

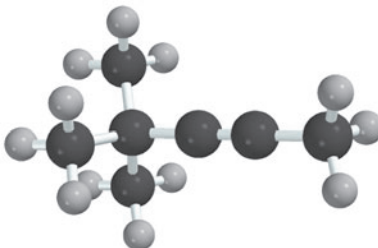
other chemical methods of structure determination, however, it has been superseded by spectroscopic methods.

PROBLEM 9.15 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*.

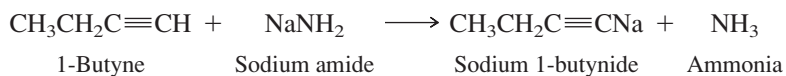


4,4-Dimethyl-2-pentyne

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 $X-C\equiv C-Y$ 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 of these carbons also has two *2p* 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 pK_a 's of approximately 26, compared with about 45 for alkenes and about 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.



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

Section 9.8 Like alkenes, alkynes undergo addition reactions.

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.	$\text{RC}\equiv\text{CH} + \text{NaNH}_2 \longrightarrow \text{RC}\equiv\text{CNa} + \text{NH}_3$ <p>Alkyne Sodium amide Sodium alkynide Ammonia</p>
	$\text{RC}\equiv\text{CNa} + \text{R}'\text{CH}_2\text{X} \longrightarrow \text{RC}\equiv\text{CCH}_2\text{R}' + \text{NaX}$ <p>Sodium alkynide Primary alkyl halide Alkyne Sodium halide</p>
	$(\text{CH}_3)_3\text{CC}\equiv\text{CH} \xrightarrow[2. \text{CH}_3\text{I}]{1. \text{NaNH}_2, \text{NH}_3} (\text{CH}_3)_3\text{CC}\equiv\text{CCH}_3$ <p>3,3-Dimethyl-1-butyne 4,4-Dimethyl-2-pentyne (96%)</p>
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.	$\begin{array}{c} \text{H} \quad \text{X} \\ \quad \\ \text{RC}-\text{CR}' \\ \quad \\ \text{H} \quad \text{X} \end{array} + 2\text{NaNH}_2 \longrightarrow \text{RC}\equiv\text{CR}' + 2\text{NaX}$ <p>Geminal dihalide Sodium amide Alkyne Sodium halide</p>
	$(\text{CH}_3)_3\text{CCH}_2\text{CHCl}_2 \xrightarrow[2. \text{H}_2\text{O}]{1. 3\text{NaNH}_2, \text{NH}_3} (\text{CH}_3)_3\text{CC}\equiv\text{CH}$ <p>1,1-Dichloro-3,3-dimethylbutane 3,3-Dimethyl-1-butyne (56–60%)</p>
	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{RC}-\text{CR}' \\ \quad \\ \text{X} \quad \text{X} \end{array} + 2\text{NaNH}_2 \longrightarrow \text{RC}\equiv\text{CR}' + 2\text{NaX}$ <p>Vicinal dihalide Sodium amide Alkyne Sodium halide</p>
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.	$\text{CH}_3\text{CH}_2\underset{\text{Br}}{\text{CH}}\text{CH}_2\text{Br} \xrightarrow[2. \text{H}_2\text{O}]{1. 3\text{NaNH}_2, \text{NH}_3} \text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$ <p>1,2-Dibromobutane 1-Butyne (78–85%)</p>

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.

