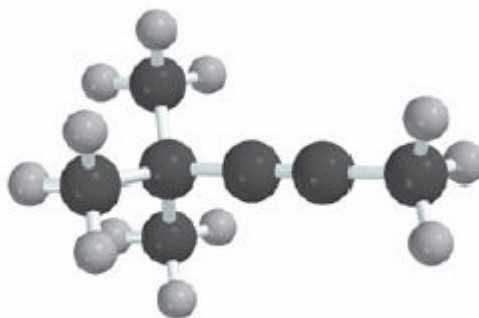


# Alkynes

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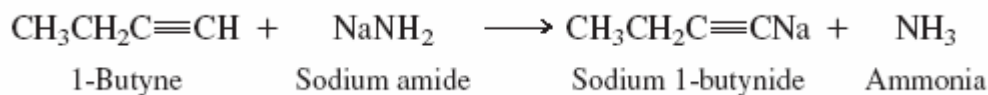
## SUMMARY

- 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  $XOCqCOY$  units. The carbon–carbon triple bond in alkynes is composed of a  $s$  and two  $p$  components. The triply bonded carbons are  $sp$ -hybridized. The  $s$  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  $p$  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.
- 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.

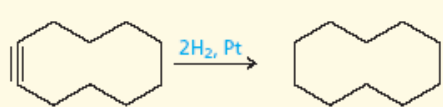
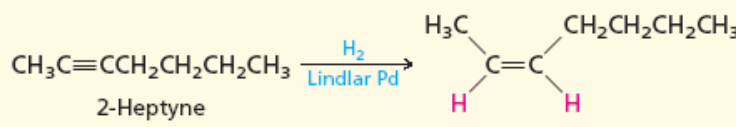
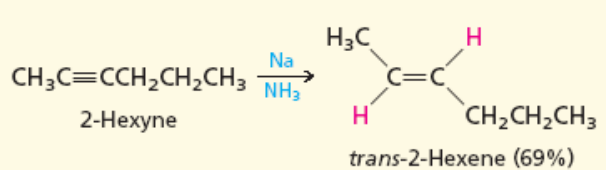
TABLE 9.2

## Preparation of Alkynes

Reaction (section) and comments	General equation and specific example
<b>Alkylation of acetylene and terminal alkynes (Section 9.6)</b> 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>
<b>Double dehydrohalogenation of geminal dihalides (Section 9.7)</b> 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>
<b>Double dehydrohalogenation of vicinal dihalides (Section 9.7)</b> Dihalides in which the halogens are on adjacent carbons undergo two elimination processes analogous to those of geminal dihalides.	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{RC}-\text{CR}' \\   \quad   \\ \text{X} \quad \text{X} \end{array} + 2\text{NaNH}_2 \longrightarrow \text{RC}\equiv\text{CR}' + 2\text{NaX}$ <p>Vicinal dihalide      Sodium amide      Alkyne      Sodium halide</p>
	$\text{CH}_3\text{CH}_2\underset{\text{Br}}{\text{CH}}\text{CH}_2\text{Br} \xrightarrow[2. \text{H}_2\text{O}]{1. 3\text{NaNH}_2, \text{NH}_3} \text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$ <p>1,2-Dibromobutane      1-Butyne (78–85%)</p>

TABLE 9.3

## Conversion of Alkynes to Alkenes and Alkanes

Reaction (section) and comments	General equation and specific example
<p><b>Hydrogenation of alkynes to alkanes (Section 9.9)</b> Alkynes are completely hydrogenated, yielding alkanes, in the presence of the customary metal hydrogenation catalysts.</p>	$\text{RC}\equiv\text{CR}' + 2\text{H}_2 \xrightarrow{\text{metal catalyst}} \text{RCH}_2\text{CH}_2\text{R}'$ <p>Alkyne      Hydrogen      Alkane</p>  <p>Cyclodecyne      Cyclodecane (71%)</p>
<p><b>Hydrogenation of alkynes to alkenes (Section 9.9)</b> 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.</p>	$\text{RC}\equiv\text{CR}' + \text{H}_2 \xrightarrow{\text{Lindlar Pd}} \begin{array}{c} \text{R} \quad \text{R}' \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$ <p>Alkyne      Hydrogen      Cis alkene</p>  <p>2-Heptyne      <i>cis</i>-2-Heptene (59%)</p>
<p><b>Metal–ammonia reduction (Section 9.10)</b> 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.</p>	$\text{RC}\equiv\text{CR}' + 2\text{Na} + 2\text{NH}_3 \longrightarrow \begin{array}{c} \text{R} \quad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{R}' \end{array} + 2\text{NaNH}_2$ <p>Alkyne      Sodium      Ammonia      Trans alkene      Sodium amide</p>  <p>2-Hexyne      <i>trans</i>-2-Hexene (69%)</p>

