated structures.

Enediynes hold substantial promise as anticancer drugs because of their potency and selectivity. Not only do they inhibit cell growth, they have a greater tendency to kill cancer cells than they do normal cells. The mechanism by which enediynes act involves novel chemistry unique to the $C\equiv C{-}C{=}C{-}C\equiv C$ unit, which leads to a species that cleaves DNA and halts tumor growth.

The history of drug development has long been based on naturally occurring substances. Often, however, compounds that might be effective drugs are produced by plants and microorganisms in such small amounts that their isolation from natural sources is not practical. If the structure is relatively simple, chemical synthesis provides an alternative source of the drug, making it more available at a lower price. Equally important, chemical synthesis, modification, or both can improve the effectiveness of a drug. Building on the enediyne core of dynemicin A, for example, Professor Kyriacos C. Nicolaou and his associates at the Scripps Research Institute and the University of California at San Diego have prepared a simpler analog that is both more potent and more selective than dynemicin A. It is a “designed enediyne” in that its structure was conceived on the basis of chemical reasoning so as to carry out its biochemical task. The designed enediyne offers the additional advantage of being more amenable to large-scale synthesis.



Dynemicin A

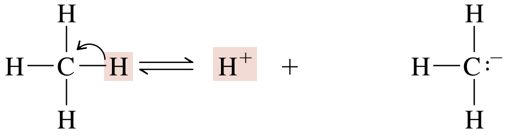


“Designed” enediyne

**Learning By Modeling* contains a model of dynemicin A, which shows that the $C\equiv C{-}C{=}C{-}C\equiv C$ unit can be incorporated into the molecule without much angle strain.

9.5 ACIDITY OF ACETYLENE AND TERMINAL ALKYNES

The C—H bonds of hydrocarbons show little tendency to ionize, and alkanes, alkenes, and alkynes are all very weak acids. The ionization constant K_a for methane, for example, is too small to be measured directly but is estimated to be about 10^{-60} (pK_a 60).



Methane Proton Methide anion (a *carbanion*)

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The conjugate base of a hydrocarbon is called a **carbanion.** It is an anion in which the negative charge is borne by carbon. Since it is derived from a very weak acid, a carbanion such as $^{-}\!:\!CH_3$ is an exceptionally strong base.

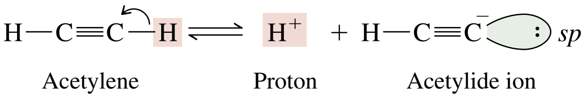
In general, the ability of an atom to bear a negative charge is related to its electronegativity. Both the electronegativity of an atom X and the acidity of H—X increase across a row in the periodic table.

CH_4	$<$	NH_3	$<$	H_2O	$<$	HF
Methane		Ammonia		Water		Hydrogen fluoride
$K_a \approx 10^{-60}$		$\approx 10^{-36}$		1.8×10^{-16}		3.5×10^{-4}
$pK_a \approx 60$		≈ 36		15.7		3.2
(weakest acid)						(strongest acid)

Using the relationship from the preceding section that the effective electronegativity of carbon in a C—H bond increases with its *s* character ($sp^3 < sp^2 < sp$), the order of hydrocarbon acidity behaves much like the preceding methane, ammonia, water, hydrogen fluoride series.

CH_3CH_3	$<$	$CH_2{=}CH_2$	$<$	$HC{\equiv}CH$
Ethane		Ethylene		Acetylene
$K_a \approx 10^{-62}$		$\approx 10^{-45}$		$= 10^{-26}$
$pK_a \approx 62$		≈ 45		$= 26$
(weakest acid)				(strongest acid)

The acidity increases as carbon becomes more electronegative. Ionization of acetylene gives an anion in which the unshared electron pair occupies an orbital with 50% *s* character.



In the corresponding ionizations of ethylene and ethane, the unshared pair occupies an orbital with 33% (sp^2) and 25% (sp^3) *s* character, respectively.

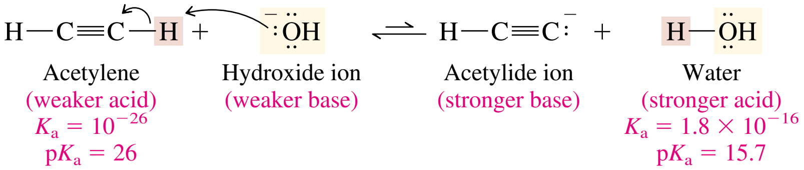
Terminal alkynes (RC≡CH) resemble acetylene in acidity.

$$(CH_3)_3CC{\equiv}CH \qquad K_a = 3 \times 10^{-26}\ (pK_a = 25.5)$$

3,3-Dimethyl-1-butyne

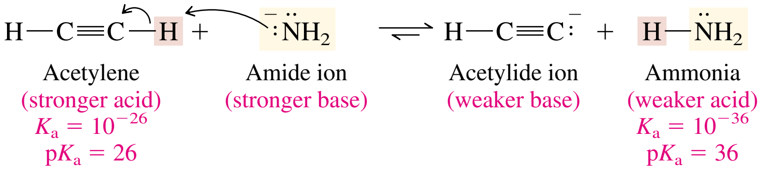
The electrostatic potential map of $(CH_3)_3CC{\equiv}CH$ on *Learning By Modeling* clearly shows the greater positive character of the acetylenic hydrogen relative to the methyl hydrogens.

Although acetylene and terminal alkynes are far stronger acids than other hydrocarbons, we must remember that they are, nevertheless, very weak acids—much weaker than water and alcohols, for example. Hydroxide ion is too weak a base to convert acetylene to its anion in meaningful amounts. The position of the equilibrium described by the following equation lies overwhelmingly to the left:



Because acetylene is a far weaker acid than water and alcohols, these substances are not suitable solvents for reactions involving acetylide ions. Acetylide is instantly converted to acetylene by proton transfer from compounds that contain hydroxyl groups.

Amide ion is a much stronger base than acetylide ion and converts acetylene to its conjugate base quantitatively.



Solutions of sodium acetylide ($HC\equiv CNa$) may be prepared by adding *sodium amide* ($NaNH_2$) to acetylene in liquid ammonia as the solvent. Terminal alkynes react similarly to give species of the type $RC\equiv CNa$.

PROBLEM 9.4 Complete each of the following equations to show the conjugate acid and the conjugate base formed by proton transfer between the indicated species. Use curved arrows to show the flow of electrons, and specify whether the position of equilibrium lies to the side of reactants or products.

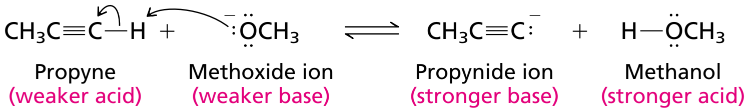
(a) $CH_3C\equiv CH + {}^{-}{:}\ddot{\underset{..}{O}}CH_3 \rightleftharpoons$

(b) $HC\equiv CH + H_2\overset{-}{\ddot{C}}CH_3 \rightleftharpoons$

(c) $CH_2{=}CH_2 + {}^{-}{:}\ddot{N}H_2 \rightleftharpoons$

(d) $CH_3C\equiv CCH_2OH + {}^{-}{:}\ddot{N}H_2 \rightleftharpoons$

SAMPLE SOLUTION (a) The equation representing the acid–base reaction between propyne and methoxide ion is:



Alcohols are stronger acids than acetylene, and so the position of equilibrium lies to the left. Methoxide ion is not a strong enough base to remove a proton from acetylene.

Anions of acetylene and terminal alkynes are nucleophilic and react with methyl and primary alkyl halides to form carbon–carbon bonds by nucleophilic substitution. Some useful applications of this reaction will be discussed in the following section.

9.6 PREPARATION OF ALKYNES BY ALKYLATION OF ACETYLENE AND TERMINAL ALKYNES

Organic synthesis makes use of two major reaction types:

1. Functional group transformations
2. Carbon–carbon bond-forming reactions

Both strategies are applied to the preparation of alkynes. In this section we shall see how to prepare alkynes while building longer carbon chains. By attaching alkyl groups to acetylene, more complex alkynes can be prepared.

$$\mathrm{H{-}C{\equiv}C{-}H} \longrightarrow \mathrm{R{-}C{\equiv}C{-}H} \longrightarrow \mathrm{R{-}C{\equiv}C{-}R'}$$

Acetylene — Monosubstituted or terminal alkyne — Disubstituted derivative of acetylene

Reactions that attach alkyl groups to molecular fragments are called **alkylation** reactions. One way in which alkynes are prepared is by alkylation of acetylene.

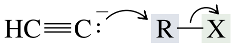
Alkylation of acetylene involves a sequence of two separate operations. In the first one, acetylene is converted to its conjugate base by treatment with sodium amide.

$$\mathrm{HC{\equiv}CH} + \mathrm{NaNH_2} \longrightarrow \mathrm{HC{\equiv}CNa} + \mathrm{NH_3}$$

Acetylene — Sodium amide — Sodium acetylide — Ammonia

Next, an alkyl halide (the *alkylating agent*) is added to the solution of sodium acetylide. Acetylide ion acts as a nucleophile, displacing halide from carbon and forming a new carbon–carbon bond. Substitution occurs by an S_N2 mechanism.

$$\mathrm{HC{\equiv}CNa} + \mathrm{RX} \longrightarrow \mathrm{HC{\equiv}CR} + \mathrm{NaX} \quad \text{via}$$



$$\mathrm{HC{\equiv}C{:}^{-}\ \ R{-}X}$$

Sodium acetylide — Alkyl halide — Alkyne — Sodium halide

The synthetic sequence is usually carried out in liquid ammonia as the solvent. Alternatively, diethyl ether or tetrahydrofuran may be used.

$$\mathrm{HC{\equiv}CNa} + \mathrm{CH_3CH_2CH_2CH_2Br} \xrightarrow{\mathrm{NH_3}} \mathrm{CH_3CH_2CH_2CH_2C{\equiv}CH}$$

Sodium acetylide — 1-Bromobutane — 1-Hexyne (70–77%)

An analogous sequence using terminal alkynes as starting materials yields alkynes of the type $\mathrm{RC{\equiv}CR'}$.

$$\mathrm{(CH_3)_2CHCH_2C{\equiv}CH} \xrightarrow[\mathrm{NH_3}]{\mathrm{NaNH_2}} \mathrm{(CH_3)_2CHCH_2C{\equiv}CNa} \xrightarrow{\mathrm{CH_3Br}} \mathrm{(CH_3)_2CHCH_2C{\equiv}CCH_3}$$

4-Methyl-1-pentyne — 5-Methyl-2-hexyne (81%)

Dialkylation of acetylene can be achieved by carrying out the sequence twice.

$$\mathrm{HC{\equiv}CH} \xrightarrow[\text{2. } \mathrm{CH_3CH_2Br}]{\text{1. } \mathrm{NaNH_2,\ NH_3}} \mathrm{HC{\equiv}CCH_2CH_3} \xrightarrow[\text{2. } \mathrm{CH_3Br}]{\text{1. } \mathrm{NaNH_2,\ NH_3}} \mathrm{CH_3C{\equiv}CCH_2CH_3}$$

Acetylene — 1-Butyne — 2-Pentyne (81%)

As in other nucleophilic substitution reactions, alkyl *p*-toluenesulfonates may be used in place of alkyl halides.

PROBLEM 9.5 Outline efficient syntheses of each of the following alkynes from acetylene and any necessary organic or inorganic reagents:

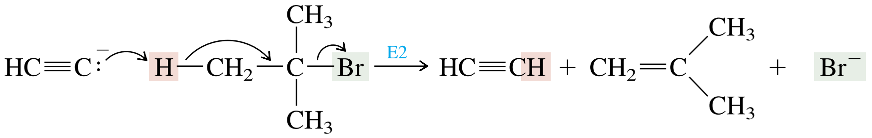
(a) 1-Heptyne
(b) 2-Heptyne
(c) 3-Heptyne

SAMPLE SOLUTION (a) An examination of the structural formula of 1-heptyne reveals it to have a pentyl group attached to an acetylene unit. Alkylation of acetylene, by way of its anion, with a pentyl halide is a suitable synthetic route to 1-heptyne.

$$\mathrm{HC{\equiv}CH} \xrightarrow[\mathrm{NH_3}]{\mathrm{NaNH_2}} \mathrm{HC{\equiv}CNa} \xrightarrow{\mathrm{CH_3CH_2CH_2CH_2CH_2Br}} \mathrm{HC{\equiv}CCH_2CH_2CH_2CH_2CH_3}$$

Acetylene Sodium acetylide 1-Heptyne

The major limitation to this reaction is that synthetically acceptable yields are obtained only with methyl halides and primary alkyl halides. Acetylide anions are very basic, much more basic than hydroxide, for example, and react with secondary and tertiary alkyl halides by elimination.



Acetylide *tert*-Butyl bromide Acetylene 2-Methylpropene Bromide

The desired S_N2 *substitution pathway is observed only with methyl and primary alkyl halides.*

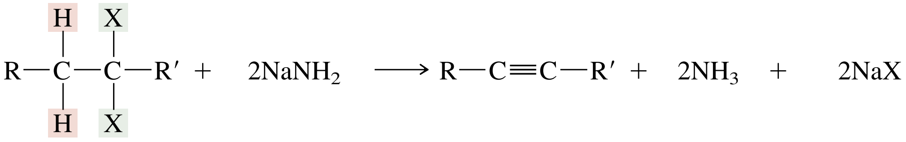
PROBLEM 9.6 Which of the alkynes of molecular formula C_5H_8 can be prepared in good yield by alkylation or dialkylation of acetylene? Explain why the preparation of the other C_5H_8 isomers would not be practical.

A second strategy for alkyne synthesis, involving functional group transformation reactions, is described in the following section.

9.7 PREPARATION OF ALKYNES BY ELIMINATION REACTIONS

Just as it is possible to prepare alkenes by dehydrohalogenation of alkyl halides, so may alkynes be prepared by a *double dehydrohalogenation* of dihaloalkanes. The dihalide may be a **geminal dihalide,** one in which both halogens are on the same carbon, or it may be a **vicinal dihalide,** one in which the halogens are on adjacent carbons.

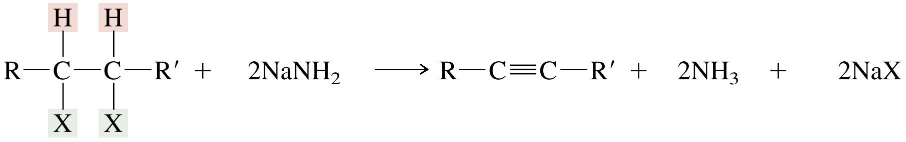
Double dehydrohalogenation of a geminal dihalide



$$\mathrm{R{-}\overset{H}{\underset{H}{C}}{-}\overset{X}{\underset{X}{C}}{-}R'} + \mathrm{2NaNH_2} \longrightarrow \mathrm{R{-}C{\equiv}C{-}R'} + \mathrm{2NH_3} + \mathrm{2NaX}$$

Geminal dihalide Sodium amide Alkyne Ammonia Sodium halide

Double dehydrohalogenation of a vicinal dihalide



$$\mathrm{R{-}\overset{H}{\underset{X}{C}}{-}\overset{H}{\underset{X}{C}}{-}R'} + \mathrm{2NaNH_2} \longrightarrow \mathrm{R{-}C{\equiv}C{-}R'} + \mathrm{2NH_3} + \mathrm{2NaX}$$

Vicinal dihalide Sodium amide Alkyne Ammonia Sodium halide

The most frequent applications of these procedures are in the preparation of terminal alkynes. Since the terminal alkyne product is acidic enough to transfer a proton to amide anion, one equivalent of base in addition to the two equivalents required for double

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dehydrohalogenation is needed. Adding water or acid after the reaction is complete converts the sodium salt to the corresponding alkyne.

Double dehydrohalogenation of a geminal dihalide

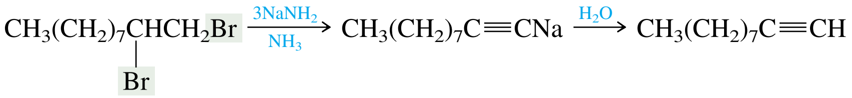
$$(CH_3)_3CCH_2CHCl_2 \xrightarrow[NH_3]{3NaNH_2} (CH_3)_3CC{\equiv}CNa \xrightarrow{H_2O} (CH_3)_3CC{\equiv}CH$$

1,1-Dichloro-3,3-dimethylbutane

Sodium salt of alkyne product (not isolated)

3,3-Dimethyl-1-butyne (56–60%)

Double dehydrohalogenation of a vicinal dihalide



$$CH_3(CH_2)_7\underset{\underset{\displaystyle Br}{|}}{C}HCH_2Br \xrightarrow[NH_3]{3NaNH_2} CH_3(CH_2)_7C{\equiv}CNa \xrightarrow{H_2O} CH_3(CH_2)_7C{\equiv}CH$$

1,2-Dibromodecane

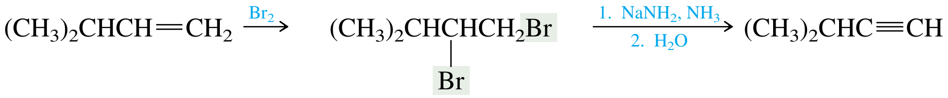
Sodium salt of alkyne product (not isolated)

1-Decyne (54%)

Double dehydrohalogenation to form terminal alkynes may also be carried out by heating geminal and vicinal dihalides with potassium *tert*-butoxide in dimethyl sulfoxide.

PROBLEM 9.7 Give the structures of three isomeric dibromides that could be used as starting materials for the preparation of 3,3-dimethyl-1-butyne.

Since vicinal dihalides are prepared by addition of chlorine or bromine to alkenes (Section 6.14), alkenes, especially terminal alkenes, can serve as starting materials for the preparation of alkynes as shown in the following example:



$$(CH_3)_2CHCH{=}CH_2 \xrightarrow{Br_2} (CH_3)_2CH\underset{\underset{\displaystyle Br}{|}}{C}HCH_2Br \xrightarrow[2.\ H_2O]{1.\ NaNH_2,\ NH_3} (CH_3)_2CHC{\equiv}CH$$

3-Methyl-1-butene

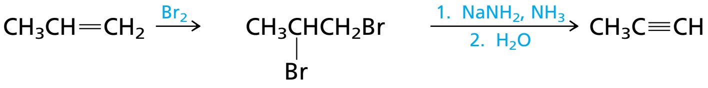
1,2-Dibromo-3-methylbutane

3-Methyl-1-butyne (52%)

PROBLEM 9.8 Show, by writing an appropriate series of equations, how you could prepare propyne from each of the following compounds as starting materials. You may use any necessary organic or inorganic reagents.

(a) 2-Propanol
(b) 1-Propanol
(c) Isopropyl bromide
(d) 1,1-Dichloroethane
(e) Ethyl alcohol

SAMPLE SOLUTION (a) Since we know that we can convert propene to propyne by the sequence of reactions



$$CH_3CH{=}CH_2 \xrightarrow{Br_2} CH_3\underset{\underset{\displaystyle Br}{|}}{C}HCH_2Br \xrightarrow[2.\ H_2O]{1.\ NaNH_2,\ NH_3} CH_3C{\equiv}CH$$

Propene

1,2-Dibromopropane

Propyne

all that remains to completely describe the synthesis is to show the preparation of propene from 2-propanol. Acid-catalyzed dehydration is suitable.

$$(CH_3)_2CHOH \xrightarrow[heat]{H^+} CH_3CH{=}CH_2$$

2-Propanol

Propene

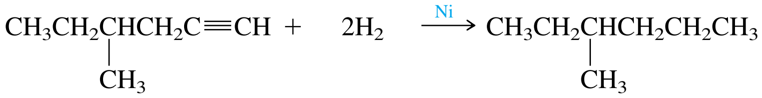
9.8 REACTIONS OF ALKYNES

We have already discussed one important chemical property of alkynes, the acidity of acetylene and terminal alkynes. In the remaining sections of this chapter several other reactions of alkynes will be explored. Most of them will be similar to reactions of alkenes. Like alkenes, alkynes undergo addition reactions. We'll begin with a reaction familiar to us from our study of alkenes, namely, catalytic hydrogenation.

9.9 HYDROGENATION OF ALKYNES

The conditions for hydrogenation of alkynes are similar to those employed for alkenes. In the presence of finely divided platinum, palladium, nickel, or rhodium, two molar equivalents of hydrogen add to the triple bond of an alkyne to yield an alkane.

$$\underset{\text{Alkyne}}{\mathrm{RC{\equiv}CR'}} + \underset{\text{Hydrogen}}{\mathrm{2H_2}} \xrightarrow{\text{Pt, Pd, Ni, or Rh}} \underset{\text{Alkane}}{\mathrm{RCH_2CH_2R'}}$$



$$\underset{\text{4-Methyl-1-hexyne}}{\mathrm{CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2C{\equiv}CH}} + \underset{\text{Hydrogen}}{\mathrm{2H_2}} \xrightarrow{\text{Ni}} \underset{\text{3-Methylhexane (77\%)}}{\mathrm{CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2CH_3}}$$

PROBLEM 9.9 Write a series of equations showing how you could prepare octane from acetylene and any necessary organic and inorganic reagents.

Substituents affect the heats of hydrogenation of alkynes in the same way they affect alkenes. Alkyl groups release electrons to *sp*-hybridized carbon, stabilizing the alkyne and decreasing the heat of hydrogenation.

	$\mathrm{CH_3CH_2C{\equiv}CH}$	$\mathrm{CH_3C{\equiv}CCH_3}$
	1-Butyne	2-Butyne
$-\Delta H°$ (hydrogenation)	292 kJ/mol (69.9 kcal/mol)	275 kJ/mol (65.6 kcal/mol)

Alkenes are intermediates in the hydrogenation of alkynes to alkanes.

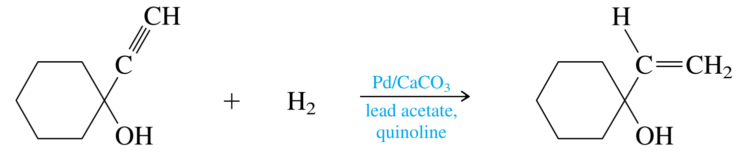
$$\underset{\text{Alkyne}}{\mathrm{RC{\equiv}CR'}} \xrightarrow[\text{catalyst}]{\mathrm{H_2}} \underset{\text{Alkene}}{\mathrm{RCH{=}CHR'}} \xrightarrow[\text{catalyst}]{\mathrm{H_2}} \underset{\text{Alkane}}{\mathrm{RCH_2CH_2R'}}$$

The heat of hydrogenation of an alkyne is greater than twice the heat of hydrogenation of the derived alkene. The first hydrogenation step of an alkyne is therefore more exothermic than the second.

The high energy of acetylene is released when it is mixed with oxygen and burned in an *oxyacetylene torch.* The temperature of the flame (about 3000°C) exceeds that of any other hydrocarbon fuel and is higher than the melting point of iron (1535°C).

Noting that alkenes are intermediates in the hydrogenation of alkynes leads us to consider the possibility of halting hydrogenation at the alkene stage. If partial hydrogenation of an alkyne could be achieved, it would provide a useful synthesis of alkenes. In practice it is a simple matter to convert alkynes to alkenes by hydrogenation in the presence of specially developed catalysts. The one most frequently used is the **Lindlar catalyst,** a palladium on calcium carbonate combination to which lead acetate and quinoline have been added. Lead acetate and quinoline partially deactivate ("poison") the catalyst, making it a poor catalyst for alkene hydrogenation while retaining its ability to catalyze the addition of hydrogen to alkynes.

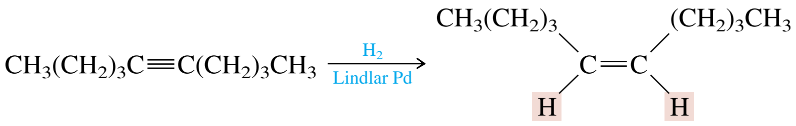
The structure of quinoline is shown on page 430.



1-Ethynylcyclohexanol Hydrogen 1-Vinylcyclohexanol (90–95%)

In subsequent equations, we will not specify the components of the Lindlar palladium catalyst in detail but will simply write "Lindlar Pd" over the reaction arrow.

Hydrogenation of alkynes to alkenes yields the cis (or *Z*) alkene by syn addition to the triple bond.

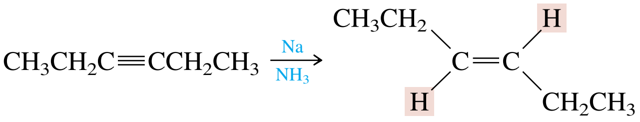


5-Decyne (*Z*)-5-Decene (87%)

PROBLEM 9.10 Oleic acid and stearic acid are naturally occurring compounds, which can be isolated from various fats and oils. In the laboratory, each can be prepared by hydrogenation of a compound known as *stearolic acid,* which has the formula $CH_3(CH_2)_7C\equiv C(CH_2)_7CO_2H$. Oleic acid is obtained by hydrogenation of stearolic acid over Lindlar palladium; stearic acid is obtained by hydrogenation over platinum. What are the structures of oleic acid and stearic acid?

9.10 METAL–AMMONIA REDUCTION OF ALKYNES

A useful alternative to catalytic partial hydrogenation for converting alkynes to alkenes is reduction by a Group I metal (lithium, sodium, or potassium) in liquid ammonia. The unique feature of metal–ammonia reduction is that it converts alkynes to trans (or *E*) alkenes whereas catalytic hydrogenation yields cis (or *Z*) alkenes. Thus, from the same alkyne one can prepare either a cis or a trans alkene by choosing the appropriate reaction conditions.



3-Hexyne (*E*)-3-Hexene (82%)

PROBLEM 9.11 Sodium–ammonia reduction of stearolic acid (see Problem 9.10) yields a compound known as *elaidic acid.* What is the structure of elaidic acid?

PROBLEM 9.12 Suggest efficient syntheses of (*E*)- and (*Z*)-2-heptene from propyne and any necessary organic or inorganic reagents.

The stereochemistry of metal–ammonia reduction of alkynes differs from that of catalytic hydrogenation because the mechanisms of the two reactions are different. The mechanism of hydrogenation of alkynes is similar to that of catalytic hydrogenation of alkenes (Sections 6.1 and 6.3). A mechanism for metal–ammonia reduction of alkynes is outlined in Figure 9.4.

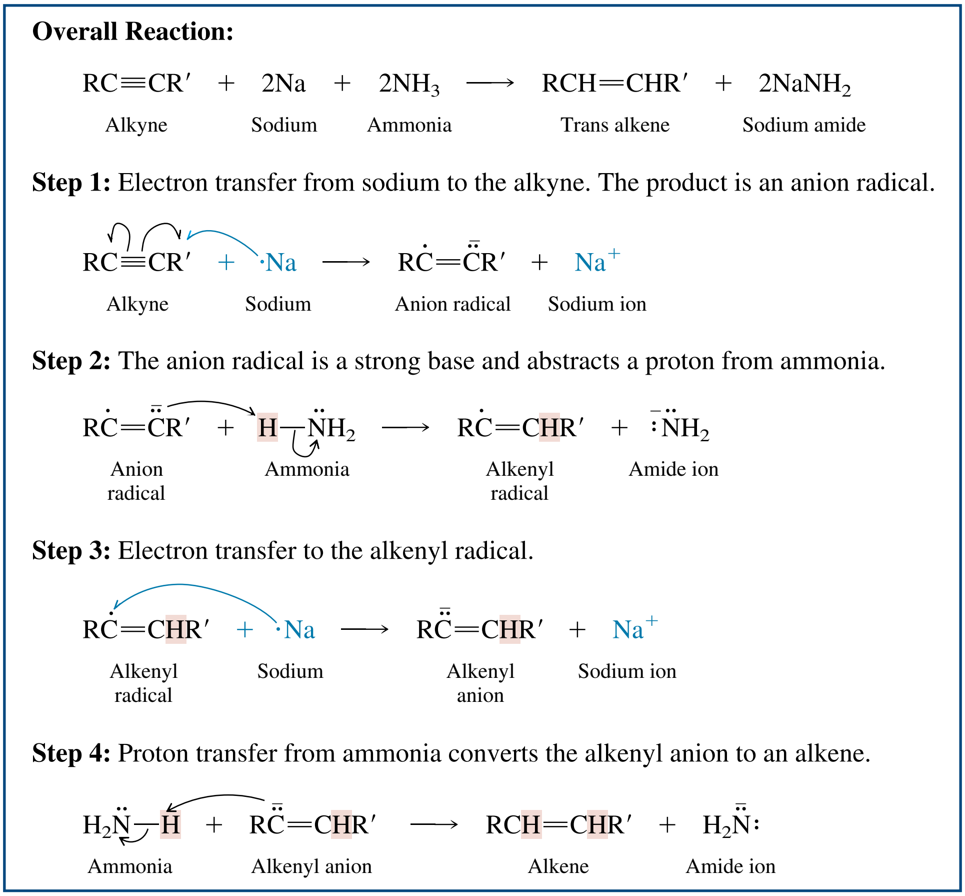
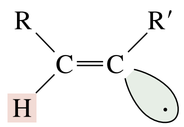
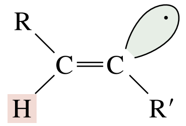


FIGURE 9.4 Mechanism of the sodium–ammonia reduction of an alkyne.

The mechanism includes two single-electron transfers (steps 1 and 3) and two proton transfers (steps 2 and 4). Experimental evidence indicates that step 2 is rate-determining, and it is believed that the observed trans stereochemistry reflects the distribution of the two stereoisomeric alkenyl radical intermediates formed in this step.



(*Z*)-Alkenyl radical
(less stable)

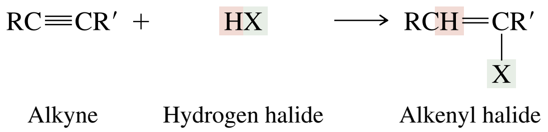


(*E*)-Alkenyl radical
(more stable)

The more stable (*E*)-alkenyl radical, in which the alkyl groups R and R′ are trans to each other, is formed faster than its *Z* stereoisomer. Steps 3 and 4, which follow, are fast, and the product distribution is determined by the *E*–*Z* ratio of radicals produced in step 2.

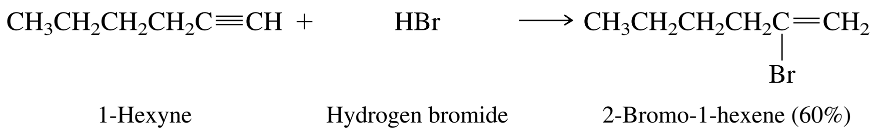
9.11 ADDITION OF HYDROGEN HALIDES TO ALKYNES

Alkynes react with many of the same electrophilic reagents that add to the carbon–carbon double bond of alkenes. Hydrogen halides, for example, add to alkynes to form alkenyl halides.



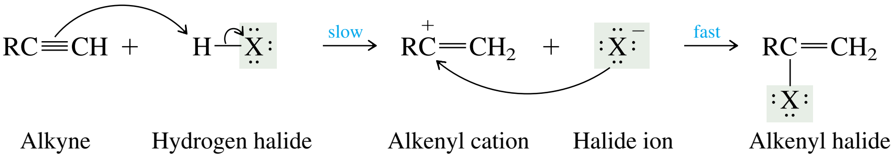
$$\mathrm{RC{\equiv}CR' + HX \longrightarrow RCH{=}\underset{\underset{\displaystyle X}{|}}{C}R'}$$

The regioselectivity of addition follows Markovnikov's rule. A proton adds to the carbon that has the greater number of hydrogens, and halide adds to the carbon with the fewer hydrogens.



$$\mathrm{CH_3CH_2CH_2CH_2C{\equiv}CH + HBr \longrightarrow CH_3CH_2CH_2CH_2\underset{\underset{\displaystyle Br}{|}}{C}{=}CH_2}$$

When formulating a mechanism for the reaction of alkynes with hydrogen halides, we could propose a process analogous to that of electrophilic addition to alkenes in which the first step is formation of a carbocation and is rate-determining. The second step according to such a mechanism would be nucleophilic capture of the carbocation by a halide ion.



Evidence from a variety of sources, however, indicates that alkenyl cations (also called *vinylic cations*) are much less stable than simple alkyl cations, and their involvement in these additions has been questioned. For example, although electrophilic addition of hydrogen halides to alkynes occurs more slowly than the corresponding additions to alkenes, the difference is not nearly as great as the difference in carbocation stabilities would suggest.

Furthermore, kinetic studies reveal that electrophilic addition of hydrogen halides to alkynes follows a rate law that is third-order overall and second-order in hydrogen halide.

$$\text{Rate} = k[\text{alkyne}][\text{HX}]^2$$

This third-order rate dependence suggests a termolecular transition state, one that involves two molecules of the hydrogen halide. Figure 9.5 depicts such a termolecular process using curved arrow notation to show the flow of electrons, and dashed-line notation to

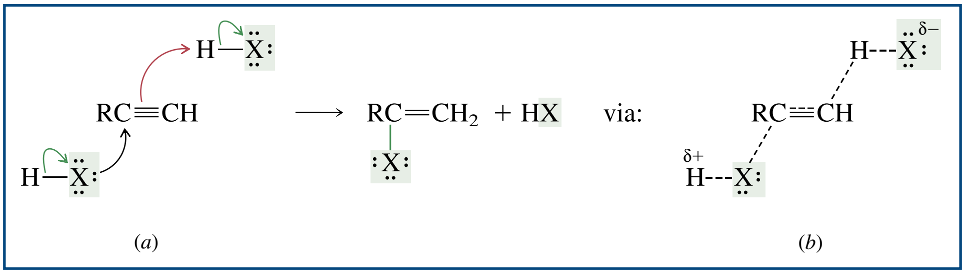
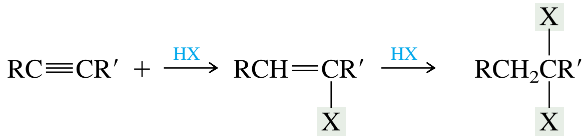


FIGURE 9.5 (*a*), Curved arrow notation and (*b*) transition-state representation for electrophilic addition of a hydrogen halide HX to an alkyne.

For further discussion of this topic, see the article "The Electrophilic Addition to Alkynes" in the November 1993 edition of the *Journal of Chemical Education* (p. 873). Additional commentary appeared in the November 1996 issue.

indicate the bonds being made and broken at the transition state. This mechanism, called *Ad$_E$3* for *addition-electrophilic-termolecular,* avoids the formation of a very unstable alkenyl cation intermediate by invoking nucleophilic participation by the halogen at an early stage. Nevertheless, since Markovnikov's rule is observed, it seems likely that some degree of positive character develops at carbon and controls the regioselectivity of addition.

In the presence of excess hydrogen halide, geminal dihalides are formed by sequential addition of two molecules of hydrogen halide to the carbon–carbon triple bond.



$$RC{\equiv}CR' + \xrightarrow{HX} RCH{=}\underset{X}{C}R' \xrightarrow{HX} RCH_2\overset{X}{\underset{X}{C}}R'$$

Alkyne Alkenyl halide Geminal dihalide

The hydrogen halide adds to the initially formed alkenyl halide in accordance with Markovnikov's rule. Overall, both protons become bonded to the same carbon and both halogens to the adjacent carbon.

$$CH_3CH_2C{\equiv}CCH_2CH_3 + 2HF \longrightarrow CH_3CH_2CH_2\overset{F}{\underset{F}{C}}CH_2CH_3$$

3-Hexyne Hydrogen fluoride 3,3-Difluorohexane (76%)

PROBLEM 9.13 Write a series of equations showing how you could prepare 1,1-dichloroethane from

(a) Ethylene
(b) Vinyl chloride ($CH_2{=}CHCl$)
(c) 1,1-Dibromoethane

SAMPLE SOLUTION (a) Reasoning backward, we recognize 1,1-dichloroethane as the product of addition of two molecules of hydrogen chloride to acetylene. Thus, the synthesis requires converting ethylene to acetylene as a key feature. As described in Section 9.7, this may be accomplished by conversion of ethylene to a vicinal dihalide, followed by double dehydrohalogenation. A suitable synthesis based on this analysis is as shown:

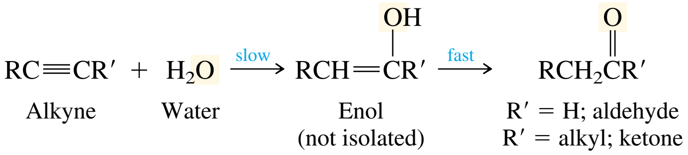
$$\underset{\text{Ethylene}}{CH_2{=}CH_2} \xrightarrow{Br_2} \underset{\text{1,2-Dibromoethane}}{BrCH_2CH_2Br} \xrightarrow[2.\ H_2O]{1.\ NaNH_2} \underset{\text{Acetylene}}{HC{\equiv}CH} \xrightarrow{2HCl} \underset{\text{1,1-Dichloroethane}}{CH_3CHCl_2}$$

Hydrogen bromide (but not hydrogen chloride or hydrogen iodide) adds to alkynes by a free-radical mechanism when peroxides are present in the reaction mixture. As in the free-radical addition of hydrogen bromide to alkenes (Section 6.8), a regioselectivity opposite to Markovnikov's rule is observed.

$$\underset{\text{1-Hexyne}}{CH_3CH_2CH_2CH_2C{\equiv}CH} + \underset{\text{Hydrogen bromide}}{HBr} \xrightarrow{\text{peroxides}} \underset{\text{1-Bromo-1-hexene (79\%)}}{CH_3CH_2CH_2CH_2CH{=}CHBr}$$

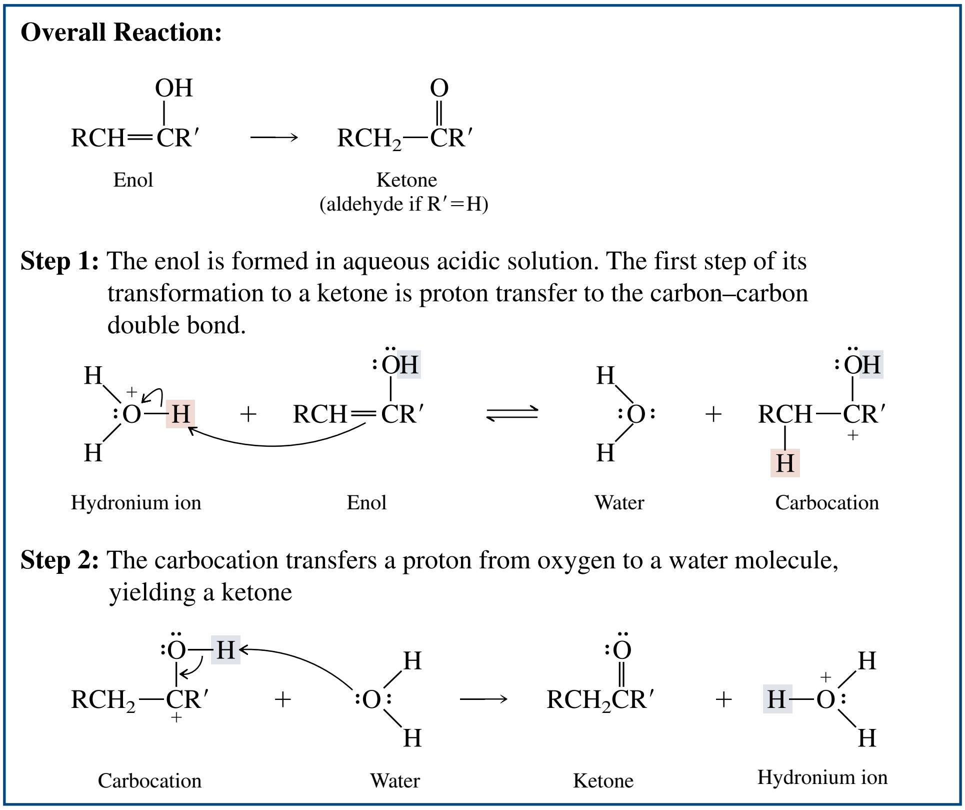
9.12 HYDRATION OF ALKYNES

By analogy to the hydration of alkenes, hydration of an alkyne is expected to yield an alcohol. The kind of alcohol, however, would be of a special kind, one in which the hydroxyl group is a substituent on a carbon–carbon double bond. This type of alcohol is called an **enol** (the double bond suffix *-ene* plus the alcohol suffix *-ol*). An important property of enols is their rapid isomerization to aldehydes or ketones under the conditions of their formation.



$$\mathrm{RC{\equiv}CR' + H_2O \xrightarrow{\text{slow}} RCH{=}\overset{\overset{\large OH}{|}}{C}R' \xrightarrow{\text{fast}} RCH_2\overset{\overset{\large O}{\|}}{C}R'}$$

The process by which enols are converted to aldehydes or ketones is called *keto–enol isomerism* (or *keto–enol tautomerism*) and proceeds by the sequence of proton transfers shown in Figure 9.6. Proton transfer to the double bond of an enol occurs readily because the carbocation that is produced is a very stable one. The positive charge on carbon is stabilized by electron release from oxygen and may be represented in resonance terms as shown on the following page.

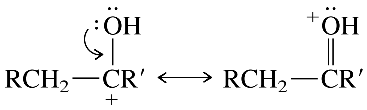


Overall Reaction:

Step 1: The enol is formed in aqueous acidic solution. The first step of its transformation to a ketone is proton transfer to the carbon–carbon double bond.

Step 2: The carbocation transfers a proton from oxygen to a water molecule, yielding a ketone

FIGURE 9.6 Conversion of an enol to a ketone takes place by way of two solvent-mediated proton transfers. A proton is transferred to carbon in the first step, then removed from oxygen in the second.



$$\mathrm{RCH_2{-}\underset{+}{\overset{:\ddot{O}H}{\overset{|}{C}}}R'} \longleftrightarrow \mathrm{RCH_2{-}\overset{^{+}\ddot{O}H}{\overset{\|}{C}}R'}$$

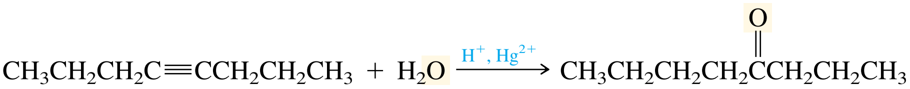
A B

Delocalization of an oxygen lone pair stabilizes the cation. All the atoms in B have octets of electrons, making it a more stable structure than A. Only six electrons are associated with the positively charged carbon in A.

PROBLEM 9.14 Give the structure of the enol formed by hydration of 2-butyne, and write a series of equations showing its conversion to its corresponding ketone isomer.

Mercury(II) sulfate and mercury(II) oxide are also known as *mercuric* sulfate and oxide, respectively.

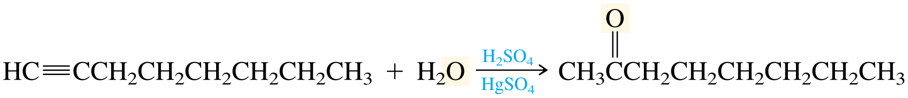
In general, ketones are more stable than their enol precursors and are the products actually isolated when alkynes undergo acid-catalyzed hydration. The standard method for alkyne hydration employs aqueous sulfuric acid as the reaction medium and mercury(II) sulfate or mercury(II) oxide as a catalyst.



$$\mathrm{CH_3CH_2CH_2C{\equiv}CCH_2CH_2CH_3 + H_2O \xrightarrow{H^+,\ Hg^{2+}} CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3}$$

4-Octyne 4-Octanone (89%)

Hydration of alkynes follows Markovnikov's rule; terminal alkynes yield methyl-substituted ketones.

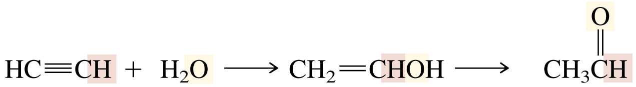


$$\mathrm{HC{\equiv}CCH_2CH_2CH_2CH_2CH_2CH_3 + H_2O \xrightarrow[HgSO_4]{H_2SO_4} CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_2CH_2CH_3}$$

1-Octyne 2-Octanone (91%)

PROBLEM 9.15 Show by a series of equations how you could prepare 2-octanone from acetylene and any necessary organic or inorganic reagents. How could you prepare 4-octanone?

Because of the regioselectivity of alkyne hydration, acetylene is the only alkyne structurally capable of yielding an aldehyde under these conditions.



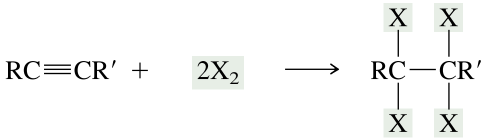
$$\mathrm{HC{\equiv}CH + H_2O \longrightarrow CH_2{=}CHOH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}H}$$

Acetylene Water Vinyl alcohol (not isolated) Acetaldehyde

At one time acetaldehyde was prepared on an industrial scale by this method. Modern methods involve direct oxidation of ethylene and are more economical.

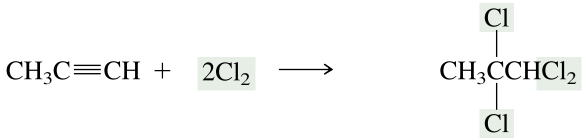
9.13 ADDITION OF HALOGENS TO ALKYNES

Alkynes react with chlorine and bromine to yield tetrahaloalkanes. Two molecules of the halogen add to the triple bond.



$$RC\equiv CR' + 2X_2 \longrightarrow R\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}R'$$

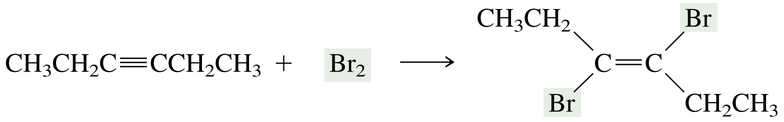
Alkyne Halogen (chlorine or bromine) Tetrahaloalkane



$$CH_3C\equiv CH + 2Cl_2 \longrightarrow CH_3\underset{Cl}{\overset{Cl}{C}}CHCl_2$$

Propyne Chlorine 1,1,2,2-Tetrachloropropane (63%)

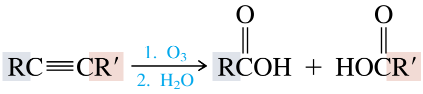
A dihaloalkene is an intermediate and is the isolated product when the alkyne and the halogen are present in equimolar amounts. The stereochemistry of addition is anti.



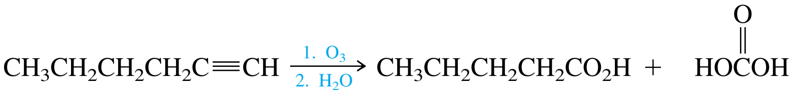
3-Hexyne Bromine (*E*)-3,4-Dibromo-3-hexene (90%)

9.14 OZONOLYSIS OF ALKYNES

Carboxylic acids are produced when alkynes are subjected to ozonolysis.



$$RC\equiv CR' \xrightarrow[2.\ H_2O]{1.\ O_3} R\overset{O}{\overset{\|}{C}}OH + HO\overset{O}{\overset{\|}{C}}R'$$



$$CH_3CH_2CH_2CH_2C\equiv CH \xrightarrow[2.\ H_2O]{1.\ O_3} CH_3CH_2CH_2CH_2CO_2H + HO\overset{O}{\overset{\|}{C}}OH$$

1-Hexyne Pentanoic acid (51%) Carbonic acid

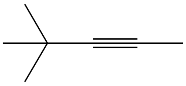
Recall that when carbonic acid is formed as a reaction product, it dissociates to carbon dioxide and water.

Ozonolysis is sometimes used as a tool in structure determination. By identifying the carboxylic acids produced, we can deduce the structure of the alkyne. As with many other chemical methods of structure determination, however, it has been superseded by spectroscopic methods.

PROBLEM 9.16 A certain hydrocarbon had the molecular formula $C_{16}H_{26}$ and contained two triple bonds. Ozonolysis gave $CH_3(CH_2)_4CO_2H$ and $HO_2CCH_2CH_2CO_2H$ as the only products. Suggest a reasonable structure for this hydrocarbon.

9.15 SUMMARY

Section 9.1	**Alkynes** are hydrocarbons that contain a carbon–carbon *triple bond.* Simple alkynes having no other functional groups or rings have the general formula C_nH_{2n-2}. Acetylene is the simplest alkyne.
Section 9.2	Alkynes are named in much the same way as alkenes, using the suffix *-yne* instead of *-ene.*



4,4-Dimethyl-2-pentyne

Section 9.3 The physical properties (boiling point, solubility in water, dipole moment) of alkynes resemble those of alkanes and alkenes.

Section 9.4 Acetylene is linear and alkynes have a linear geometry of their X—C≡C—Y units. The carbon–carbon triple bond in alkynes is composed of a σ and two π components. The triply bonded carbons are *sp*-hybridized. The σ component of the triple bond contains two electrons in an orbital generated by the overlap of *sp*-hybridized orbitals on adjacent carbons. Each to these carbons also has two 2*p* orbitals, which overlap in pairs so as to give two π orbitals, each of which contains two electrons.

Section 9.5 Acetylene and terminal alkynes are more *acidic* than other hydrocarbons. They have a K_a's for ionization of approximately 10^{-26}, compared with about 10^{-45} for alkenes and about 10^{-60} for alkanes. Sodium amide is a strong enough base to remove a proton from acetylene or a terminal alkyne, but sodium hydroxide is not.

$$\underset{\text{1-Butyne}}{CH_3CH_2C{\equiv}CH} + \underset{\text{Sodium amide}}{NaNH_2} \longrightarrow \underset{\text{Sodium 1-butynide}}{CH_3CH_2C{\equiv}CNa} + \underset{\text{Ammonia}}{NH_3}$$

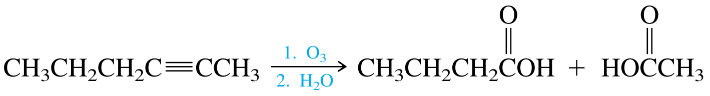
Sections 9.6–9.7 Table 9.2 summarizes the methods for preparing alkynes.

Section 9.8 Like alkenes, alkynes undergo addition reactions.

Sections 9.9–9.10 Table 9.3 summarizes reactions that reduce alkynes to alkenes and alkanes.

Sections 9.11–9.13 Table 9.4 summarizes electrophilic addition to alkynes.

Section 9.14 Carbon–carbon triple bonds can be cleaved by ozonolysis. The cleavage products are carboxylic acids.



$$\underset{\text{2-Hexyne}}{CH_3CH_2CH_2C{\equiv}CCH_3} \xrightarrow[\text{2. } H_2O]{\text{1. } O_3} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}OH} + \underset{\text{Acetic acid}}{HO\overset{O}{\overset{\|}{C}}CH_3}$$

2-Hexyne Butanoic acid Acetic acid

PROBLEMS

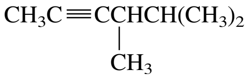
9.17 Write structural formulas and give the IUPAC names for all the alkynes of molecular formula C_6H_{10}.

9.18 Provide the IUPAC name for each of the following alkynes:

(a) $CH_3CH_2CH_2C{\equiv}CH$

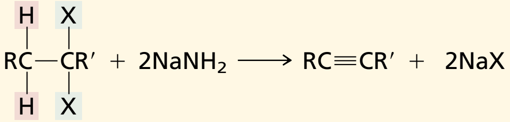
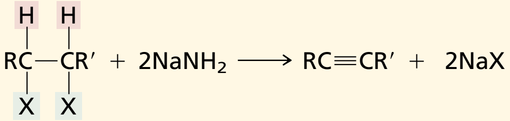
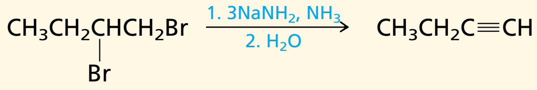
(b) $CH_3CH_2C{\equiv}CCH_3$

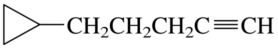
(c)

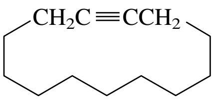


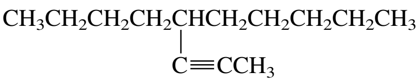
$CH_3C{\equiv}C\underset{CH_3}{\underset{|}{C}}HCH(CH_3)_2$

TABLE 9.2 Preparation of Alkynes

Reaction (section) and comments	General equation and specific example
Alkylation of acetylene and terminal alkynes (Section 9.6) The acidity of acetylene and terminal alkynes permits them to be converted to their conjugate bases on treatment with sodium amide. These anions are good nucleophiles and react with methyl and primary alkyl halides to form carbon–carbon bonds. Secondary and tertiary alkyl halides cannot be used, because they yield only elimination products under these conditions.	$\underset{\text{Alkyne}}{RC\equiv CH} + \underset{\text{Sodium amide}}{NaNH_2} \longrightarrow \underset{\text{Sodium alkynide}}{RC\equiv CNa} + \underset{\text{Ammonia}}{NH_3}$ $\underset{\text{Sodium alkynide}}{RC\equiv CNa} + \underset{\text{Primary alkyl halide}}{R'CH_2X} \longrightarrow \underset{\text{Alkyne}}{RC\equiv CCH_2R'} + \underset{\text{Sodium halide}}{NaX}$ $\underset{\text{3,3-Dimethyl-1-butyne}}{(CH_3)_3CC\equiv CH} \xrightarrow[2.\ CH_3I]{1.\ NaNH_2,\ NH_3} \underset{\text{4,4-Dimethyl-2-pentyne (96\%)}}{(CH_3)_3CC\equiv CCH_3}$
Double dehydrohalogenation of geminal dihalides (Section 9.7) An E2 elimination reaction of a geminal dihalide yields an alkenyl halide. If a strong enough base is used, sodium amide, for example, a second elimination step follows the first and the alkenyl halide is converted to an alkyne.	 $RCH_2CX_2R' + 2NaNH_2 \longrightarrow RC\equiv CR' + 2NaX$ Geminal dihalide Sodium amide Alkyne Sodium halide $\underset{\text{1,1-Dichloro-3,3-dimethylbutane}}{(CH_3)_3CCH_2CHCl_2} \xrightarrow[2.\ H_2O]{1.\ 3NaNH_2,\ NH_3} \underset{\text{3,3-Dimethyl-1-butyne (56–60\%)}}{(CH_3)_3CC\equiv CH}$
Double dehydrohalogenation of vicinal dihalides (Section 9.7) Dihalides in which the halogens are on adjacent carbons undergo two elimination processes analogous to those of geminal dihalides.	 $RCHXCHXR' + 2NaNH_2 \longrightarrow RC\equiv CR' + 2NaX$ Vicinal dihalide Sodium amide Alkyne Sodium halide  $CH_3CH_2CH(Br)CH_2Br \xrightarrow[2.\ H_2O]{1.\ 3NaNH_2,\ NH_3} CH_3CH_2C\equiv CH$ 1,2-Dibromobutane 1-Butyne (78–85%)

(d) 

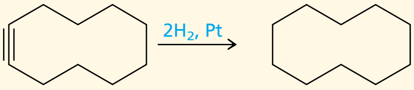
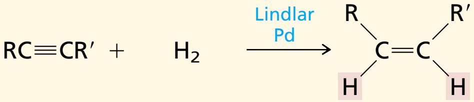
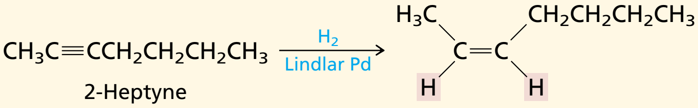
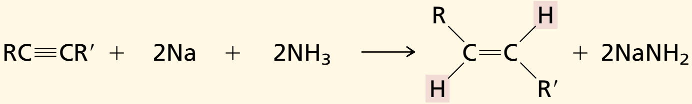
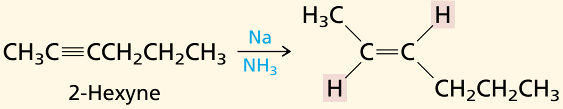
(e) 

(f) 

$CH_3CH_2CH_2CH_2CH(C\equiv CCH_3)CH_2CH_2CH_2CH_2CH_3$

(g) $(CH_3)_3CC\equiv CC(CH_3)_3$

TABLE 9.3 Conversion of Alkynes to Alkenes and Alkanes

Reaction (section) and comments	General equation and specific example
Hydrogenation of alkynes to alkanes (Section 9.9) Alkynes are completely hydrogenated, yielding alkanes, in the presence of the customary metal hydrogenation catalysts.	$RC\equiv CR' + 2H_2 \xrightarrow{\text{metal catalyst}} RCH_2CH_2R'$ Alkyne Hydrogen Alkane  Cyclodecyne Cyclodecane (71%)
Hydrogenation of alkynes to alkenes (Section 9.9) Hydrogenation of alkynes may be halted at the alkene stage by using special catalysts. Lindlar palladium is the metal catalyst employed most often. Hydrogenation occurs with syn stereochemistry and yields a cis alkene.	 Alkyne Hydrogen Cis alkene  2-Heptyne *cis*-2-Heptene (59%)
Metal–ammonia reduction (Section 9.10) Group I metals—sodium is the one usually employed—in liquid ammonia as the solvent convert alkynes to trans alkenes. The reaction proceeds by a four-step sequence in which electron-transfer and proton-transfer steps alternate.	 Alkyne Sodium Ammonia Trans alkene Sodium amide  2-Hexyne *trans*-2-Hexene (69%)

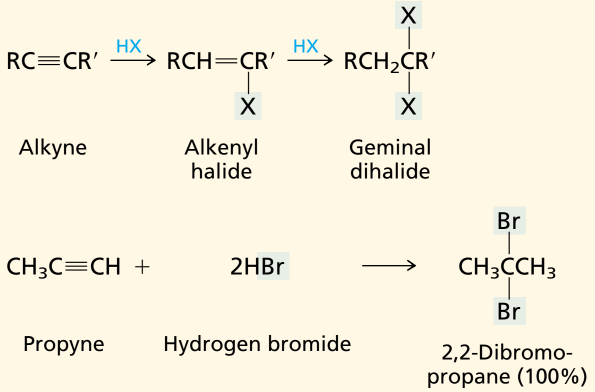
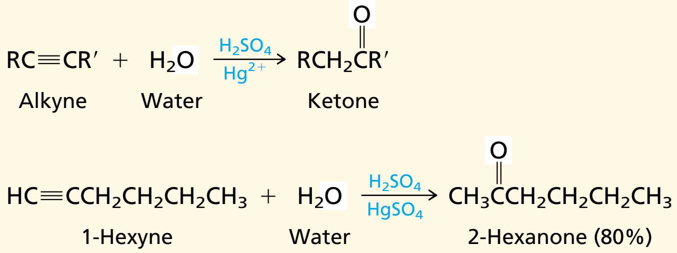
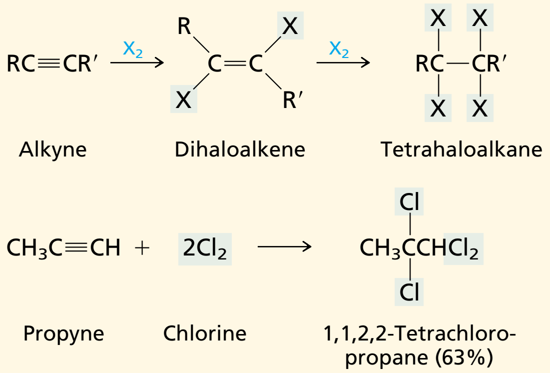
9.19 Write a structural formula or build a molecular model of each of the following:

(a) 1-Octyne
(b) 2-Octyne
(c) 3-Octyne
(d) 4-Octyne
(e) 2,5-Dimethyl-3-hexyne
(f) 4-Ethyl-1-hexyne
(g) Ethynylcyclohexane
(h) 3-Ethyl-3-methyl-1-pentyne

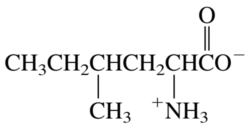
9.20 All the compounds in Problem 9.19 are isomers except one. Which one?

9.21 Write structural formulas for all the alkynes of molecular formula C_8H_{14} that yield 3-ethylhexane on catalytic hydrogenation.

TABLE 9.4 Electrophilic Addition to Alkynes

Reaction (section) and comments	General equation and specific example
Addition of hydrogen halides (Section 9.11) Hydrogen halides add to alkynes in accordance with Markovnikov's rule to give alkenyl halides. In the presence of 2 eq of hydrogen halide, a second addition occurs to give a geminal dihalide.	
Acid-catalyzed hydration (Section 9.12) Water adds to the triple bond of alkynes to yield ketones by way of an unstable enol intermediate. The enol arises by Markovnikov hydration of the alkyne. Enol formation is followed by rapid isomerization of the enol to a ketone.	
Halogenation (Section 9.13) Addition of 1 equivalent of chlorine or bromine to an alkyne yields a trans dihaloalkene. A tetrahalide is formed on addition of a second equivalent of the halogen.	

9.22 An unknown acetylenic amino acid obtained from the seed of a tropical fruit has the molecular formula $C_7H_{11}NO_2$. On catalytic hydrogenation over platinum this amino acid yielded homoleucine (an amino acid of known structure shown here) as the only product. What is the structure of the unknown amino acid?



$$CH_3CH_2\underset{CH_3}{\underset{|}{CH}}CH_2\underset{^+NH_3}{\underset{|}{CH}}\overset{O}{\overset{\|}{C}}O^-$$

Homoleucine

9.23 Show by writing appropriate chemical equations how each of the following compounds could be converted to 1-hexyne:

(a) 1,1-Dichlorohexane
(b) 1-Hexene
(c) Acetylene
(d) 1-Iodohexane

9.24 Show by writing appropriate chemical equations how each of the following compounds could be converted to 3-hexyne:

(a) 1-Butene
(b) 1,1-Dichlorobutane
(c) Acetylene

9.25 When 1,2-dibromodecane was treated with potassium hydroxide in aqueous ethanol, it yielded a mixture of three isomeric compounds of molecular formula $C_{10}H_{19}Br$. Each of these compounds was converted to 1-decyne on reaction with sodium amide in dimethyl sulfoxide. Identify these three compounds.

9.26 Write the structure of the major organic product isolated from the reaction of 1-hexyne with

(a) Hydrogen (2 mol), platinum
(b) Hydrogen (1 mol), Lindlar palladium
(c) Lithium in liquid ammonia
(d) Sodium amide in liquid ammonia
(e) Product in part (d) treated with 1-bromobutane
(f) Product in part (d) treated with *tert*-butyl bromide
(g) Hydrogen chloride (1 mol)
(h) Hydrogen chloride (2 mol)
(i) Chlorine (1 mol)
(j) Chlorine (2 mol)
(k) Aqueous sulfuric acid, mercury(II) sulfate
(l) Ozone followed by hydrolysis

9.27 Write the structure of the major organic product isolated from the reaction of 3-hexyne with

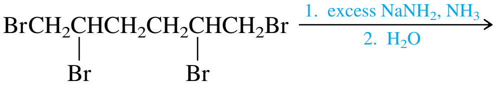
(a) Hydrogen (2 mol), platinum
(b) Hydrogen (1 mol), Lindlar palladium
(c) Lithium in liquid ammonia
(d) Hydrogen chloride (1 mol)
(e) Hydrogen chloride (2 mol)
(f) Chlorine (1 mol)
(g) Chlorine (2 mol)
(h) Aqueous sulfuric acid, mercury(II) sulfate
(i) Ozone followed by hydrolysis

9.28 When 2-heptyne was treated with aqueous sulfuric acid containing mercury(II) sulfate, two products, each having the molecular formula $C_7H_{14}O$, were obtained in approximately equal amounts. What are these two compounds?

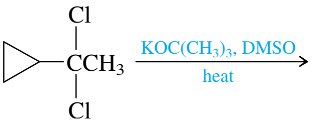
9.29 The alkane formed by hydrogenation of (*S*)-4-methyl-1-hexyne is optically active, but the one formed by hydrogenation of (*S*)-3-methyl-1-pentyne is not. Explain. Would you expect the products of hydrogenation of these two compounds in the presence of Lindlar palladium to be optically active?

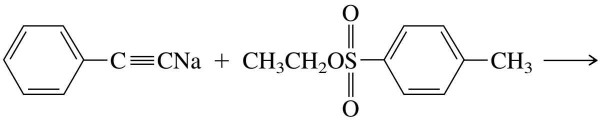
9.30 All the following reactions have been described in the chemical literature and proceed in good yield. In some cases the reactants are more complicated than those we have so far encountered. Nevertheless, on the basis of what you have already learned, you should be able to predict the principal product in each case.

(a) $\mathrm{NaC{\equiv}CH + ClCH_2CH_2CH_2CH_2CH_2CH_2I} \longrightarrow$

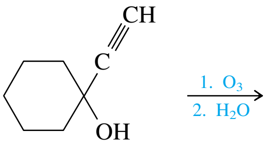
(b) 

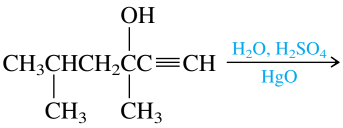
$\mathrm{BrCH_2\underset{Br}{CH}CH_2CH_2\underset{Br}{CH}CH_2Br} \xrightarrow[\text{2. } \mathrm{H_2O}]{\text{1. excess } \mathrm{NaNH_2, NH_3}}$

(c) 

(d) 

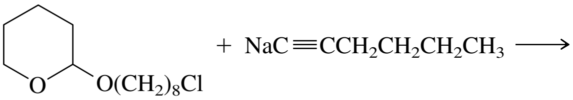
(e) Cyclodecyne $\xrightarrow[\text{2. } \mathrm{H_2O}]{\text{1. } \mathrm{O_3}}$

(f) 

(g) 

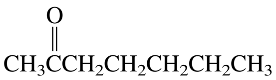
$\mathrm{CH_3\underset{CH_3}{CH}CH_2\overset{OH}{\underset{CH_3}{C}}C{\equiv}CH} \xrightarrow[\mathrm{HgO}]{\mathrm{H_2O,\ H_2SO_4}}$

(h) (*Z*)-$\mathrm{CH_3CH_2CH_2CH_2CH{=}CHCH_2(CH_2)_7C{\equiv}CCH_2CH_2OH} \xrightarrow[\text{2. } \mathrm{H_2O}]{\text{1. } \mathrm{Na, NH_3}}$

(i) 

(j) Product of part (i) $\xrightarrow[\text{Lindlar Pd}]{\mathrm{H_2}}$

9.31 The ketone 2-heptanone has been identified as contributing to the odor of a number of dairy products, including condensed milk and cheddar cheese. Describe a synthesis of 2-heptanone from acetylene and any necessary organic or inorganic reagents.



$\mathrm{CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH_2CH_2CH_3}$

2-Heptanone

9.32 (*Z*)-9-Tricosene [(*Z*)-$\mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_{12}CH_3}$] is the sex pheromone of the female housefly. Synthetic (*Z*)-9-tricosene is used as bait to lure male flies to traps that contain insecticide. Using acetylene and alcohols of your choice as starting materials, along with any necessary inorganic reagents, show how you could prepare (*Z*)-9-tricosene.

9.33 Show by writing a suitable series of equations how you could prepare each of the following compounds from the designated starting materials and any necessary organic or inorganic reagents:

(a) 2,2-Dibromopropane from 1,1-dibromopropane

(b) 2,2-Dibromopropane from 1,2-dibromopropane

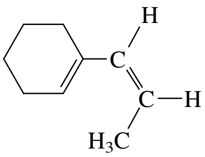
(c) 1,1,2,2-Tetrachloropropane from 1,2-dichloropropane

(d) 2,2-Diiodobutane from acetylene and ethyl bromide

(e) 1-Hexene from 1-butene and acetylene

(f) Decane from 1-butene and acetylene

(g) Cyclopentadecyne from cyclopentadecene

(h)


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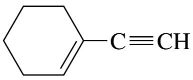

and methyl bromide

(i) *meso*-2,3-Dibromobutane from 2-butyne

9.34 Assume that you need to prepare 4-methyl-2-pentyne and discover that the only alkynes on hand are acetylene and propyne. You also have available methyl iodide, isopropyl bromide, and 1,1-dichloro-3-methylbutane. Which of these compounds would you choose in order to perform your synthesis, and how would you carry it out?

9.35 Compound A has the molecular formula $C_{14}H_{25}Br$ and was obtained by reaction of sodium acetylide with 1,12-dibromododecane. On treatment of compound A with sodium amide, it was converted to compound B ($C_{14}H_{24}$). Ozonolysis of compound B gave the diacid $HO_2C(CH_2)_{12}CO_2H$. Catalytic hydrogenation of compound B over Lindlar palladium gave compound C ($C_{14}H_{26}$), and hydrogenation over platinum gave compound D ($C_{14}H_{28}$). Sodium–ammonia reduction of compound B gave compound E ($C_{14}H_{26}$). Both C and E yielded $O{=}CH(CH_2)_{12}CH{=}O$ on ozonolysis. Assign structures to compounds A through E so as to be consistent with the observed transformations.

9.36 Use molecular models to compare $—C{\equiv}CH$, $—CH{=}CH_2$, and $—CH_2CH_3$ with respect to their preference for an equatorial orientation when attached to a cyclohexane ring. One of these groups is very much different from the other two. Which one? Why?

9.37 Try making a model of a hydrocarbon that contains three carbons, only one of which is *sp*-hybridized. What is its molecular formula? Is it an alkyne? What must be the hybridization state of the other two carbons? (You will learn more about compounds of this type in Chapter 10.)