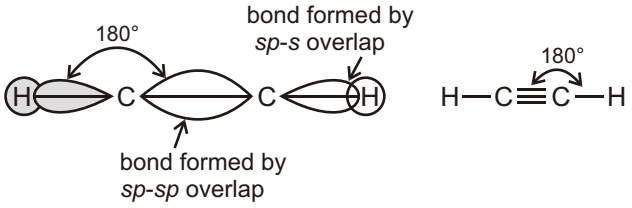
CHAPTER

30

Alkyne

INTRODUCTION



A triple bond consist of a -bond formed by (*sp* *sp*) overlap *p* and 2*p*-bonds formed by *p*-*p* overlap.

- These are the acyclic hydrocarbons which contains carbon-carbon triple bond are called alkyne.
- Hybridization state of triply bonded carbon in alkyne is sp or also called as diagonal hybridisation.
- Geometry of carbon is linear in alkynes.
- Bond angle in alkyne is 180 .
- Their general formula is $C_nH_{2n\ 2}$.
- C — C triple bond length is 1.20 Å.
- C — H bond length is 1.08 Å.
- C — C triple bond energy is 190 kcal./mol.
- C — H bond energy is 102.38 kcal./mol.
- Alkyne shows chain, position and functional isomerism. They are functional isomer with cycloalkene and alkadiene.

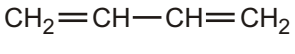
(i) C_1 — C_4 compounds do not show chain isomerism.

(ii) Functional isomers of C_4H_6

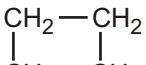
e.g.,

$CH_3—CH_2—C\equiv CH$ 1-Butyne

$CH_3—CH=C=CH_2$ 1, 2-Butadiene



1,3-Butadiene



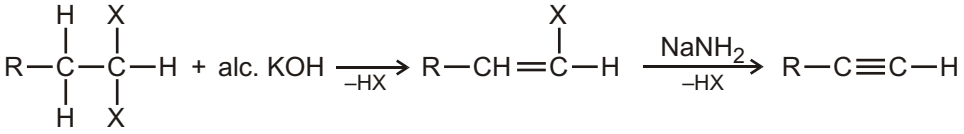
Cyclobutene

Physical Properties

- Alkynes are colourless, odourless and tasteless.
- Lower alkynes are partially soluble in H_2O. (It is due to its polarisibility).
- Higher alkynes are insoluble in water due to more % of covalent character.
- Completely soluble in organic solvents.
- Melting point and boiling point increases with molecular mass and decreases with number of branches.
- Upto C_4 alkynes are gaseous.C_5 — C_{11} are liquid, C_{12} & above are solids.
- Pure acetylene is odourless and impure acetylene has odour like garlic. It is due to impurities of Arsene (AsH_3) & Phosphine (PH_3).
- Acetylene & 1- alkyne are acidic in nature. It is due to greater electronegativity of *sp* hybridised 'C'.
- Acetylene has two acidic hydrogen atoms. It can neutralise two equivalents of base at the same time. So it is also called as dibasic acid. But the base should be very stronger as $-NH_2$ or $-CH_3$ etc.

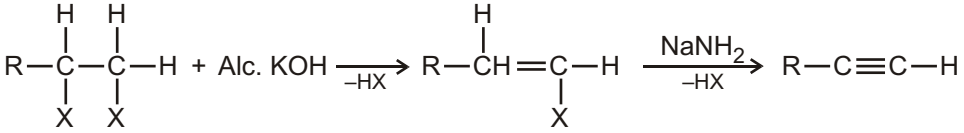
Preparation Methods :

1. **From Gem Dihalides (Dehydrohalogenation) :**



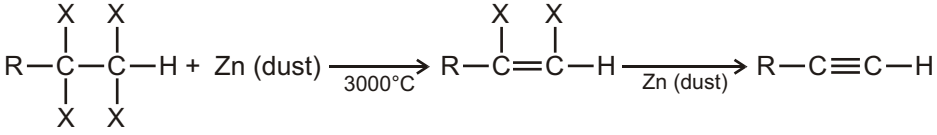
❑ **NOTE :** Alc.KOH is not used for elimination in second step because in this case elimination takes place from doubly bonded carbon atom which is stable due to resonance so strong base $NaNH_2$ is used for elimination of HX.

2. **From Vicinal Dihalides (Dehydrohalogenation) :**



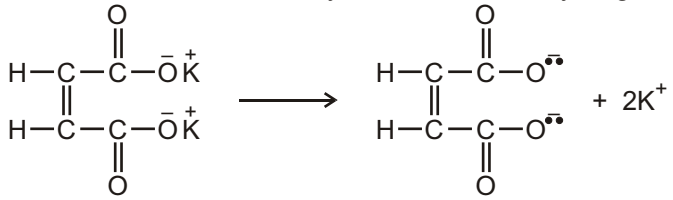
❑ **NOTE :** In the above reaction if the reactant secondary butylene chloride is taken then the products are 2-butyne, 1, 2-butadiene and 1, 3- butadiene in which 2-butyne is the chief product.

3. From Tetrahaloalkanes (Dehalogenation) :



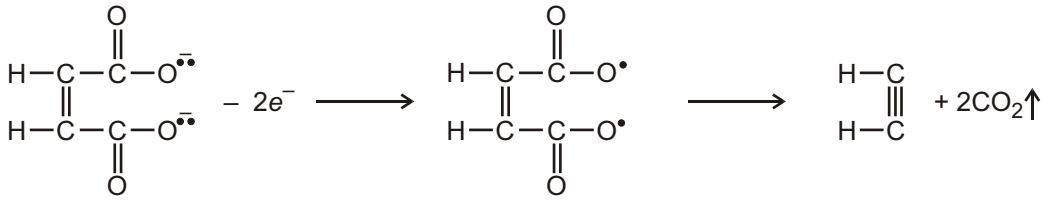
In the above reaction it is necessary that the four halogen atoms must be attached at vicinal carbons. If they are attached at the two ends then the product cyclo alkene is obtained.

4. **From Kolbe's Synthesis :** Potassium salt of carboxylic acid on electrolysis give hydrocarbon:



Potassium Malaete

At Anode :

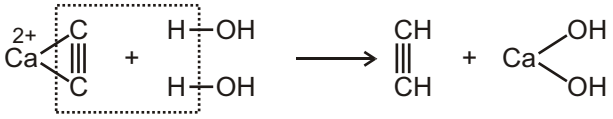


At Cathode :

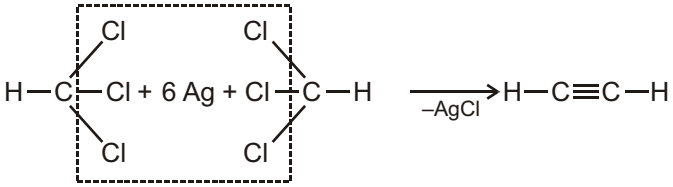
$2K \quad 2e \quad 2K$; $2K \quad 2H_2O \quad 2KOH \quad H_2$

5. Laboratory method of preparation of Acetylene :

(a) In laboratory acetylene is prepared by hydrolysis of calcium carbide.



(b) It can also be prepared from $CHCl_3$ with Ag dust.



6. From Lower Homologues to Higher Homologues

Because of the acidic characters of H-atom in acetylens.

$H—C \quad C—H \quad NaNH_2 \qquad H—C \quad C\ Na \quad NH_3$

or $\quad H—C \quad C—H \quad 2NaNH_2 \qquad NaC^- \quad C^-Na \quad 2NH_3$

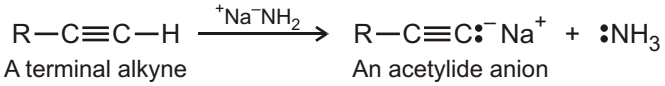
$H—C \quad C^-Na \quad R—X \qquad H—C \quad C—R \quad NaX$

$NaC^- \quad C^-Na \quad R—X \qquad R—C \quad C—R \quad NaX$

Chemical Properties :

1. 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 an **acetylide anion** is formed.



According to the Bronsted–Lowry definition, an acid is a substance that donates H . Although we usually think of oxyacids (H_2SO_4, HNO_3) or halogen acids (HCl, HBr) in this context, any compound containing a hydrogen atom can be an acid under the right circumstances. By measuring dissociation constants of different acids and expressing the results as pK_a values, an acidity order can be established. Recall that a lower pK_a corresponds to a stronger acid and a higher pK_a corresponds to a weaker acid.

Where do hydrocarbons lie on the acidity scale? As the data in show, both methane (pK_a 60) and ethylene (pK_a = 44) are very weak acids and thus do not react with any of the common bases. Acetylene, however, has pK_aa = 25 and can be deprotonated by the conjugate base of any acid whose pKa is greater

than 25. Amide ion (NH_2), for example, the conjugate base of ammonia (pK_a = 35), is often used to deprotonate terminal alkynes.

Acidity of Simple Hydrocarbons

Family	Example	K_a	pK_a	
Alkyne	HC CH	10^{25}	25	Stronger acid
Alkene	H_2C CH_2	10^{44}	44	⇑
Alkane	CH_4	10^{60}	60	Weaker acid

Alkyne alkylation is not limited to acetylene itself. Any terminal alkyne can be converted into its corresponding anion and then alkylated by treatment with an alkyl halide, yielding an internal alkyne. For example, conversion of 1-hexyne into its anion, followed by reaction with 1-bromobutane, yields 5-decyne.

$$\underset{\text{1-Hexyne}}{CH_3CH_2CH_2CH_2C{\equiv}CH} \xrightarrow[2.\ CH_3CH_2CH_2CH_2Br]{1.\ NaNH_2,\ NH_3} \underset{\text{5-Decyne (76\%)}}{CH_3CH_2CH_2CH_2C{\equiv}CCH_2CH_2CH_2CH_3}$$

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.

$$\underset{\text{Acetylene}}{H{-}C{\equiv}CH} \xrightarrow{NaNH_2} [H{-}C{\equiv}C{:}^{-}\ Na^{+}] \xrightarrow{RCH_2Br} \underset{\text{A terminal alkyne}}{H{-}C{\equiv}C{-}CH_2Br}$$

$$\underset{\text{A terminal alkyne}}{R{-}C{\equiv}C{-}H} \xrightarrow{NaNH_2} [R{-}C{\equiv}C{:}^{-}\ Na^{+}] \xrightarrow{R'CH_2Br} \underset{\text{An internal alkyne}}{R{-}C{\equiv}C{-}CH_2R'}$$

The alkylation reaction is limited to the use of 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 bromocyclohexane with propyne anion yields the elimination product cyclohexene rather than the substitution product 1-propynylcyclohexane.

$$CH_3CH_2C{\equiv}\overset{\cdot\cdot}{C}^{-} + CH_3CH_2CH_2{-}\overset{+}{Br}{}^{-} \longrightarrow CH_3CH_2C{\equiv}CCH_2CH_2CH_3 + Br^{-}$$

$$\underset{\text{1-pentyne}}{CH_3CH_2CH_2C{\equiv}CH} \xrightarrow[2.\ CH_3CH_2CH_2CH_2CH_2Cl]{1.\ NaNH_2} \underset{\text{4-decyne}}{CH_3CH_2CH_2C{\equiv}CCH_2CH_2CH_2CH_2CH_3}$$

Distinction Between Terminal And Non-Terminal Alkynes :

All terminal alkynes contain acidic H-atom. Hence such H-atom may be replaced by metals while non-terminal alkynes do not have acidic H-atoms hence they will not react with metals

(a) Tollen's Reagent

Ammoniacal Silver nitrate solution is called Tollen's reagent.

Alkynes containing acidic H-atoms will react with Ammoniacal silver nitrate solution

$$HC \quad CH \quad 2[Ag(NH_3)_2]\ OH \qquad \underset{\text{White ppt (Silver acetylide)}}{GC \quad CAg}$$

$$R{-}C \quad CH \quad [Ag(NH_3)_2]\ OH^{\ominus} \qquad \underset{\text{White ppt}}{R{-}C \quad CAg}$$

(b) Ammoniacal Cuprous chloride

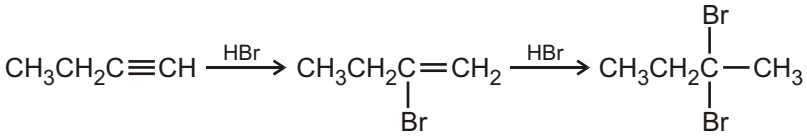
$$CuCl \quad NH_4OH \qquad NH_4Cl \quad CuOH$$

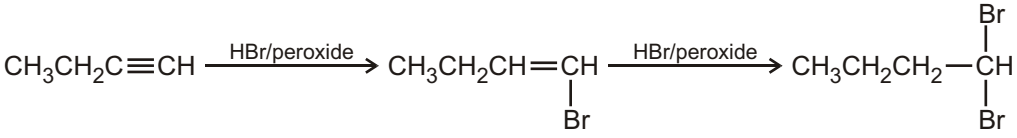
$$CuOH \quad NH_4OH \qquad (Cu(NH_3)_2)OH \quad 2H_2O$$

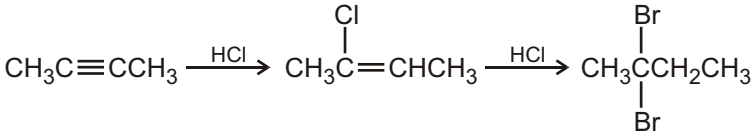
HC CH $2[Cu(NH_3)_2]OH$ CuC CCu (Cuprous acetylide) Red ppt.

RC CH $[CH(NH_3)_2OH$ R — C C — Cu

2. **Reaction with halogen acid :** Halogen acid (H-X) adds on unsymmetric alkyne to give product according to Markovnikov's rule where as in the presence of peroxide, anti Markovnikov's rule is followed :





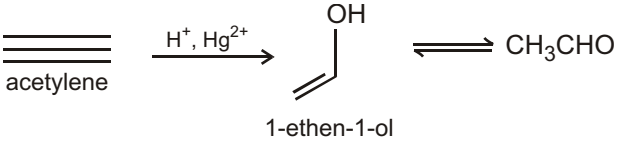


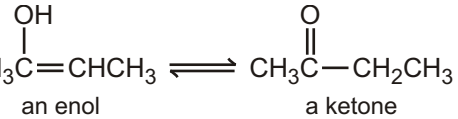
3. **Acid catalyzed hydration :**

Alkyne hydration : Kucherov-reaction :

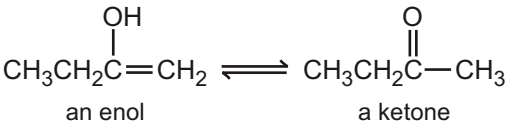
Alkyne readily combine with water in the presence of acid (usually sulfuric acid) and mercury (II) salts (usually the sulfate is used) to form carbonyl compounds, in a process known as Kucherov's reaction. In the case of acetylene (ethyne) the product is acetaldehyde (ethanal), while other alkynes form ketones.

Ex. : (a)



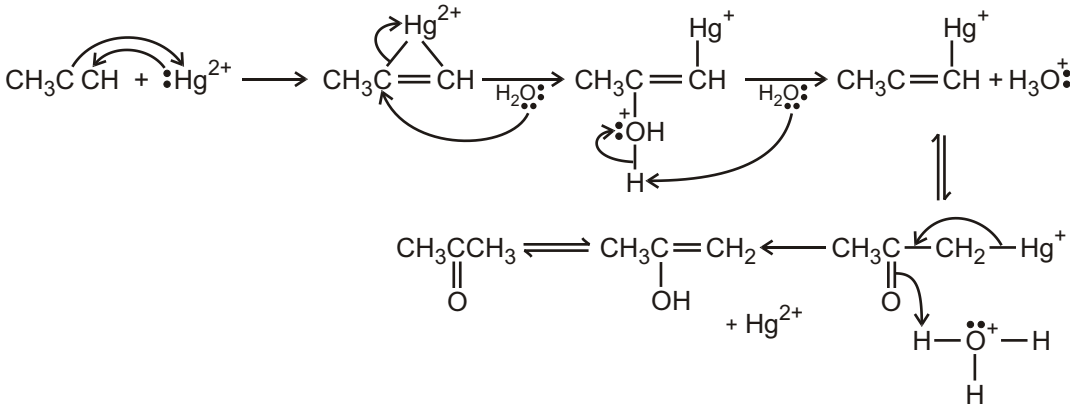
(b) $CH_3C{\equiv}CCH_3 + H_2O \xrightarrow{H_2SO_4}$ 

an enol a ketone

(c) $CH_3CH_2C{\equiv}CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4}$ 

an enol a ketone

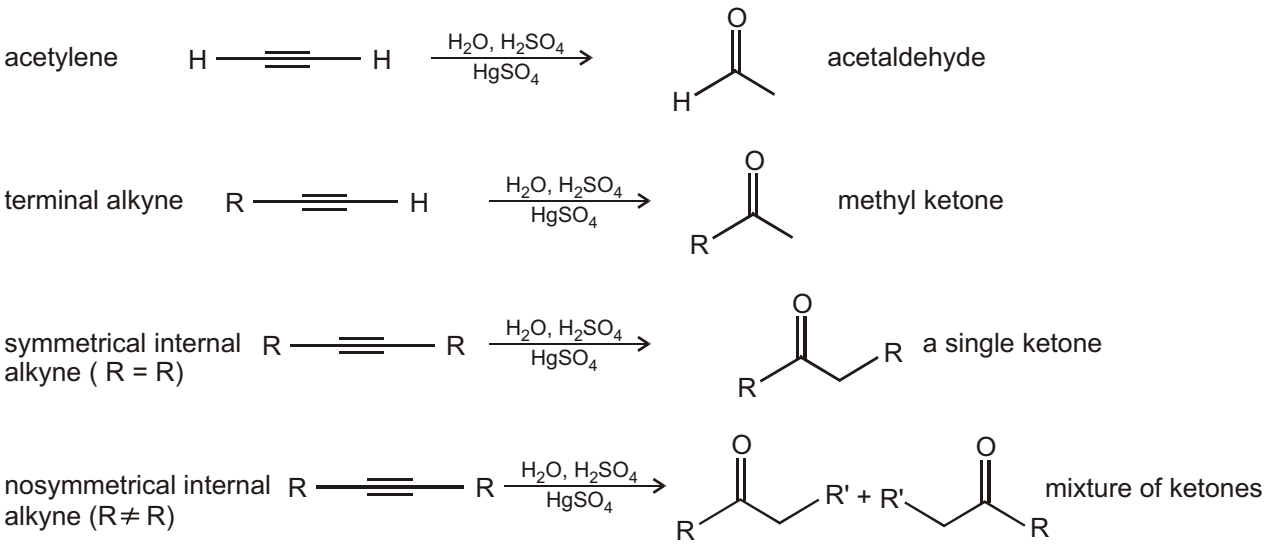
Mercuric-ion-catalyzed Mechanism :



The intermediate product is an enol (an alkene with a hydroxyl group attached to a doubly bonded carbon), which then transforms to its keto tautomer through keto-enol tautomerization.

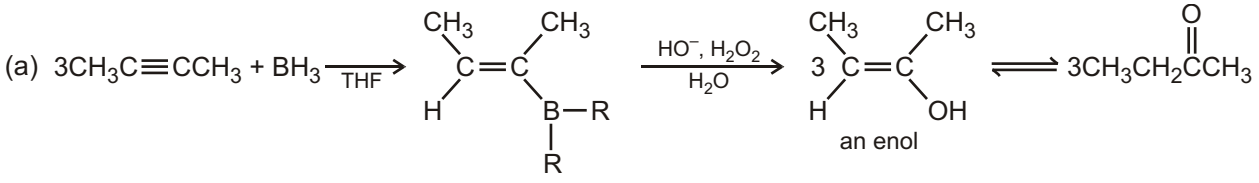
Alkene hydration only requires acid catalysis and proceeds through the most stable carbocation available Terminal alkynes selectively produce a methyl ketone. But unsymmetrical internal alkynes can produce two different vinyl cations, whose stabilities may be similar if the alkyne's substituents are different.

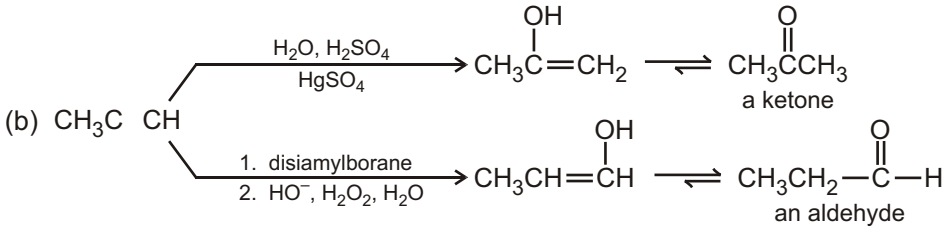
Different results occur for this reaction depending on the substitution pattern of the alkyne.



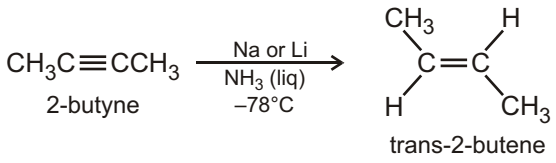
4. Hydroboronation oxidation of alkyne :

It is a two-step organic reaction that converts an alkene into a neutral alcohol by the net addition of water across the double bond. The hydrogen and hydroxyl group are added in a syn addition leading to cis stereochemistry. It is an antiMarkovnikov reaction, with the hydroxyl group attaching to the less-substituted carbon.





5. Birch Reduction :

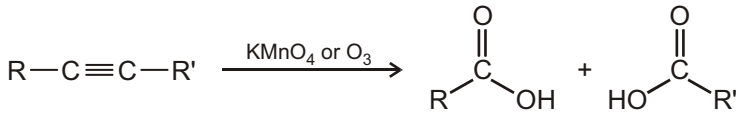


6. Oxidative Cleavage of Alkynes :

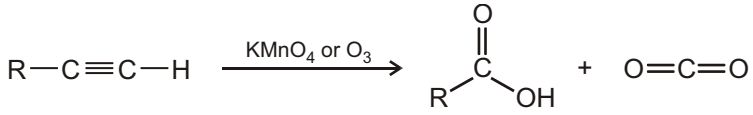
Alkynes, like alkenes, can be cleaved by reaction with powerful oxidizing agents such as ozone or $KMnO_4$, although the reaction is of little value and we mention it only for completeness. A triple bond is generally

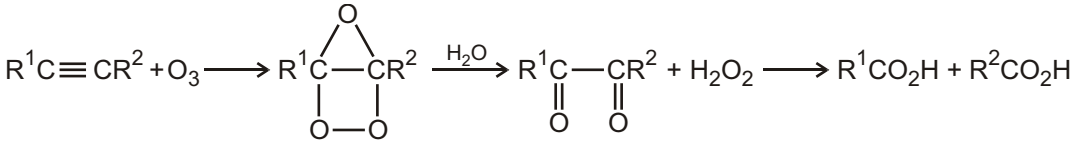
less reactive than a double bond, and yields of cleavage products are sometimes low. The products obtained from cleavage of an internal alkyne are carboxylic acids; from a terminal alkyne, CO_2 is formed as one product.

An internal alkyne

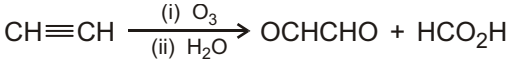


A terminal alkyne



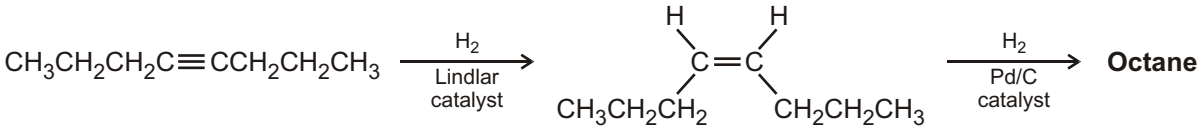


Acetylene is exceptional in that it gives glyoxal as well as formic acid

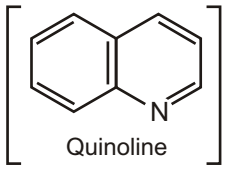


7. Reduction :

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.

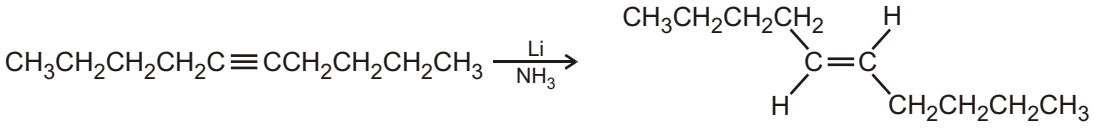


cis-4-Octene



Quinoline

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.



5-Decyne trans-5-Decene (78%)