other chemical methods of structure determination, however, it has been superseded by spectroscopic methods.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  $HO_2CCH_2CO_2H$  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  $\sigma$  and two  $\pi$  components. The triply bonded carbons are *sp*-hybridized. The  $\sigma$  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  $\pi$  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.

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

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

Section 9.8 Like alkenes, alkynes undergo addition reactions.

#### TABLE 9.2

#### Preparation of Alkynes

#### Reaction (section) and comments

# 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.

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.

**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.

#### General equation and specific example

$$(CH_3)_3CC \equiv CH$$
  $\xrightarrow{1. \text{ NaNH}_2, \text{ NH}_3}$   $(CH_3)_3CC \equiv CCH_3$   
3,3-Dimethyl-1-butyne 4,4-Dimethyl-2-pentyne (96%)

Geminal Sodium Alkyne Sodium dihalide amide halide

$$(CH_3)_3CCH_2CHCl_2$$
  $\xrightarrow{1.3NaNH_2, NH_3}$   $(CH_3)_3CC \equiv CH$  1,1-Dichloro-3,3-dimethylbutane 3,3-Dimethyl-1-butyne (56–60%)

$$\begin{array}{c|c} H & H \\ | & | \\ RC - CR' + 2NaNH_2 \longrightarrow RC \equiv CR' + 2NaX \\ | & | \\ X & X \end{array}$$

Vicinal Sodium Alkyne Sodium dihalide amide halide

$$\begin{array}{ccc} \text{CH}_{3}\text{CH}_{2}\text{CHCH}_{2}\text{Br} & \xrightarrow{\text{1. 3NaNH}_{2}, \text{ NH}_{3}} & \text{CH}_{3}\text{CH}_{2}\text{C} \!\!\equiv\! \text{CH} \\ & \text{Br} & \end{array}$$

1,2-Dibromobutane 1-Butyne (78–85%)

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

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

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

$$CH_3CH_2CH_2C \equiv CCH_3 \xrightarrow{1. O_3} CH_3CH_2CH_2COH + HOCCH_3$$
2-Hexyne Butanoic acid Acetic acid

#### TABLE 9.3

#### Conversion of Alkynes to Alkenes and Alkanes

#### Reaction (section) and comments

## **Hydrogenation of alkynes to alkanes (Section 9.9)** Alkynes are completely hydrogenated, yielding alkanes, in the presence of the customary metal hydrogenation catalysts.

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.

### 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.

#### General equation and specific example

RC
$$\equiv$$
CR' + 2H<sub>2</sub>  $\xrightarrow{\text{metal catalyst}}$  RCH<sub>2</sub>CH<sub>2</sub>R'

Alkyne Hydrogen Alkane

Cyclodecyne Cyclodecane (71%)

RC $\equiv$ CR' + H<sub>2</sub>  $\xrightarrow{\text{Lindlar R}}$   $\xrightarrow{\text{Pd}}$   $\xrightarrow{\text{R'}}$   $\xrightarrow{\text{R'}}$   $\xrightarrow{\text{H}}$   $\xrightarrow{\text{H}}$   $\xrightarrow{\text{H}}$   $\xrightarrow{\text{H}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{CH}_2}$ CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

Alkyne Hydrogen Cis alkene

CH<sub>3</sub>C $\equiv$ CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>  $\xrightarrow{\text{H}_2}$   $\xrightarrow{\text{Lindlar Pd}}$   $\xrightarrow{\text{H}_3}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{H}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{H}}$   $\xrightarrow{\text{Pd}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{H}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{H}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{H}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{H}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{H}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{H}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{H}}$   $\xrightarrow{\text{C}}$   $\xrightarrow{\text{C$ 

#### **PROBLEMS**

- **9.16** Write structural formulas and give the IUPAC names for all the alkynes of molecular formula  $C_6H_{10}$ .
- **9.17** 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<sub>3</sub>C≡CCHCH(CH<sub>3</sub>)<sub>2</sub> | CH<sub>3</sub>
  - (d)  $\longrightarrow$  CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C  $\equiv$  CH

(e) 
$$CH_2C \equiv CCH_2$$