Alkynes

- Alkynes contain a triple bond.
- General formula is C_nH_{2n-2}

Alkynes contain a carbon—carbon triple bond.

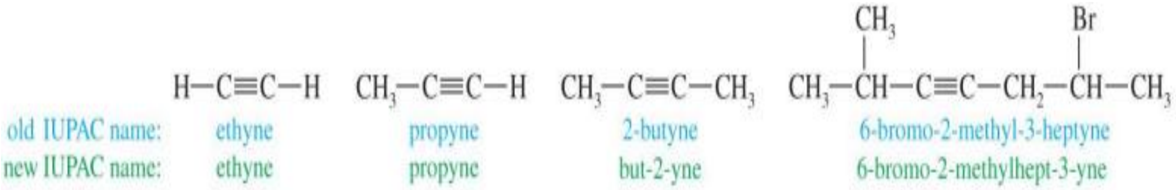
• Terminal alkynes have the triple bond at the end of the carbon chain so that a hydrogen atom is directly bonded to a carbon atom of the triple bond

. • Internal alkynes have a carbon atom bonded to each carbon atom of the triple bond.

• An alkyne has the general molecular formula CnH2n-2, giving it four fewer hydrogens than the maximum possible for the number of carbons present. Thus, the triple bond introduces two degrees of unsaturation.

Nomenclature of Alkynes

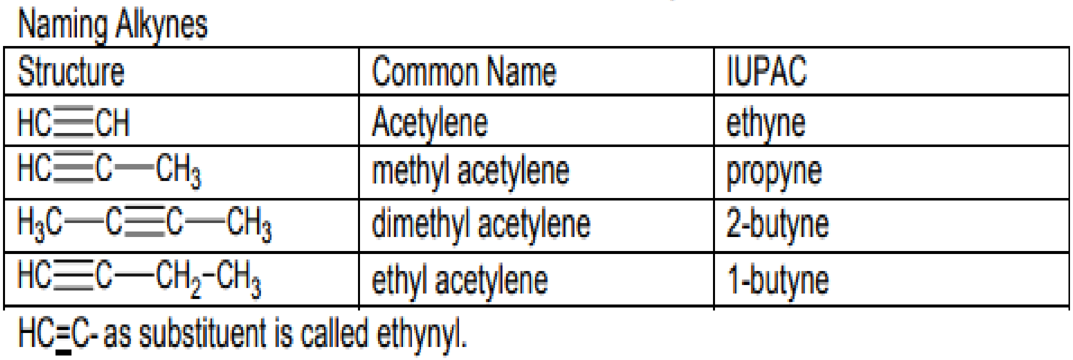
IUPAC nomenclature is similar to that for alkenes, except the –ane ending is replaced with –yne. The chain is numbered from the end closest to the triple bond



$H—C\equiv C—H$
ethyne
(acetylene)

$CH_3—C\equiv C—H$
propyne
(methylacetylene)

$CH_3—C\equiv C—CH_3$
2-butyne
(dimethylacetylene)



Naming Alkynes

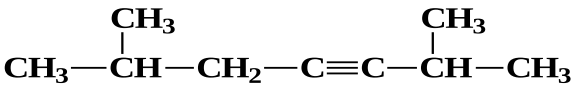
Structure	Common Name	IUPAC
$HC\equiv CH$	Acetylene	ethyne
$HC\equiv C—CH_3$	methyl acetylene	propyne
$H_3C—C\equiv C—CH_3$	dimethyl acetylene	2-butyne
$HC\equiv C—CH_2$-CH_3	ethyl acetylene	1-butyne

HC≡C- as substituent is called ethynyl.

Common name: the simplest alkyne is acetylene and the common name of any memberderived from acetylene

$CH_3—C\equiv CH$

Common : Methyl acetylene



$$CH_3—\underset{}{\overset{CH_3}{\overset{|}{C}H}}—CH_2—C\equiv C—\overset{CH_3}{\overset{|}{C}H}—CH_3$$

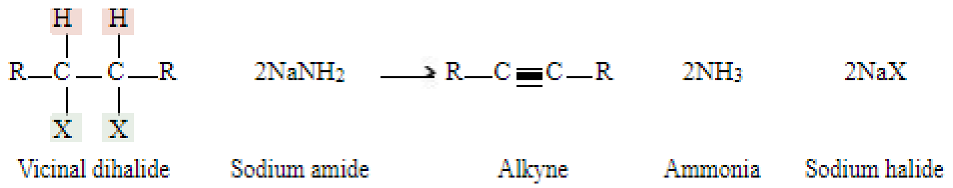
Common : Isobutyisopropylacetylene

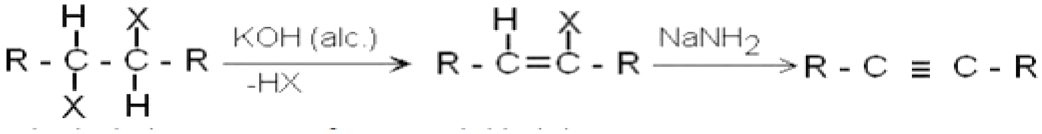
PREPARATION OF ALKYNES BY ELIMINATION REACTIONS

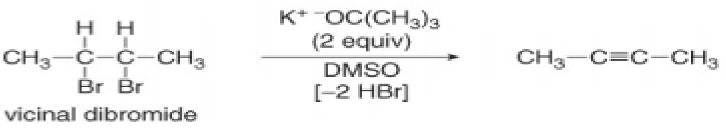
alkynes are prepared by elimination reactions. A strong base removes two equivalents of HX from a vicinal or geminal dihalide to yield an alkyne through two successive E2 elimination reactions.

it is possible to prepare alkenes by dehydrohalogenation of alkyl halides, so may alkynes be prepared by a *double dehydrohalogenation* of dihaloalkanes. The dihalide may be a geminal dihalide, one in which both halogens are on the same carbon, or it may be a vicinal dihalide, one in which the halogens are on adjacent carbons.

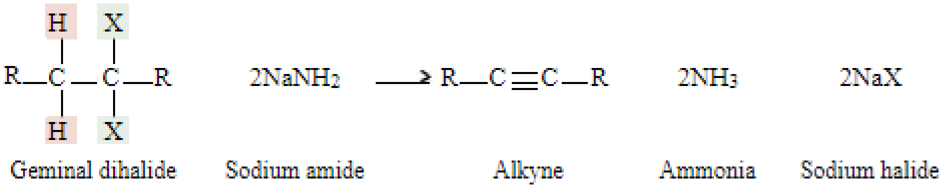
1-Double dehydrohalogenation of a vicinal dihalides

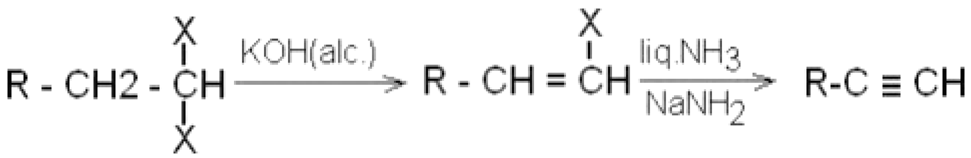


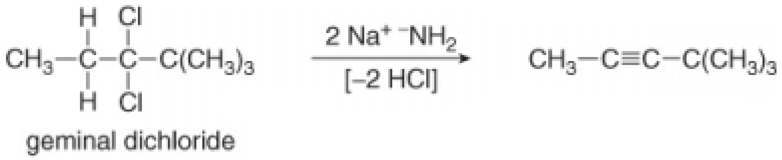




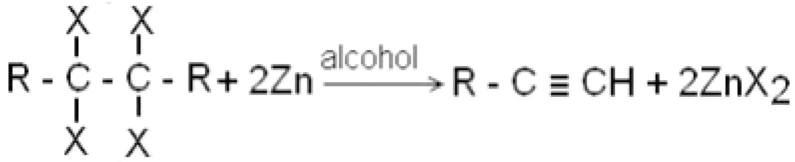
2-Double dehydrohalogenation of a geminal dihalides







3-Dehalogenation of tetrahalides

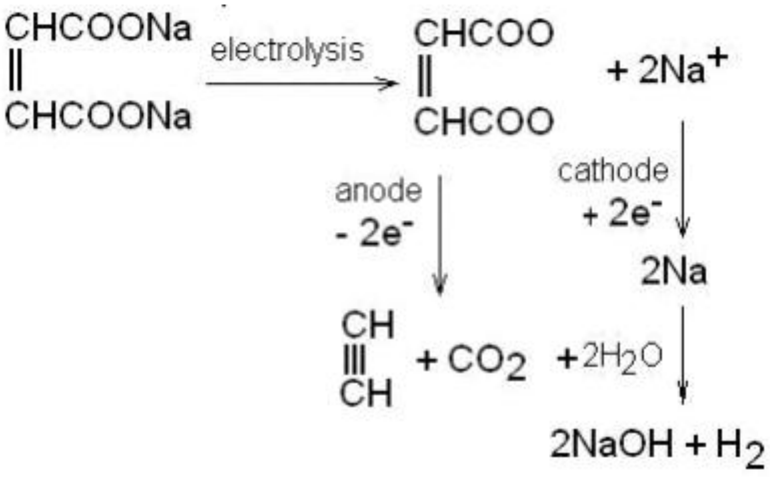


$$R-CX_2-CX_2-R + 2Zn \xrightarrow{\text{alcohol}} R-C\equiv CH + 2ZnX_2$$

4. Reaction of iodoform with silver

$$CHI_3 + 6Ag + I_3CH \xrightarrow{alcohol} CH \equiv CH + 6AgI$$

5. Kolbe's electrolysis



6. From calcium carbide

Pure acetylene is obtained from calcium carbide, a substance produced from carbon and calcium oxide.

$$3\ C + CaO \xrightarrow[\text{electrical arc}]{2500\text{-}3000^{\circ}} CaC_2 + CO$$

$$CaC_2 + 2\ H_2O \longrightarrow Ca(OH)_2 + CH\equiv CH$$

Acetylene can be converted to the sodium salt, sodium acetylide, that will displace the halogen atom in certain haloalkanes. The process is nucleophilic substitution

$$HC\equiv CNa + BrCH_3 \longrightarrow HC\equiv CCH_3$$

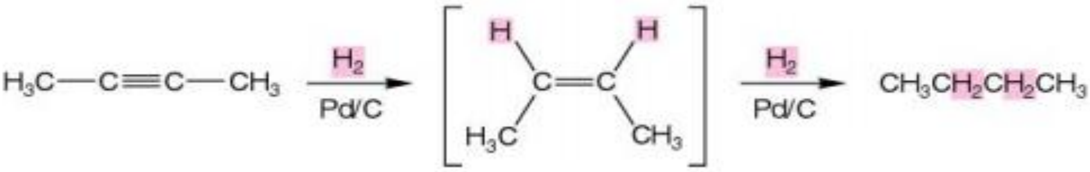
Reactions of Alkynes

Like alkenes, alkynes undergo addition reactions because they contain relatively weak π bonds.

- **Two sequential reactions can take place: addition of one equivalent of reagent forms an alkene, which can then add a second equivalent of reagent to yield a product having four new bonds.**

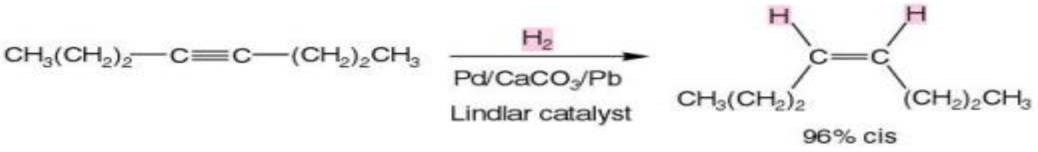
Catalytic hydrogenation

H_2 reduces alkynes to alkenes and then to alkanes in the presence of catalyst such as Ni ,Pt or Pd.. The fact that the reaction is exothermic and takes place on the surface of Pt or Pd. **more so for alkynes than alkenes, the reaction is hard to stop.**

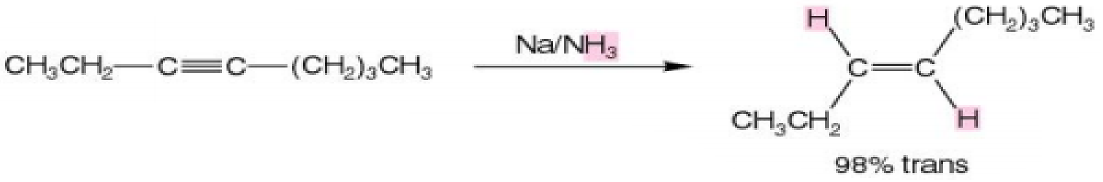


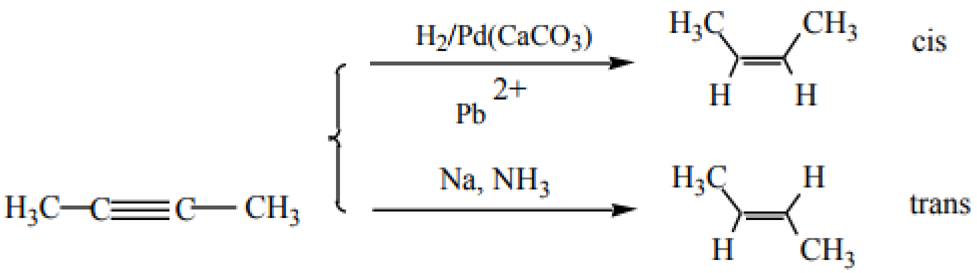
Reduction of alkynes to cis or (Z) alkenes

Lindlar's catalyst: Pd, quinoline, Pb and CaCO3 poisons the metal catalyst, so that one molecule of H2 adds only to the alkyne to form alkenes.



Reduction of alkynes to trans or (E) alkenes reaction of alkyne with hydrogen in the presence of Na radical dissolved in liquid NH3 gives trans alkene .

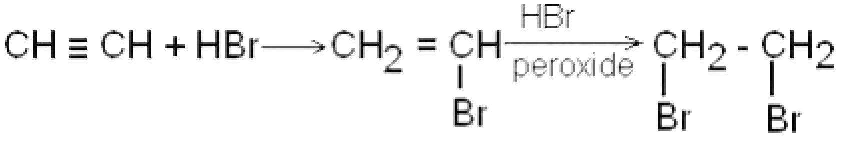




Addition of Hydrogen halides

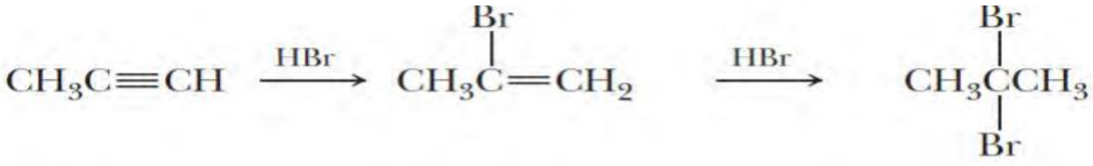
Alkynes undergo hydrohalogenation, i.e the, addition of hydrogen halides, HX (X = Cl, Br, I).

Two equivalents of HX are usually used: addition of one mole forms a vinyl halide, which then reacts with a second mole of HX to form a geminal dihalid so Alkynes undergo regioselective addition of either 1 or 2 moles of HX, depending on the ratios in which the alkyne and halogen acid are mixed



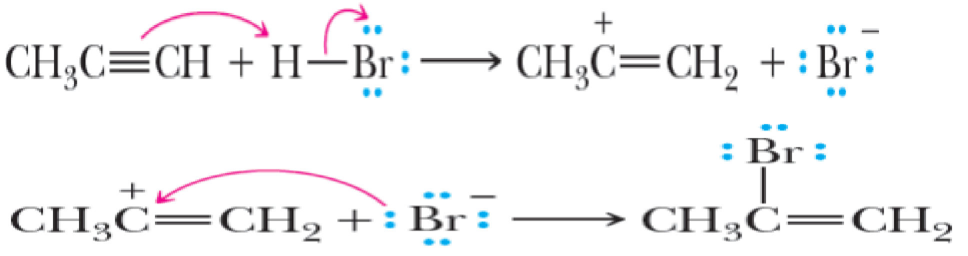
$CH\equiv CH + HBr \longrightarrow CH_2=CH(Br) \xrightarrow[peroxide]{HBr} CH_2(Br)-CH_2(Br)$

1,2-dibromo ethane



$CH_3C\equiv CH \xrightarrow{HBr} CH_3C(Br)=CH_2 \xrightarrow{HBr} CH_3CBr_2CH_3$

Mechanism of the addition :



$CH_3C\equiv CH + H-\ddot{Br}: \longrightarrow CH_3\overset{+}{C}=CH_2 + :\ddot{Br}:^-$

$CH_3\overset{+}{C}=CH_2 + :\ddot{Br}:^- \longrightarrow CH_3C(Br)=CH_2$

$HC\equiv CH + HCl \longrightarrow CH_2=CHCl$

$CH_3C\equiv CCH_3 + 2H_2 \xrightarrow[3\ atm]{Pd,\ Pt,\ or\ Ni} CH_3CH_2CH_2CH_3$

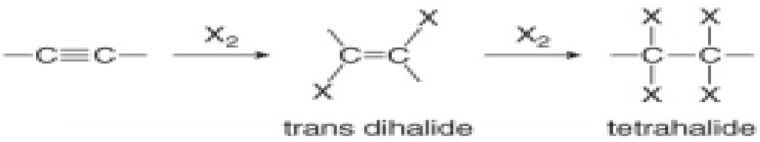
2-Butyne Butane

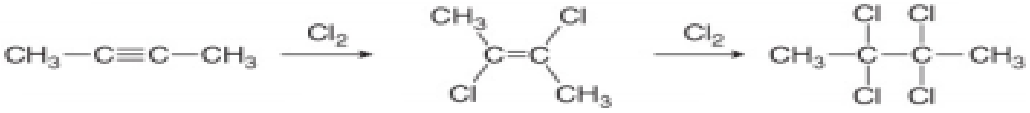
Show how you might convert 1-pentene to 1-pentyne

Addition of Halogen(Halogenation)

- **Halogens X2 (X = Cl or Br) add to alkynes just as they do to alkenes.**

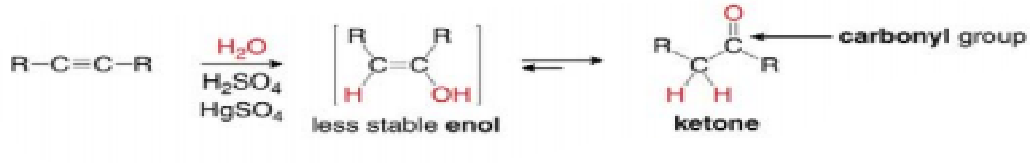
Addition of one mole of X2 forms a trans dihalide, which can then react with a second mole of X2 to yield a tetrahalide.

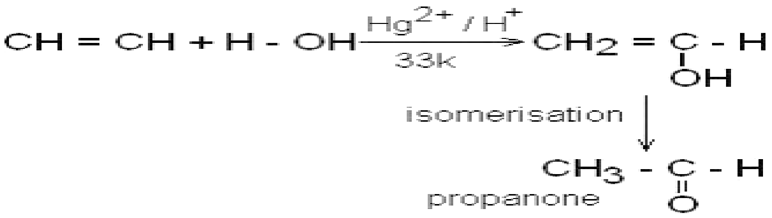




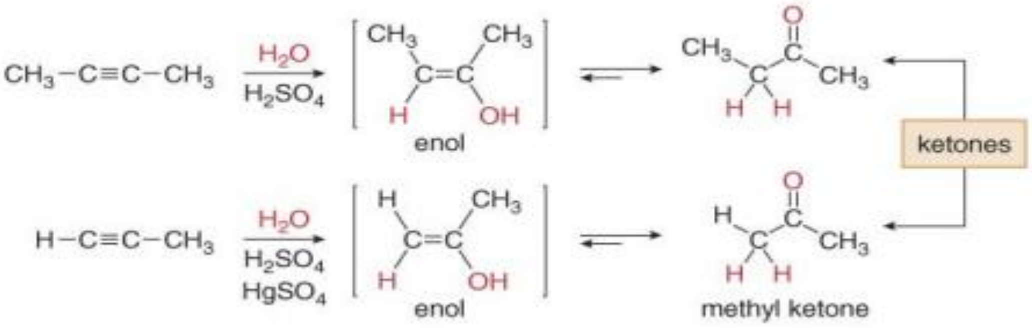
Addition of Water

In the presence of strong acid or Hg^{2+} catalyst, the elements of H2O add to the triple bond, but the initial addition product, an enol, is unstable and rearranges to a product containing a carbonyl group— that is, a C=O. A carbonyl compound having two alkyl groups bonded to the C=O carbon is called a ketone.





Internal alkynes undergo hydration with concentrated acid, whereas terminal alkynes require the presence of an additional Hg2+ catalyst— usually $HgSO_4$—to yield methyl ketones by Markovnikov's addition of water.



Alkyne can be hydrated to form enol form which tautomerised to ketone
Regioselectivity predicted by Markovnikov's rule
Tautomerization, the process of converting one tautomer into another, is catalyzed by both acid and base.

Acetylide anions

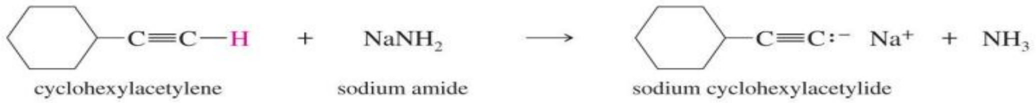
Because sp hybridized C—H bonds are more acidic than sp2 and sp3 hybridized C—H bonds, terminal alkynes are readily deprotonated with strong base in a Bronsted-Lowry acid-base reaction. The resulting ion is called the acetylide ion

$$R-C\equiv CH + B:^- \rightleftharpoons R-C\equiv C:^{\ominus} + BH$$

Acidity of Alkynes Terminal alkynes are acidic, the end hydrogen can be removed as a proton by a strong base.

$$CH_3CH_2-C\equiv C-H + Na^+ \ ^-:NH_2 \longrightarrow CH_3CH_2-C\equiv C:^- \ Na^+ + NH_3$$

but-1-yne, a terminal alkyne — sodium amide — sodium butynide

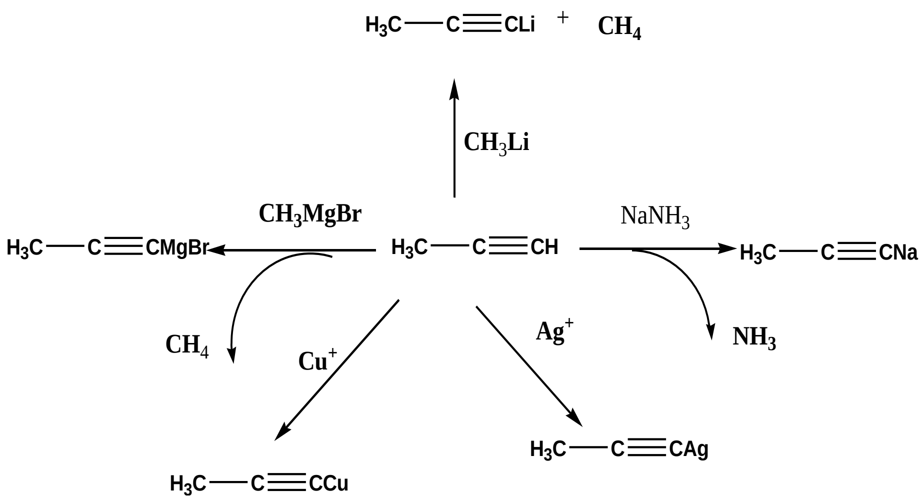


$$CH_3-C\equiv C-CH_3 \xrightarrow{NaNH_2} \text{no reaction}$$

(no acetylenic proton)

but-2-yne, an internal alkyne

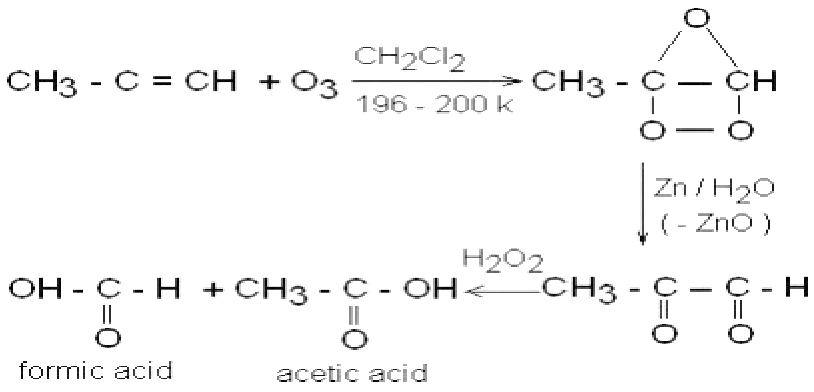
Acetylene and terminal alkynes have acidic character and can be deprotonated by strong base to form acetylide the bases used are sodamide Grignard reagent or organo lithum compounds

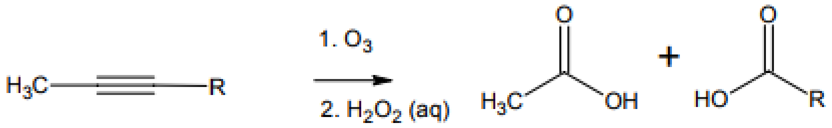


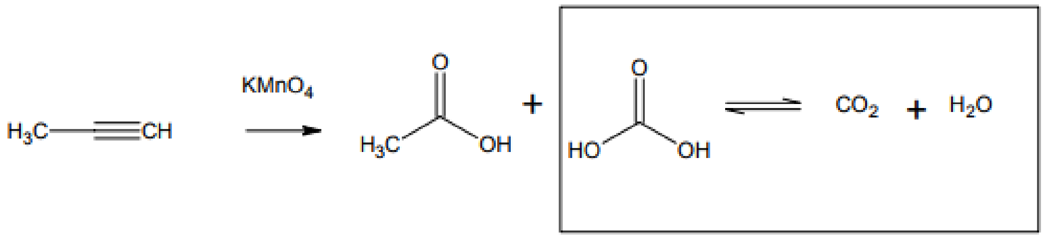
Sodium acetylidecan reacted with primary alkyl halide to form higher alkyne

Oxidation

Oxidation Like alkenes, either with O_3 (ozone) or $KMnO_4$. Because of the added unsaturation of alkynes, it is hard to stop at an aldehyde. So, the reaction goes mostly to carboxylic acids. Terminal alkynes will make fizzy water.







Polymerization

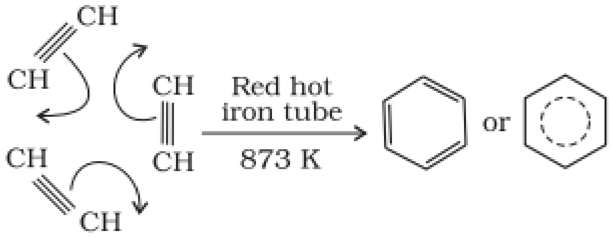
(vi) Polymerisation

(a) Linear polymerization

$$CH \equiv CH + CH \equiv CH \xrightarrow{Cu_2Cl_2, NH_4Cl} CH_2 = CH - C \equiv CH \xrightarrow{CH\equiv CH}$$

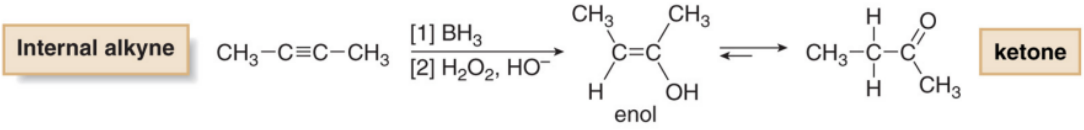
$CH_2 = CH - C \equiv C - CH = CH_2$ (divinyl acetylene)

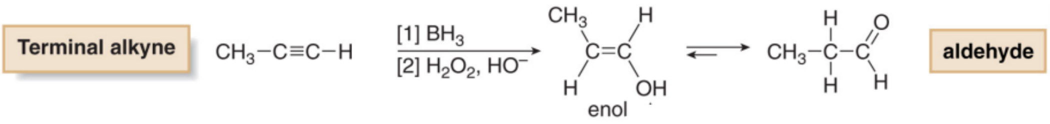
(b) Cyclic polymerization



Hydroboration-oxidation of alkynes

is the same as for alkenes • Regioselective for anti-Markovnikov addition • It also produces an enol that tautomerizes to aldehyde




Terminal alkyne
CH3−C≡C−H
[1] BH3
[2] H2O2, HO−
enol
aldehyde