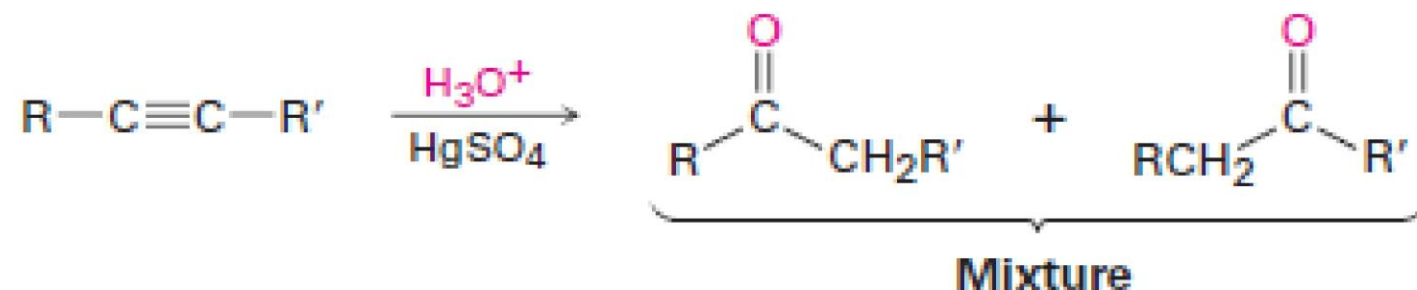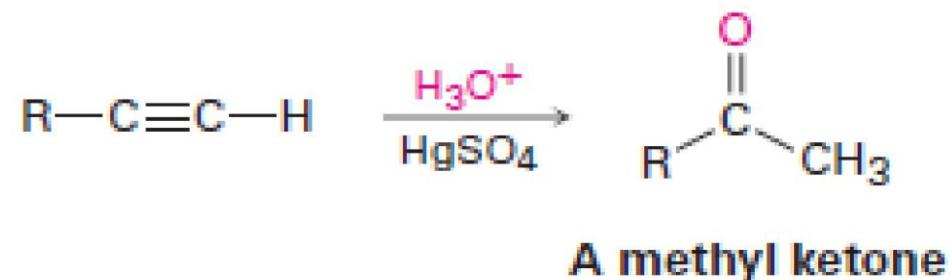A mixture of both possible ketones results when an unsymmetrically substituted internal alkyne $(RC \equiv CR')$ is hydrated. The reaction is therefore most useful when applied to a terminal alkyne $(RC \equiv CH)$ because only a methyl ketone is formed.

An internal alkyne

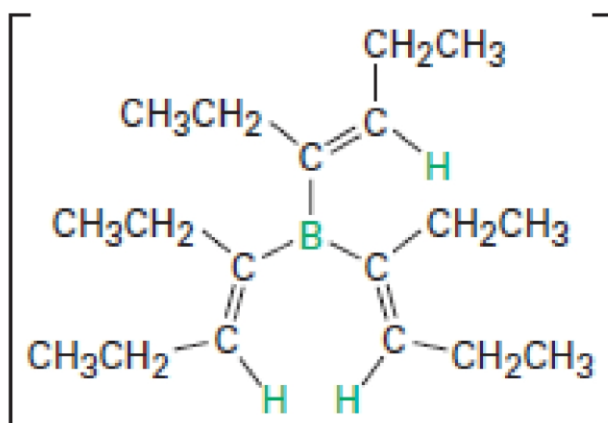$$R-C \equiv C-R' \xrightarrow[\text{HgSO}_4]{\text{H}_3\text{O}^+}$$

$$\underbrace{R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2R' \quad + \quad RCH_2-\overset{\overset{\displaystyle O}{\|}}{C}-R'}_{\textbf{Mixture}}$$

A terminal alkyne

$$R-C \equiv C-H \xrightarrow[\text{HgSO}_4]{\text{H}_3\text{O}^+} R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$
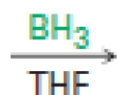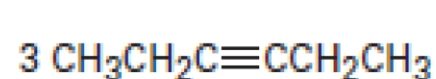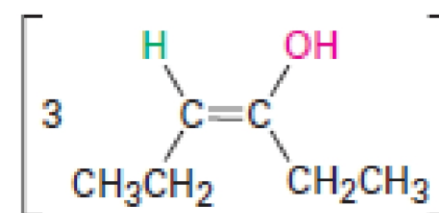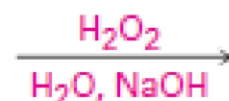
A methyl ketone

Hydroboration–Oxidation of Alkynes

Borane adds rapidly to an alkyne just as it does to an alkene, and the resulting vinylic borane can be oxidized by H_2O_2 to yield an enol. Tautomerization then gives either a ketone or an aldehyde, depending on the structure of the alkyne reactant. Hydroboration–oxidation of an internal alkyne such as 3-hexyne gives a ketone and hydroboration–oxidation of a terminal alkyne gives an aldehyde. Note that the relatively unhindered terminal alkyne undergoes two additions, giving a doubly hydroborated intermediate. Oxidation with H_2O_2 at pH 8 then replaces both boron atoms with oxygen and generates the aldehyde.

An internal alkyne

$$3 \ CH_3CH_2C{\equiv}CCH_2CH_3 \quad \xrightarrow[\text{THF}]{BH_3}$$

A vinylic borane

$$\xrightarrow[\text{H}_2\text{O, NaOH}]{\text{H}_2\text{O}_2}$$

An enol

$$3 \ CH_3CH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_3$$
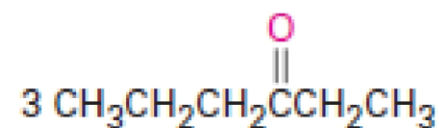
3-Hexanone

A terminal alkyne

$$CH_3CH_2CH_2CH_2C{\equiv}CH \quad \xrightarrow[\text{THF}]{BH_3} \quad CH_3CH_2CH_2CH_2CH_2-\overset{\displaystyle R{\diagdown}\underset{\displaystyle R{\diagup}\overset{B}{\diagup}R}{B}{\diagup}R}{CH} \quad \xrightarrow[\text{H}_2\text{O, pH 8}]{\text{H}_2\text{O}_2} \quad CH_3CH_2CH_2CH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}H$$
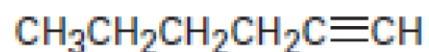
1-Hexyne
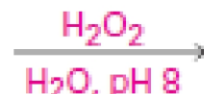
Hexanal (70%)

The hydroboration–oxidation sequence is complementary to the direct, mercury(II)-catalyzed hydration reaction of a terminal alkyne because different products result. Direct hydration with aqueous acid and m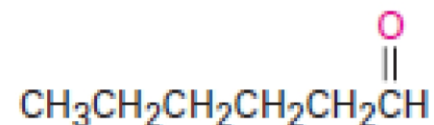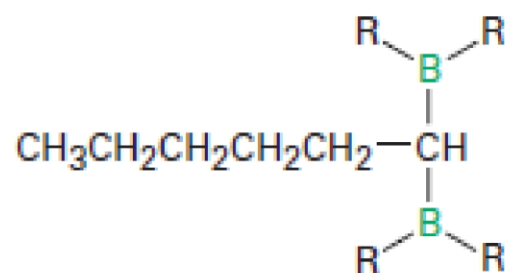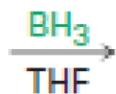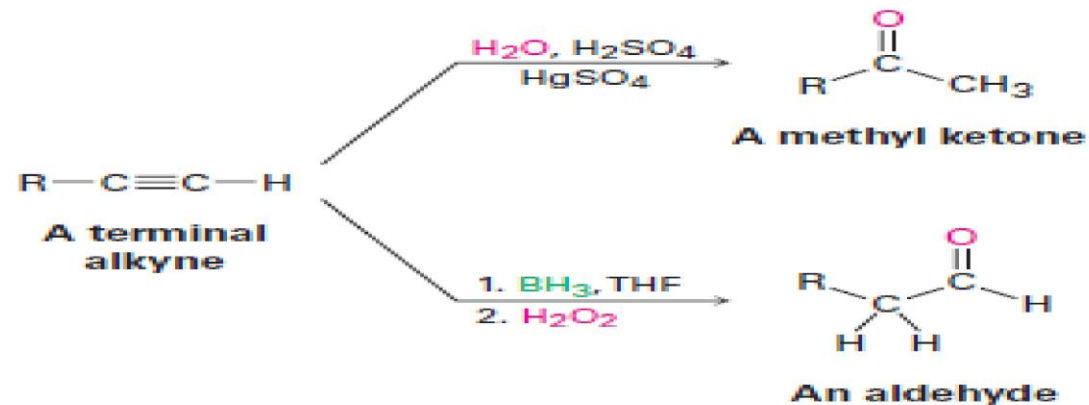ercury (II) sulfate leads to a methyl ketone, whereas hydroboration–oxidation of the same terminal alkyne leads to an aldehyde.
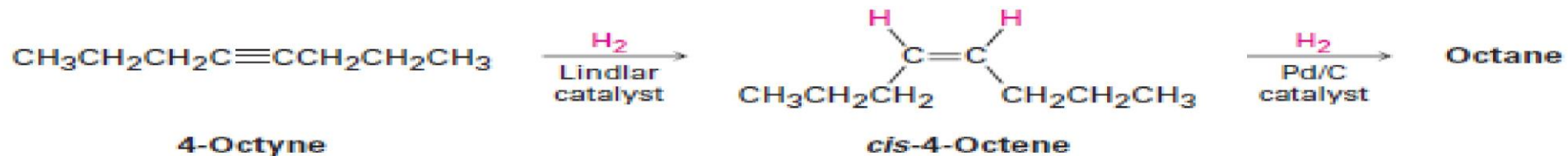
$$R-C\equiv C-H \quad \text{A terminal alkyne}$$

$$\xrightarrow[\text{HgSO}_4]{\text{H}_2\text{O, H}_2\text{SO}_4}$$

A methyl ketone

$$\xrightarrow[\text{2. H}_2\text{O}_2]{\text{1. BH}_3\text{, THF}}$$

An aldehyde

Reduction of Alkynes

Alkynes are reduced to alkanes by addition of H_2 over a metal catalyst. The reaction occurs in two steps through an alkene intermediate, and measurements show that the first step in the reaction is more exothermic than the second.

$$HC\equiv CH \xrightarrow[\text{Catalyst}]{\text{H}_2} H_2C=CH_2 \qquad \Delta H°_{\text{hydrog}} = -176 \text{ kJ/mol } (-42 \text{ kcal/mol})$$

$$H_2C=CH_2 \xrightarrow[\text{Catalyst}]{\text{H}_2} CH_3-CH_3 \qquad \Delta H°_{\text{hydrog}} = -137 \text{ kJ/mol } (-33 \text{ kcal/mol})$$

Complete reduction to the alkane occurs when palladium on carbon (Pd/C) is used as catalyst, but hydrogenation can be stopped at the alkene stage if the less active *Lindlar catalyst* is used. The Lindlar catalyst is a finely divided palladium metal that has been precipitated onto a calcium carbonate support and then deactivated by treatment with lead acetate and quinoline, an aromatic amine. The hydrogenation occurs with syn stereochemistry, giving a cis alkene product.

$CH_3CH_2CH_2C{\equiv}CCH_2CH_2CH_3$ $\xrightarrow[\text{catalyst}]{\text{H}_2 \atop \text{Lindlar}}$

4-Octyne

cis-**4-Octene**

$\xrightarrow[\text{catalyst}]{\text{H}_2 \atop \text{Pd/C}}$ **Octane**
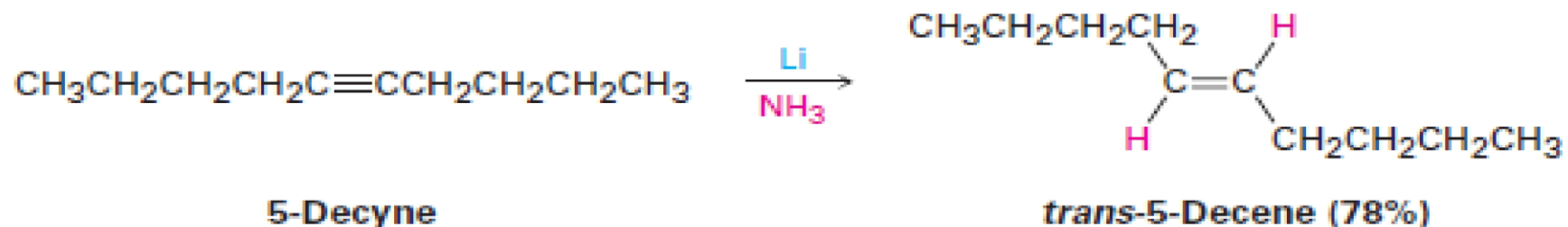
Quinoline

The alkyne hydrogenation reaction has been explored extensively by the Hoffmann–LaRoche pharmaceutical company, where it is used in the commercial synthesis of vitamin A. The cis isomer of vitamin A produced initially on hydrogenation is converted to the trans isomer by heating.

7-cis-Retinol
(7-cis-vitamin A; vitamin A has
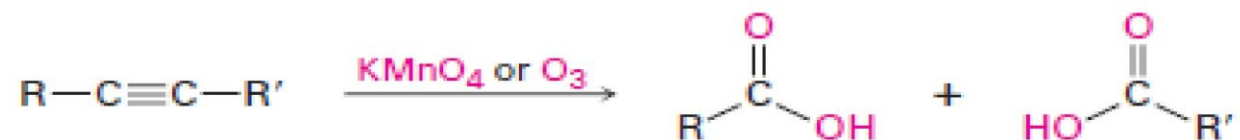**a trans double bond at C7)**
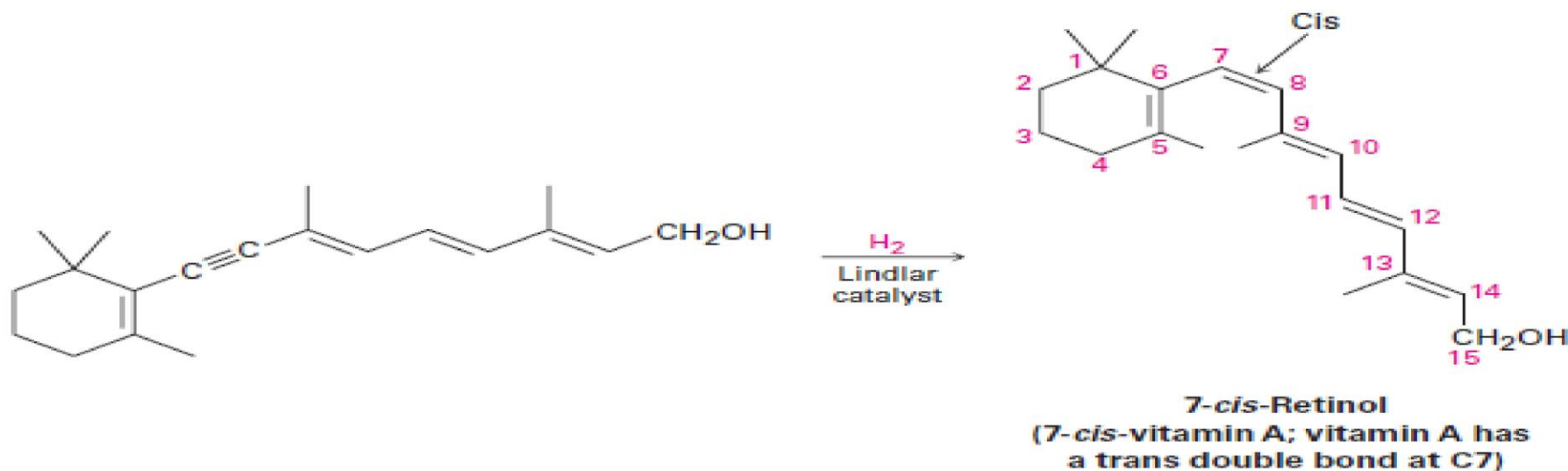
An alternative method for the conversion of an alkyne to an alkene uses sodium or lithium metal as the reducing agent in liquid ammonia as solvent. This method is complementary to the Lindlar reduction because it produces trans rather than cis alkenes. For example, 5-decyne gives *trans*-5-decene on treatment with lithium in liquid ammonia.

$$CH_3CH_2CH_2CH_2C{\equiv}CCH_2CH_2CH_2CH_3 \xrightarrow[NH_3]{Li}$$

5-Decyne

$$CH_3CH_2CH_2CH_2 \diagdown \; \diagup H$$
$$C{=}C$$
$$H \diagup \; \diagdown CH_2CH_2CH_2CH_3$$

trans-5-Decene (78%)

Oxidative Cleavage of Alkynes

Alkynes, like alkenes, can be cleaved by reaction with powerful oxidizing agents such as ozone or $KMnO_4$, although the reaction is of little value and we mention it only for completeness. A triple bond is generally less reactive than a double bond, and yields of cleavage products can be low. The products obtained from cleavage of an internal alkyne are carboxylic acids; from a terminal alkyne, CO_2 is formed as one product.

An internal alkyne

$$R-C\equiv C-R' \xrightarrow{\text{KMnO}_4 \text{ or O}_3} \underset{\underset{\text{OH}}{R}}{\overset{O}{\overset{\|}{C}}} + \underset{\underset{R'}{\text{HO}}}{\overset{O}{\overset{\|}{C}}}$$

A terminal alkyne

$$R-C\equiv C-H \xrightarrow{\text{KMnO}_4 \text{ or O}_3} \underset{\underset{\text{OH}}{R}}{\overset{O}{\overset{\|}{C}}} + O=C=O$$
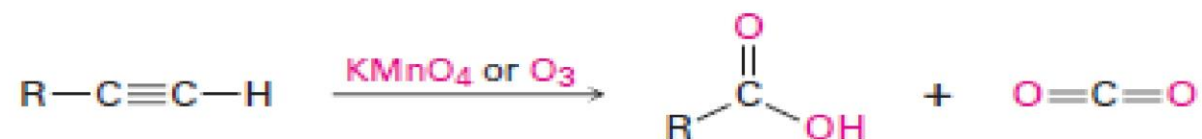
Alkyne Acidity: Formation of Acetylide Anions

The most striking difference between alkenes and alkynes is that terminal alkynes are relatively acidic. When a terminal alkyne is treated with a strong base, such as sodium amide, Na^+ $^-NH_2$, the terminal hydrogen is removed and the corresponding **acetylide anion** is formed.

$$R-C\equiv C-H + :\ddot{N}H_2 \ Na^+ \longrightarrow R-C\equiv C:^- \ Na^+ + :NH_3$$

Acetylide anion

Alkylation of Acetylide Anions

The negative charge and unshared electron pair on carbon make an acetylide anion strongly nucleophilic. As a result, an acetylide anion can react with electrophiles, such as alkyl halides, in a process that replaces the halide and yields a new alkyne product.
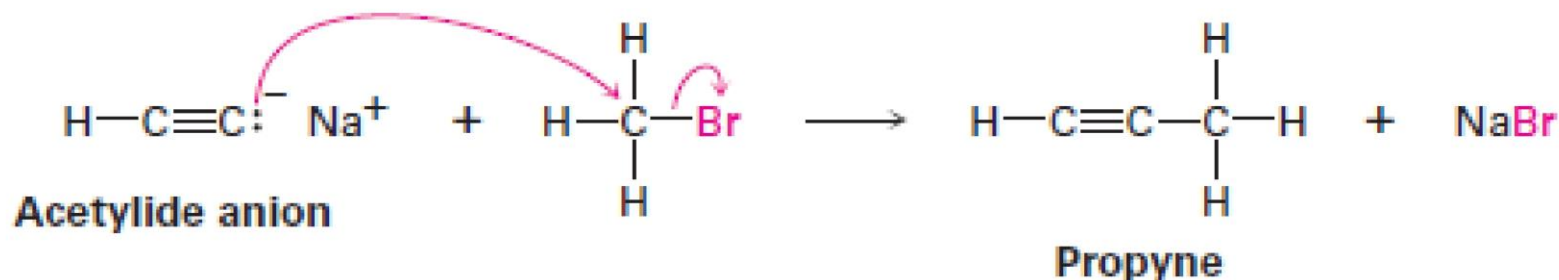
For now you can picture it as happening by the pathway shown in **Figure 9-6**. The nucleophilic acetylide ion uses an electron pair to form a bond to the positively polarized, electrophilic carbon atom of bromomethane. As the new C-C bond forms, Br^- departs, taking with it the electron pair from the former C-Br bond and yielding propyne as product. We call such a reaction an **alkylation** because a new alkyl group has become attached to the starting alkyne.

① The nucleophilic acetylide anion uses its electron lone pair to form a bond to the positively polarized, electrophilic carbon atom of bromomethane. As the new C–C bond begins to form, the C–Br bond begins to break in the transition state.
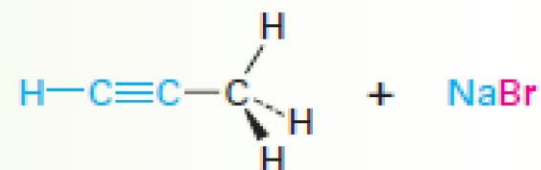
Transition state

② The new C–C bond is fully formed and the old C–Br bond is fully broken at the end of the reaction.
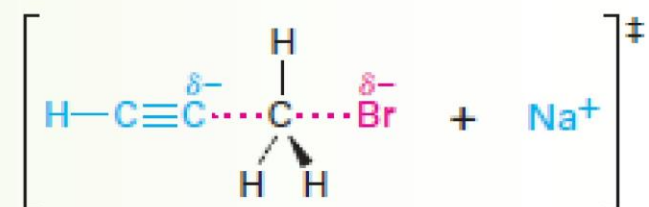
Figure 9-6A mechanism for the alkylation reaction of acetylide anion with bromomethane to give propyne.

Alkyne alkylation is not limited to acetylene itself. *Any* terminal alkyne can be converted into its corresponding anion and then allowed to react with an alkyl halide to give an internal alkyne product. Hex-1-yne, for instance, gives dec-5-yne when treated first with $NaNH_2$ and then with 1-bromobutane.

$$CH_3CH_2CH_2CH_2C{\equiv}CH \xrightarrow[\text{2. } CH_3CH_2CH_2CH_2Br]{\text{1. } NaNH_2,\ NH_3} CH_3CH_2CH_2CH_2C{\equiv}CCH_2CH_2CH_2CH_3$$

1-Hexyne   5-Decyne (76%)

Because of its generality, acetylide alkylation is a good method for preparing substituted alkynes from simpler precursors. A terminal alkyne can be prepared by alkylation of acetylene itself, and an internal alkyne can be prepared by further alkylation of a terminal alkyne.

$$H{-}C{\equiv}C{-}H \xrightarrow{NaNH_2} \left[H{-}C{\equiv}C{:}^- \ Na^+ \right] \xrightarrow{RCH_2Br} H{-}C{\equiv}C{-}CH_2R$$

Acetylene   A terminal alkyne

$$R{-}C{\equiv}C{-}H \xrightarrow{NaNH_2} \left[R{-}C{\equiv}C{:}^- \ Na^+ \right] \xrightarrow{R'CH_2Br} R{-}C{\equiv}C{-}CH_2R'$$

A terminal alkyne   An internal alkyne

The alkylation reaction can only use primary alkyl bromides and alkyl iodides because acetylide ions are sufficiently strong bases to cause elimination instead of substitution when they react with secondary and tertiary alkyl halides. For example, reaction of bromo cyclohexane with propyne anion yields the elimination product cyclohexene rather than the substitution product 1-propynyl cyclohexane.

Bromocyclohexane
(a secondary alkyl halide)

$+$ $CH_3C\equiv C:^- Na^+$

Cyclohexene

$+$ $CH_3C\equiv CH$ $+$ NaBr

Not formed