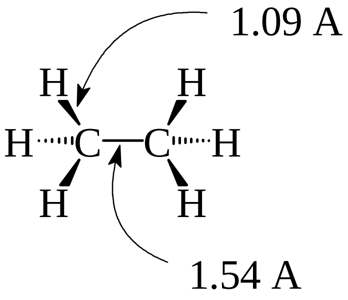
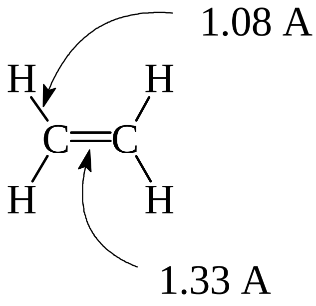
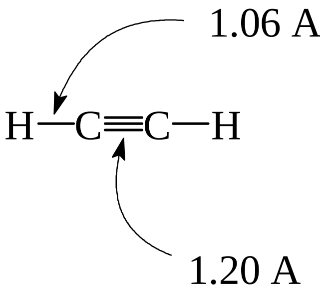
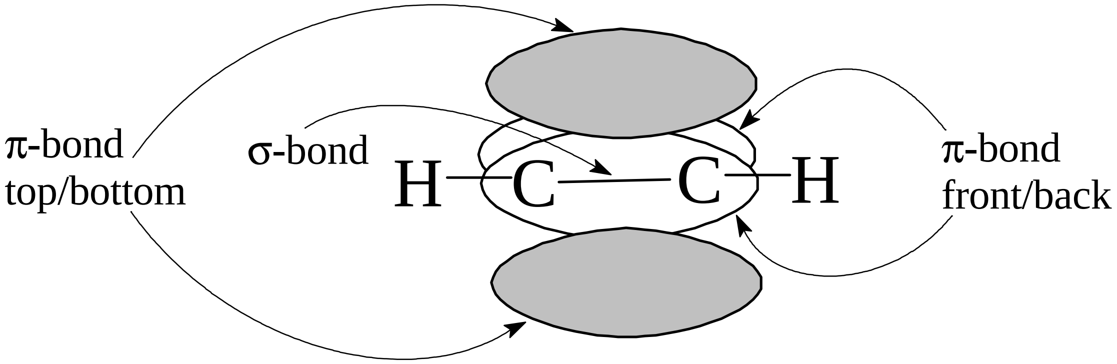
Alkynes, -C≡C-

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





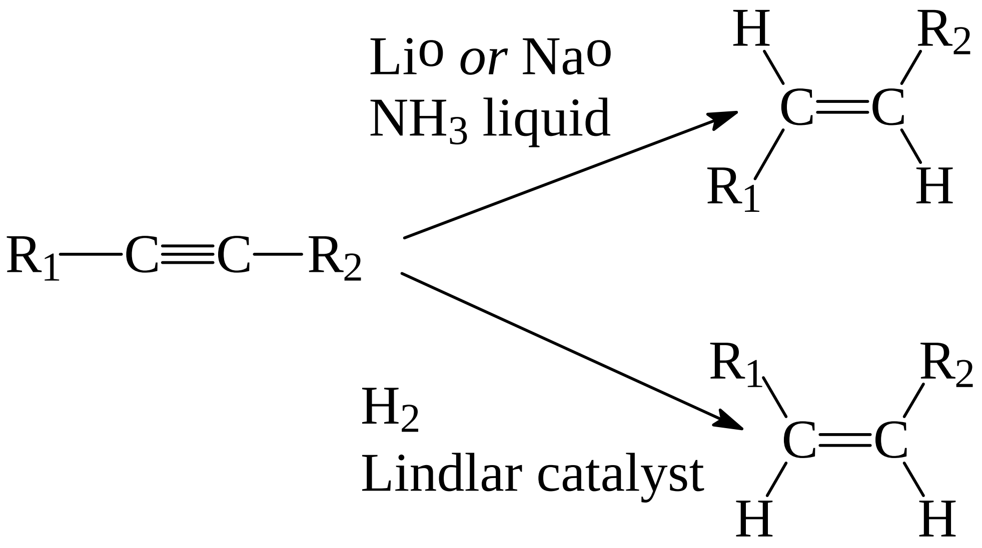




Reactions of Alkynes

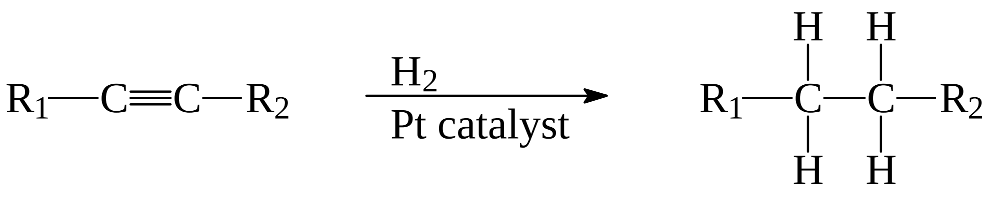
Reduction to an alkene ---

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

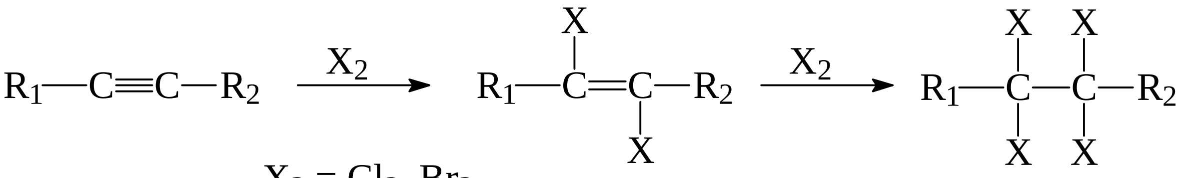


Each of these reactions is *stereoselective* in that each yields predominantly one stereoisomer of two or more possible ones.

Reduction to an alkane ---



Addition of halogens:

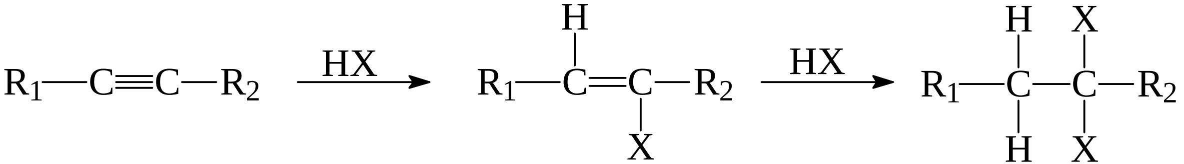


$X_2 = Cl_2, Br_2$

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 ---

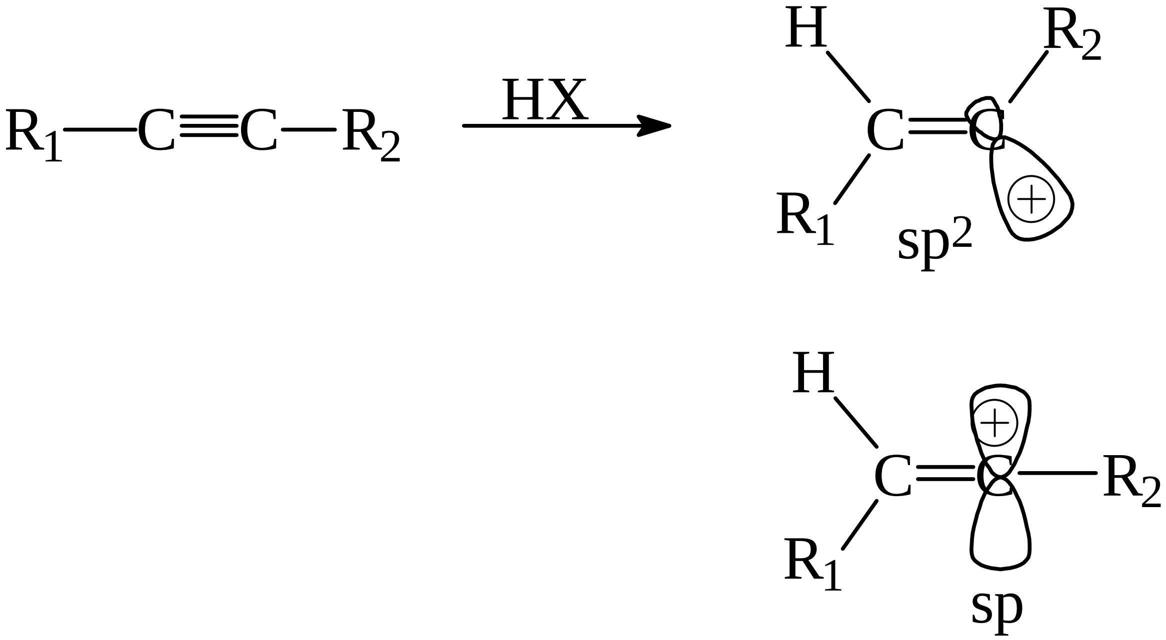


HX = HCl, HBr, HI

typically anti addition

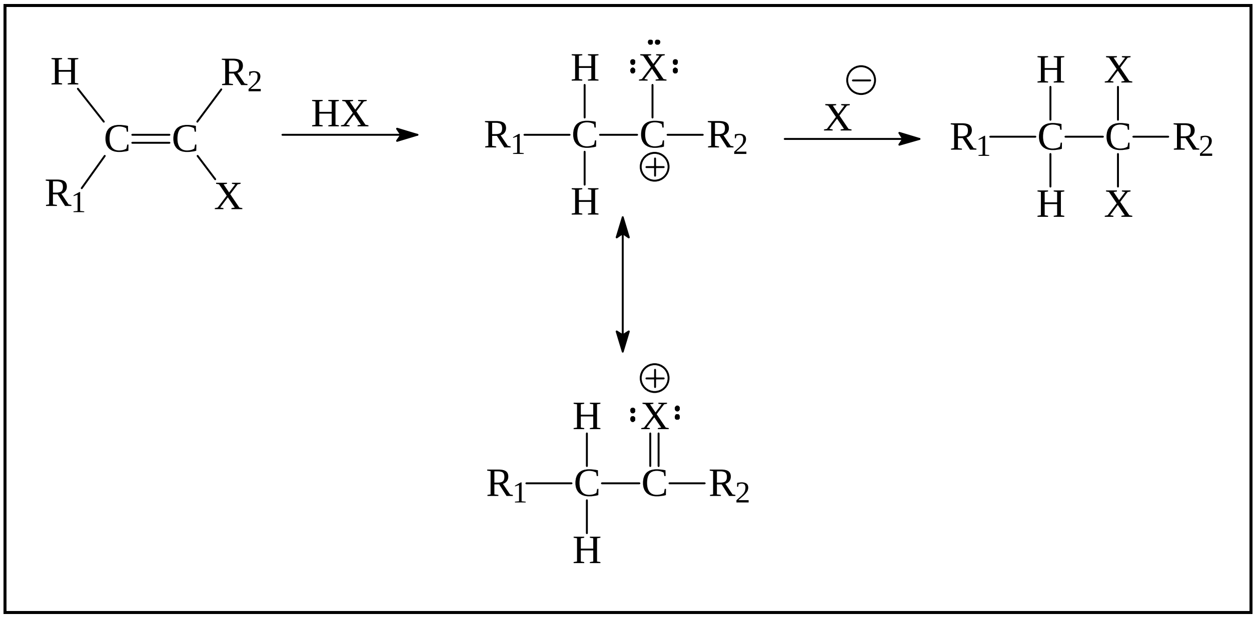
Terminal alkynes show Markovnikov addition in first step.

The anti addition could be explained by a vinylic carbocation with a vacant sp^2 orbital although calculations suggest that a carbocation with a vacant p orbital (sp hybrid) would be more stable.



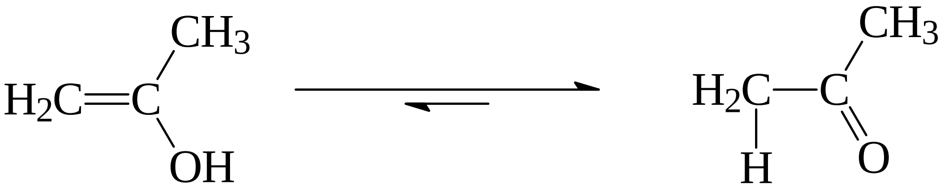
Reaction can often be stopped after the first step even though alkynes are less reactive toward electrophilic addition than alkenes. This lower reactivity of alkynes is at least partly due to vinylic cations being less stable than comparable alkyl cations --- 2° vinylic ~ 1° alkyl;
1° vinylic ~ methyl.

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*

$$\mathrm{H{-}C{\equiv}C{-}CH_3} \xrightarrow[\mathrm{HgSO_4}]{\mathrm{H_2O,\ H_2SO_4}}$$

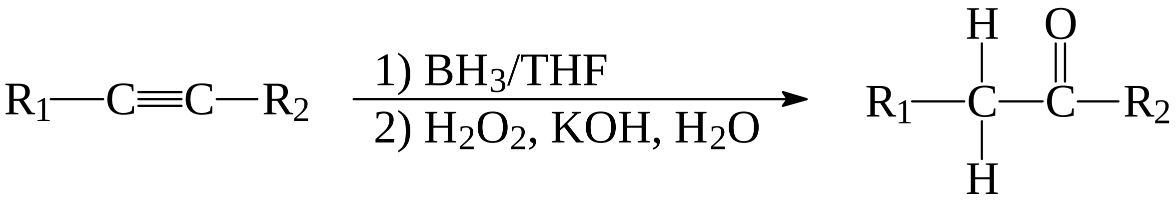


an enol a ketone

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.

Hydroboration of Alkynes ---



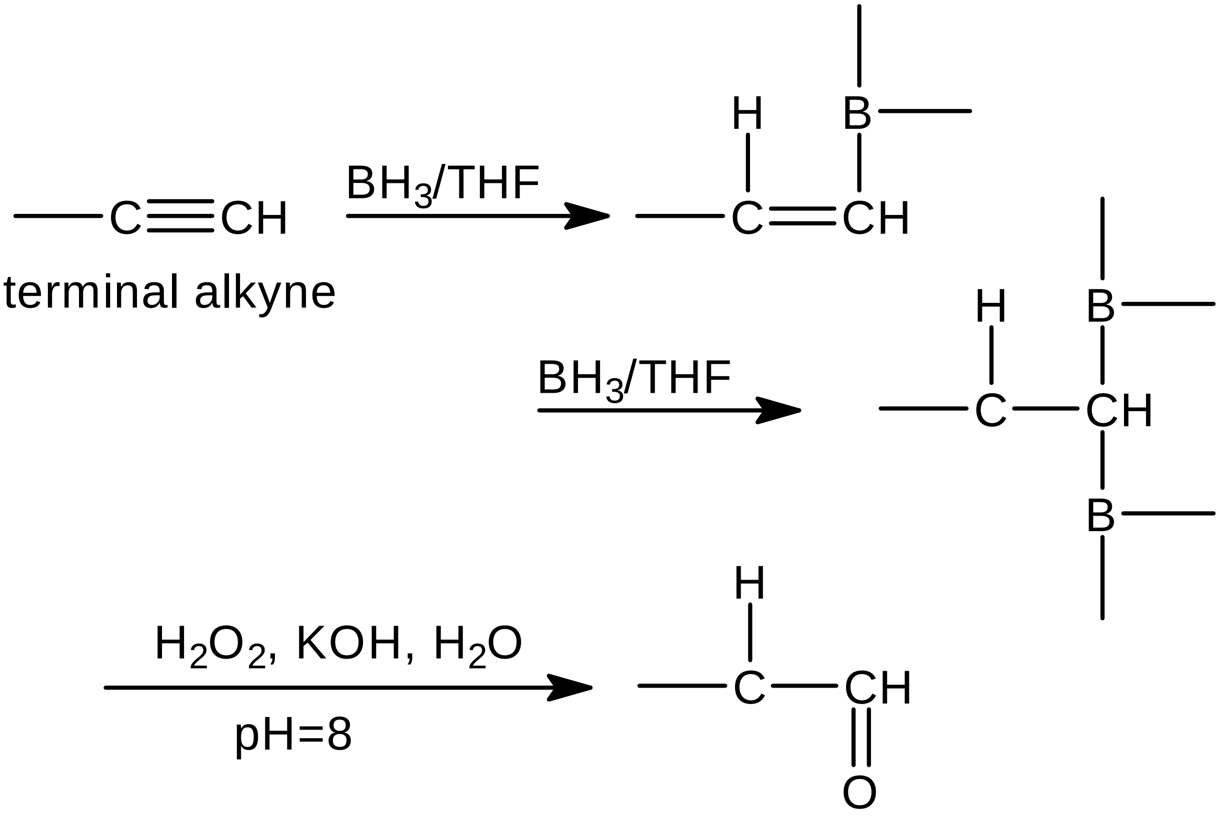
$$R_1-C\equiv C-R_2 \xrightarrow[\text{2) } H_2O_2,\ KOH,\ H_2O]{\text{1) } BH_3/THF} R_1-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-R_2$$

internal alkyne: $R_1, R_2 \neq H$

Ketone is formed via enol.

Symmetrical alkyne gives one ketone, unsymmetrical alkyne gives a mixture of two ketones.

In the case of terminal alkynes borane will add twice to the triple bond, in anti-Markovnikov fashion. This product can be converted to an aldehyde by reaction with hydrogen peroxide at a pH of 8.



Synthesis – Making Larger Alkynes from Smaller Ones

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 ---

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

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

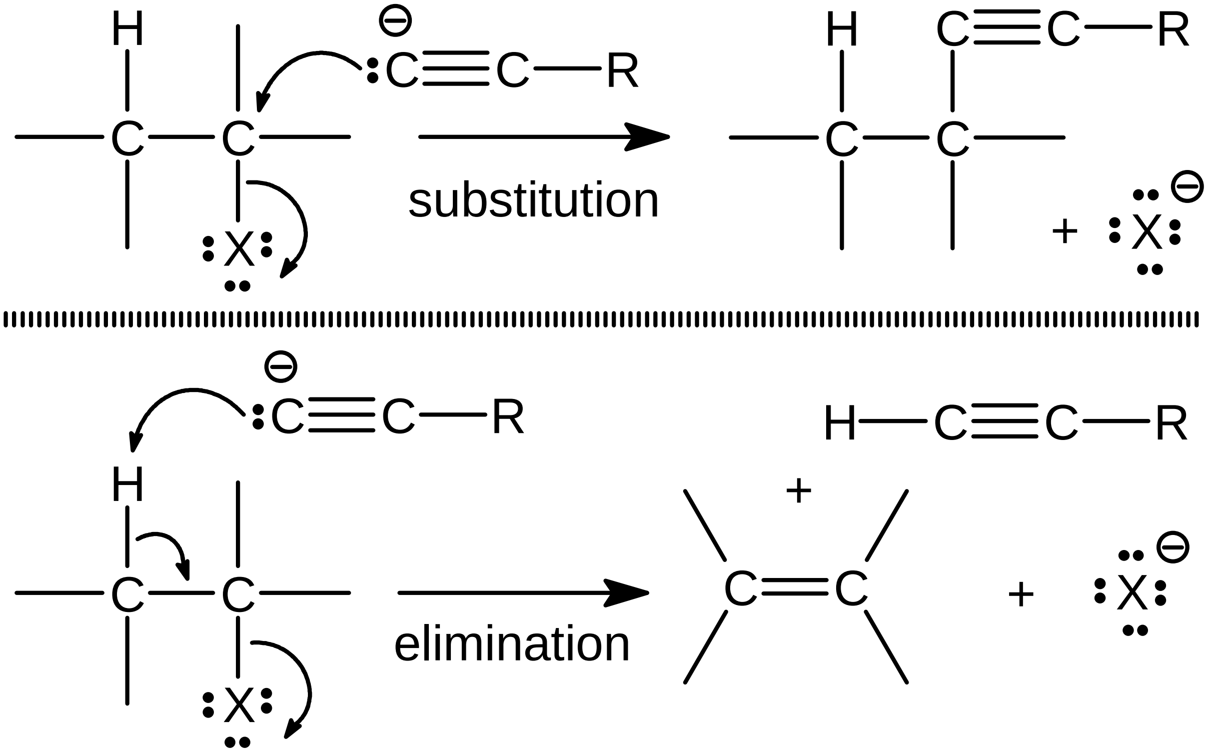
$H\text{-}C{\equiv}C\text{-}CH_2\text{-}C_2H_5 + NaNH_2 \longrightarrow$
$Na^{+\,-}C{\equiv}C\text{-}CH_2\text{-}C_2H_5 + NH_3$

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

Example problem 3 ---
Synthesize 2,2-dimethyl-3-octyne, $(CH_3)_3C\text{-}C{\equiv}C\text{-}(CH_2)_3CH_3$, from starting materials which do not contain more than 6 carbons.

Reaction of acetylides with alkyl halides --- Substitution *vs.* Elimination

So far, the reaction of acetylide anion with alkyl halide has resulted in a substitution, producing a larger alkyne. This is not the only reaction which can occur between an acetylide anion and an alkyl halide; a B/L acid-base reaction leading to an elimination is also possible.



(E2) Elimination usually increases

————————————————————————>

R-X = 1^o 2^o 3^o

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(S_N2) Substitution usually increases

With a strong base like acetylide, substitution is successful only if R-X is 1^o.

Solution 3 ---

$(CH_3)_3C\text{-}C{\equiv}C\text{-}H + NaNH_2 \longrightarrow (CH_3)_3C\text{-}C{\equiv}C^- \; Na^+$
$(CH_3)_3C\text{-}C{\equiv}C^- \; Na^+ + CH_3\text{-}CH_2Cl \longrightarrow$
$(CH_3)_3C\text{-}C{\equiv}C\text{-}CH_2CH_2CH_2CH_3$

Note that reacting sodium pentynide with 2-chloro-2-methylpropane will **NOT** work. 2-Chloro-2-methylpropane is a 3^o alkyl halide and will undergo elimination to form 2-methyl-1-propene.