DIENES

Dienes are alkenes with 2 double bonds.
IUPAC: Same as alkene, but change -ene to -adiene and use two numbers to locate the two double bonds (number from the end of the chain which makes the smaller of these numbers smaller).

Double bonds separated by more than one single bond are *isolated.* Compounds with isolated double bonds have the same chemical properties as alkenes.

Double bonds that alternate with single bonds, *eg* C=C-C=C, are *conjugated*.

Double bond arrangements like C=C=C are *cumulated*. Compounds containing two carbon-carbon cumulated double bonds are called *allenes.*

Conjugated dienes differ from simple alkenes in that they

☞   are more stable,
☞   undergo 1,4-addition, and
☞   are more reactive.

Stability —

In conjugated systems, not only is there π bonding between the first and second and again between the third and fourth carbon atoms, as indicated in the structural formulas, but there is also *some* π bonding between the second and third carbons. [Remember: The more bonding the more stable the molecule.]

We can see this using the resonance model –
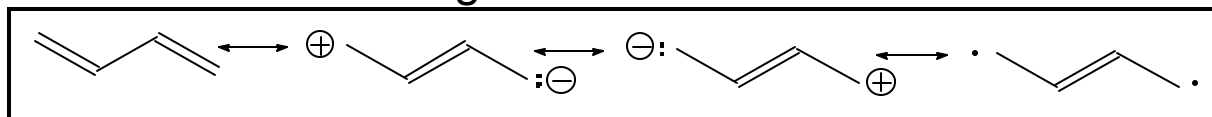
Clearly, none of the three structures on the right contributes very much to the hybrid (the actual structure of the molecule); but there are three of them, so taken together they would produce some double bond character between the second and third carbons.

Although it is beyond the scope of this course, molecular orbital theory – the theory that deals with molecular orbitals and how they form from atomic orbitals – also predicts π bonding between the second and third carbons. This bonding arises from the first π orbital (see below) which unites all four p atomic orbitals (one from each of the sp^2 hybridized carbons in the conjugated system).

Energy (Huckel) of Two Isolated *vs* Conjugated Double Bonds
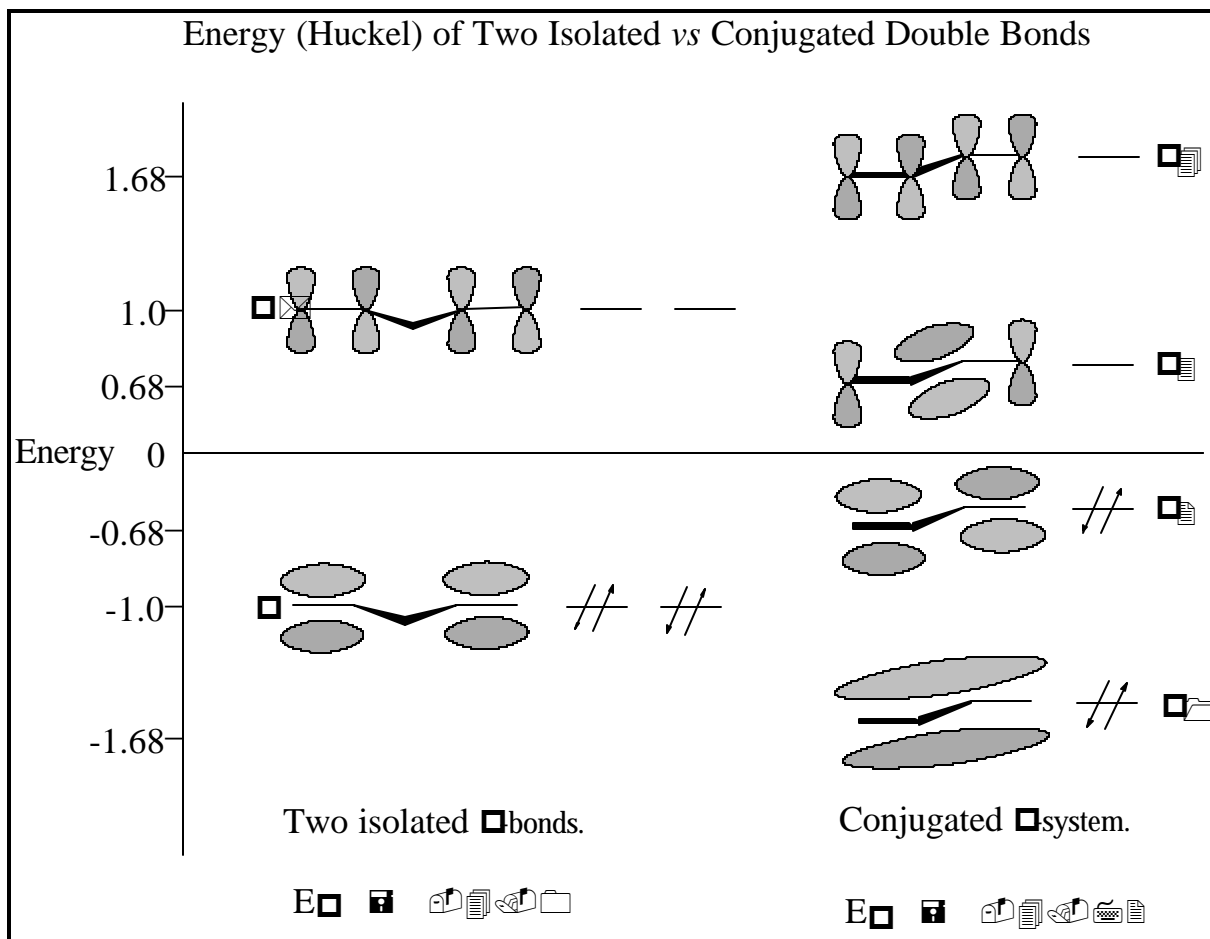
We see that the calculated π bonding energy is lower in the conjugated system by 0.72 units, meaning that the conjugated molecule is more stable than the non-conjugated one.

Electrophilic Addition to Conjugated Dienes:
1,2- vs. 1,4- Addition –

1,2-addition   1,4-addition
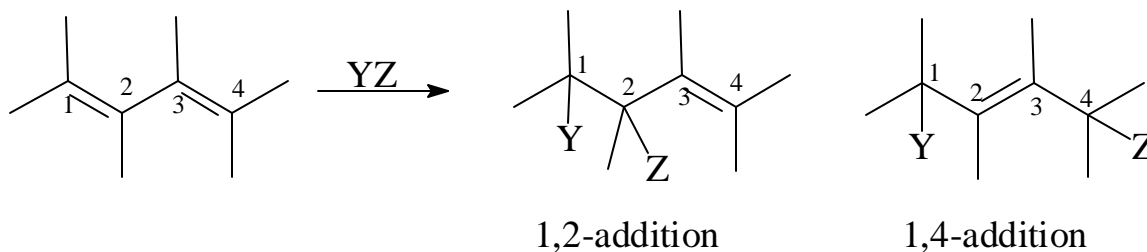
Note the "shift"
of the π-bond.

eg CH$_3$CH=CH-CH=CHCH$_3$ + HCl)))))))>

CH$_3$-CH$_2$-CHCl-CH=CHCH$_3$ *via* 1,2-addition
            +
CH$_3$-CH$_2$CH=CH-CHCl-CH$_3$ *via* 1,4-addition

This reaction occurs in the usual way – that is to say, via a carbocation. However, in this case the carbocation that forms preferentially is a resonance stabilized one. It has the positive charge on a carbon that is attached to a carbon with a double bond; these carbocations are called *allylic* and they are particularly stable.
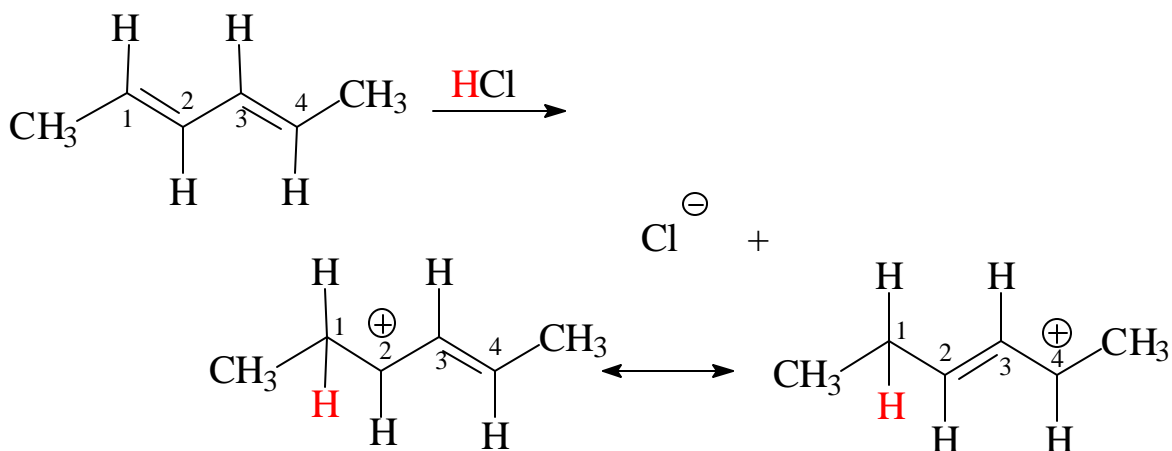
2º allylic type of carbocation; ~ stability of 3º carbocation.

Since the positive charge is shared between the carbons labeled 2 & 4, $\overset{\ominus}{Cl}$ can attack either.

Not formed:

ordinary 2º carbocation
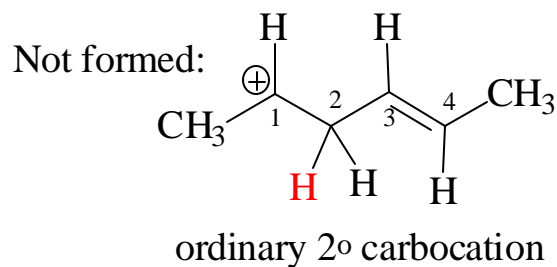
Reactivity of Conjugated Dienes —

Owing to the formation of resonance stabilized allylic carbocations when undergoing electrophilic addition, conjugated dienes are especially reactive.

Alkynes, -C≡C-

The triple bond consists of an sp-sp σ-bond and two π-bonds. The remaining sp orbital on each carbon is oriented 180° from the former sp orbital and forms a σ-bond with another atom.

1.09 A   1.08 A   1.06 A

1.54 A   1.33 A   1.20 A

π-bond   σ-bond   π-bond
top/bottom   front/back
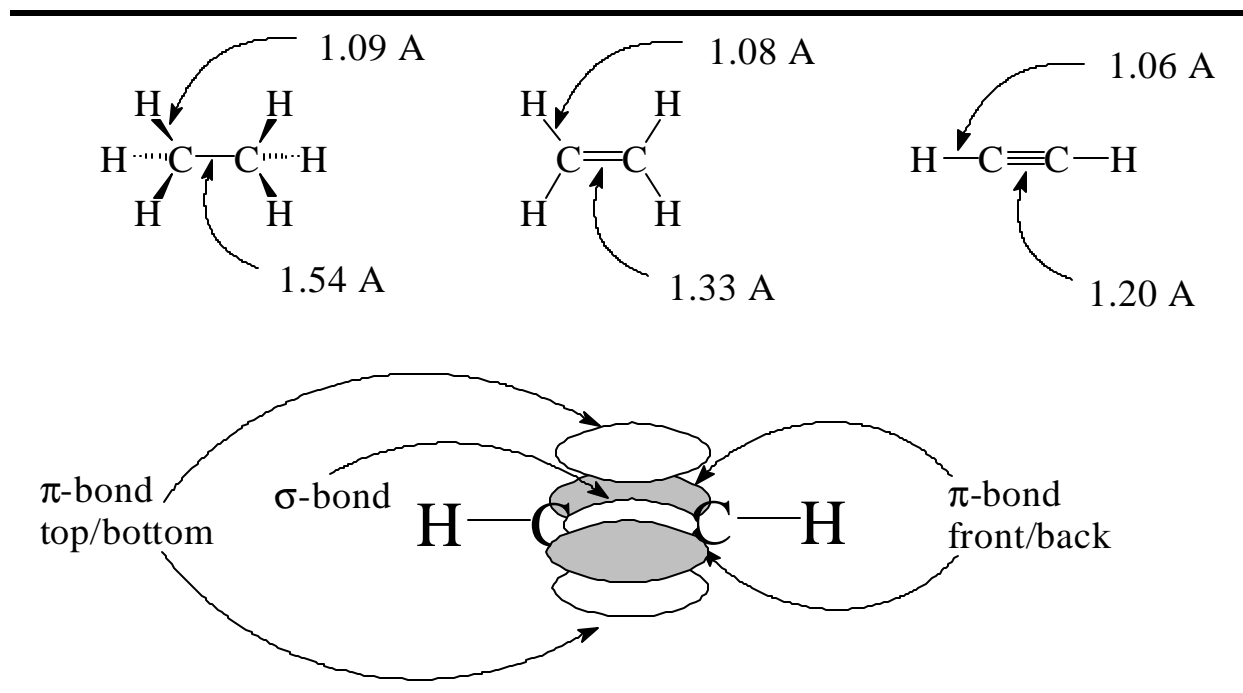
Reactions of Alkynes

Reduction to an alkene –

Geometrical isomerism possible for product, except when alkyne is terminal (has triple bond at end).

$$R_1-C\equiv C-R_2$$

$\xrightarrow{\text{Li}^0 \text{ or Na}^0 \\ \text{NH}_3 \text{ liquid}}$
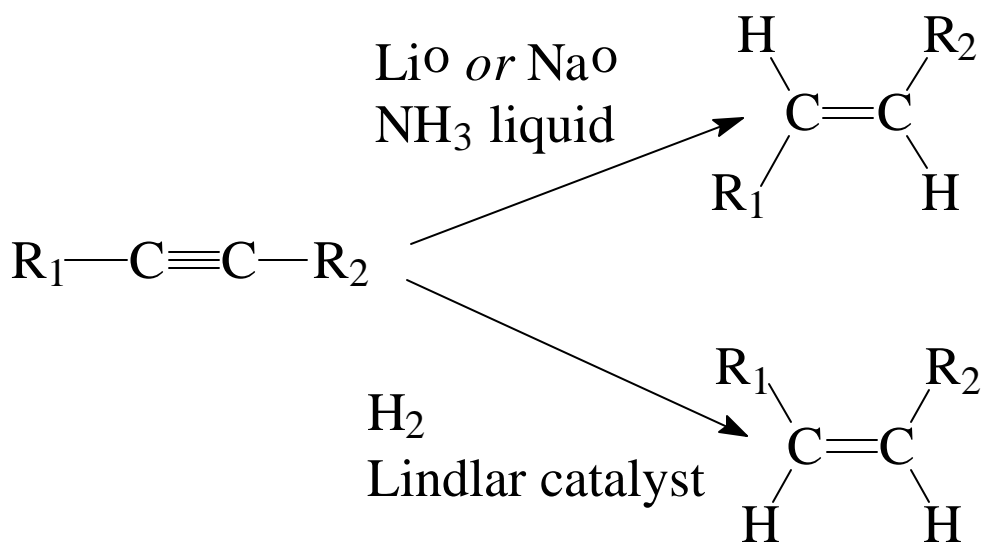
$$\begin{array}{c} H \qquad\quad R_2 \\ \diagdown\;\;\;\diagup \\ C=C \\ \diagup\;\;\;\diagdown \\ R_1 \qquad\quad H \end{array}$$

$\xrightarrow{\text{H}_2 \\ \text{Lindlar catalyst}}$

$$\begin{array}{c} R_1 \qquad\quad R_2 \\ \diagdown\;\;\;\diagup \\ C=C \\ \diagup\;\;\;\diagdown \\ H \qquad\quad H \end{array}$$

Each of these reactions is *stereoselective* in that each yields predominantly one stereoisomer of two or more possible ones.

Reduction to an alkane –

$$R_1 - C \equiv C - R_2 \quad \xrightarrow[\text{Pt catalyst}]{H_2} \quad R_1 - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - R_2$$

Addition of halogens –

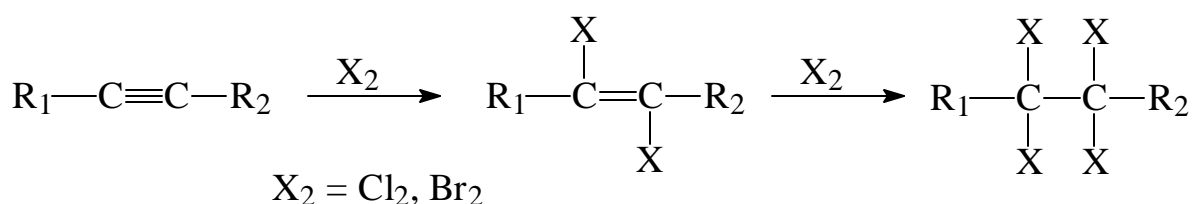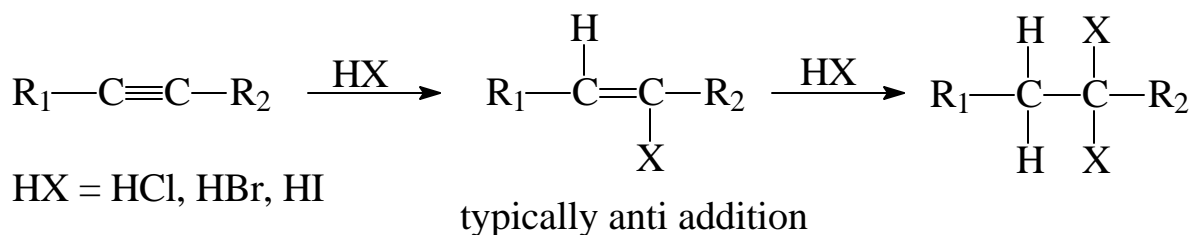$$R_1 - C \equiv C - R_2 \quad \xrightarrow{X_2} \quad R_1 - \underset{\underset{X}{|}}{\overset{\overset{X}{|}}{C}} = C - R_2 \quad \xrightarrow{X_2} \quad R_1 - \underset{\underset{X}{|}}{\overset{\overset{X}{|}}{C}} - \underset{\underset{X}{|}}{\overset{\overset{X}{|}}{C}} - R_2$$

$$X_2 = Cl_2, Br_2$$
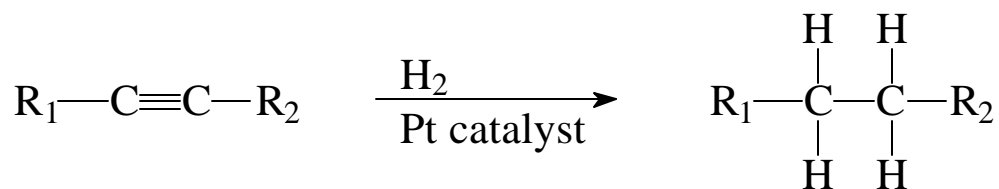
Both steps generally show *anti* addition.

Although triple bonds are usually less reactive than double bonds toward electrophilic addition, this reaction can often be stopped at the first step.

Addition of hydrogen halides –

$$R_1 - C \equiv C - R_2 \quad \xrightarrow{HX} \quad R_1 - \overset{\overset{H}{|}}{C} = \underset{\underset{X}{|}}{C} - R_2 \quad \xrightarrow{HX} \quad R_1 - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{X}{|}}{\overset{\overset{X}{|}}{C}} - R_2$$

$$HX = HCl, HBr, HI$$

typically anti addition

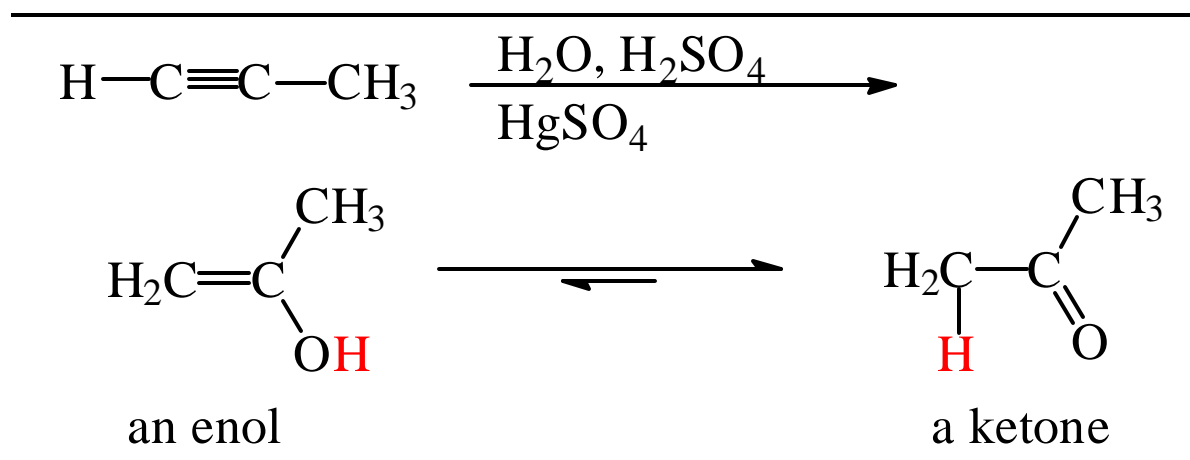Terminal alkynes show Markovnikov addition in first step. Reaction can often be stopped after the first step even though alkynes are less reactive toward electrophilic addition than alkenes. This lower reactivity of alkynes is at least partly due to vinylic cations being less stable than comparable alkyl cations --- 2º vinylic ~ 1º alkyl; 1º vinylic ~ methyl.

Note formation of *geminal* dihalide in the second step. This is the result of resonance stabilization of the intermediate carbocation (and the transition state leading to it), as shown below. Evidently, this has more importance than the destabilizing inductive effect of the electronegative element.
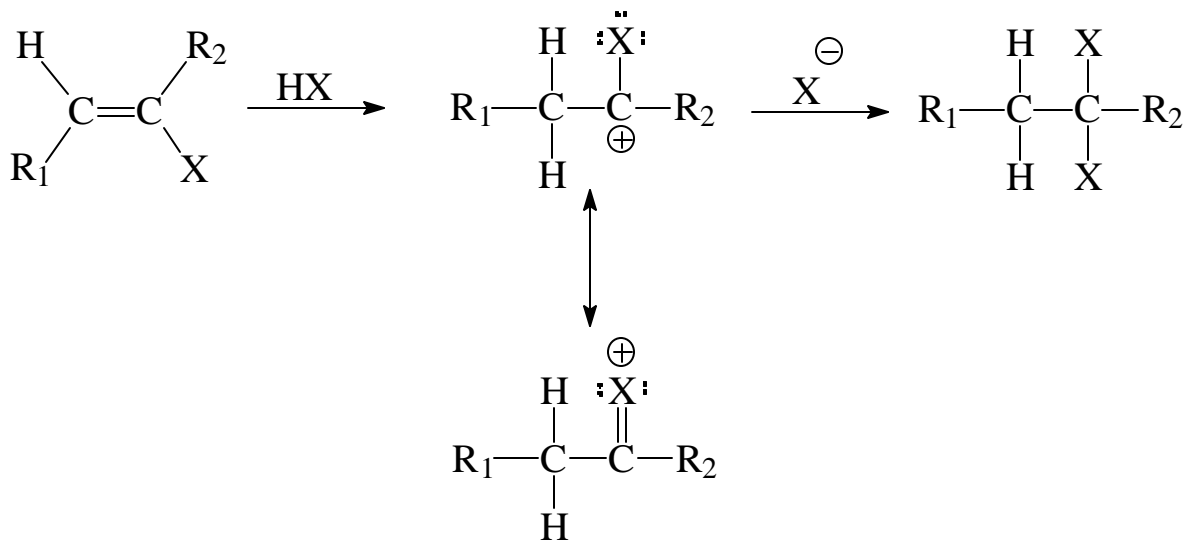
Hydration of Alkynes - *Tautomerism* –

$$H-C\equiv C-CH_3 \quad \xrightarrow[\text{HgSO}_4]{\text{H}_2\text{O, H}_2\text{SO}_4}$$

$$H_2C=C\overset{CH_3}{\underset{OH}{\diagup}} \quad \longrightarrow \quad H_2C-C\overset{CH_3}{\underset{\overset{|}{H} \quad O}{\diagdown}}$$

an enol   a ketone

     Usually the equilibrium favors the ketone
(or CH_3 - CHO, when the alkyne is acetylene).
This is an acid - base equilibrium and -OH is a stronger
acid than -CH_3.

     Structural isomers which exist in equilibrium with
each other are called *tautomers*. The particular type of
tautomerism shown above is *keto - enol* tautomerism.

Acidity of Alkynes – Alkynes in Synthesis —

In general, it is possible to convert a *terminal* alkyne to an anion by removing the terminal hydrogen. This is usually accomplished by using a base which is stronger than an acetylide anion:
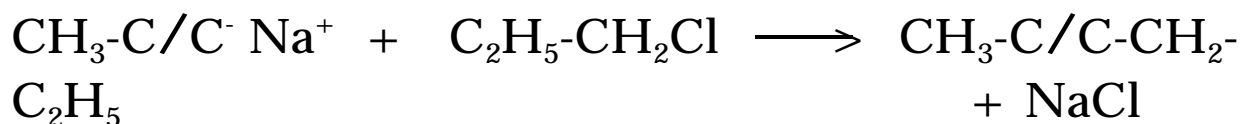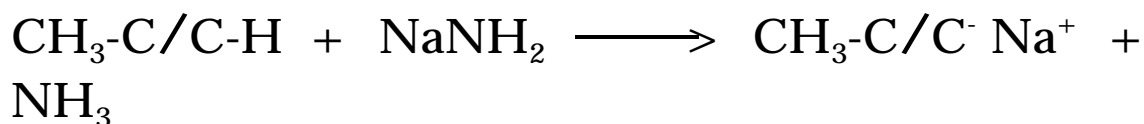
$R\text{-}C\equiv C\text{-}H \; + \; Na^+NH_2^- \longrightarrow R\text{-}C\equiv C^- \; Na^+ \; + \; NH_3$
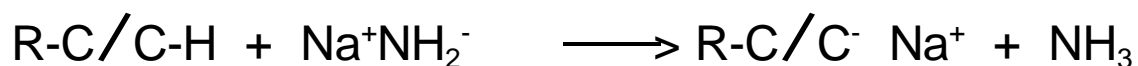
The acetylide anion can be used in synthesis, to make larger molecules, by reacting it with alkyl halides in a substitution reaction:

$R\text{-}C\equiv C^- \; Na^+ \; + \; ClCH_2\text{-}R' \longrightarrow R\text{-}C\equiv C\text{-}CH_2\text{-}R' \; + \; Na^+Cl^-$

Example problem 1 –
Synthesize 2-hexyne from starting materials which do not contain more than 3 carbons.

Solution 1 –

$CH_3\text{-}C\equiv C\text{-}H \; + \; NaNH_2 \longrightarrow CH_3\text{-}C\equiv C^- \; Na^+ \; + \; NH_3$

$CH_3\text{-}C\equiv C^- \; Na^+ \; + \; C_2H_5\text{-}CH_2Cl \longrightarrow CH_3\text{-}C\equiv C\text{-}CH_2\text{-}C_2H_5 \; + \; NaCl$

Example problem 2 –
Synthesize 4-octyne from starting materials which do not contain more than 3 carbons.

Solution 2 –

H-C/C-H + NaNH$_2$ $\longrightarrow$ H-C/C$^-$ Na$^+$ + NH$_3$

H-C/C$^-$ Na$^+$ + C$_2$H$_5$-CH$_2$Cl $\longrightarrow$

   H-C/C-CH$_2$-C$_2$H$_5$ + NaCl

H-C/C-CH$_2$-C$_2$H$_5$ + NaNH$_2$ $\longrightarrow$

   Na$^+$ $^-$C/C-CH$_2$-C$_2$H$_5$ +   NH$_3$

Na$^+$ $^-$C/C-CH$_2$-C$_2$H$_5$ +   C$_2$H$_5$-CH$_2$Cl $\longrightarrow$

   C$_2$H$_5$-CH$_2$-C/C-CH$_2$-C$_2$H$_5$ + NaCl