Alkynes

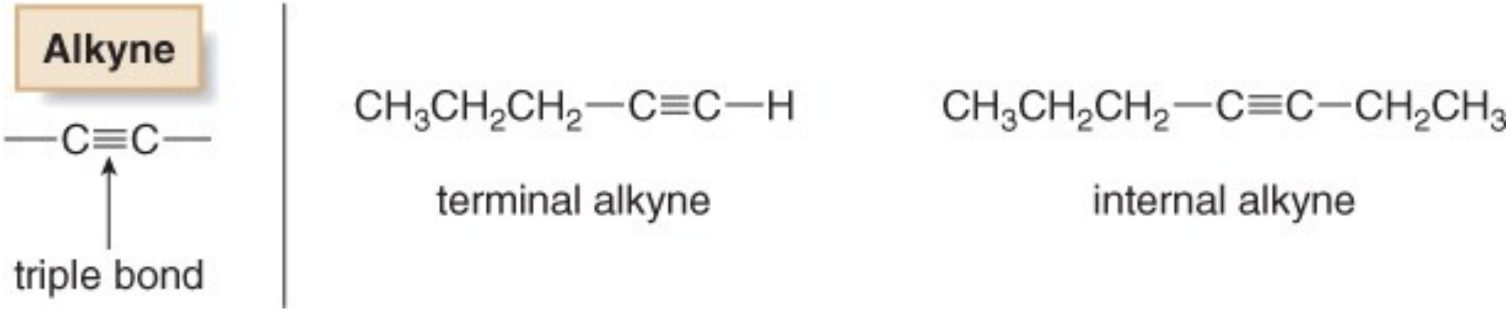
Chapter 9

Organic Chemistry, *8th Edition*

John E. McMurry

Structure and Bonding

General molecular formula C_nH_{2n-2}, Thus, the triple bond introduces two degrees of unsaturation.



Alkyne

$-C{\equiv}C-$

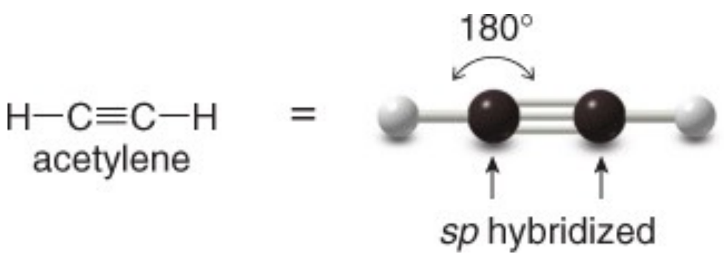
triple bond

$CH_3CH_2CH_2-C{\equiv}C-H$

terminal alkyne

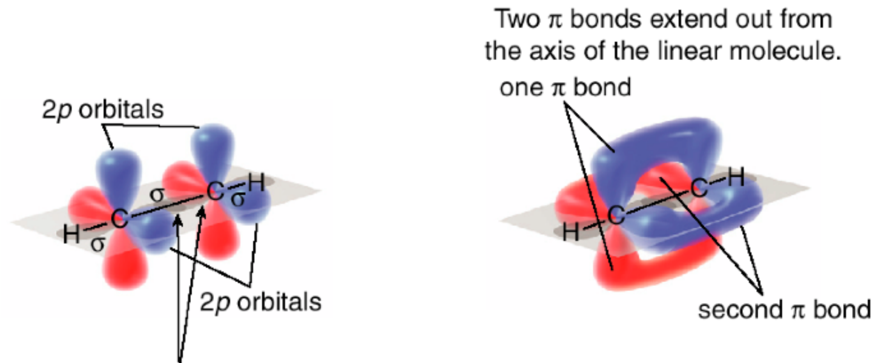
$CH_3CH_2CH_2-C{\equiv}C-CH_2CH_3$

internal alkyne



$H-C{\equiv}C-H$

acetylene



Overlap of the two *sp* hybrid orbitals forms the C–C σ bond.

Overlap of two sets of two 2*p* orbitals forms two C–C π bonds.

- **The σ bond is formed by end-on overlap of the two *sp* hybrid orbitals.**
- **Each π bond is formed by side-by-side overlap of two 2*p* orbitals.**

Structure and Bonding

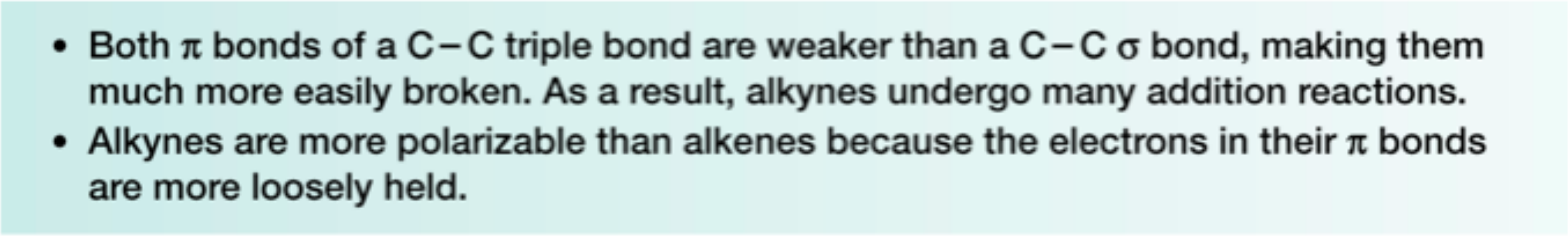
Alkynes are more reactive than alkenes

$$H_2C{=}CH_2 \longrightarrow H_3C{-}CH_3$$

152 Kcal/mol - 88 Kcal/mol = 64 Kcal/mol

$$HC{\equiv}CH \longrightarrow H_2C{=}CH_2$$

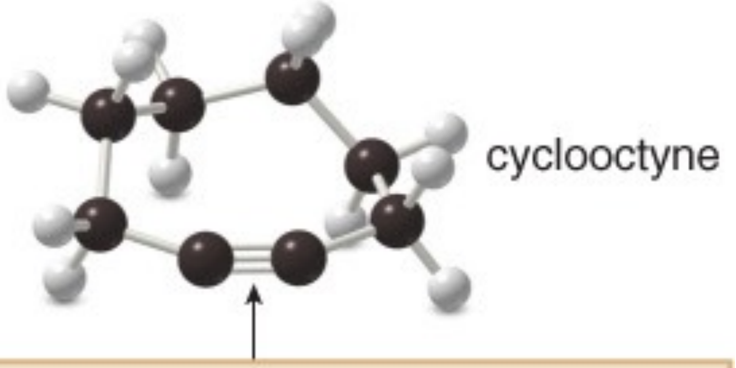
200 Kcal/mol - 152 Kcal/mol. = 48 Kcal/mol



- Both π bonds of a C–C triple bond are weaker than a C–C σ bond, making them much more easily broken. As a result, alkynes undergo many addition reactions.
- Alkynes are more polarizable than alkenes because the electrons in their π bonds are more loosely held.

Structure and Bonding

- Like trans cycloalkenes, cycloalkynes with small rings are unstable.
- **Cyclooctyne** is the smallest isolable cycloalkyne, though it decomposes upon standing at room temperature after a short time.

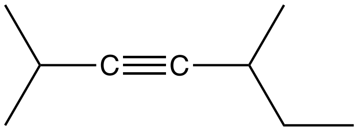


To accommodate the triple bond in a ring, bending occurs around the *sp* hybridized C's, destabilizing the molecule.

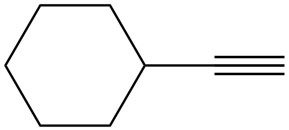
Nomenclature

$H-C\equiv C-H$ ethyne (acetylene)

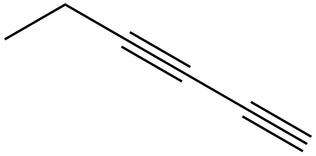
$H-C\equiv C-$ ethynyl



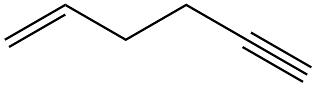
2,5-dimethyl-3-heptyne



ethynylcyclohexane



1,3-hexadiyne



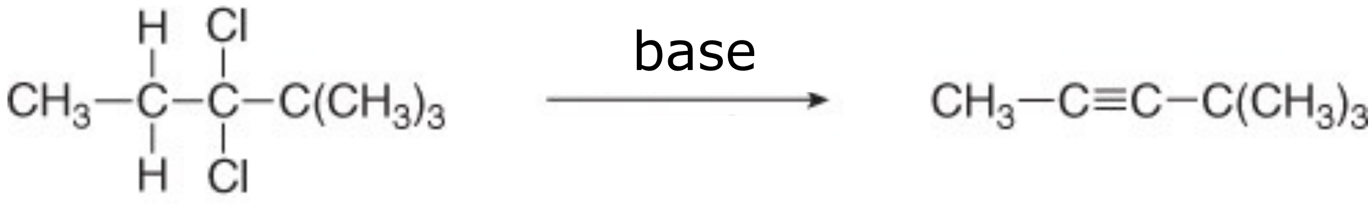
1-hexen-5-yne

Physical Properties

- The physical properties of alkynes resemble those of hydrocarbons of similar shape and molecular weight.
- Alkynes have low melting points and boiling points.
- Melting point and boiling point increase as the number of carbons increases.
- Alkynes are soluble in organic solvents and insoluble in water.

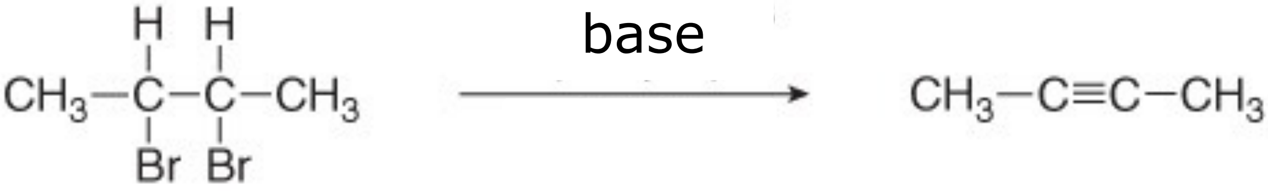
Preparation of Alkynes

Alkynes are prepared by elimination reactions.



$$CH_3-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{Cl}{C}}-C(CH_3)_3 \xrightarrow{\text{base}} CH_3-C\equiv C-C(CH_3)_3$$

geminal dichloride

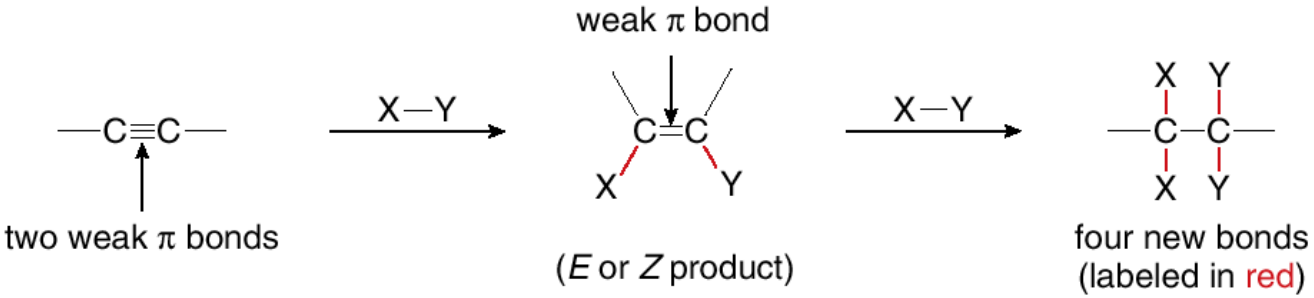


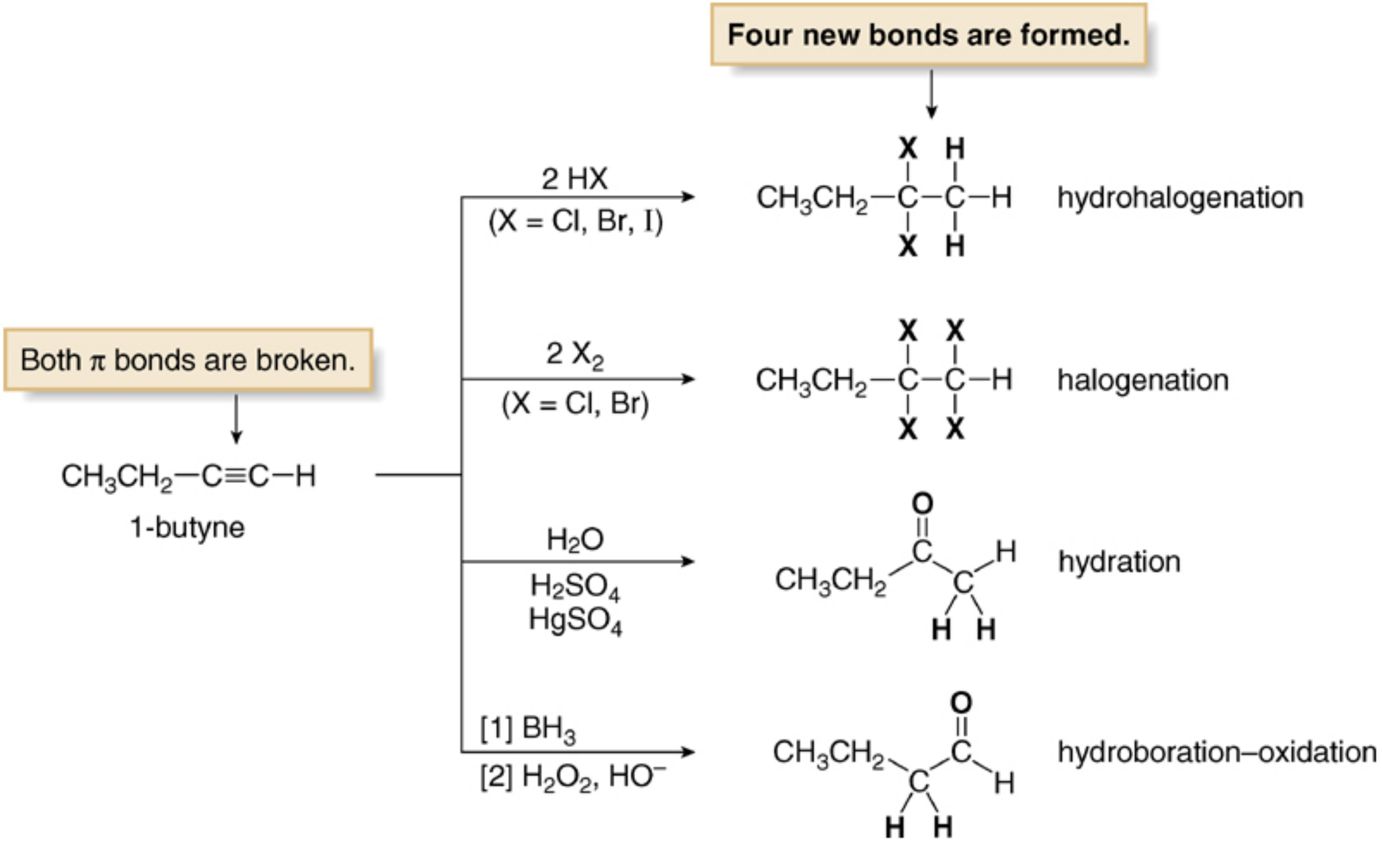
$$CH_3-\overset{H}{\underset{Br}{C}}-\overset{H}{\underset{Br}{C}}-CH_3 \xrightarrow{\text{base}} CH_3-C\equiv C-CH_3$$

vicinal dibromide

Alkyne Reactions—Additions

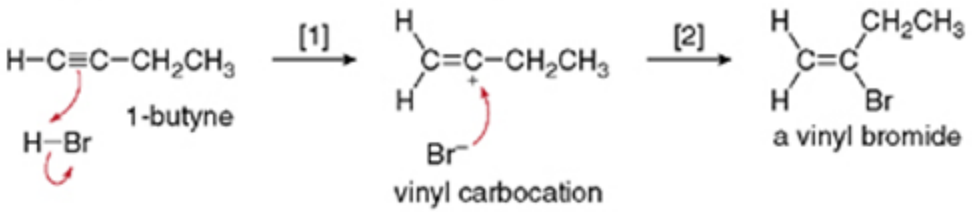
Addition reaction





Hydrohalogenation

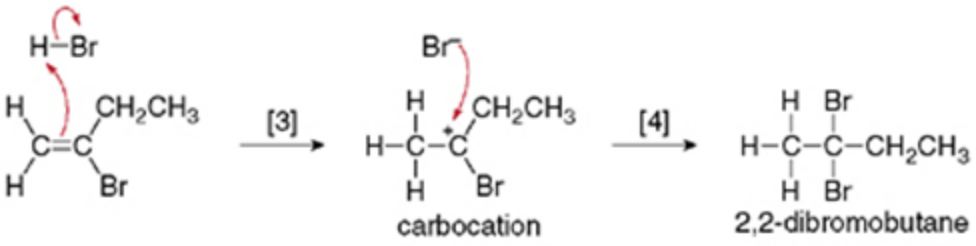
Part [1] Addition of HBr to form a vinyl halide



slower

(less stable vinyl cation)

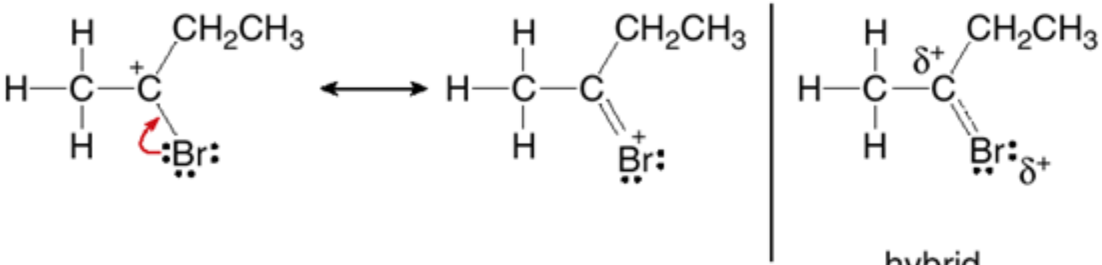
Part [2] Addition of HBr to form a geminal dihalide



faster

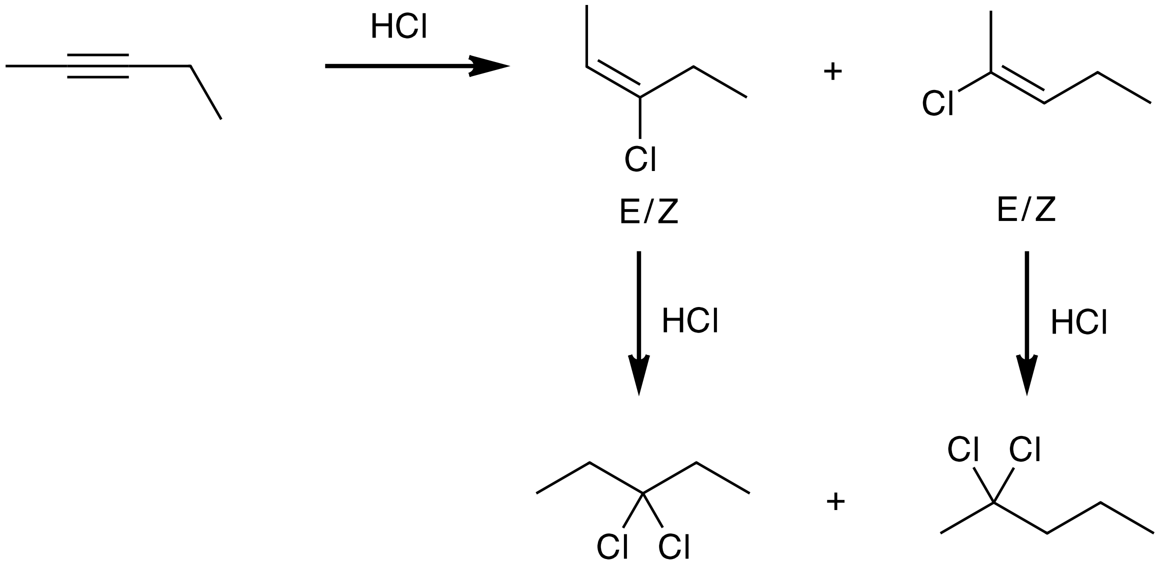
(more stable,

tertiary alkyl cation)



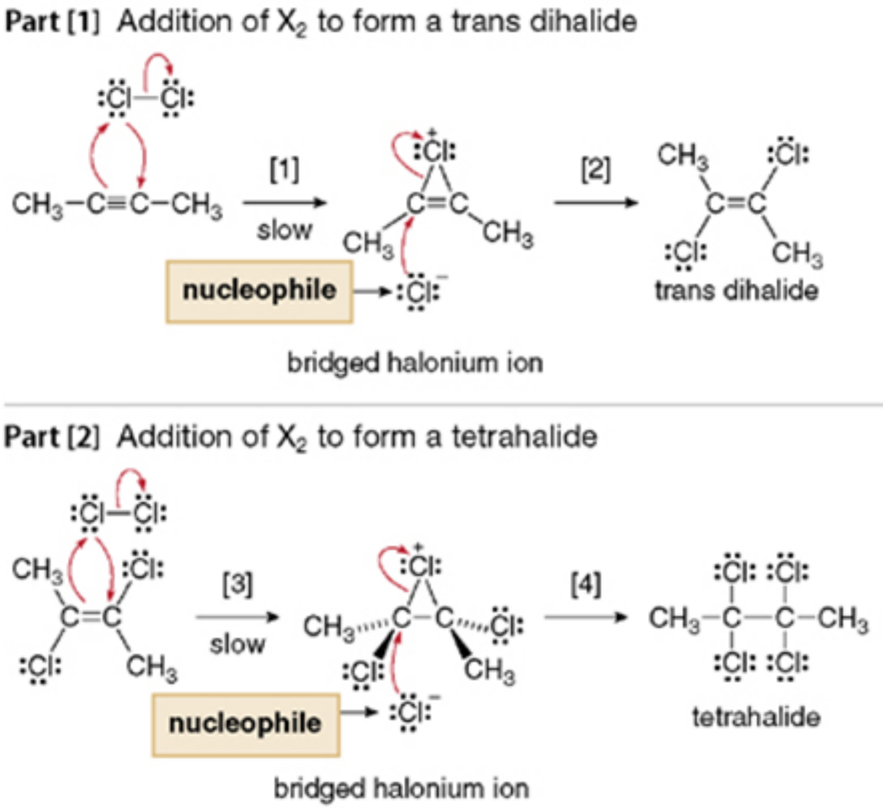
The positive charge is delocalized.

Hydrohalogenation



Not regioselective with internal alkynes

Halogenation



Part [1] Addition of X_2 to form a trans dihalide

Part [2] Addition of X_2 to form a tetrahalide

Hydration

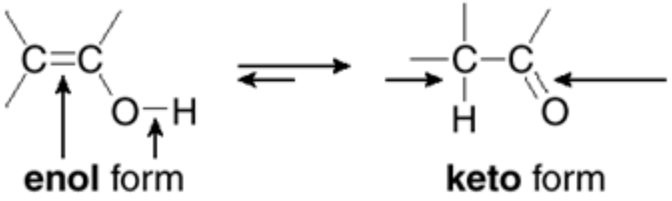
Hydration

H_2O has been added.

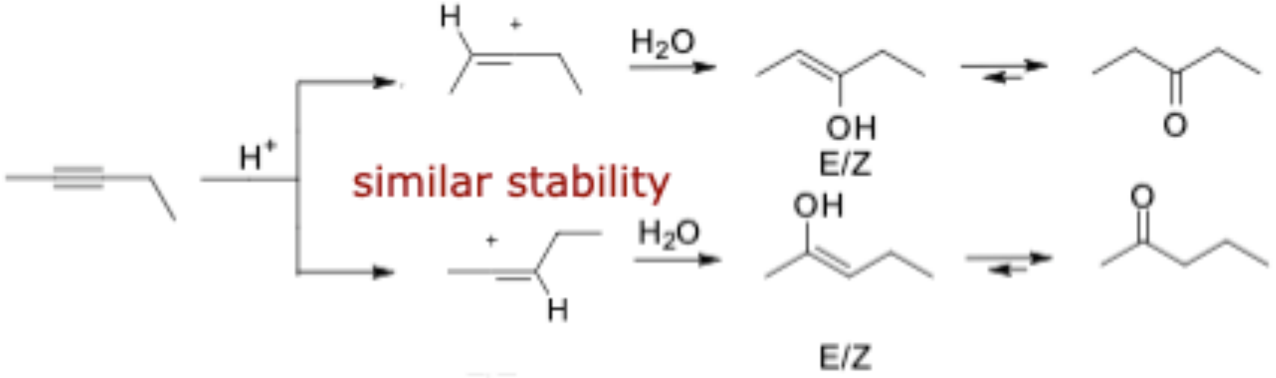
Equilibrium favors the keto form largely because the C=O is much stronger than a C=C.

- *Tautomers* are constitutional isomers that differ in the location of a double bond and a hydrogen atom. Two tautomers are in equilibrium with each other.

enol **ketone**



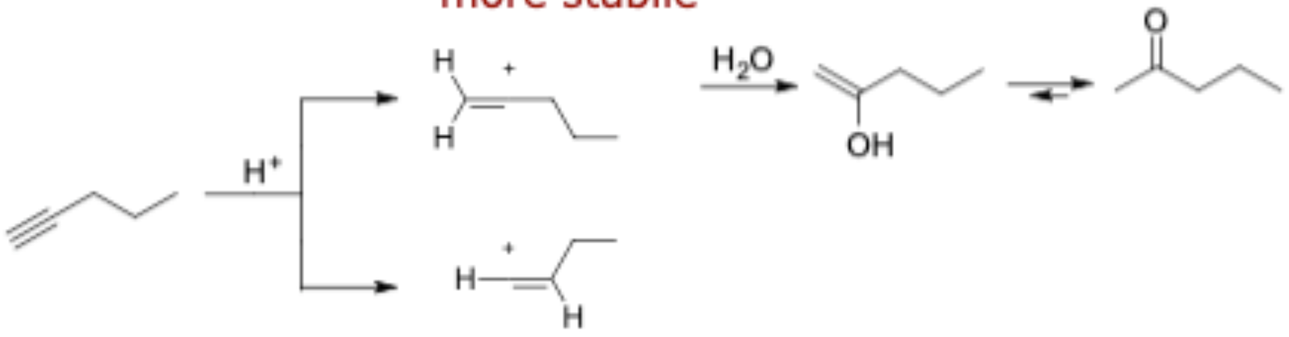
Hydration



similar stability

not regioselective

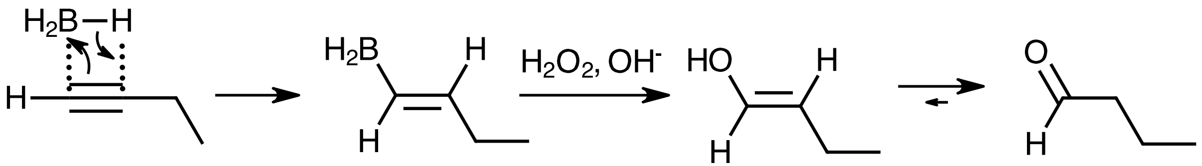
more stabile



less stabile

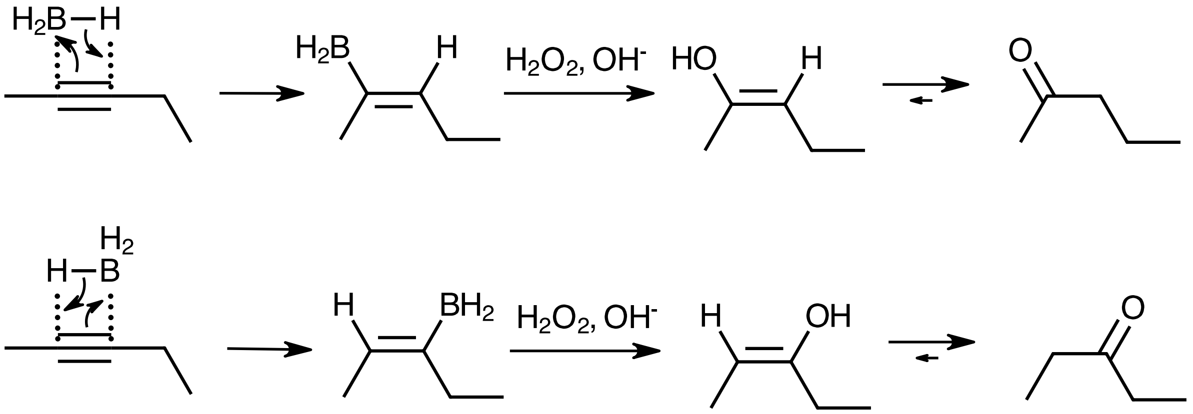
regioselective

Hydroboration—Oxidation



terminal
alkyne

aldehyde

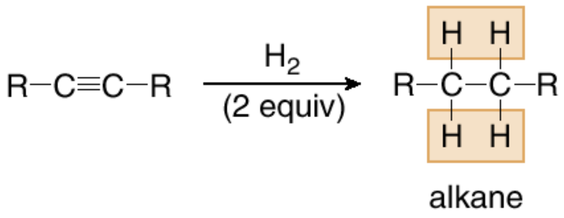


internal
alkyne

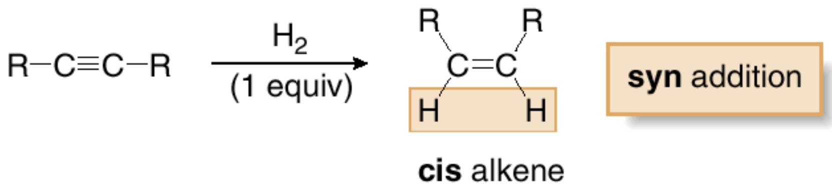
isomeric
Ketones

Reduction of Alkynes

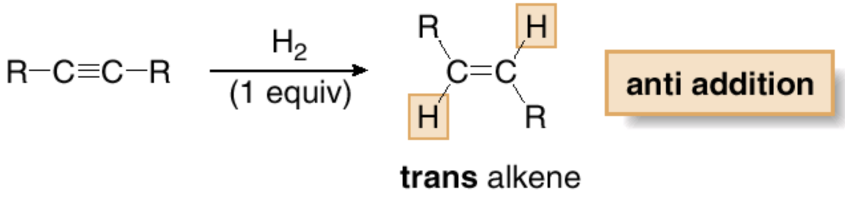
- Adding two equivalents of H_2 forms an alkane.



- Adding one equivalent of H_2 in a syn fashion forms a cis alkene.



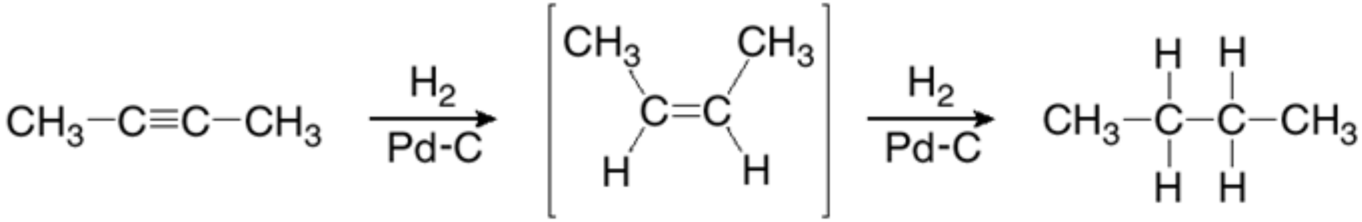
- Adding one equivalent of H_2 in an anti fashion forms a trans alkene.



Catalytic Hydrogenation

Alkanes:

Example

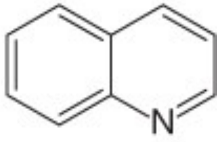


Cis-Alkenes:

- Palladium metal is too reactive to allow hydrogenation of an alkyne to stop after one equivalent of H_2 adds.
- To stop at a cis alkene, a less active Pd catalyst is used - Pd adsorbed onto $CaCO_3$ with added lead(II) acetate and quinoline. This is called Lindlar's catalyst.

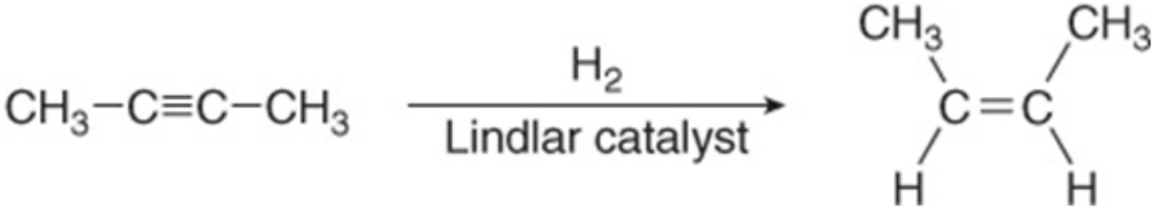
Pd on $CaCO_3$
+ $Pb(OCOCH_3)_2$ + quinoline

Lindlar catalyst

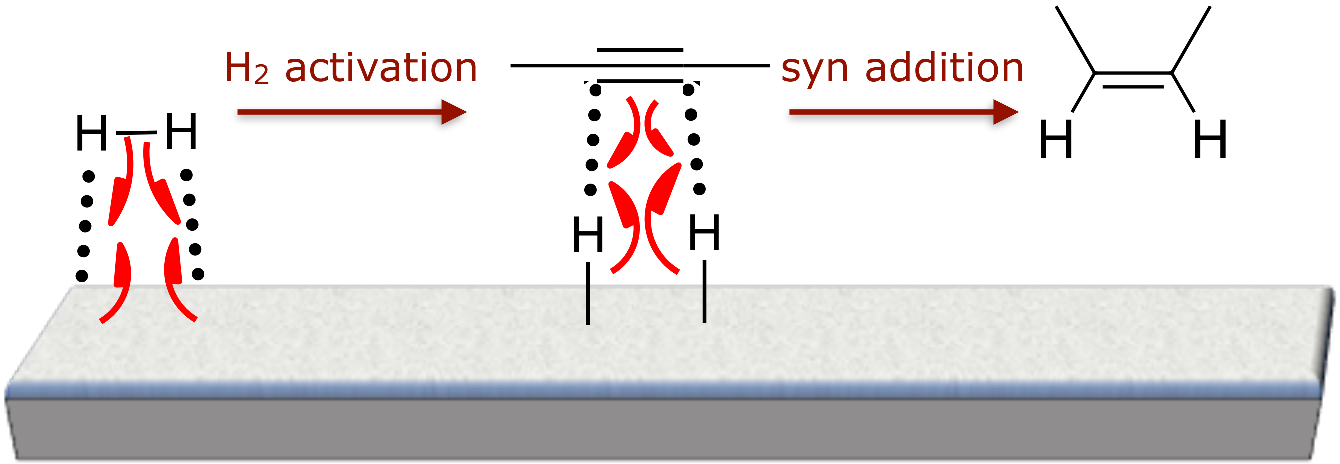


quinoline

Example



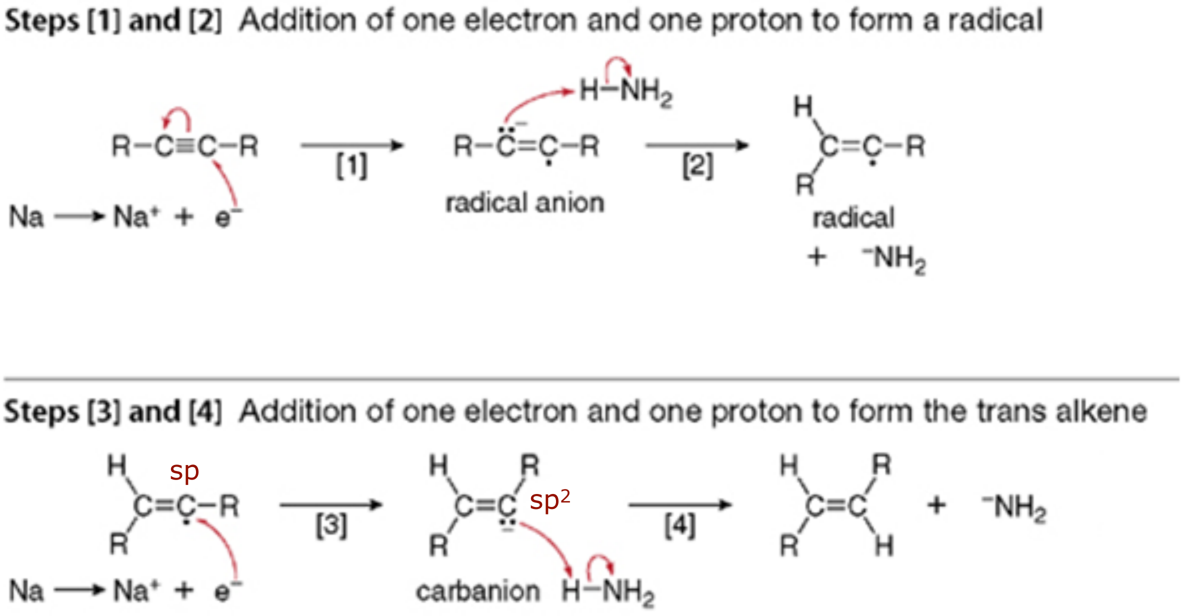
Catalytic Hydrogenation



H_2 activation

syn addition

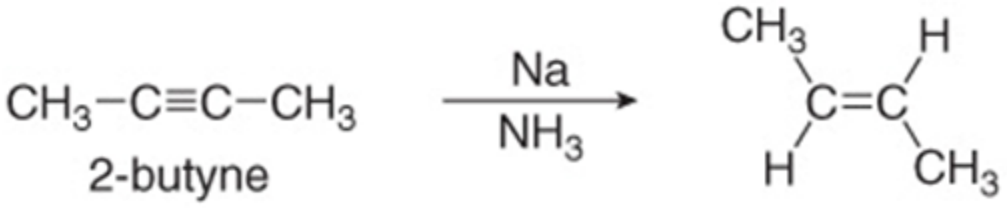
Dissolving Metal Reduction



Steps [1] and [2] Addition of one electron and one proton to form a radical

Steps [3] and [4] Addition of one electron and one proton to form the trans alkene

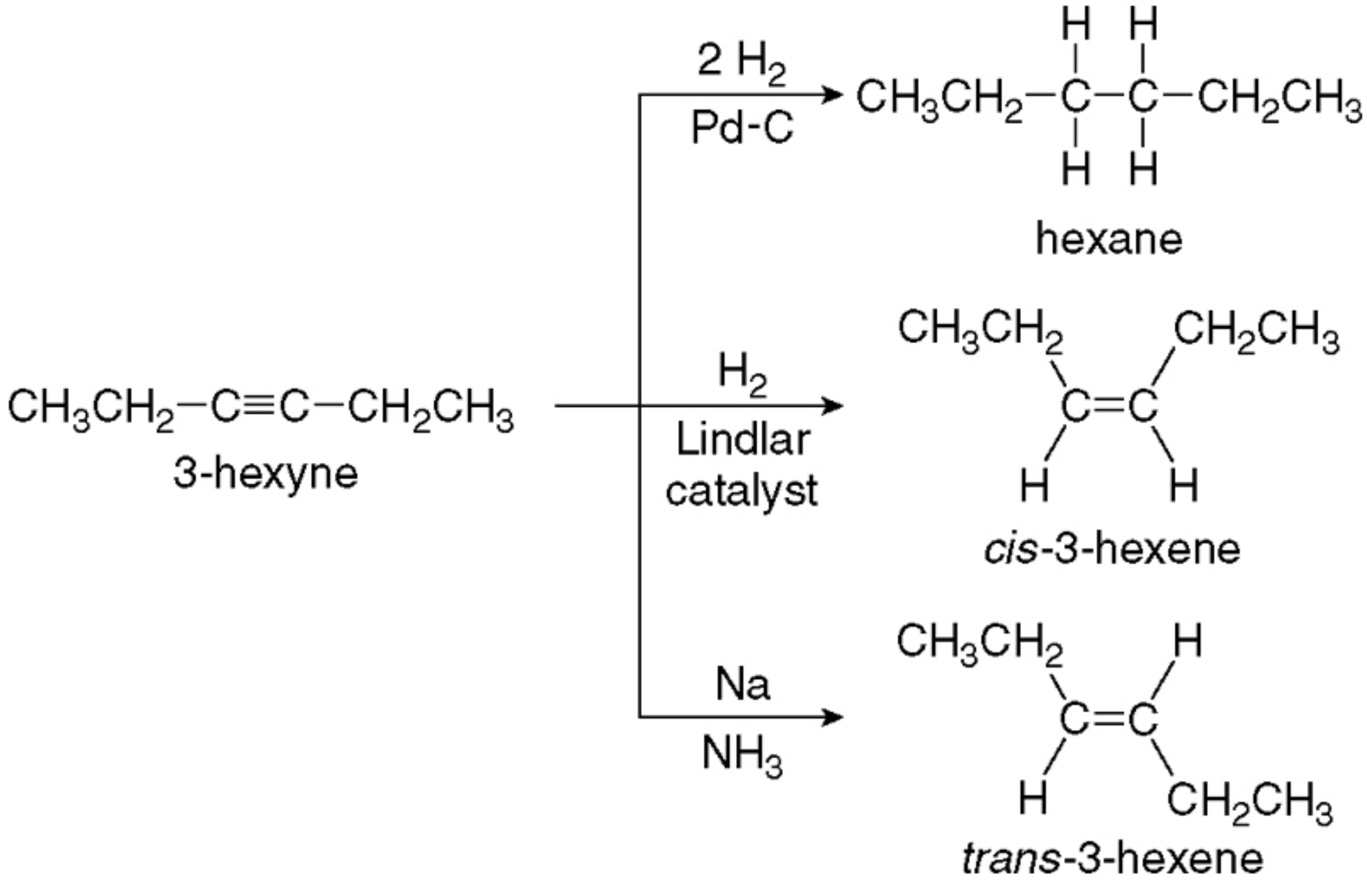
Example



$CH_3-C\equiv C-CH_3 \xrightarrow[NH_3]{Na}$

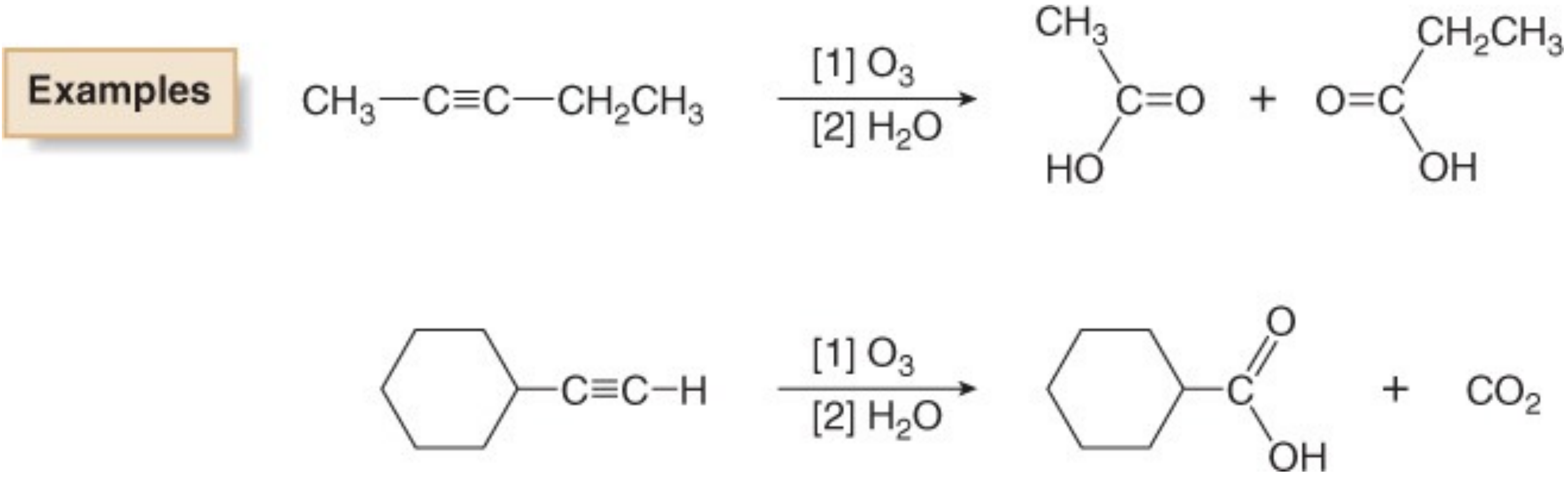
trans-2-butene

Summary of Alkyne Reductions

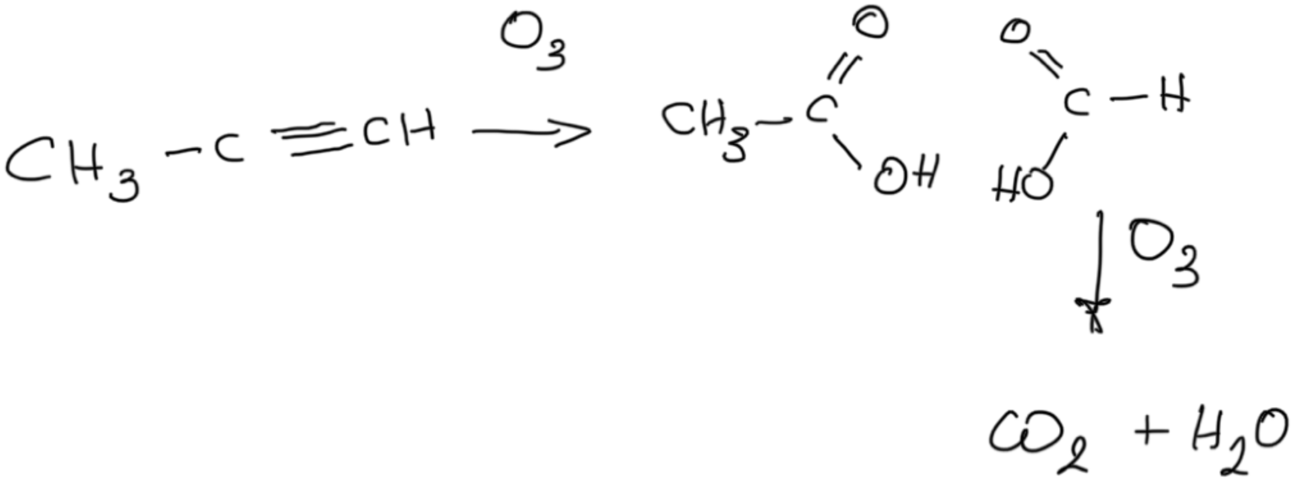


Oxidative Cleavage of Alkynes

- Internal alkynes are oxidized to carboxylic acids (RCOOH).
- Terminal alkynes afford a carboxylic acid and CO_2 from the *sp* hybridized C—H bond.



Oxidative Cleavage of Alkynes



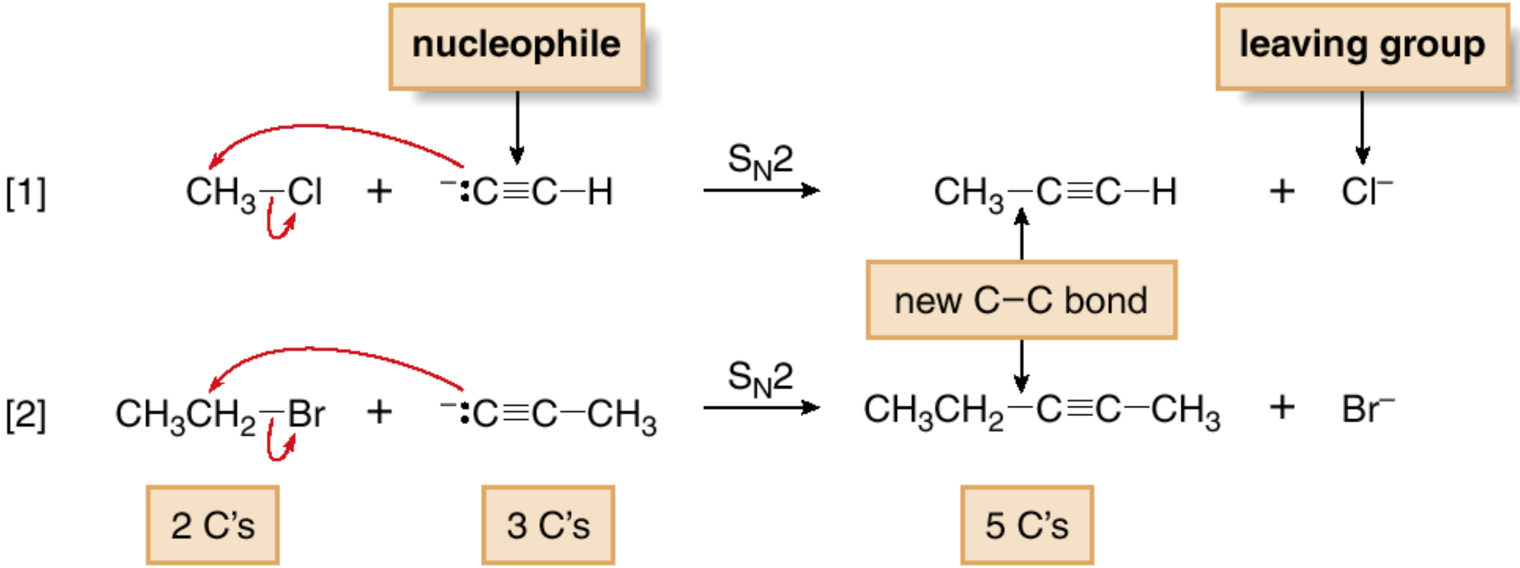
Acetylide anions

	Base	pK_a of the conjugate acid
These bases are **strong** enough to deprotonate an alkyne.	$^-NH_2$	38
	H^-	35
These bases are ***not*** strong enough to deprotonate an alkyne.	^-OH	15.7
	^-OR	15.5–18

Acetylide Anions

- Acetylide anions are strong nucleophiles and react with methyl and 1° alkyl halides to yield products of nucleophilic substitution.

- Acetylide anions do not react with 2° and 3° alkyl halides.

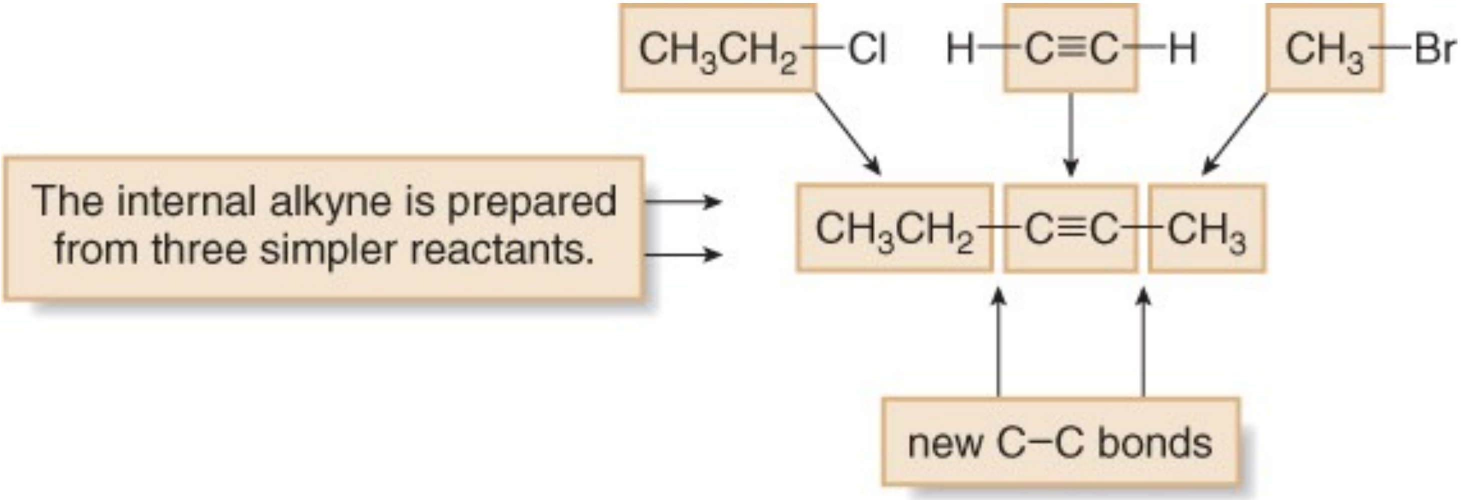


$$[1]\quad CH_3{-}Cl + {}^{-}{:}C{\equiv}C{-}H \xrightarrow{S_N2} CH_3{-}C{\equiv}C{-}H + Cl^-$$

$$[2]\quad CH_3CH_2{-}Br + {}^{-}{:}C{\equiv}C{-}CH_3 \xrightarrow{S_N2} CH_3CH_2{-}C{\equiv}C{-}CH_3 + Br^-$$

- Nucleophilic substitution with acetylide anions forms new carbon–carbon bonds.

Acetylide anions



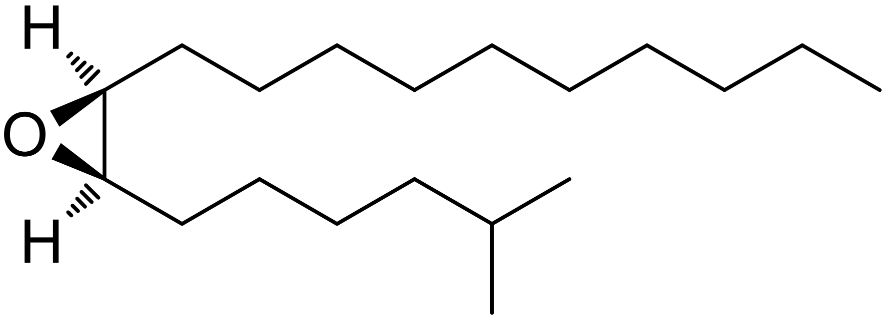
CH_3CH_2-Cl $H-C\equiv C-H$ CH_3-Br

The internal alkyne is prepared from three simpler reactants.

$CH_3CH_2-C\equiv C-CH_3$

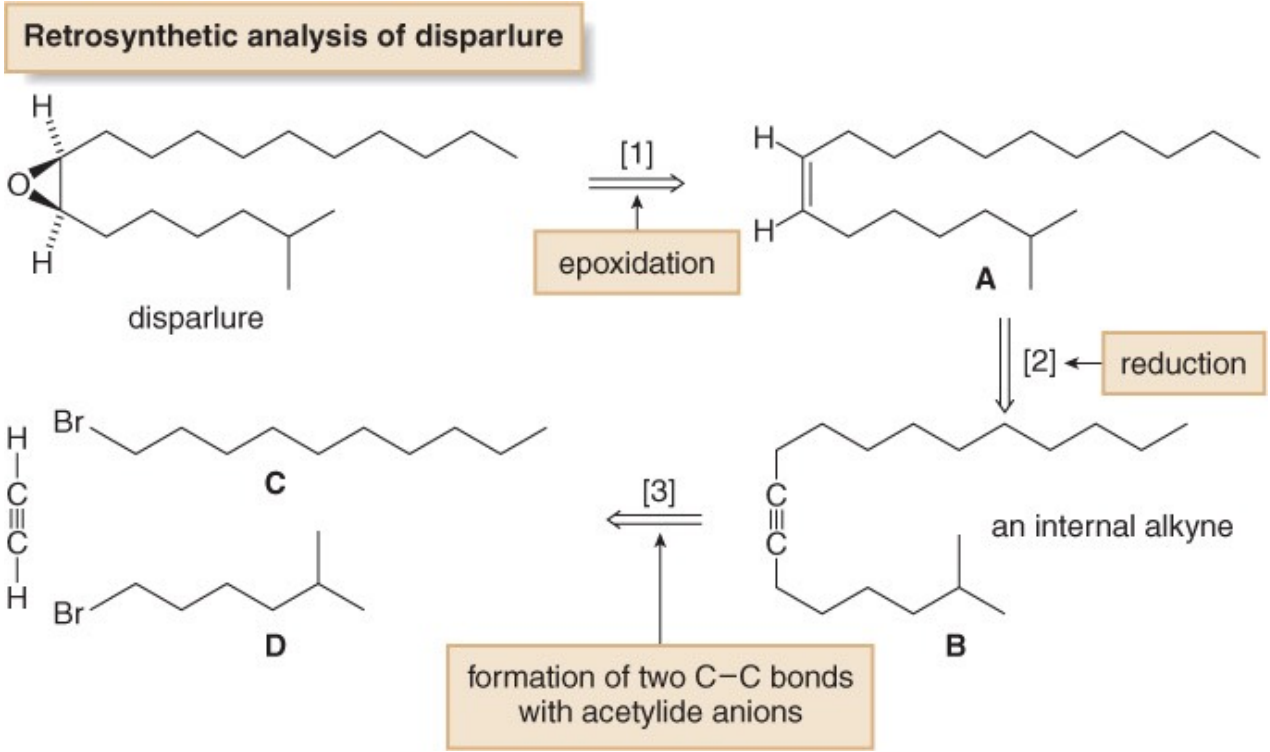
new C–C bonds

Synthesis

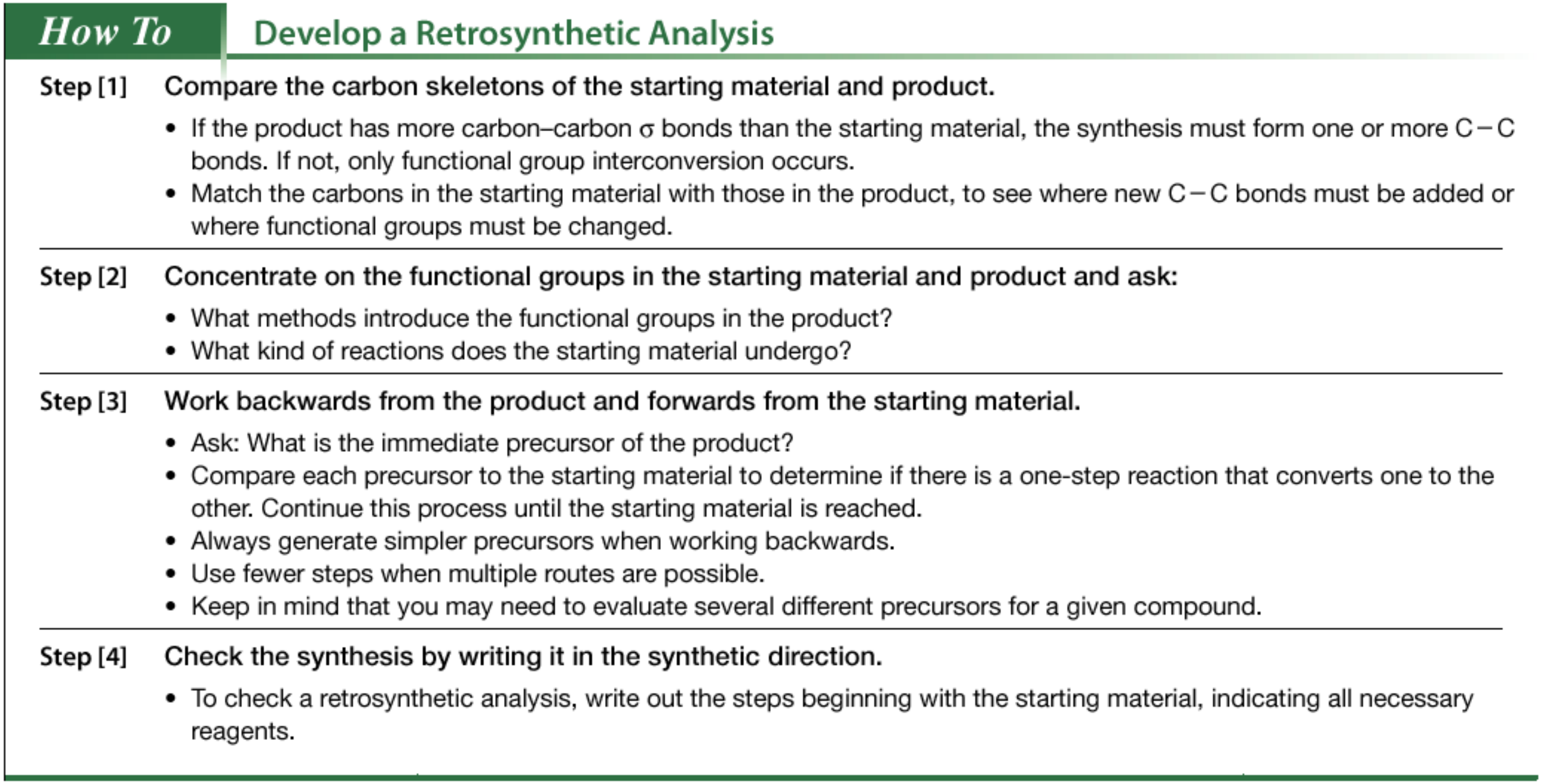


Disparlure – a pheromone

Synthesis


Retrosynthetic analysis of disparlure
H
O
H
disparlure
[1]
epoxidation
H
H
A
[2]
reduction
C
C
an internal alkyne
B
[3]
formation of two C–C bonds with acetylide anions
H
C
C
H
Br
C
Br
D

Synthesis



How To Develop a Retrosynthetic Analysis

Step [1] **Compare the carbon skeletons of the starting material and product.**

- If the product has more carbon–carbon σ bonds than the starting material, the synthesis must form one or more C – C bonds. If not, only functional group interconversion occurs.
- Match the carbons in the starting material with those in the product, to see where new C – C bonds must be added or where functional groups must be changed.

Step [2] **Concentrate on the functional groups in the starting material and product and ask:**

- What methods introduce the functional groups in the product?
- What kind of reactions does the starting material undergo?

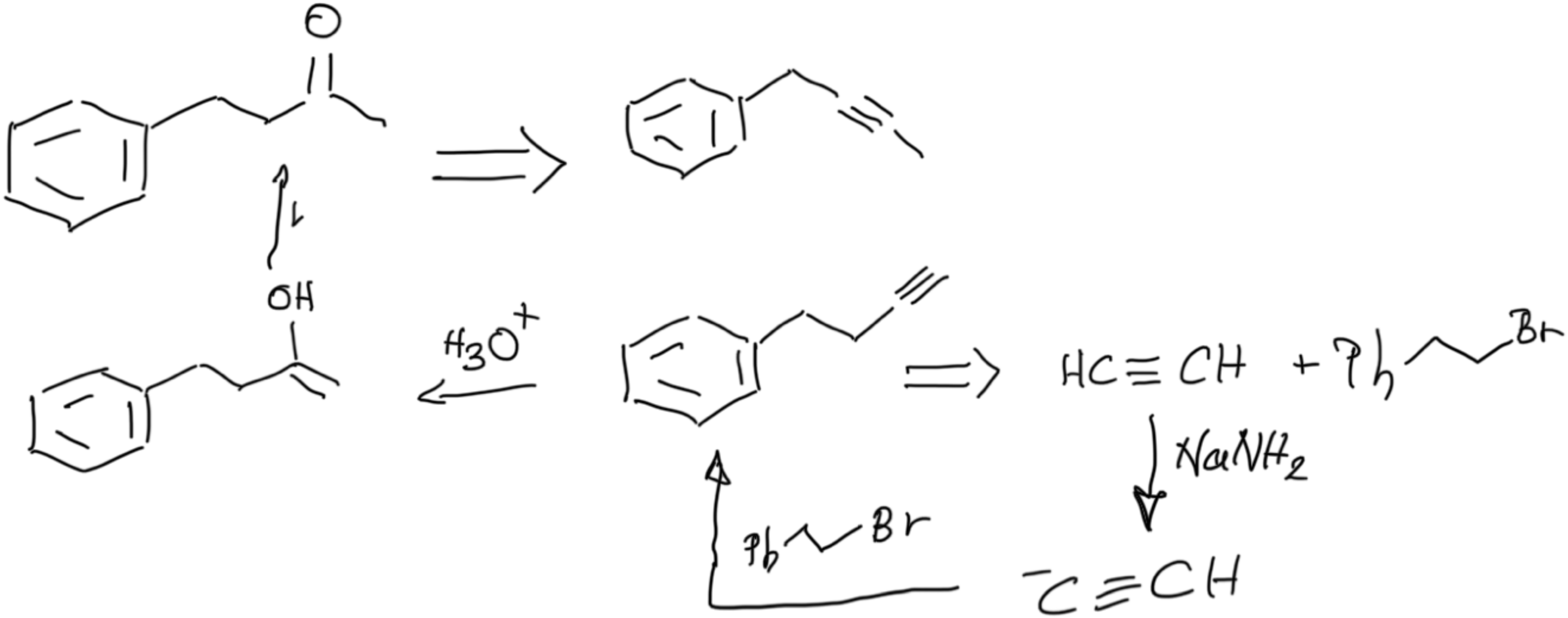
Step [3] **Work backwards from the product and forwards from the starting material.**

- Ask: What is the immediate precursor of the product?
- Compare each precursor to the starting material to determine if there is a one-step reaction that converts one to the other. Continue this process until the starting material is reached.
- Always generate simpler precursors when working backwards.
- Use fewer steps when multiple routes are possible.
- Keep in mind that you may need to evaluate several different precursors for a given compound.

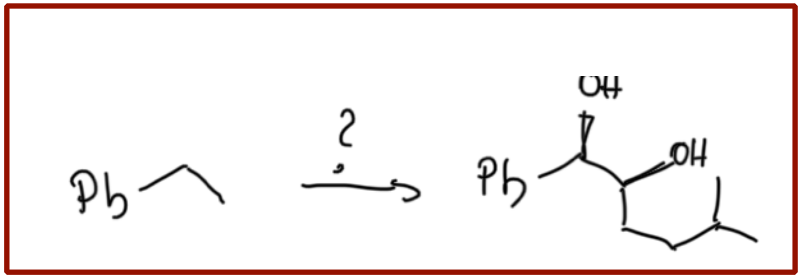
Step [4] **Check the synthesis by writing it in the synthetic direction.**

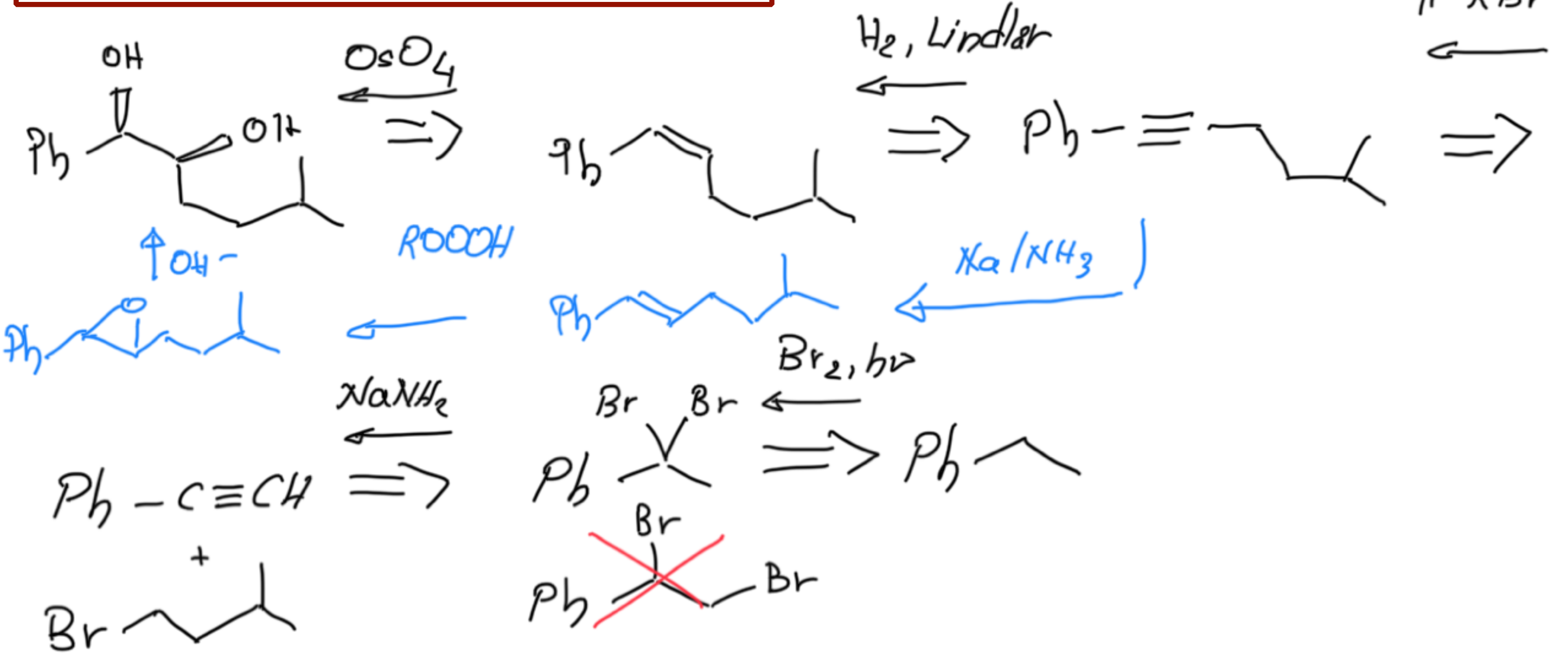
- To check a retrosynthetic analysis, write out the steps beginning with the starting material, indicating all necessary reagents.

Synthesis



Synthesis


Ph
?
Ph
OH
OH


i NaNH2
ii RBr
H2, Lindlar
OsO4
OH
Ph
OH
Ph
Ph–≡
ROOOH
Na/NH3
OH⁻
Ph
O
Ph
Br2, hν
NaNH2
Br
Br
Ph
Ph
Ph–C≡CH
+
Br
Br
Ph
Br