Alkynes

Alkynes or acetylenes are compounds that contain a carbon–carbon triple bond.

E.g.

$$H-C{\equiv}C-H \qquad CH_3CH_2-C{\equiv}C-H \qquad H_3C-C{\equiv}C-CH_3$$
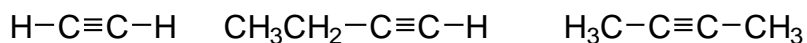
  acetylene

The triple bond results in a molecular formula of C_nH_{2n-2}
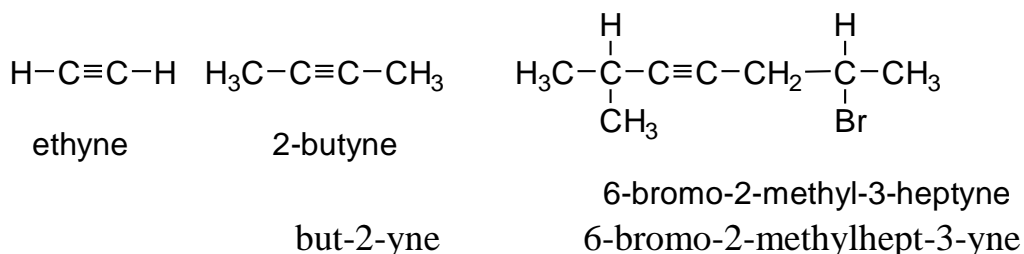
Ethane	C_2H_6	0 elements of unsaturation
Ethene	C_2H_4	1 element of unsaturation
Ethyne	C_2H_2	2 elements of unsaturation

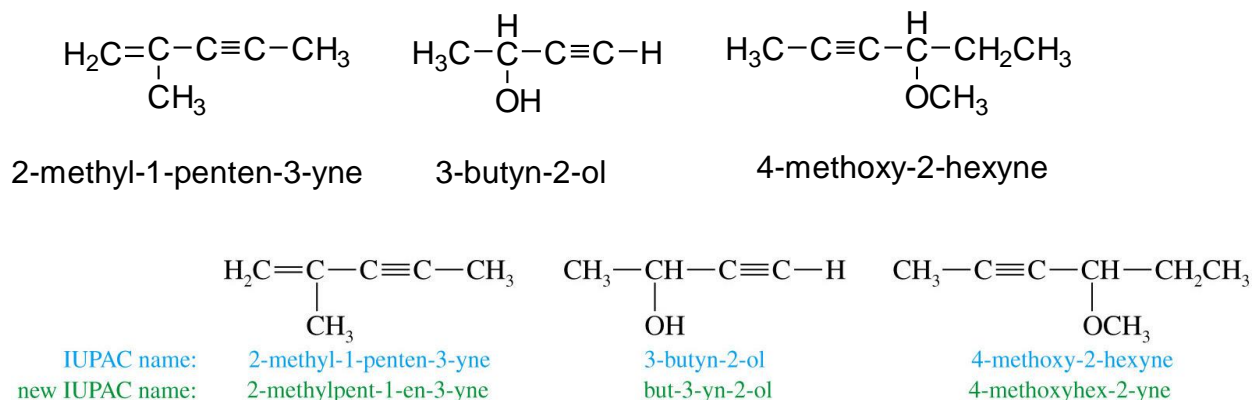The triple bond contributes two elements of unsaturation.

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 <u>closest</u> to the triple bond.

$$H-C{\equiv}C-H \qquad H_3C-C{\equiv}C-CH_3 \qquad H_3C-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}-C{\equiv}C-CH_2-\overset{\displaystyle H}{\underset{\displaystyle Br}{C}}-CH_3$$

  ethyne   2-butyne

                                    6-bromo-2-methyl-3-heptyne

                but-2-yne   6-bromo-2-methylhept-3-yne

When additional functional groups are present, the suffixes are combined.

$$H_2C{=}\overset{\displaystyle }{\underset{\displaystyle CH_3}{C}}-C{\equiv}C-CH_3 \qquad H_3C-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-C{\equiv}C-H \qquad H_3C-C{\equiv}C-\overset{\displaystyle H}{\underset{\displaystyle OCH_3}{C}}-CH_2CH_3$$

2-methyl-1-penten-3-yne   3-butyn-2-ol   4-methoxy-2-hexyne

$$H_2C{=}\overset{\displaystyle }{\underset{\displaystyle CH_3}{C}}-C{\equiv}C-CH_3 \qquad CH_3-\overset{\displaystyle }{\underset{\displaystyle OH}{CH}}-C{\equiv}C-H \qquad CH_3-C{\equiv}C-\overset{\displaystyle }{\underset{\displaystyle OCH_3}{CH}}-CH_2CH_3$$

| IUPAC name: | 2-methyl-1-penten-3-yne | 3-butyn-2-ol | 4-methoxy-2-hexyne |
| new IUPAC name: | 2-methylpent-1-en-3-yne | but-3-yn-2-ol | 4-methoxyhex-2-yne |

Terminal and Internal Alkynes
The position of the triple bond can alter the reactivity of the alkyne.

Compounds with triple bonds at the end of a molecule are called <u>terminal</u> alkynes. (Terminal C-H groups are called acetylenic hydrogens).

$H_3C-C\equiv C-H$ $H_3C-C\equiv C-CH_3$
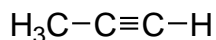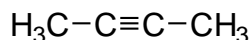
terminal   internal
alkyne   alkyne

If the triple bond is flanked by alkyl groups on both sides it is an <u>internal</u> alkyne.

Electronic Structure of Alkynes
The triple bond consists of one σ bond and two π bonds.

Each carbon is bonded to two other atoms, and there are no nonbonding electrons.

Carbon requires two hybrid orbitals to bond to the atoms, thus sp hybrids are used.

The sp orbitals are linear and oriented at 180°.

The C-C bond is formed from sp-sp overlap
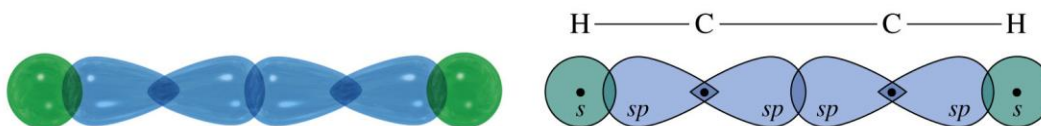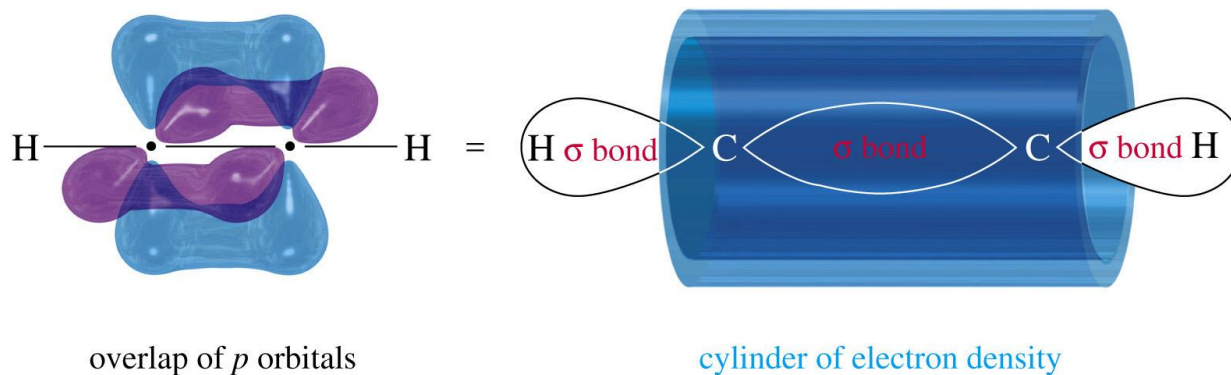The C-H bond is formed from sp-s overlap.

Diagram 9-5
The creation of sp hybrids leaves 2 free p orbitals – these create the two π bonds.

The p orbitals overlap just as for an alkene, except there are two π bonds at right angles to one another.

overlap of *p* orbitals   cylinder of electron density

Diagrams 9-5b,c

This generates a cylinder of electron density around the sigma bond.

The C-C bond length for ethyne is 1.20Å which is shorter than ethane (1.54Å) and ethene (1.33Å).

The C-H bond length in ethyne is 1.06Å which is also shorter than in ethane (1.09Å) or ethene (1.08Å).

This is because the C-H bond contains more s character ($sp^3 \rightarrow sp^2 \rightarrow sp$) which gives stronger bonds.

1.54 Å   1.33 Å   1.20 Å

1.09 Å   1.08 Å   1.06 Å
ethane   ethene   ethyne
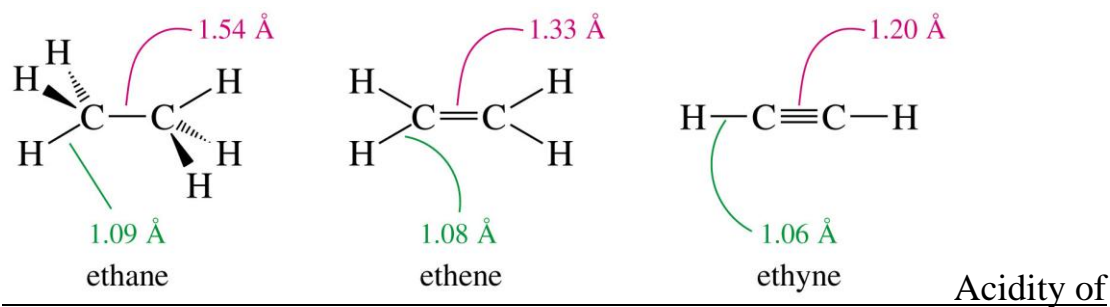
Acidity of Alkynes

Terminal alkynes are <u>acidic</u>, the end hydrogen can be removed as a proton by a strong base.

E.g.

$$H_3C-C\equiv C-H \xrightarrow{\text{CH}_3\text{-Li}} H_3C-C\equiv C-Li \qquad + CH_4$$

$$Ph-C\equiv C-H \xrightarrow{\text{CH}_3\text{CH}_2\text{MgBr}} Ph-C\equiv C-MgBr \quad + CH_3CH_3$$

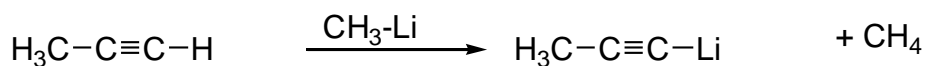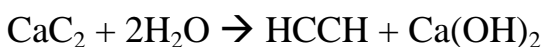$$CH_3CH_2-C\equiv C-H \xrightarrow{\text{NaNH}_2} CH_3CH_2-C\equiv C:^- \ ^+Na \quad + NH_3$$
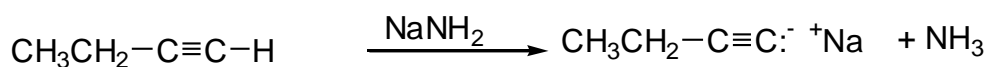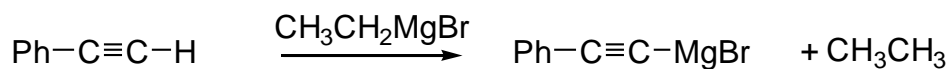
TABLE 9-2

Compound	Conjugate Base	Hybridization	s Character	pK$_a$	
H H H—C—C—H H H	H H H—C—C :$^-$ H H	sp^3	25%	50	weakest acid
H,C=C,H / H H	H,C=C :$^-$ / H H	sp^2	33%	44	
:NH$_3$	:N̈H$_2^-$	(ammonia)		35	
H—C≡C—H	H—C≡C :$^-$	sp	50%	25	
R—OH	R—Ö:$^-$	(alcohols)		16–18	stronger acid

Heavy Metal Acetylides

These form more covalent type structures, and the silver and copper acetylides will precipitate from solution. (Test for terminal alkynes).

$$H_3C-C\equiv C-H \xrightarrow{\text{Ag}^+} H_3C-C\equiv C-Ag \qquad + H^+$$
$$\text{(Precipitate)}$$

$$H_3C-C\equiv C-CH_3 \xrightarrow{\text{Ag}^+} \text{No reaction}$$

$$CaC_2 + 2H_2O \rightarrow HCCH + Ca(OH)_2$$
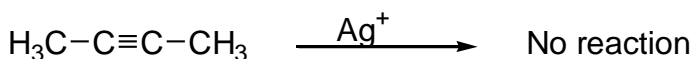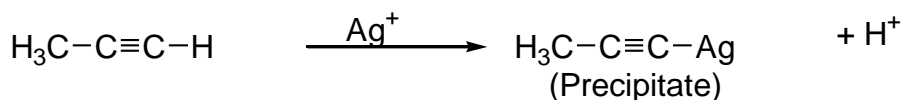
Synthesis of Alkynes
The carbanions produced are called acetylides, and are strong nucleophiles.

$$R-C\equiv C:\quad R'-X \longrightarrow \quad R-C\equiv C-R' \ + X^-$$
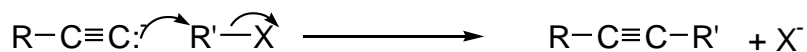
They can react in S_N2 displacements of halides or tosylates from primary unhindered substrates to produce internal alkynes.

E.g.

⬡—C≡C–H 1) NaNH₂ 2) CH₃CH₂Br ⬡—C≡C–CH₂CH₃
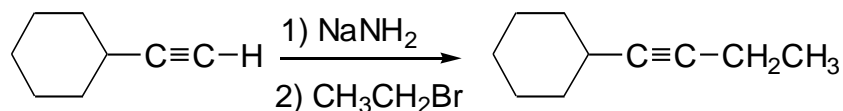
Carbonyl and Epoxide Reactions

$$R-C\equiv C: \quad \overset{\delta+}{C}\overset{\delta-}{=O} \longrightarrow R-C\equiv C-\underset{|}{\overset{|}{C}}-O^- \xrightarrow{H_2O} R-C\equiv C-\underset{|}{\overset{|}{C}}-OH$$
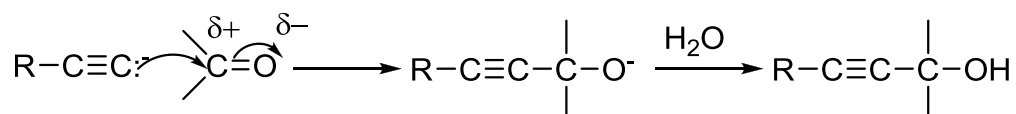
Acetylides will also attack other standard electrophiles like carbonyls and epoxides to generate alcohols. (These reactions are very similar to Grignard type reactions).
E.g.

⬡—C≡C–H 1) NaNH₂ 2) H₂C=O 3) H₂O ⬡—C≡C–CH₂-OH
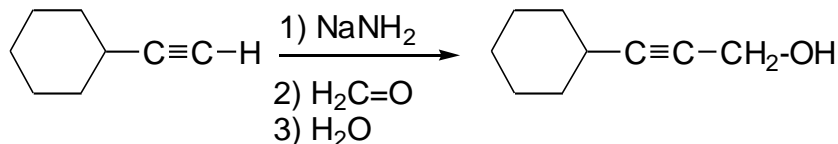
Epoxides also generate longer chain alcohols.

$$Ph-C\equiv C:^- \quad H_2C-\underset{CH_3}{\overset{O}{C}}-CH_3 \longrightarrow Ph-C\equiv C-\overset{H_2}{C}-\underset{CH_3}{\overset{O^-}{C}}-CH_3$$

$$\xrightarrow{H_2O}$$

$$Ph-C\equiv C-\overset{H_2}{C}-\underset{CH_3}{\overset{OH}{C}}-CH_3$$

$$R-C\equiv C:^- \quad + \quad R'-X \quad \xrightarrow{S_N2} \quad R-C\equiv C-R' \quad + \quad X^-$$

(R'—X must be a primary alkyl halide)

$$CH_3CH_2-C\equiv C:^- \quad + \quad \underset{\text{isopropyl bromide}}{H_3C-\overset{\overset{\displaystyle Br}{|}}{CH}-CH_3} \quad \xrightarrow{E2} \quad \underset{\text{butyne}}{CH_3CH_2-C\equiv C-H} \quad + \quad \underset{\text{propene}}{H_2C=CH-CH_3} \quad + \quad Br^-$$

butynide ion
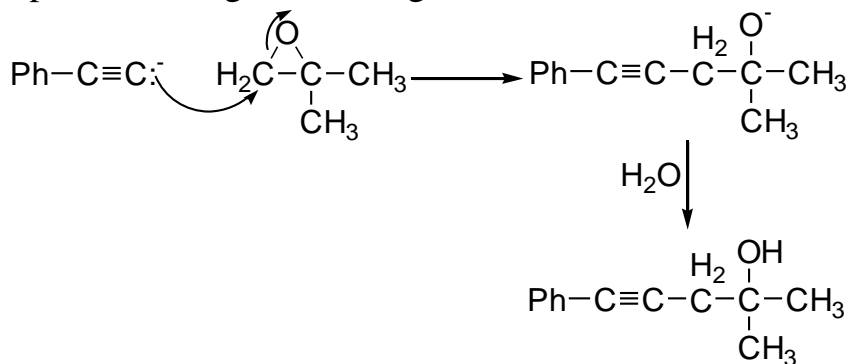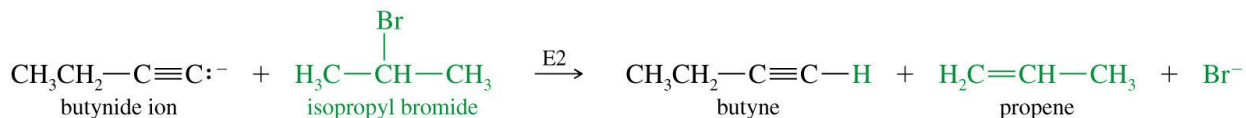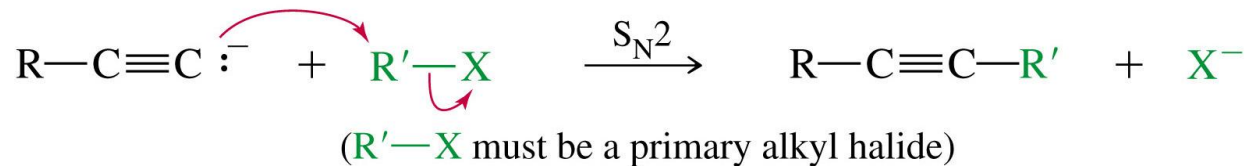
Synthesis of Alkynes via Elimination

In the same way that alkenes are produced by elimination of H-X, alkynes can be produced by elimination of 2 moles of H-X from a geminal or vicinal dihalide.
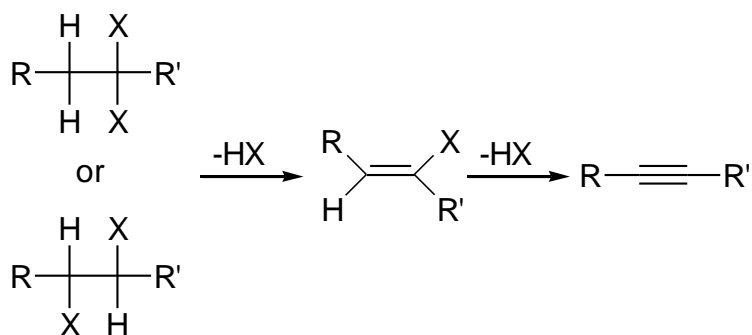
Strongly basic conditions (KOH or NaNH$_2$, high temps) are required for this transformation, and often the molecule may not be stable to these conditions and may be destroyed or will rearrange.

Base Catalyzed Rearrangements
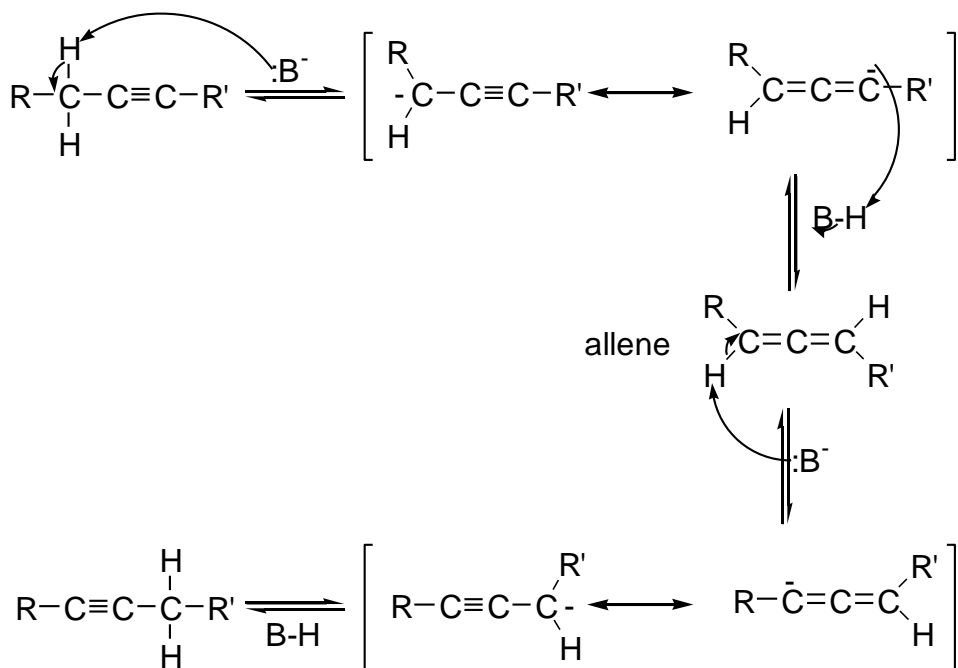
Often the deprotonated acetylide will rearrange to give a more stable product.

More highly substituted alkynes are more stable.

Sodium amide is such a strong base that during the equilibrating of all triple bond isomers, the terminal alkyne gets deprotonated and exists as the sodium salt, and is therefore prevented from equilibrating further.

one component of
the equilibrium

cannot equilibrate:
eventually becomes
major product
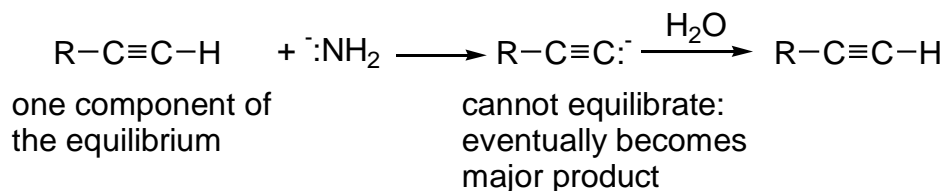
Eventually all the alkynes are trapped as the terminal sodium acetylide salts, and on addition of water generates the terminal alkyne.
E.g.
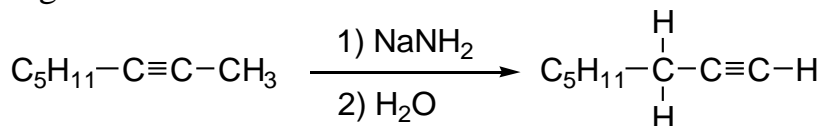
Bond Strengths
Recall that the π bond of an alkene is weaker than its σ bond.

Compound	Total Energy	Class	Approx. Energy
Alkane	83kcal/mol	alkane σ	83kcal/mol
Alkene	146kcal/mol	alkene π	63kcal/mol
Alkyne	200kcal/mol	alkyne 2nd π	54kcal/mol

The sum of the two π bonds in an alkyne are **weaker** than the sum of two alkene π bonds.

The triple bond is **electron rich** and acts as a <u>nucleophile</u> (just like a double bond).

$$R-C\equiv C-R' \xrightarrow{A-B} \underset{R \quad R'}{\overset{A \quad B}{C=C}} \xrightarrow{A-B} A-\underset{R \quad R'}{\overset{A \quad B}{C-C}}-B$$
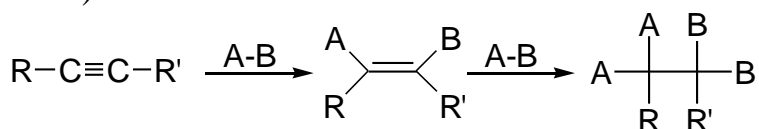
Since addition reactions convert π bonds into σ bonds, these reactions are typically exothermic.

Alkynes can add up to two molecules across the triple bond.

Addition of Hydrogen
Hydrogen in the presence of a catalyst will add twice to alkynes to generate alkanes.

$$R-C\equiv C-R' \xrightarrow{H_2, Pt} \left[\underset{R \quad R'}{\overset{H \quad H}{C=C}} \right] \longrightarrow H-\underset{R \quad R'}{\overset{H \quad H}{C-C}}-H$$
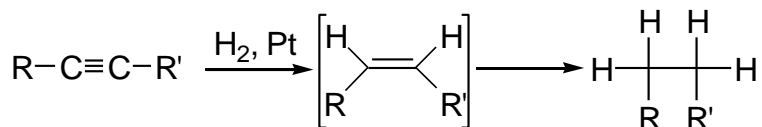
This reaction proceeds through a cis alkene intermediate, but **cannot** be stopped at this stage <u>except</u> with the use of a special catalyst.

Lindlar's catalyst
This is a partially deactivated (poisoned) catalyst consisting of barium sulfate, palladium and quinoline (the poison).

$$R-C\equiv C-R' \xrightarrow[\text{Quinoline, CH}_3\text{OH}]{H_2, Pd/BaSO_4} \underset{R \quad \quad R'}{\overset{H \quad \quad H}{C=C}}$$
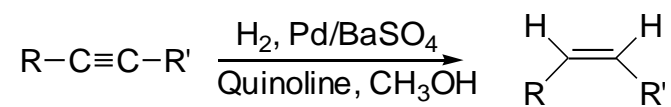
The hydrogens are delivered simultaneously to the same side of the alkyne, creating syn addition (cis alkenes).

Trans Alkenes
These can be produced by the action of sodium metal in liquid ammonia.

$$H_3C-C{\equiv}C-C_2H_5 \xrightarrow{\text{Na, NH}_3} \begin{array}{c} H_3C \\ \diagdown \\ H \end{array} C{=}C \begin{array}{c} H \\ \diagup \\ C_2H_5 \end{array}$$
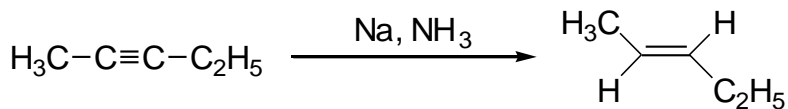
An electron is added to the triple bond, generating a radical anion, which is protonated to generate a vinyl radical.
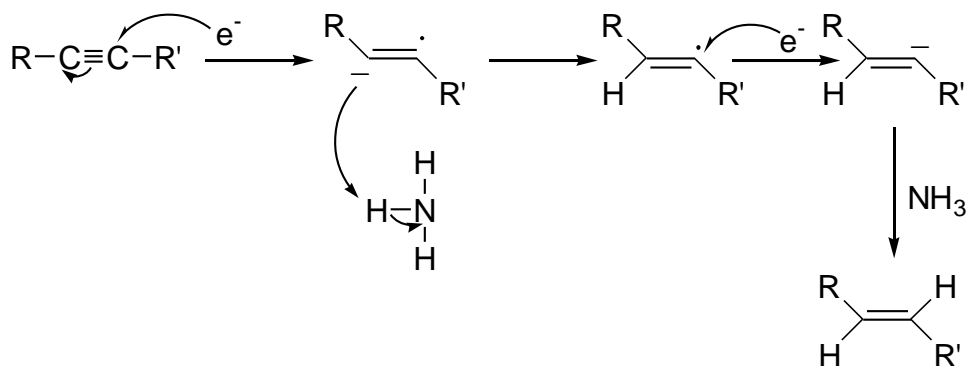
The radical accepts another electron which produces an anion, which in turn gets protonated, giving the alkene with **anti** stereochemistry.

The anti stereochemistry arises from the two alkyl groups being as far away from each other as possible at the vinyl radical stage.

Addition of Halogens
Chlorine and bromine add in an analogous fashion as for alkenes.

If only one mole of halogen is added then a dihaloalkene is produced, and a mixture of syn and anti addition is observed.

$$R-C{\equiv}C-R' \xrightarrow{X_2} \begin{array}{c} X \\ \diagdown \\ R \end{array} C{=}C \begin{array}{c} X \\ \diagup \\ R' \end{array} \qquad \begin{array}{c} X \\ \diagdown \\ R \end{array} C{=}C \begin{array}{c} R' \\ \diagup \\ X \end{array}$$
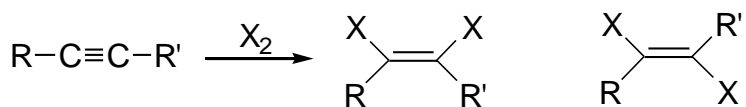
It is usually hard to control the addition of just one equivalent of halogen and it is more common to add two equivalents to generate tetrahalides.

$$R-C\equiv C-R' \xrightarrow{2\ X_2} \underset{R\quad R'}{X-\overset{X\quad X}{\underset{|\quad|}{C-C}}-X}$$
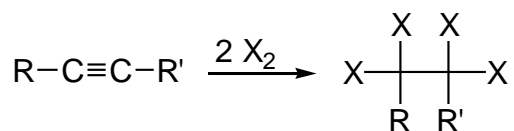
Addition of Hydrogen Halides
H-X can be added to alkynes just like to alkenes.

$$R-C\equiv C-H \xrightarrow{H\text{-}X} \underset{R\qquad H}{\overset{X\qquad H}{\diagup\!\!=\!\!\diagdown}} \xrightarrow{H\text{-}X} \underset{R\quad H}{X-\overset{X\quad H}{\underset{|\quad|}{C-C}}-H}$$
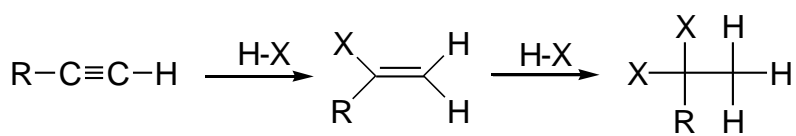
For **terminal** alkynes, the products have orientation as dictated by Markovnikov's rule.

The vinyl cation is more stable with positive charge on the **more** substituted carbon.

$$R-C\overset{\frown}{\equiv}C-H \xrightarrow{H\overset{\frown}{-}X} \underset{:X^-}{\underset{\quad}{R\diagup\!\!=\!\!\diagdown H \atop {}^+ \quad H}} \longrightarrow R\diagup\!\!=\!\!\diagdown H \atop X\qquad H$$

Markovnikov
Addition
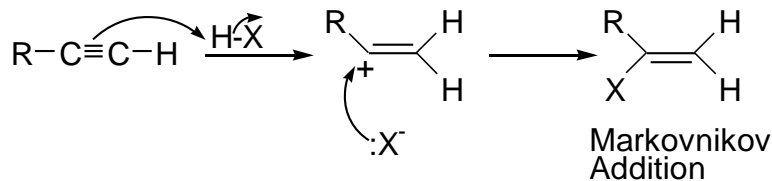
The second mole of H-X will usually add with the same orientation as the first.

Internal alkynes show little selectivity since both intermediate cations are equally substituted.

$$CH_3CH_2-C\equiv C-CH_3 \xrightarrow{H\text{-}Br} \underset{\underset{Br\qquad CH_3}{}}{CH_3CH_2\diagup\!\!=\!\!\diagdown H} \qquad \underset{\underset{H\qquad CH_3}{}}{CH_3CH_2\diagup\!\!=\!\!\diagdown Br}$$

E and Z   E and Z

The peroxide effect is also observed with the addition of H-Br and peroxides to generate anti-Markovnikov products.

$$C_2H_5-C\equiv C-H \xrightarrow[\text{R-OO-R}]{\text{H-Br}} \begin{matrix} C_2H_5 \\ \end{matrix} \diagup\!\!\!=\!\!\!\diagdown \begin{matrix} Br \\ H \end{matrix}$$

Anti-Markovnikov
Addition

Hydration of Alkynes to Ketones and Aldehydes
There are two different methods:

Mercuric-ion catalyzed hydrations
A mixture of mercuric sulfate and aqueous sulfuric acid is used to perform addition of water across the triple bond.

The orientation is Markovnikov, and the initial products are enols.

$$C_2H_5-C\equiv C-H \xrightarrow[\text{R-OO-R}]{\text{H-Br}} \begin{matrix} C_2H_5 \\ HO \end{matrix} \diagup\!\!\!=\!\!\!\diagdown \begin{matrix} H \\ H \end{matrix} \rightleftharpoons \begin{matrix} C_2H_5 \\ \\ O \end{matrix} \diagdown\!\!\!-CH_3$$

Markovnikov
Addition

enol form   keto form

Electrophilic addition of the Hg^{2+} ion generates a vinyl cation, which is attacked by a nucleophilic water molecule.

Deprotonation gives an organomercurial alcohol which, under acidic conditions, has the mercury replaced by a hydrogen, to generate a vinyl alcohol (enol).

$$C_2H_5-C\equiv C-H \xrightarrow{Hg^{2+}} \begin{matrix} C_2H_5 \\ + \end{matrix} \diagup\!\!\!=\!\!\!\diagdown \begin{matrix} H \\ Hg^+ \end{matrix} \rightarrow \begin{matrix} C_2H_5 \\ H_2O \\ + \end{matrix} \diagup\!\!\!=\!\!\!\diagdown \begin{matrix} H \\ Hg^+ \end{matrix}$$

H_2O⦂

$-H^+$

$$\begin{matrix} C_2H_5 \\ HO \end{matrix} \diagup\!\!\!=\!\!\!\diagdown \begin{matrix} H \\ H \end{matrix} \xleftarrow{H_3O^+} \begin{matrix} C_2H_5 \\ HO \end{matrix} \diagup\!\!\!=\!\!\!\diagdown \begin{matrix} H \\ Hg^+ \end{matrix}$$

enol form

Enols tend to be unstable, and isomerise to their more stable ketone form.

enol form

keto form

Enols are always in equilibrium with their ketone form – this is an example of keto-enol tautomerism.

Hydroboration-Oxidation

Previously we saw hydroboration-oxidation of alkenes gave anti-Markovnikov addition of water across the double bond.

The same occurs for alkynes, except a sterically hindered dialkylborane must be used to prevent the addition of two borane molecules. (Usually di(sec-isoamyl)borane is used).

aldehyde

A vinyl borane is produced with anti-Markovnikov orientation, which then is oxidized using basic hydrogen peroxide to an enol, which tautomerises into the more stable keto form.

Terminal alkynes are converted into aldehydes.

Oxidation of Alkynes

Under mild (cold, neutral) conditions the reaction of potassium permanganate with an alkyne can generate a diketone.

$$R\!\!=\!\!R' \xrightarrow[\text{H}_2\text{O, neutral}]{\text{KMnO}_4} \left[\begin{array}{c} \text{HO} \quad \text{OH} \\ R\!-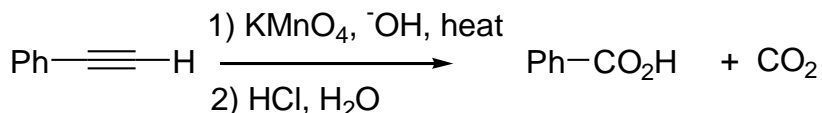\!\!\!-\!\!\!-R' \\ \text{HO} \quad \text{OH} \end{array} \right] \xrightarrow{-2\ \text{H}_2\text{O}} \underset{\text{diketone}}{\overset{\text{O} \quad \text{O}}{R \qquad R'}}$$

If the mixture becomes too warm or basic, the oxidation proceeds further to generate two carboxylate anions, which on acidification generates two carboxylic acids.

$$R\!\!=\!\!R' \xrightarrow[\text{‾OH, heat}]{\text{KMnO}_4} \begin{array}{c} R\!-\!CO_2^- \\ \\ \text{‾O}_2C\!-\!R' \end{array} \xrightarrow{\text{H}_3\text{O}^+} \begin{array}{c} R\!-\!CO_2H \\ \\ R'\!-\!CO_2H \end{array}$$

Terminal alkynes are similarly cleaved to give a carboxylic acid and carbon dioxide.

$$Ph\!\!=\!\!H \xrightarrow[\text{2) HCl, H}_2\text{O}]{\text{1) KMnO}_4,\ \text{‾OH, heat}} Ph\!-\!CO_2H \quad + \quad CO_2$$

Ozonolysis

Ozonolysis of an alkyne followed by hydrolysis gives similar products to those obtained from permanganate oxidative cleavage.

$$H_3C\!\!=\!\!C_2H_5 \xrightarrow[\text{2) H}_2\text{O}]{\text{1) O}_3} \begin{array}{c} H_3C\!-\!CO_2H \\ \\ HO_2C\!-\!C_2H_5 \end{array}$$