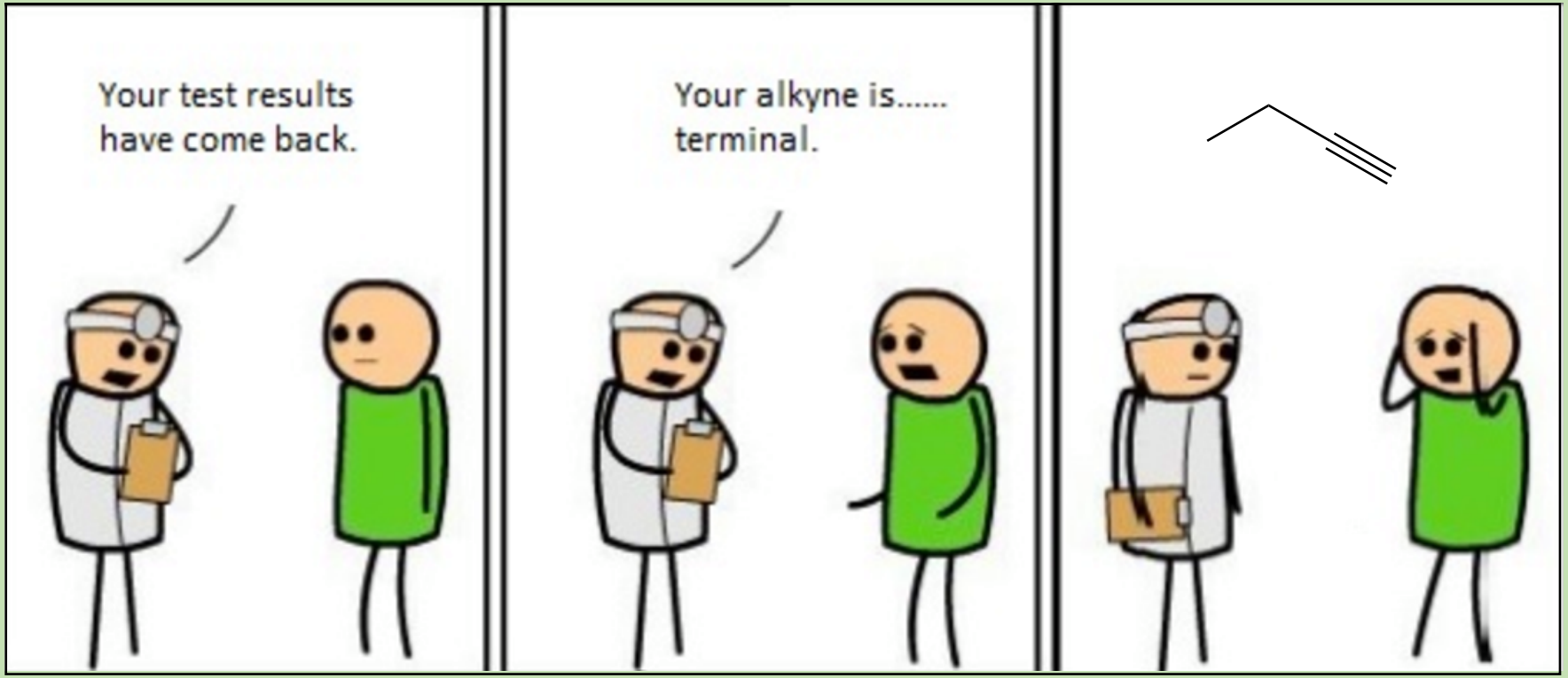
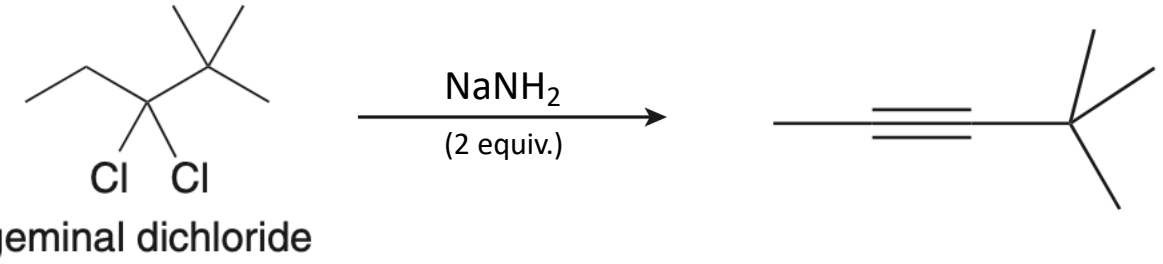
"ALKYNES" OF REACTIONS



Preparation of Alkynes

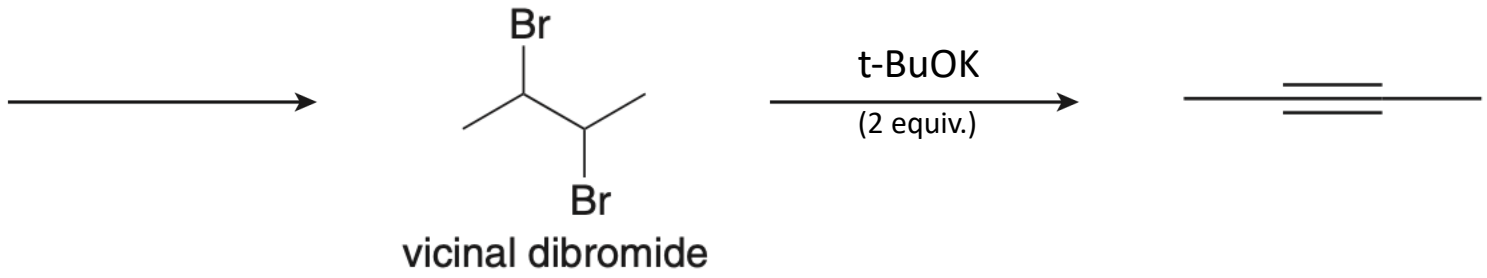
To create alkynes (i.e. 2 π bonds), the substrate must have 2 leaving groups with 2 β-hydrogens to remove.
To remove the hydrogens, 2 equivalents of strong base are added (NaH or $NaNH_2$ are best).



geminal dichloride



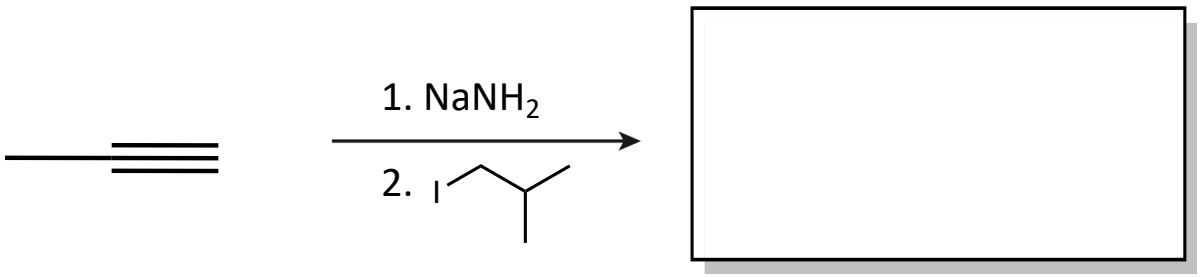
STARTING ALKENE

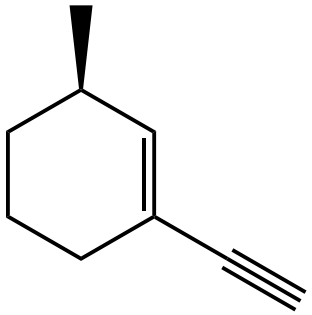


vicinal dibromide

FORMATION OF COMPLEX ALKYNES

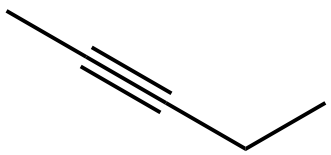
Note: works best with methyl or 1° alkyl halides





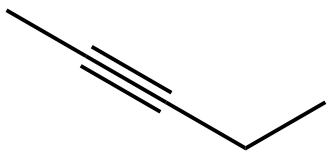
xs H_2

Pd / C



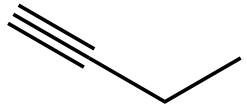
H_2

Lindlar's Cat. or Ni_2B



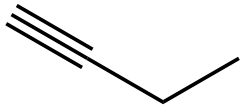
Na

NH_3 (*liq.*)



HBr (1 equiv.)

CH_2Cl_2

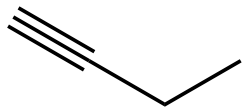


xs HBr

CH_2Cl_2

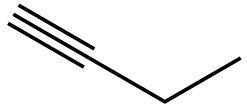
1. $NaNH_2$ / NH_3

2. H_2O



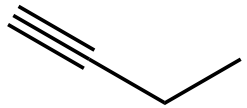
HBr

ROOR



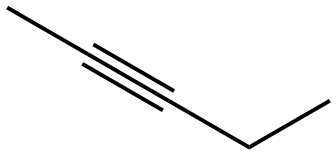
H_2SO_4, H_2O

$HgSO_4$



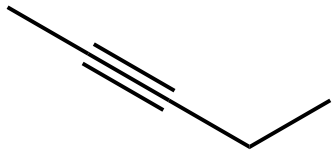
1. $(sia)_2BH$ or 9-BBN

2. H_2O_2, NaOH



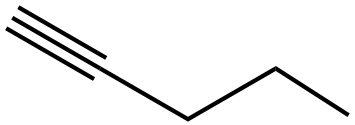
Cl_2 (1 equiv.)

CH_2Cl_2



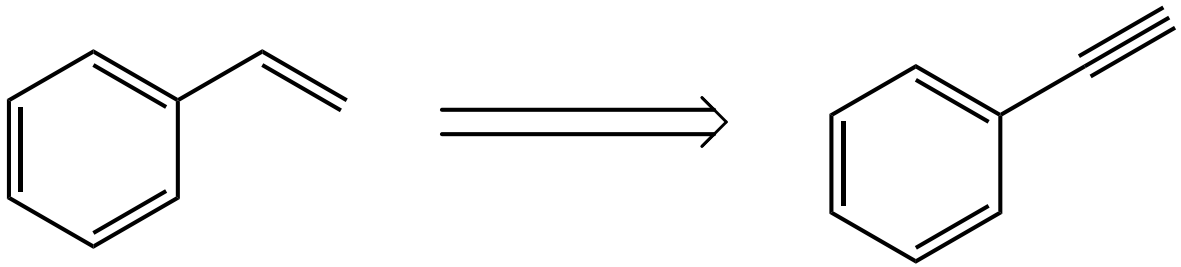
1. O_3

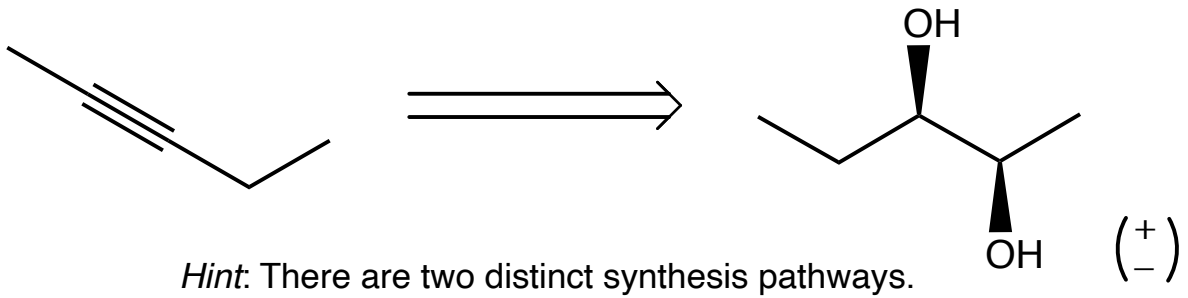
2. H_2O



1. O_3

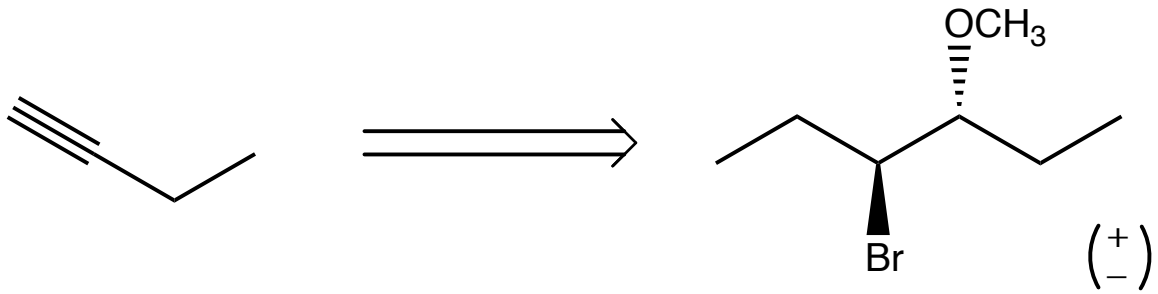
2. H_2O





(±)

Hint: There are two distinct synthesis pathways.

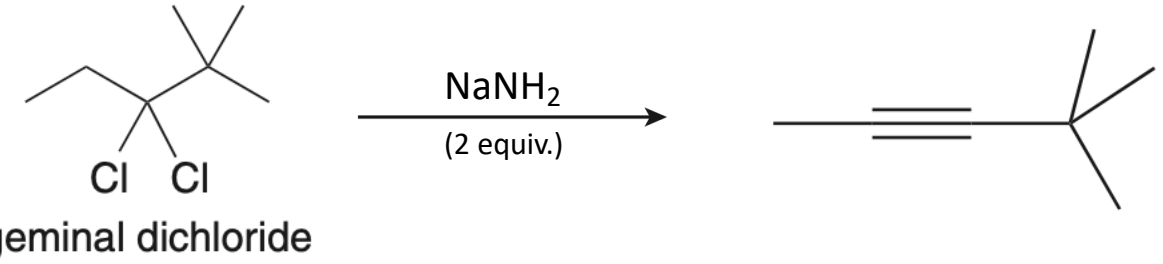


(±)

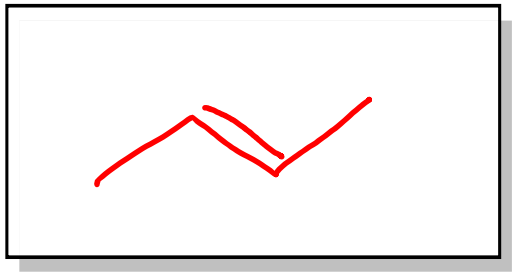
ANSWER KEY

Preparation of Alkynes

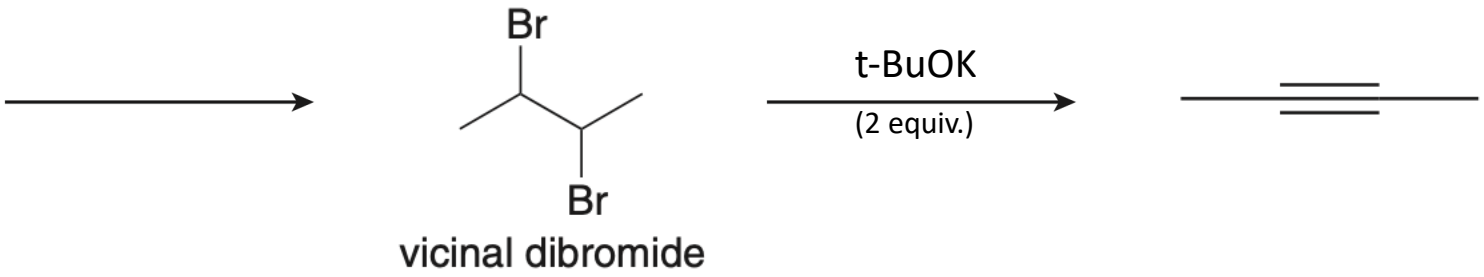
To create alkynes (i.e. 2 π bonds), the substrate must have 2 leaving groups with 2 β-hydrogens to remove.
To remove the hydrogens, 2 equivalents of strong base are added (NaH or $NaNH_2$ are best).



geminal dichloride



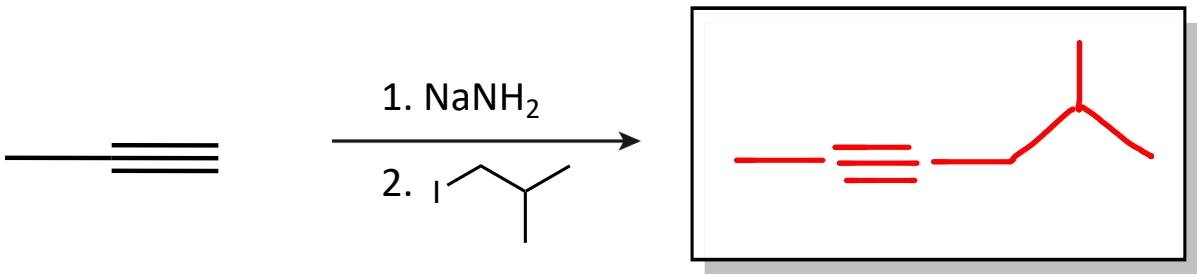
STARTING ALKENE

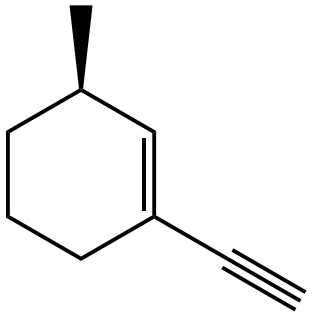


vicinal dibromide

FORMATION OF COMPLEX ALKYNES

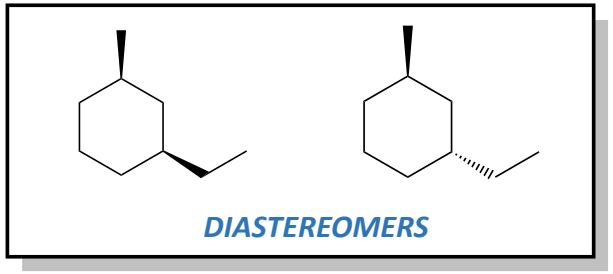
Note: works best with methyl or 1° alkyl halides





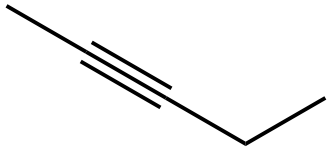
xs H_2

Pd / C



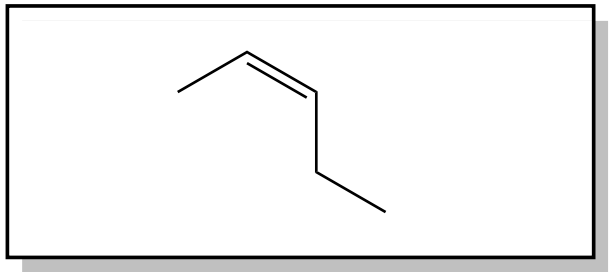
"xs" = "excess" results in the hydrogenation of all pi bonds.

Without excess, reduces least stable (i.e. least substituted) alkene first.



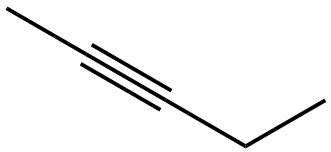
H_2

Lindlar's Cat. or Ni_2B



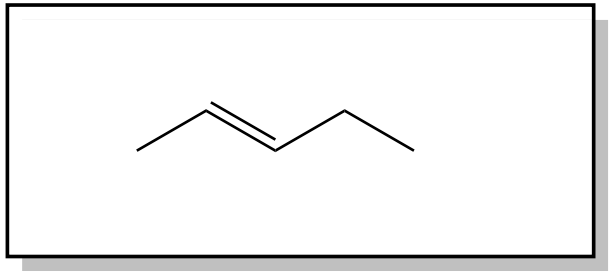
Forms *cis*-alkene.

Lindlar's catalyst is sometimes written as: Pd-$CaCO_3$-PbO_2



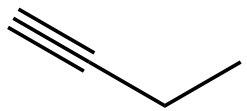
Na

NH_3 (*liq.*)



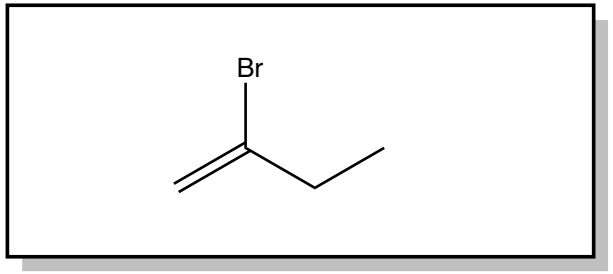
Forms *trans*-alkene.

- Mechanism is important. Know how to identify the **radical-ion intermediate**.



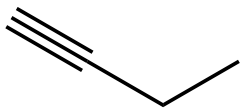
HBr (1 equiv.)

CH_2Cl_2



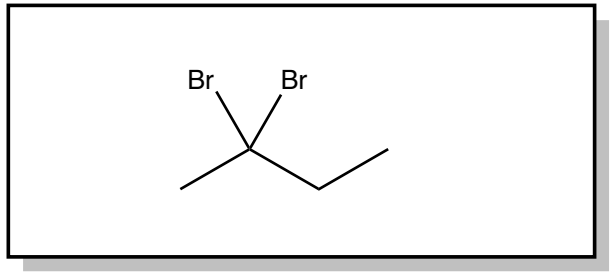
"Markovnikov" addition of Br

Mechanism unclear. Possible mechanisms:
- via **vinylic carbocation**
- via **termolecular** mechanism:
  Rate = *k* [alkyne][HX]^2



xs HBr

CH_2Cl_2

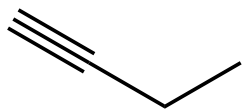


Forms above product first.
Br adds to same position in second reaction.
- can interconvert with $NaNH_2$.

1. $NaNH_2$ / NH_3

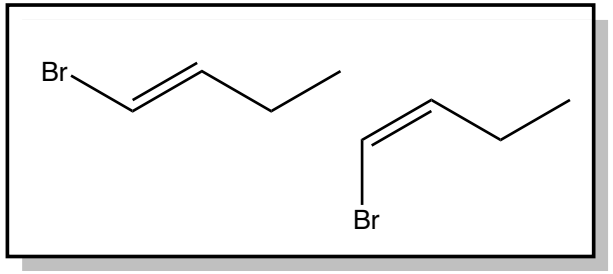
2. H_2O

Only useful for forming *terminal* alkynes
(due to triple bond migration, see p. 5).

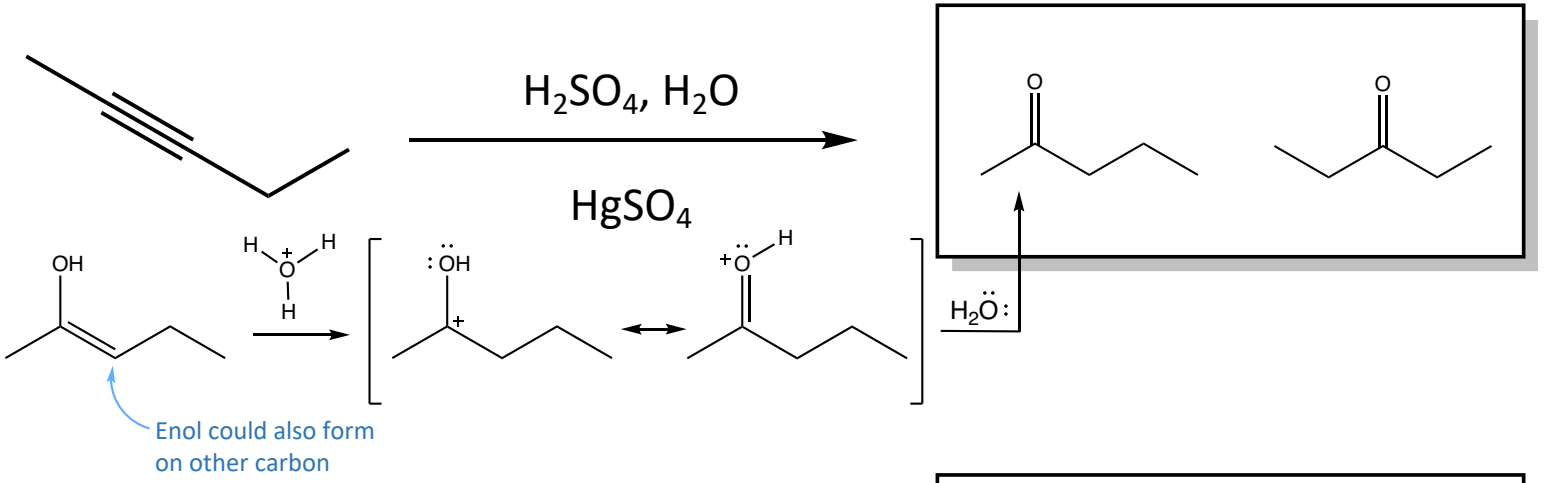


HBr

ROOR

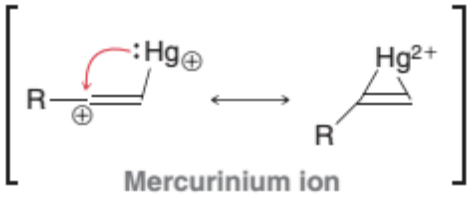


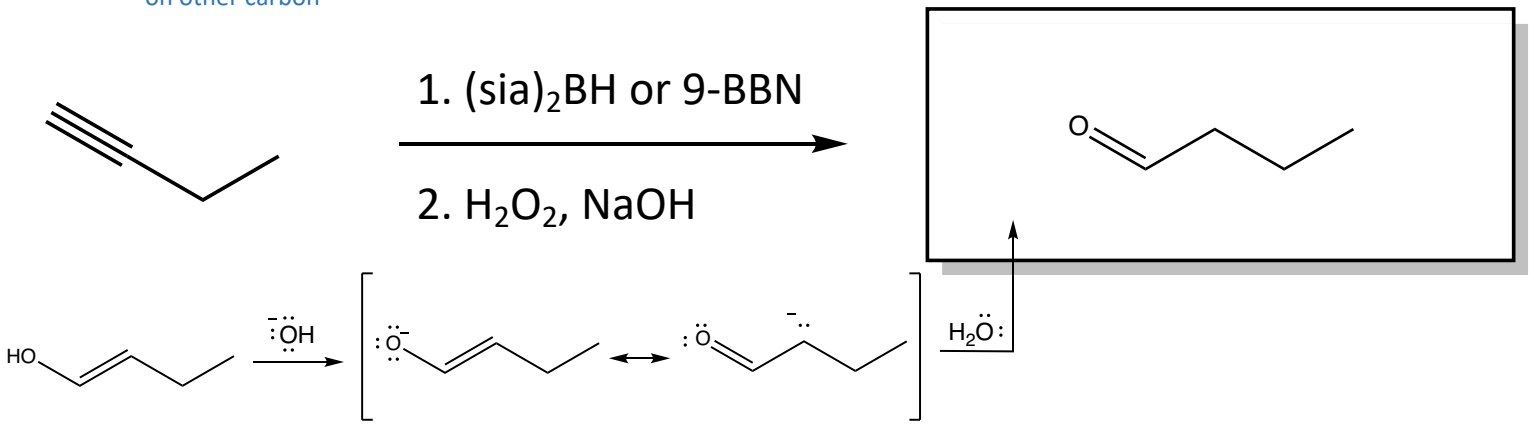
Forms mixture of *E* + *Z* alkenes



Markovnikov; Forms ketone via **acid-catalyzed tautomerization**

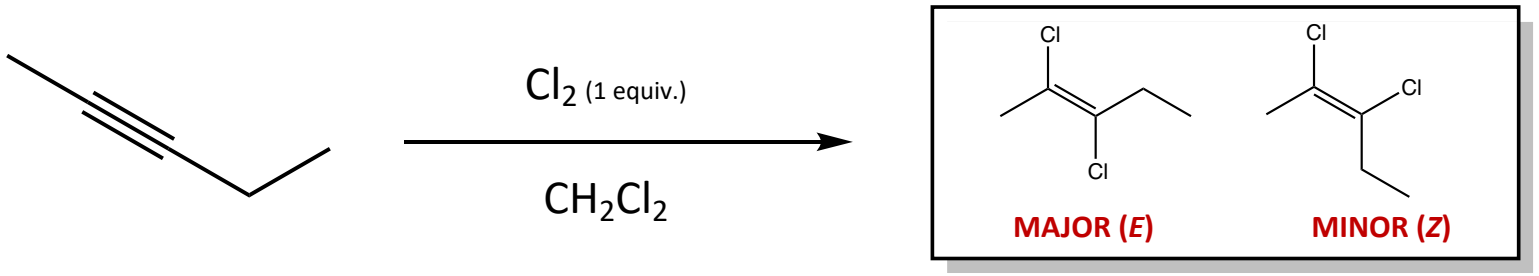
- proceeds via mercurinium ion





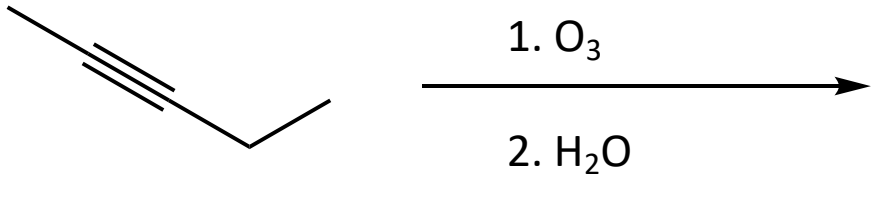
Anti-Markovnikov; Forms aldehyde (or ketone, if internal alkyne) via **base-catalyzed tautomerization.**

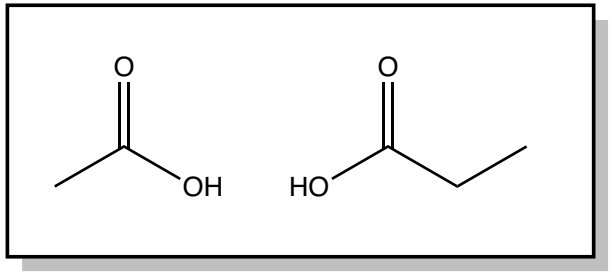
Bulky borane reagents preferred instead of BH_3•THF.



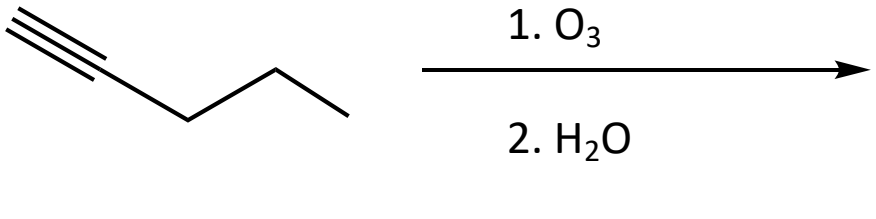
Works for Cl_2 or Br_2.

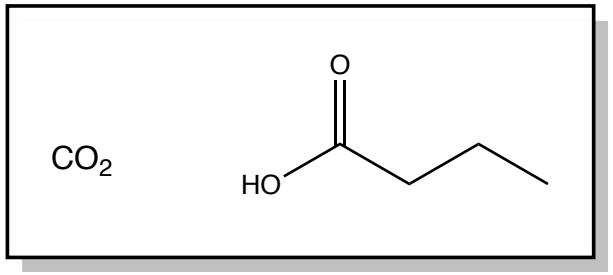
Single equiv. of X_2 forms (*E*)-product as major and (*Z*)-product as minor.



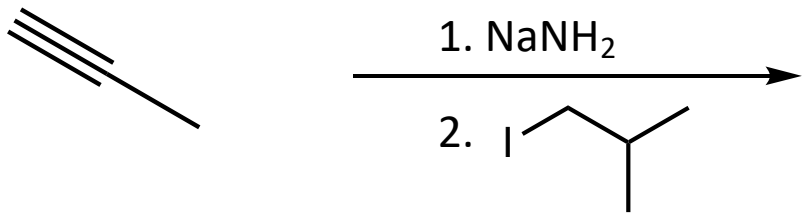


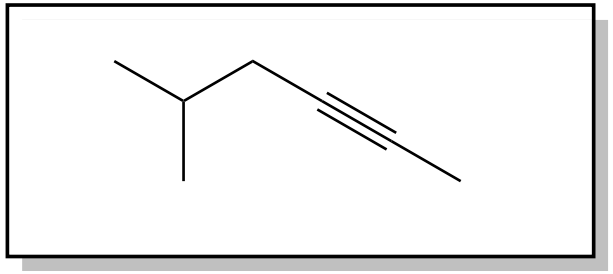
Oxidative cleavage of **internal alkyne** forms two COOH.



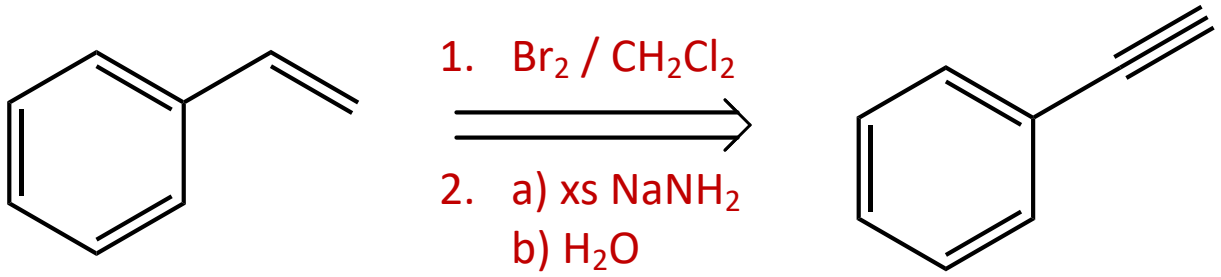


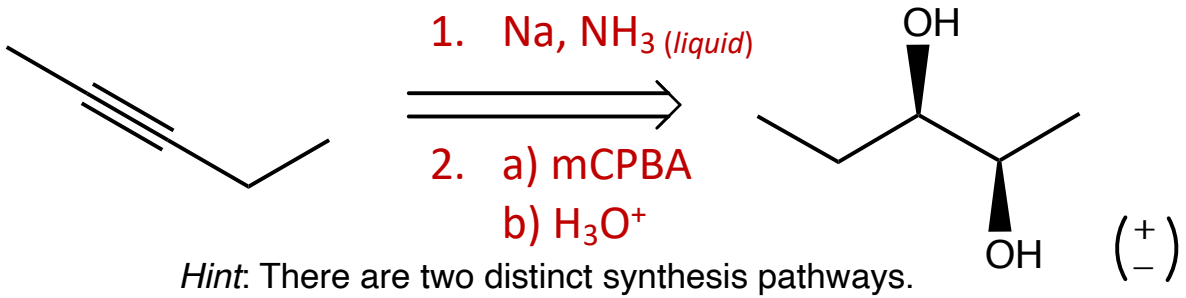
Oxidative cleavage of **terminal alkyne** forms one COOH and one CO_2.





Alkylation via S_N2
- only efficient for methyl or 1° alkyl halides





Hint: There are two distinct synthesis pathways.

OR

1. H_2, Lindlar's Cat. (or Ni_2B)
2. $KMnO_4$, NaOH, cold
(or 1. OsO_4 2. NMO)

