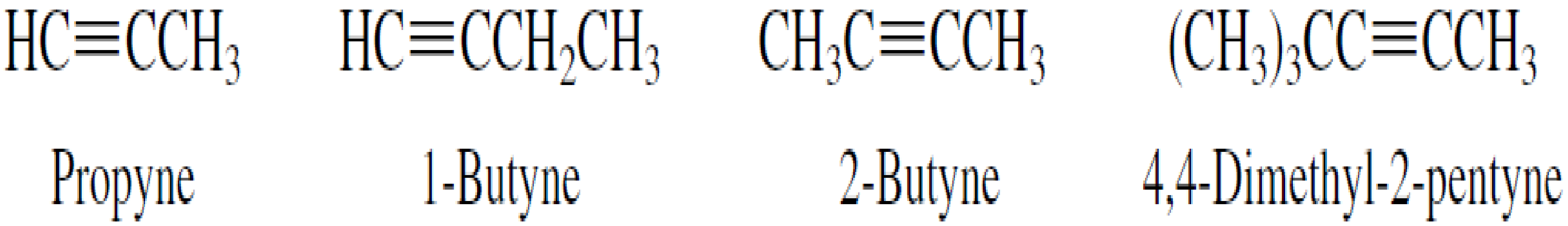
Alkynes

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

Acetylene; Monosubstituted alkynes

Sources of alkynes

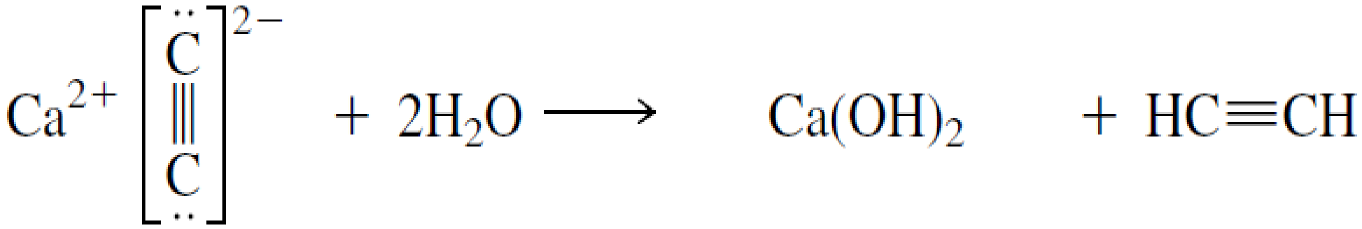
$$\mathrm{CaO} + 3\mathrm{C} \xrightarrow{1800\text{–}2100^{\circ}\mathrm{C}} \mathrm{CaC_2} + \mathrm{CO}$$

Calcium oxide (from limestone)

Carbon (from coke)

Calcium carbide

Carbon monoxide



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

Calcium carbide

Water

Calcium hydroxide

Acetylene

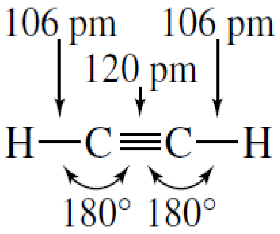
$$\mathrm{CH_2{=}CH_2} \overset{1150\ ^{o}\mathrm{C}}{\underset{}{\xrightleftharpoons{\text{heat}}}} \mathrm{HC{\equiv}CH} + \mathrm{H_2}$$

Ethylene

Acetylene

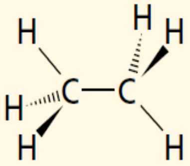
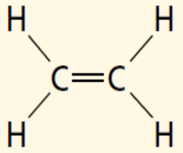
Hydrogen

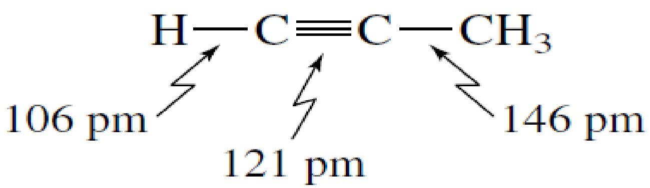
9.3 PHYSICAL PROPERTIES OF ALKYNES



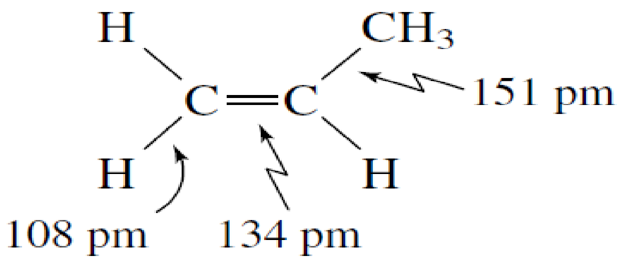
Alkynes resemble alkanes and alkenes in their physical properties. They share with these other hydrocarbons the properties of low density and low water-solubility. They are slightly more polar and generally have slightly higher boiling points than the corresponding alkanes and alkenes.

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			$H-C\equiv C-H$
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)

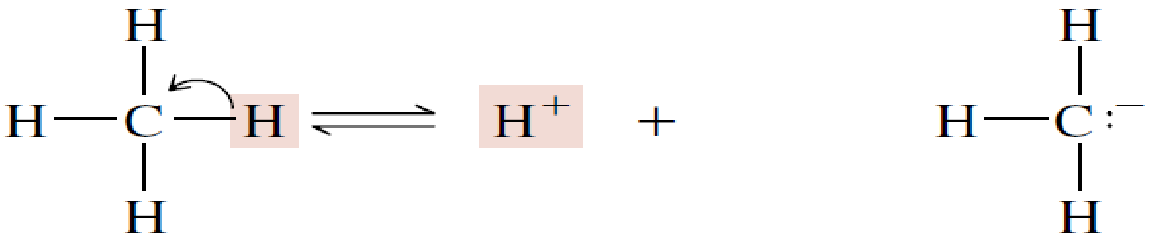


Propyne



Propene

Acidity of acetylene



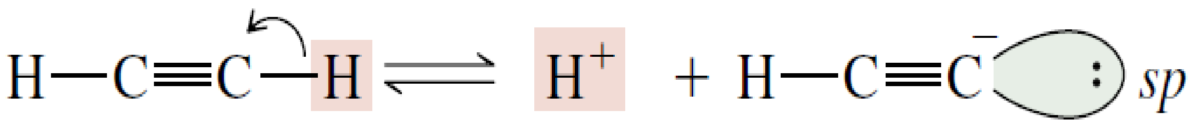
Methane Proton Methide anion (a *carbanion*)

$CH_4 < NH_3 < H_2O < HF$

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)

$CH_3CH_3 < CH_2{=}CH_2 < HC{\equiv}CH$

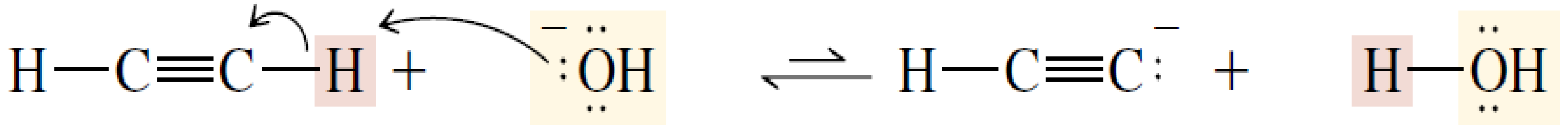
Ethane	Ethylene	Acetylene
$K_a \approx 10^{-62}$	$\approx 10^{-45}$	$= 10^{-26}$
$pK_a \approx 62$	≈ 45	$= 26$
(weakest acid)		(strongest acid)



Acetylene   Proton   Acetylide ion

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

3,3-Dimethyl-1-butyne



Acetylene
(weaker acid)
$K_a = 10^{-26}$
$pK_a = 26$

Hydroxide ion
(weaker base)

Acetylide ion
(stronger base)

Water
(stronger acid)
$K_a = 1.8 \times 10^{-16}$
$pK_a = 15.7$

Acetylene
(stronger acid)
$K_a = 10^{-26}$
$pK_a = 26$

Amide ion
(stronger base)

Acetylide ion
(weaker base)

Ammonia
(weaker acid)
$K_a = 10^{-36}$
$pK_a = 36$

Preparation of acetylenes

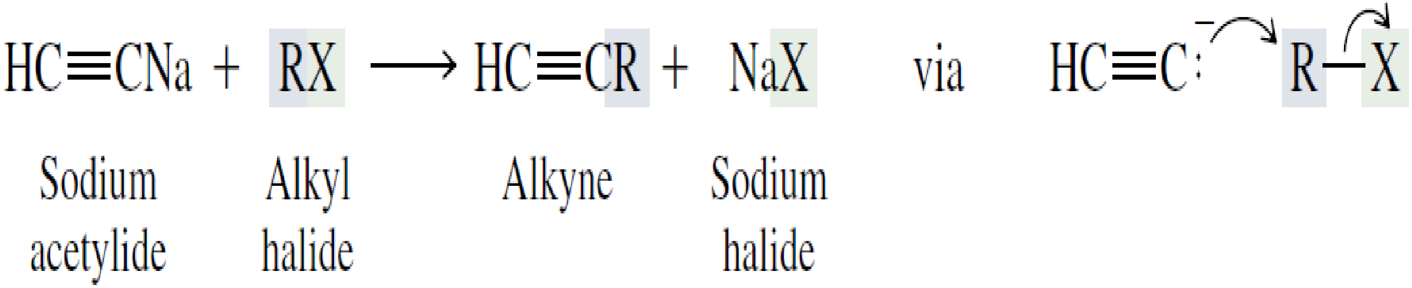
$$\mathrm{H{-}C{\equiv}C{-}H} \longrightarrow \mathrm{R{-}C{\equiv}C{-}H} \longrightarrow \mathrm{R{-}C{\equiv}C{-}R'}$$

Acetylene; Monosubstituted or terminal alkyne; Disubstituted derivative of acetylene

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

Acetylene; Sodium amide; Sodium acetylide; Ammonia

Alkylation



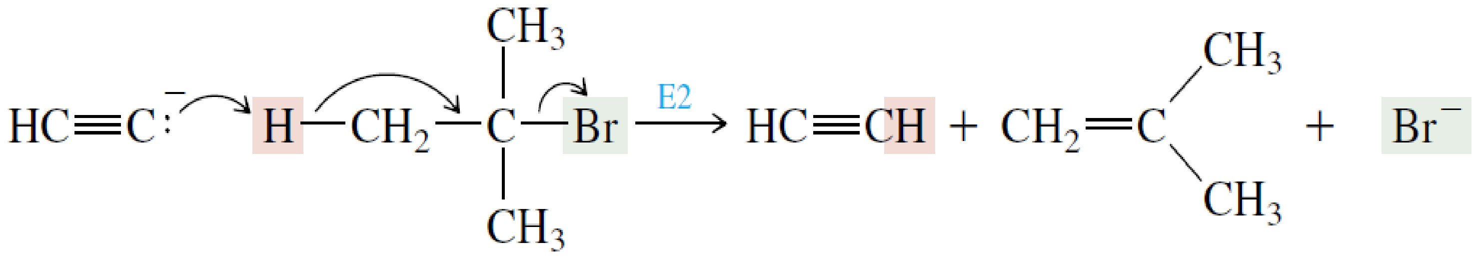
$$\mathrm{HC{\equiv}CNa} + \mathrm{RX} \longrightarrow \mathrm{HC{\equiv}CR} + \mathrm{NaX} \quad \text{via} \quad \mathrm{HC{\equiv}C{:}^{-}} \; \mathrm{R{-}X}$$

Sodium acetylide; Alkyl halide; Alkyne; Sodium halide

Functional group transformation; Carbon-carbon bond formation

$$\underset{\text{Sodium acetylide}}{HC{\equiv}CNa} + \underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br} \xrightarrow{NH_3} \underset{\text{1-Hexyne (70–77\%)}}{CH_3CH_2CH_2CH_2C{\equiv}CH}$$

Limitation

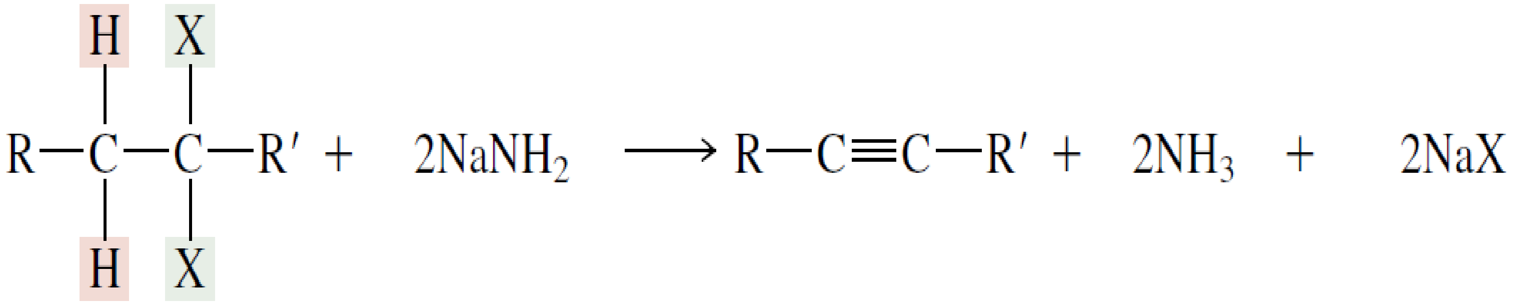


$$\underset{\text{Acetylide}}{HC{\equiv}C{:}^-} + \underset{\textit{tert}\text{-Butyl bromide}}{H{-}CH_2{-}C(CH_3)_2{-}Br} \xrightarrow{E2} \underset{\text{Acetylene}}{HC{\equiv}CH} + \underset{\text{2-Methylpropene}}{CH_2{=}C(CH_3)_2} + \underset{\text{Bromide}}{Br^-}$$

$$\underset{\text{Acetylene}}{HC{\equiv}CH} \xrightarrow[\text{2. } CH_3CH_2Br]{\text{1. } NaNH_2,\ NH_3} \underset{\text{1-Butyne}}{HC{\equiv}CCH_2CH_3} \xrightarrow[\text{2. } CH_3Br]{\text{1. } NaNH_2,\ NH_3} \underset{\text{2-Pentyne (81\%)}}{CH_3C{\equiv}CCH_2CH_3}$$

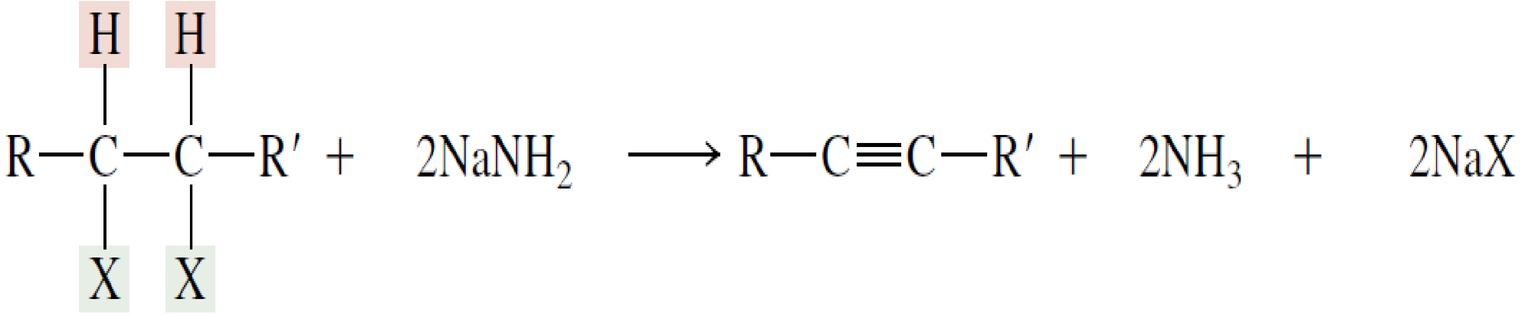
The desired S_N2 substitution pathway is observed only with methyl and primary alkyl halides.

Double dehydrohalogenation



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

Geminal dihalide　Sodium amide　Alkyne　Ammonia　Sodium halide



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

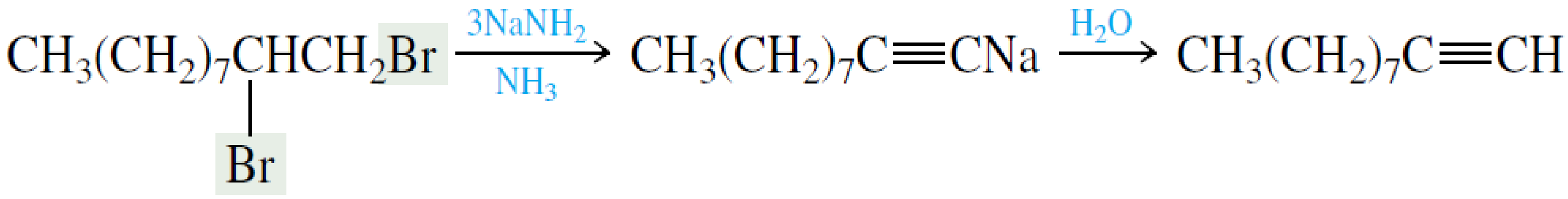
Vicinal dihalide　Sodium amide　Alkyne　Ammonia　Sodium halide

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

1,1-Dichloro-3,3-dimethylbutane

Sodium salt of alkyne product (not isolated)

3,3-Dimethyl-1-butyne (56–60%)

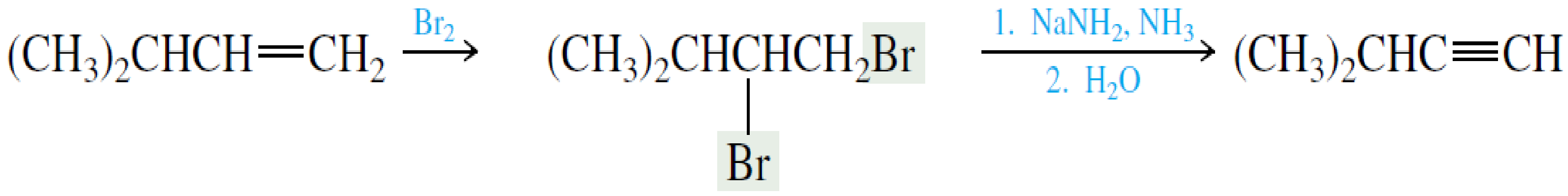


$$CH_3(CH_2)_7\underset{\displaystyle Br}{\underset{|}{C}}HCH_2Br \xrightarrow[NH_3]{3NaNH_2} CH_3(CH_2)_7C{\equiv}CNa \xrightarrow{H_2O} CH_3(CH_2)_7C{\equiv}CH$$

1,2-Dibromodecane

Sodium salt of alkyne product (not isolated)

1-Decyne (54%)



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

3-Methyl-1-butene

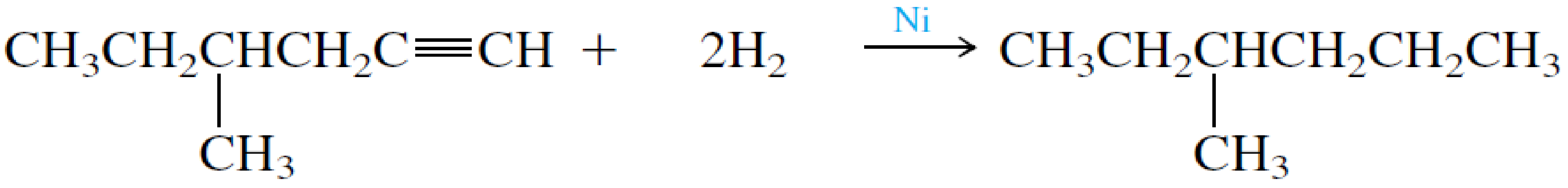
1,2-Dibromo-3-methylbutane

3-Methyl-1-butyne (52%)

Reactions

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

Alkyne Hydrogen Alkane



$$\underset{\displaystyle CH_3}{CH_3CH_2\overset{}{C}HCH_2C{\equiv}CH} + 2H_2 \xrightarrow{\text{Ni}} \underset{\displaystyle CH_3}{CH_3CH_2CHCH_2CH_2CH_3}$$

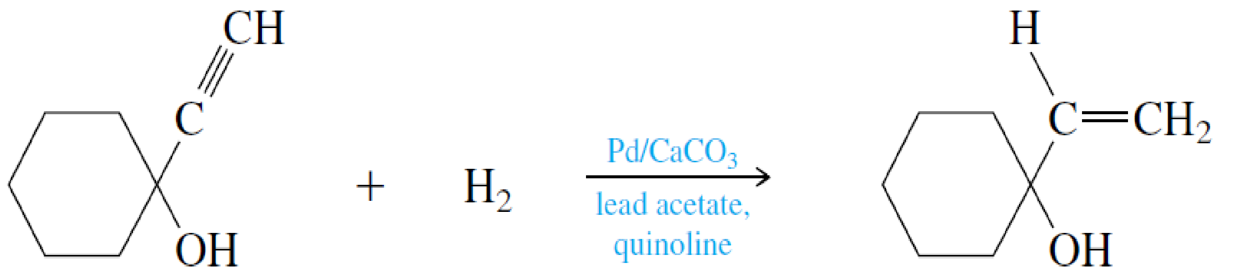
4-Methyl-1-hexyne Hydrogen 3-Methylhexane (77%)

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

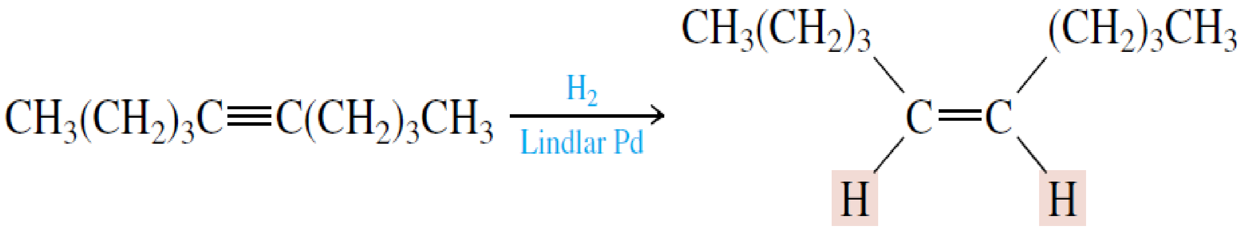
Alkenes are intermediates in the hydrogenation of alkynes to alkanes.

$$RC{\equiv}CR' \xrightarrow[\text{catalyst}]{H_2} RCH{=}CHR' \xrightarrow[\text{catalyst}]{H_2} RCH_2CH_2R'$$

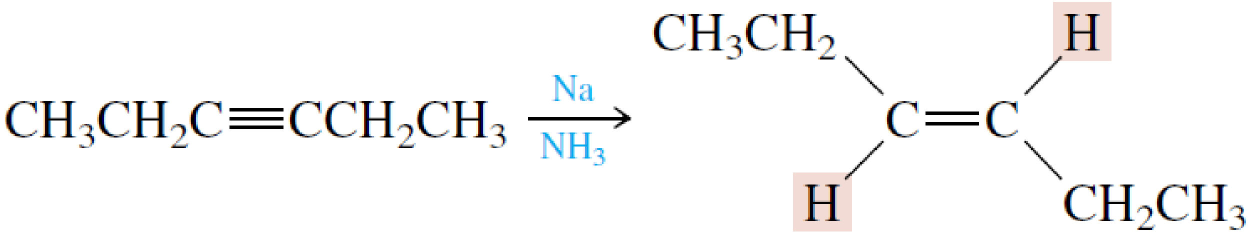
Alkyne Alkene Alkane



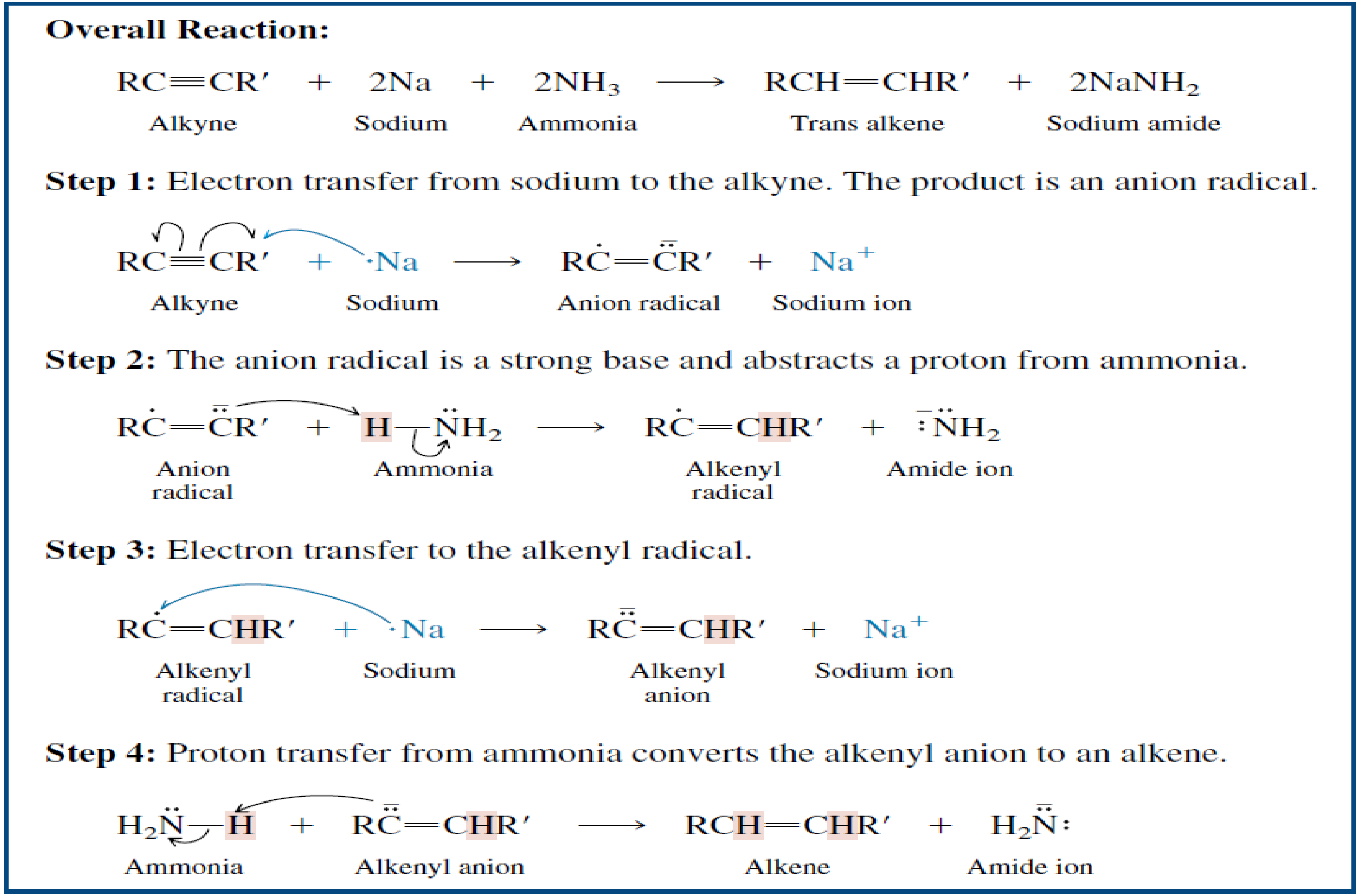
1-Ethynylcyclohexanol Hydrogen 1-Vinylcyclohexanol (90–95%)



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



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



Overall Reaction:

$$RC{\equiv}CR' + 2Na + 2NH_3 \longrightarrow RCH{=}CHR' + 2NaNH_2$$

Step 1: Electron transfer from sodium to the alkyne. The product is an anion radical.

$$RC{\equiv}CR' + \cdot Na \longrightarrow R\dot{C}{=}\ddot{C}R'^{-} + Na^{+}$$

Step 2: The anion radical is a strong base and abstracts a proton from ammonia.

$$R\dot{C}{=}\ddot{C}R'^{-} + H{-}\ddot{N}H_2 \longrightarrow R\dot{C}{=}CHR' + {}^{-}\!:\ddot{N}H_2$$

Step 3: Electron transfer to the alkenyl radical.

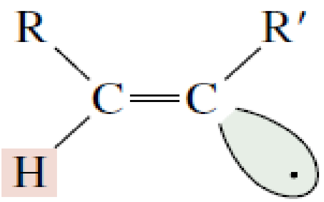
$$R\dot{C}{=}CHR' + \cdot Na \longrightarrow R\ddot{C}^{-}{=}CHR' + Na^{+}$$

Step 4: Proton transfer from ammonia converts the alkenyl anion to an alkene.

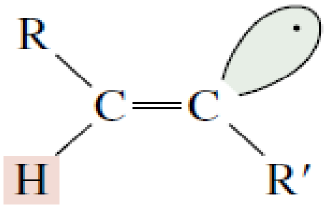
$$H_2\ddot{N}{-}H + R\ddot{C}^{-}{=}CHR' \longrightarrow RCH{=}CHR' + H_2\ddot{N}:^{-}$$

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

E radical is more stable

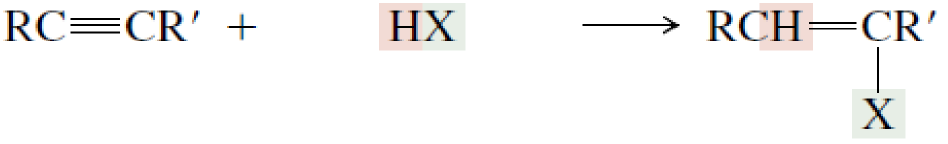


(Z)-Alkenyl radical
(less stable)



(E)-Alkenyl radical
(more stable)

Addition of hydrogen halides

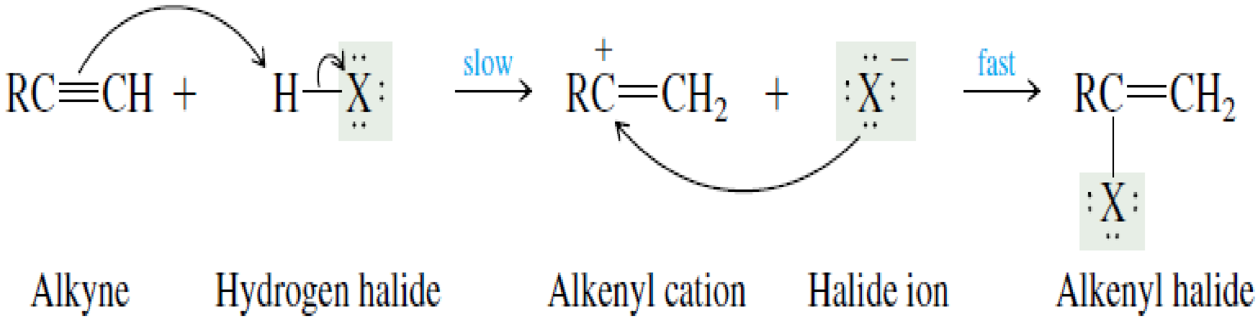


$$RC{\equiv}CR' + HX \longrightarrow RCH{=}\underset{\displaystyle X}{\underset{|}{C}}R'$$

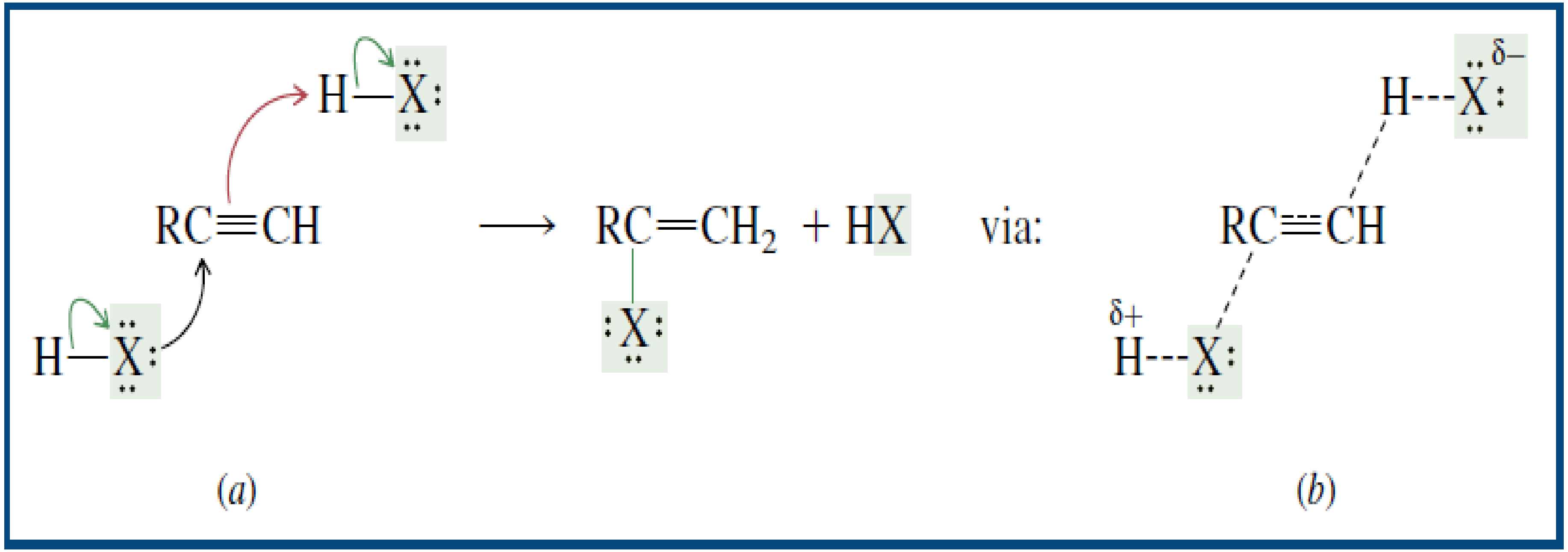
Alkyne Hydrogen halide Alkenyl halide

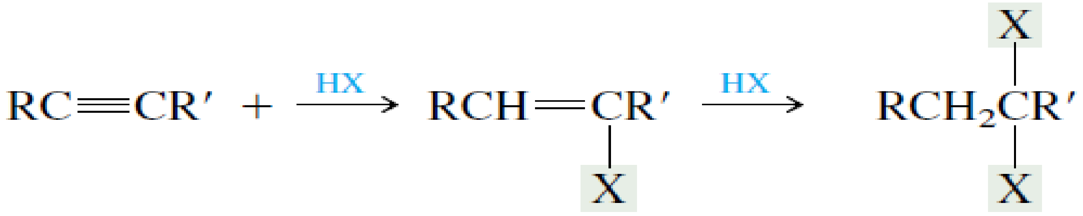
$$CH_3CH_2CH_2CH_2C{\equiv}CH + HBr \longrightarrow CH_3CH_2CH_2CH_2\underset{\displaystyle Br}{\underset{|}{C}}{=}CH_2$$

1-Hexyne Hydrogen bromide 2-Bromo-1-hexene (60%)



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



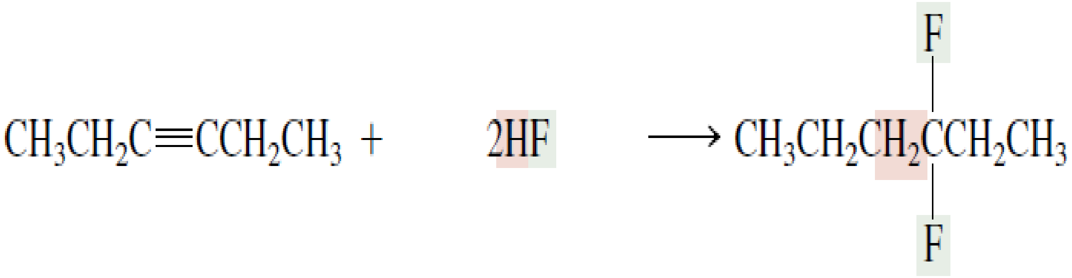


$$RC\equiv CR' + \xrightarrow{HX} RCH{=}\underset{X}{C}R' \xrightarrow{HX} RCH_2\overset{X}{\underset{X}{C}}R'$$

Alkyne

Alkenyl halide

Geminal dihalide

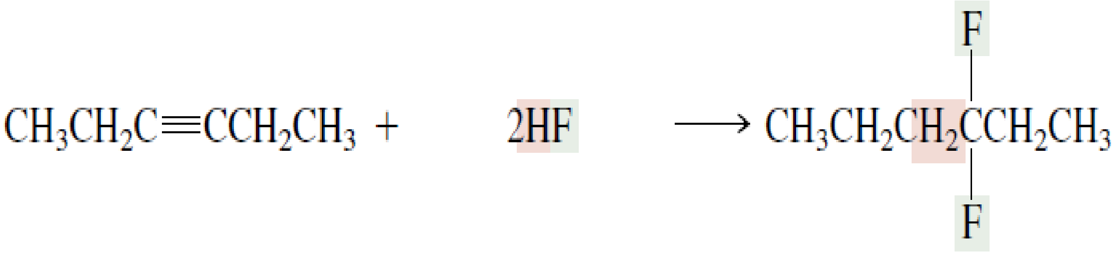


$$CH_3CH_2C\equiv CCH_2CH_3 + 2HF \longrightarrow CH_3CH_2CH_2\overset{F}{\underset{F}{C}}CH_2CH_3$$

3-Hexyne

Hydrogen fluoride

3,3-Difluorohexane (76%)

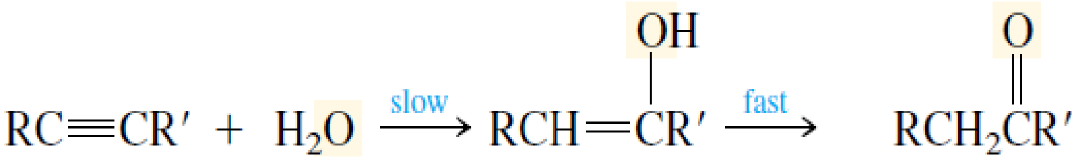


$$CH_3CH_2C\equiv CCH_2CH_3 + 2HF \longrightarrow CH_3CH_2CH_2\overset{F}{\underset{F}{C}}CH_2CH_3$$

3-Hexyne

Hydrogen fluoride

3,3-Difluorohexane (76%)



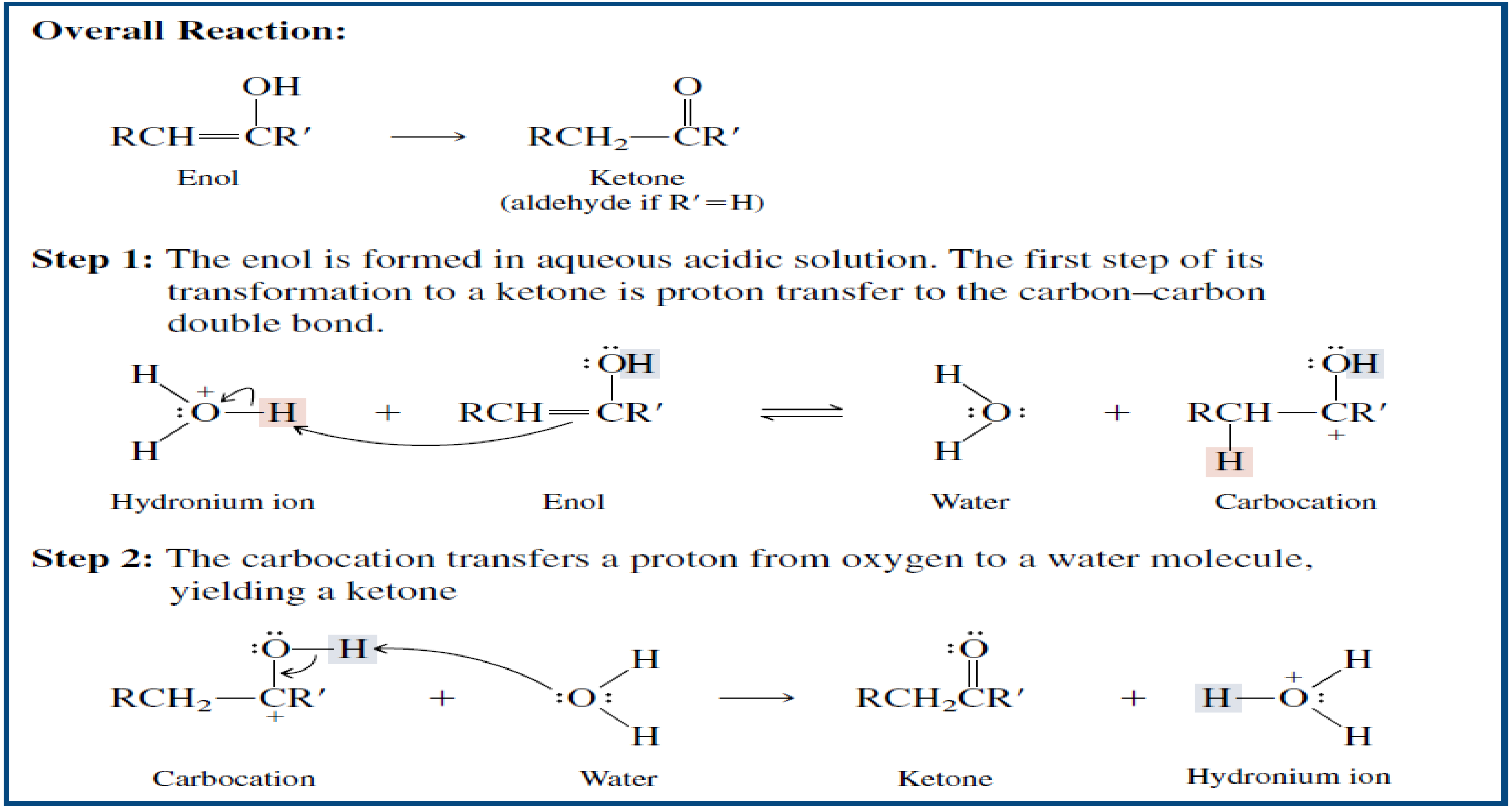
$$RC\equiv CR' + H_2O \xrightarrow{slow} RCH{=}\overset{OH}{C}R' \xrightarrow{fast} RCH_2\overset{O}{\overset{\|}{C}}R'$$

Alkyne

Water

Enol
(not isolated)

R′ = H; aldehyde
R′ = alkyl; ketone

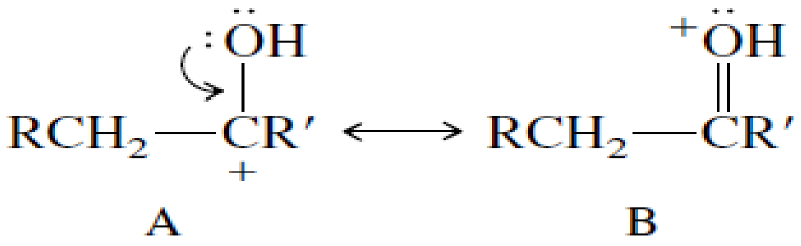


Overall Reaction:

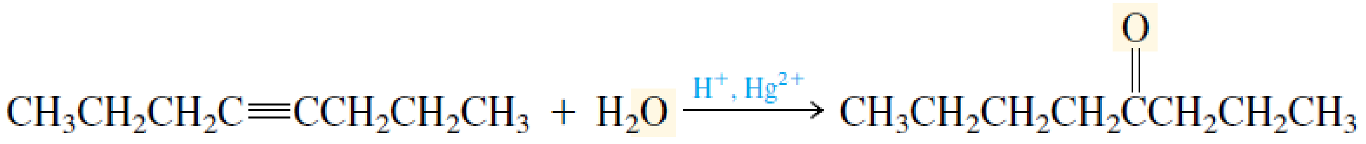
Step 1: The enol is formed in aqueous acidic solution. The first step of its transformation to a ketone is proton transfer to the carbon–carbon double bond.

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.



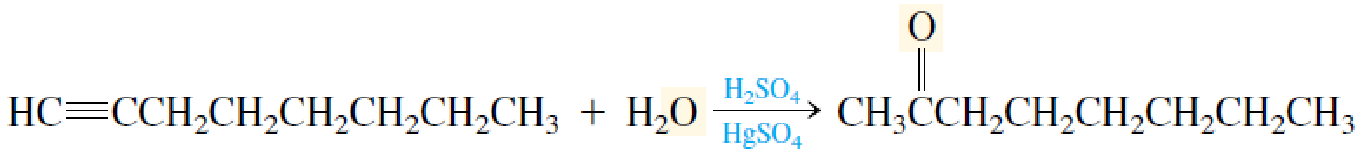
$$RCH_2-\overset{\overset{:\ddot{O}H}{|}}{\underset{+}{C}}R' \longleftrightarrow RCH_2-\overset{\overset{+\ddot{O}H}{\|}}{C}R'$$



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

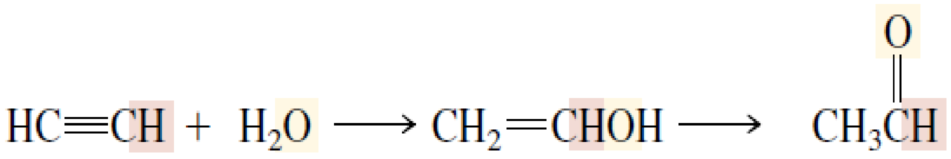
4-Octyne 4-Octanone (89%)

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



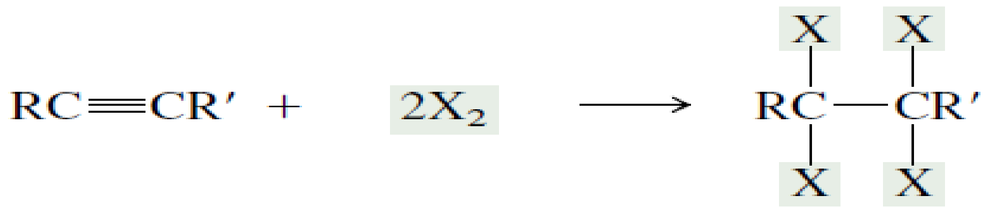
$$HC\equiv CCH_2CH_2CH_2CH_2CH_2CH_3 + H_2O \xrightarrow[HgSO_4]{H_2SO_4} CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH_2CH_2CH_2CH_3$$

1-Octyne 2-Octanone (91%)



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

Acetylene Water Vinyl alcohol (not isolated) Acetaldehyde

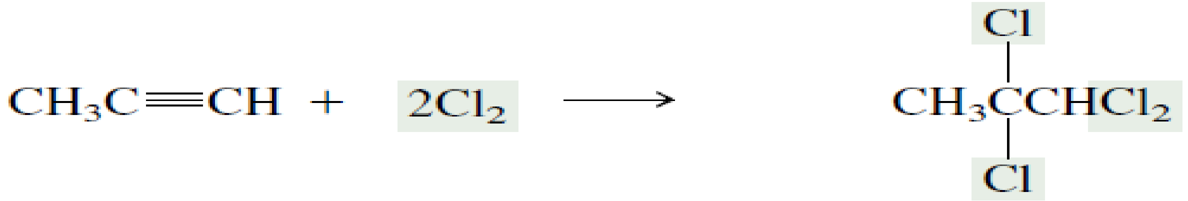


$$RC\equiv CR' + 2X_2 \longrightarrow RCX_2-CX_2R'$$

Alkyne

Halogen (chlorine or bromine)

Tetrahaloalkane

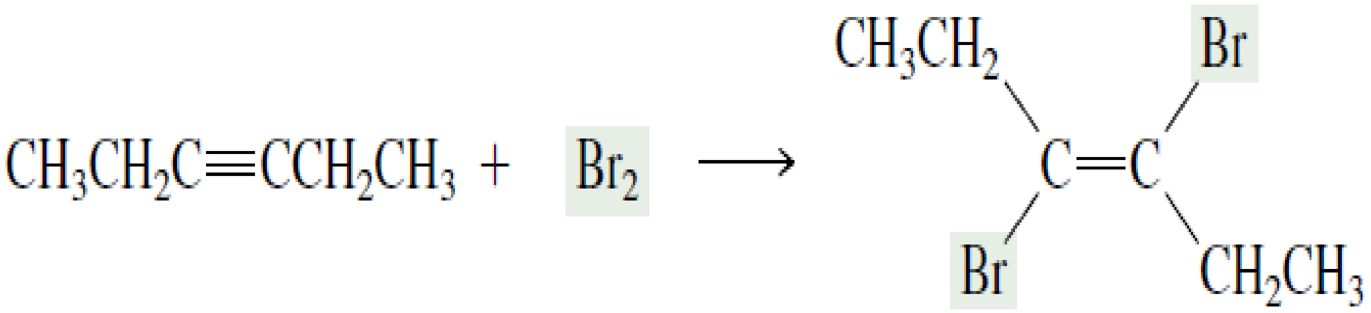


$$CH_3C\equiv CH + 2Cl_2 \longrightarrow CH_3CCl_2CHCl_2$$

Propyne

Chlorine

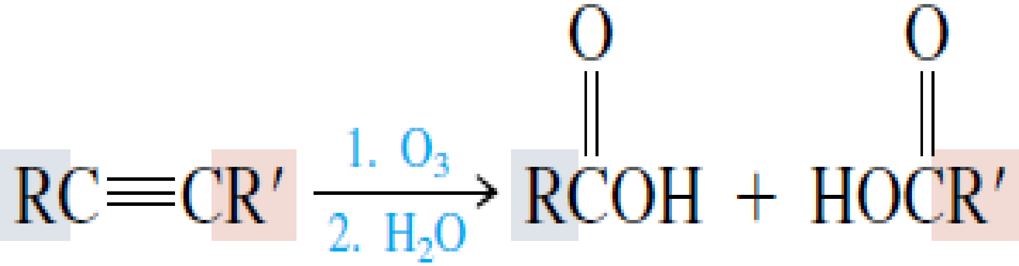
1,1,2,2-Tetrachloropropane (63%)



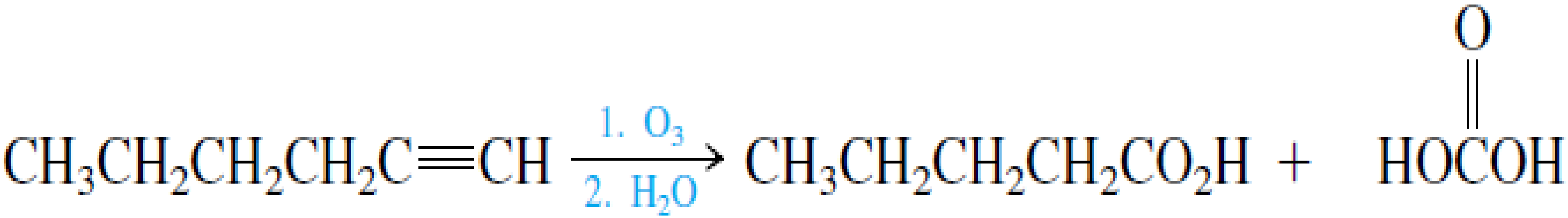
3-Hexyne

Bromine

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



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



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

1-Hexyne

Pentanoic acid (51%)

Carbonic acid

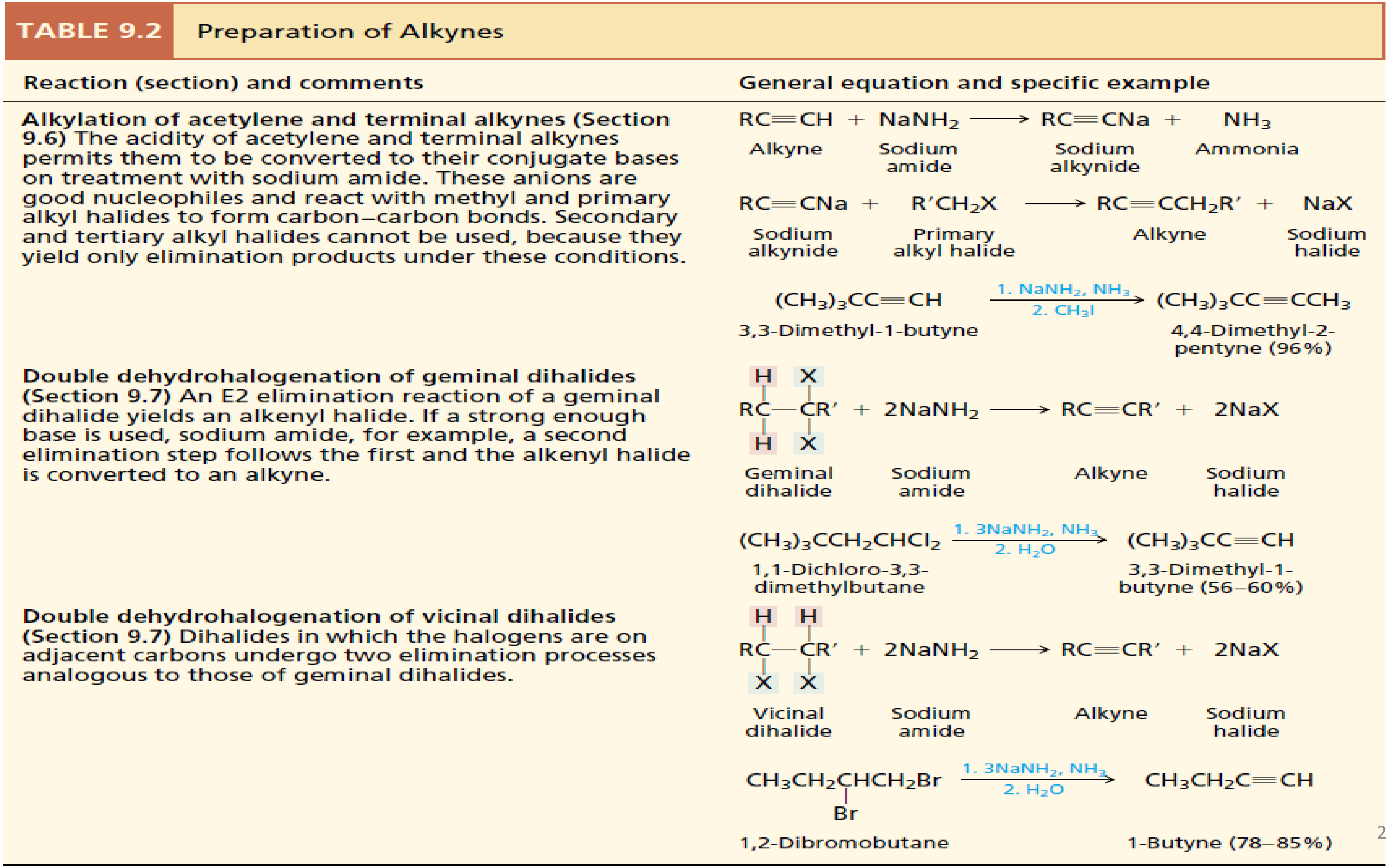


TABLE 9.2 Preparation of Alkynes

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.	$\underset{\text{Alkyne}}{RC{\equiv}CH} + \underset{\text{Sodium amide}}{NaNH_2} \longrightarrow \underset{\text{Sodium alkynide}}{RC{\equiv}CNa} + \underset{\text{Ammonia}}{NH_3}$ $\underset{\text{Sodium alkynide}}{RC{\equiv}CNa} + \underset{\text{Primary alkyl halide}}{R'CH_2X} \longrightarrow \underset{\text{Alkyne}}{RC{\equiv}CCH_2R'} + \underset{\text{Sodium halide}}{NaX}$ $\underset{\text{3,3-Dimethyl-1-butyne}}{(CH_3)_3CC{\equiv}CH} \xrightarrow[\text{2. } CH_3I]{\text{1. } NaNH_2,\ NH_3} \underset{\text{4,4-Dimethyl-2-pentyne (96\%)}}{(CH_3)_3CC{\equiv}CCH_3}$
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.	$\underset{\text{Geminal dihalide}}{R\underset{H}{\overset{H}{C}}-\underset{X}{\overset{X}{C}}R'} + \underset{\text{Sodium amide}}{2NaNH_2} \longrightarrow \underset{\text{Alkyne}}{RC{\equiv}CR'} + \underset{\text{Sodium halide}}{2NaX}$ $\underset{\text{1,1-Dichloro-3,3-dimethylbutane}}{(CH_3)_3CCH_2CHCl_2} \xrightarrow[\text{2. } H_2O]{\text{1. } 3NaNH_2,\ NH_3} \underset{\text{3,3-Dimethyl-1-butyne (56–60\%)}}{(CH_3)_3CC{\equiv}CH}$
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.	$\underset{\text{Vicinal dihalide}}{R\underset{X}{\overset{H}{C}}-\underset{X}{\overset{H}{C}}R'} + \underset{\text{Sodium amide}}{2NaNH_2} \longrightarrow \underset{\text{Alkyne}}{RC{\equiv}CR'} + \underset{\text{Sodium halide}}{2NaX}$ $\underset{\text{1,2-Dibromobutane}}{CH_3CH_2\underset{Br}{C}HCH_2Br} \xrightarrow[\text{2. } H_2O]{\text{1. } 3NaNH_2,\ NH_3} \underset{\text{1-Butyne (78–85\%)}}{CH_3CH_2C{\equiv}CH}$