Alkynes

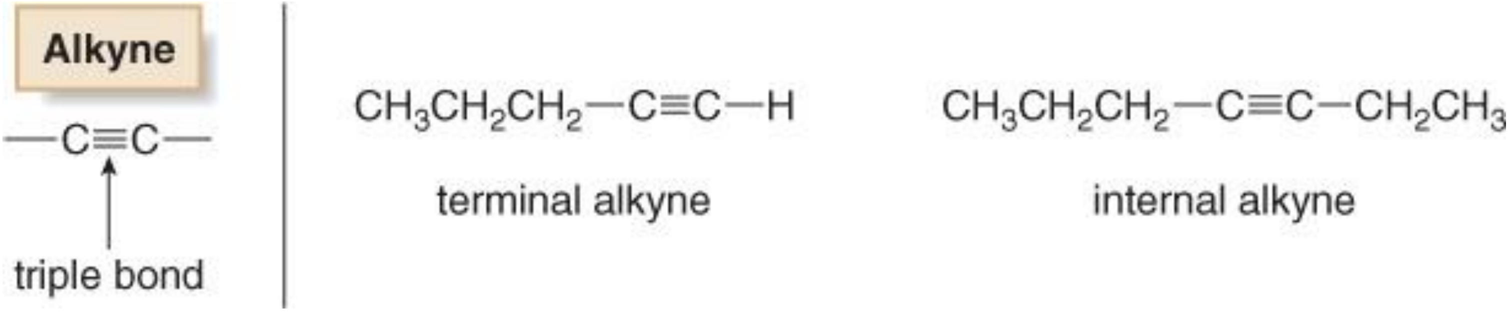
Chapter 9

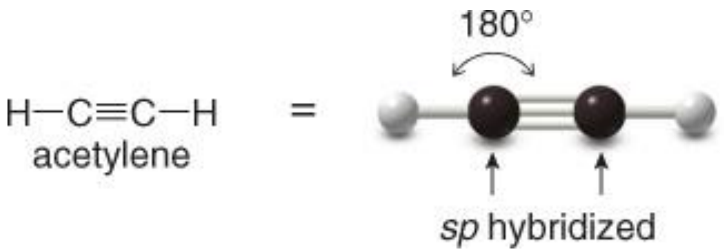
Organic Chemistry, *8th Edition*

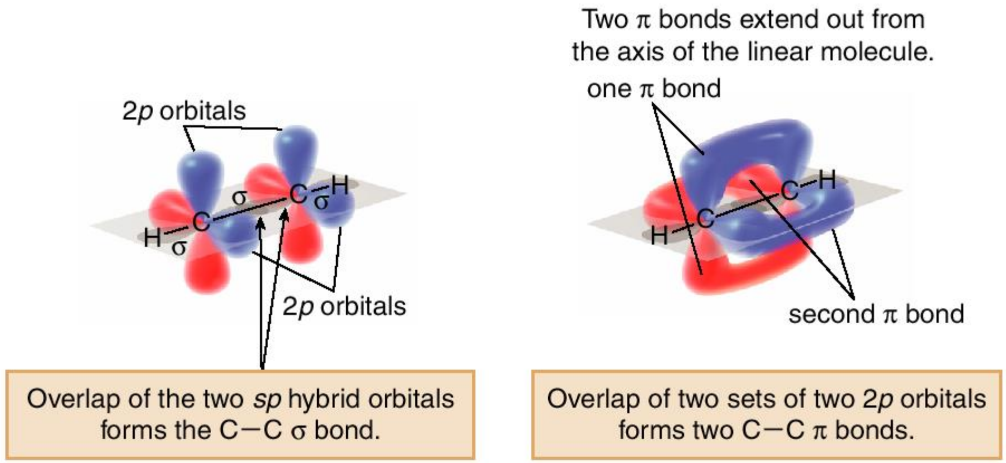
John E. McMurry

Structure and Bonding

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







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

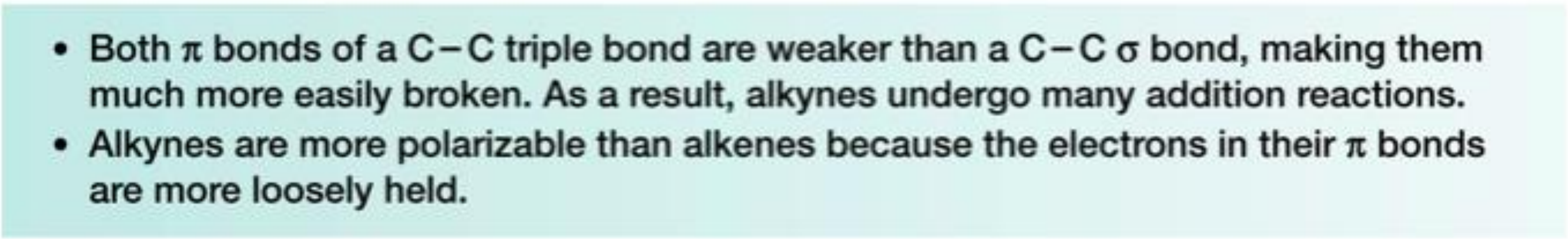
Alkynes are more reactive than alkenes

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

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

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

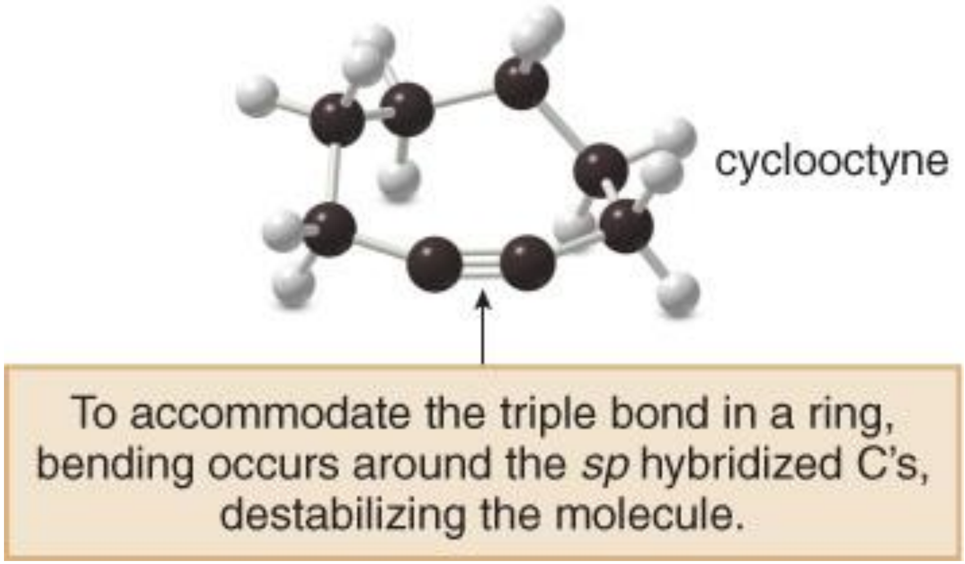
200 Kcal/mol - 152 Kcal/mol. = 48 Kcal/mol



- 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.



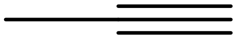
To accommodate the triple bond in a ring, bending occurs around the *sp* hybridized C's, destabilizing the molecule.

modelli 3D

Nomenclature

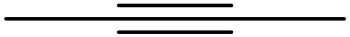
$H-C\equiv C-H$ ethyne (acetylene)

$H-C\equiv C-$ ethynyl

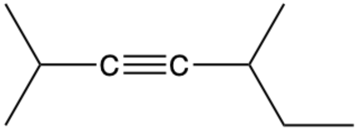


propyne

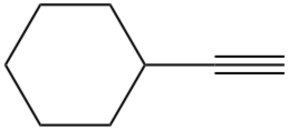
1-butyne



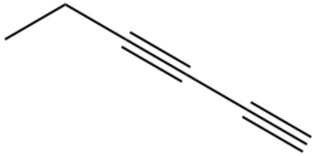
2-butyne



2,5-dimethyl-3-heptyne



ethynylcyclohexane



1,3-hexadiyne

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.

Acetylene

- The combustion of acetylene releases more energy per mole of oxygen consumed than any other hydrocarbons. It burns with a very hot flame (3300 °C) and is an excellent fuel.

Reaction	**ΔH/mol O_2 (Kcal/mol)**
$H_3C{-}CH_3 + 7/2\ O_2 \longrightarrow 2\ CO_2 + 3\ H_2O$	***-442***
$H_2C{=}CH_2 + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O$	***-467***
$HC{\equiv}CH + 5/2\ O_2 \longrightarrow 2\ CO_2 + H_2O$	***-520***

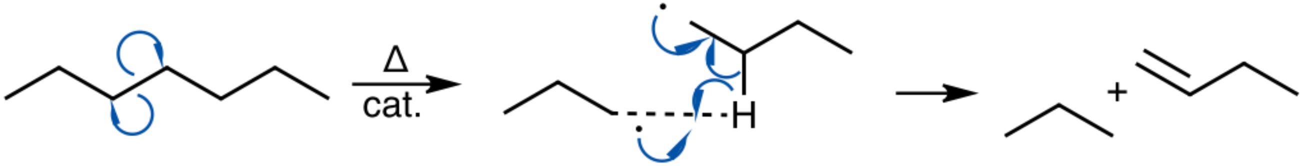
Acetylene

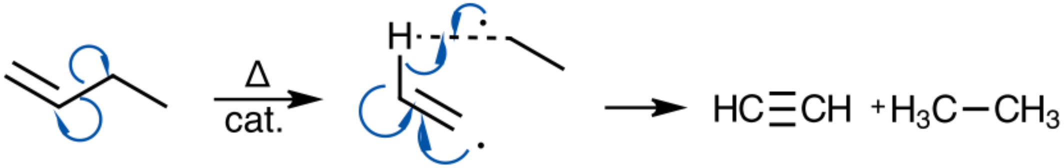
- From coal:

$$\mathrm{CaO + 3C \xrightarrow{2200\ °C} CaC_2 + CO}$$

$$\mathrm{CaC_2 + 2\,H_2O \longrightarrow Ca(OH)_2 + C_2H_2}$$

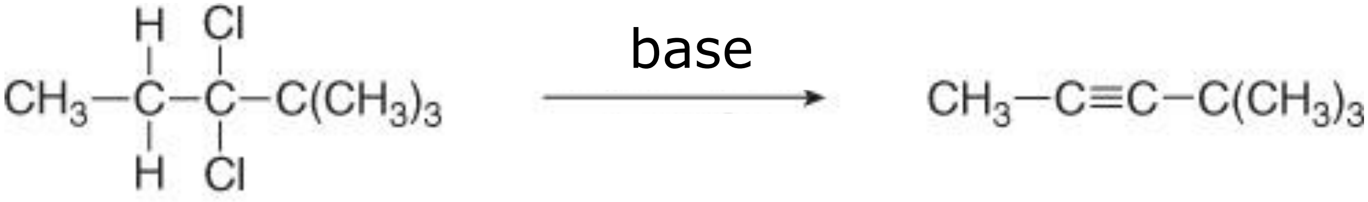
- From oil (cracking):





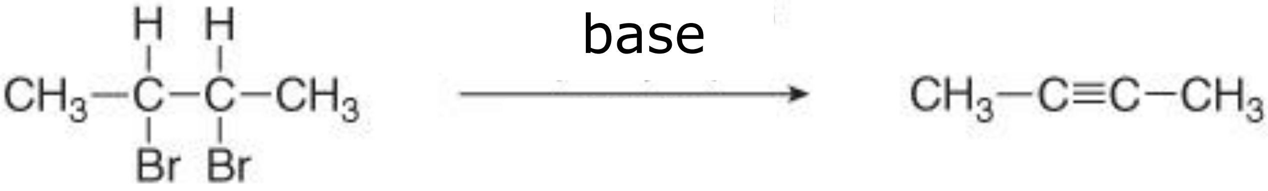
Preparation of Alkynes

Alkynes are prepared by elimination reactions.



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

geminal dichloride

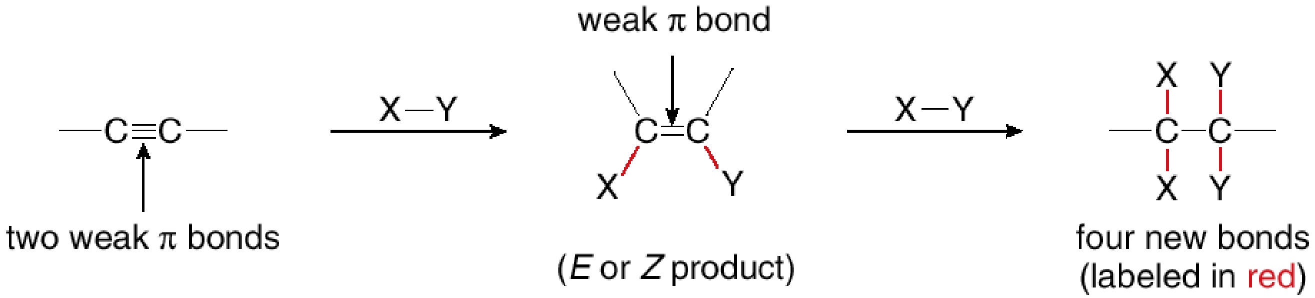


$$CH_3-\underset{Br}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}-CH_3 \xrightarrow{\text{base}} CH_3-C\equiv C-CH_3$$

vicinal dibromide

Alkyne Reactions—Additions

Addition reaction



$-C\equiv C-$ two weak π bonds

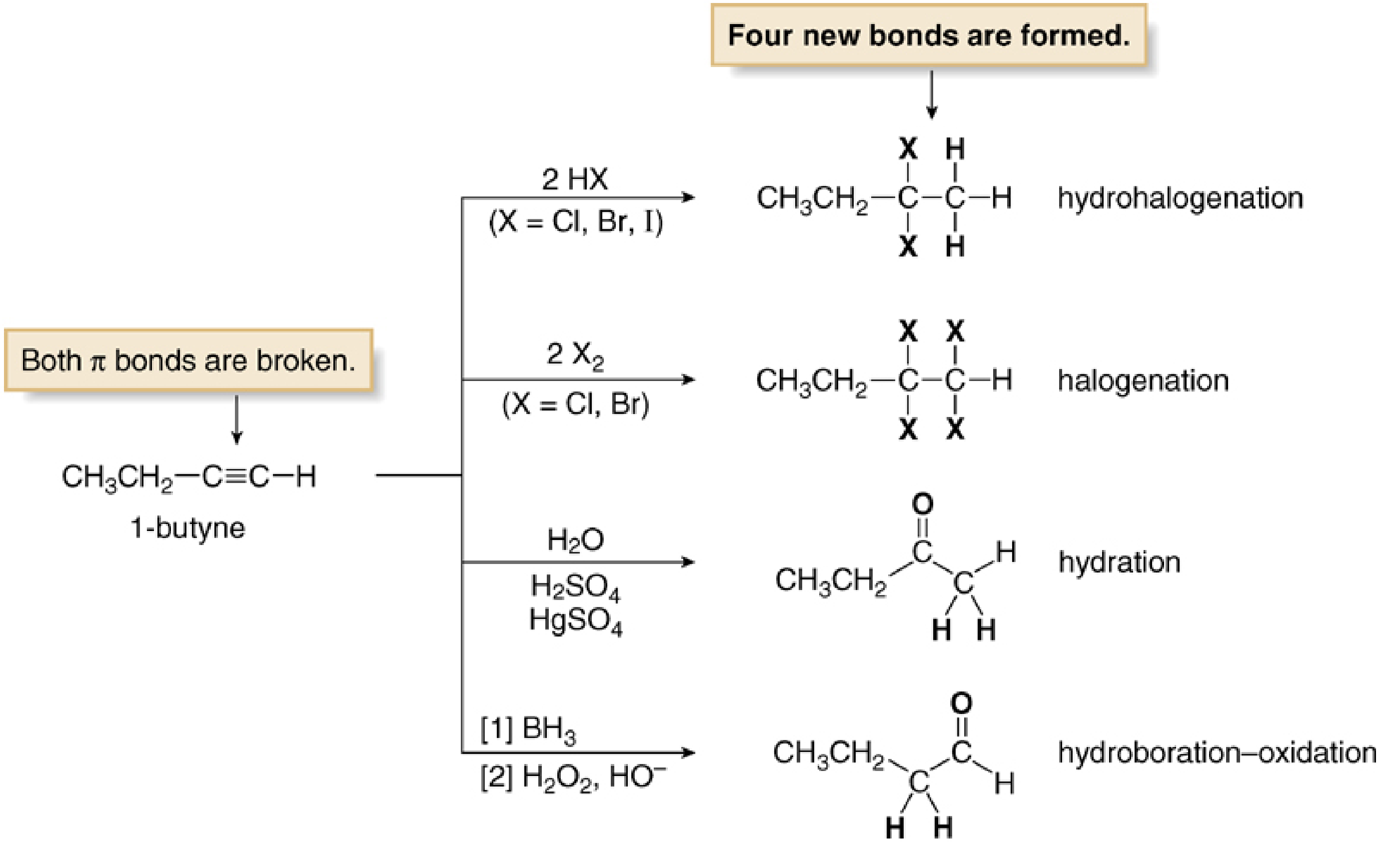
$\xrightarrow{X-Y}$

weak π bond

(*E* or *Z* product)

$\xrightarrow{X-Y}$

four new bonds (labeled in red)



Four new bonds are formed.

Both π bonds are broken.

$CH_3CH_2-C\equiv C-H$

1-butyne

2 HX (X = Cl, Br, I) → hydrohalogenation

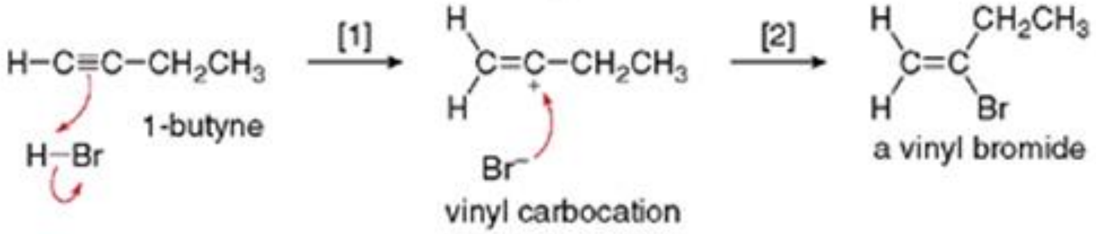
$2\ X_2$ (X = Cl, Br) → halogenation

H_2O, H_2SO_4, $HgSO_4$ → hydration

[1] BH_3 [2] H_2O_2, HO^- → hydroboration–oxidation

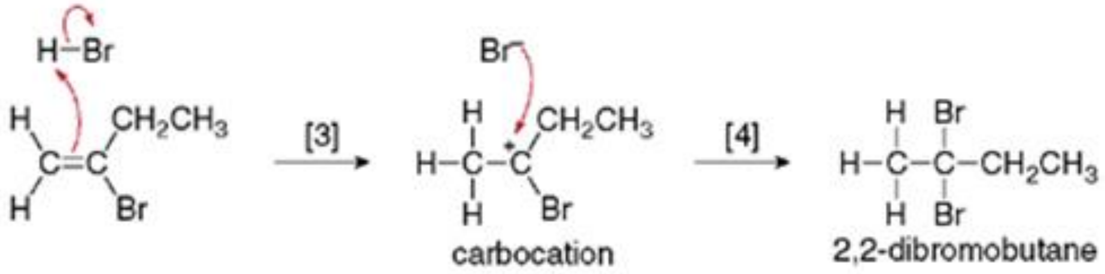
Hydrohalogenation

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

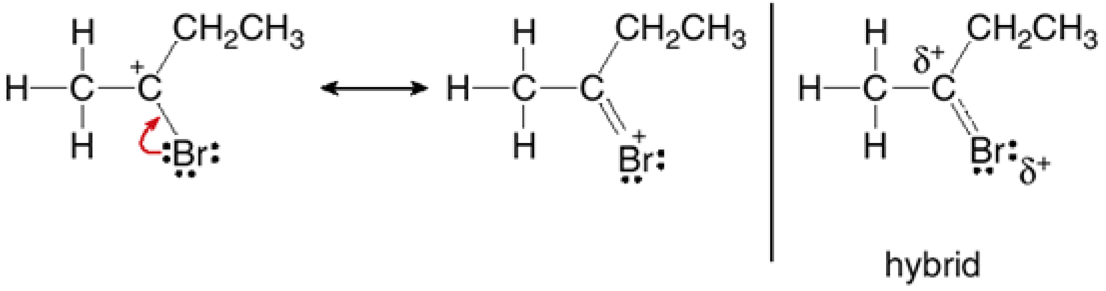


slower
(less stable vinyl cation)

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

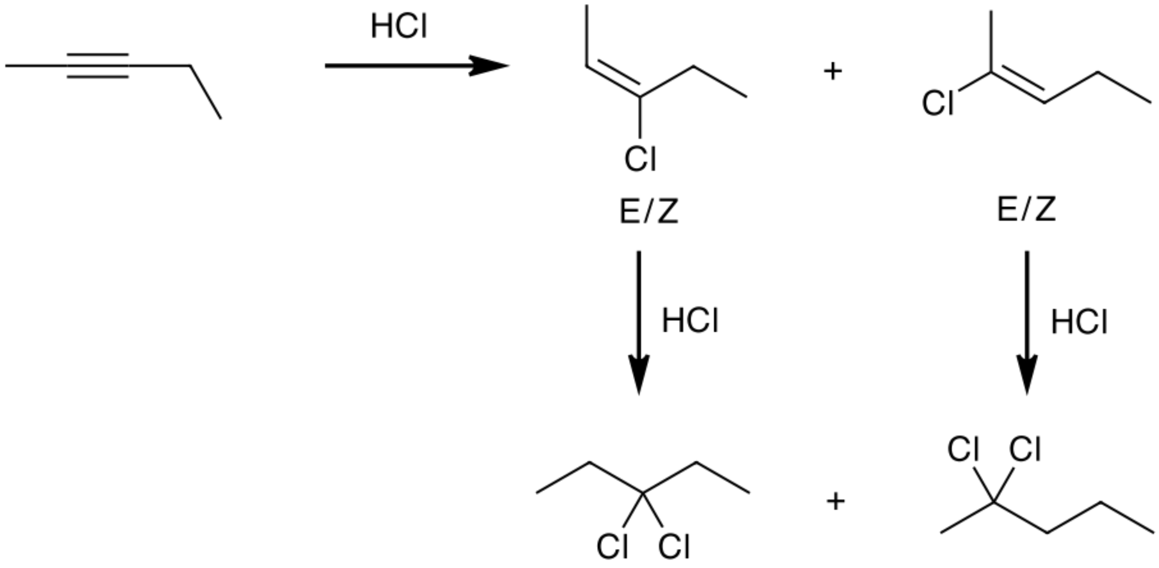


faster
(more stable,
secondary alkyl cation)



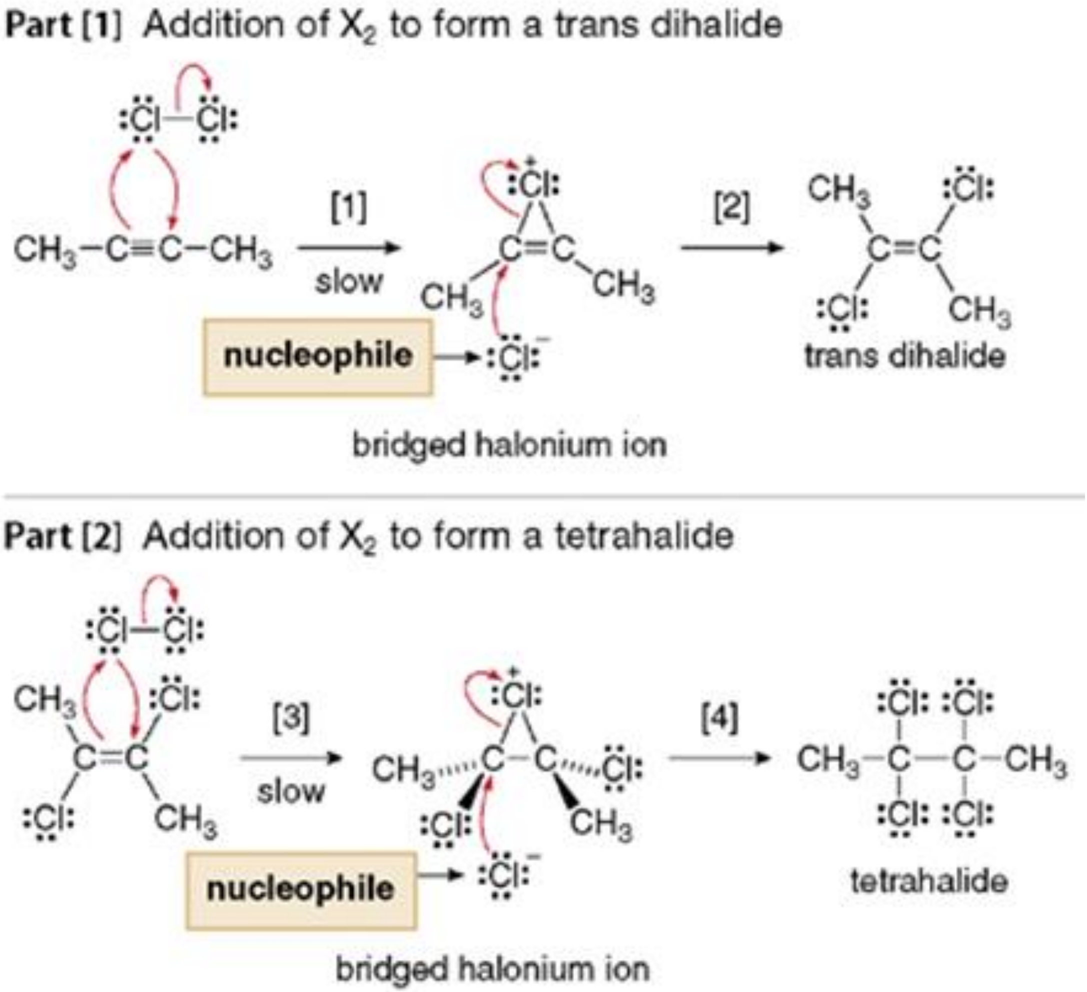
The positive charge is delocalized.

Hydrohalogenation



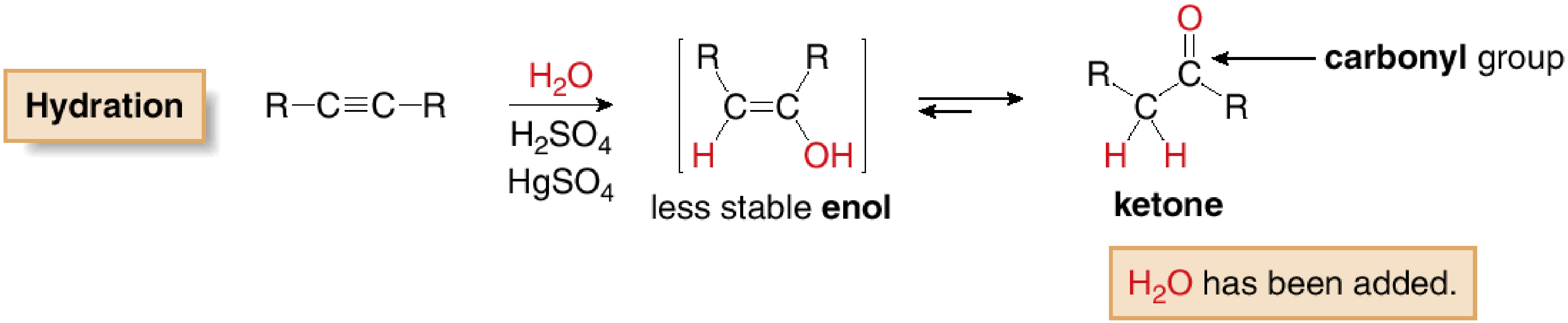
Not regioselective with internal alkynes

Halogenation


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

Part [2] Addition of X_2 to form a tetrahalide

Hydration



Hydration

$R-C\equiv C-R \xrightarrow[H_2SO_4,\ HgSO_4]{H_2O}$

less stable **enol**

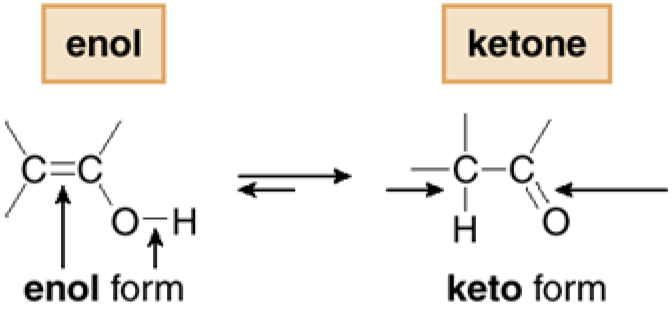
ketone

carbonyl group

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

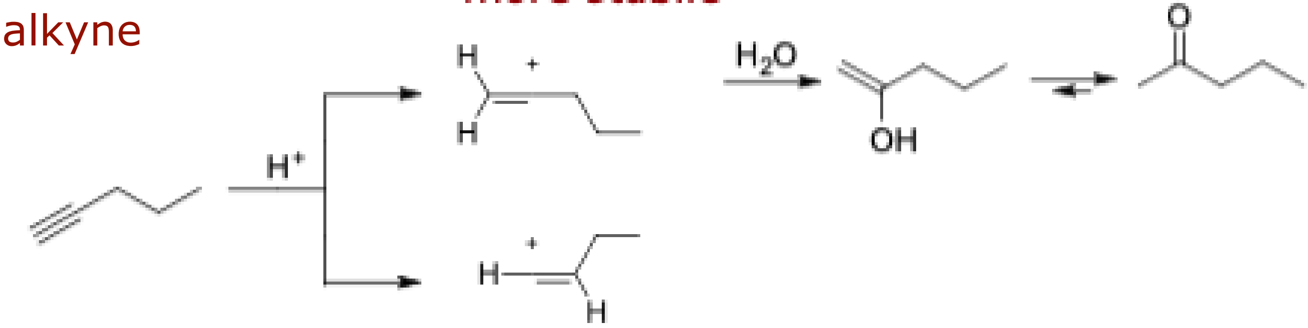
ketone

enol form

keto form

Hydration

terminal
alkyne

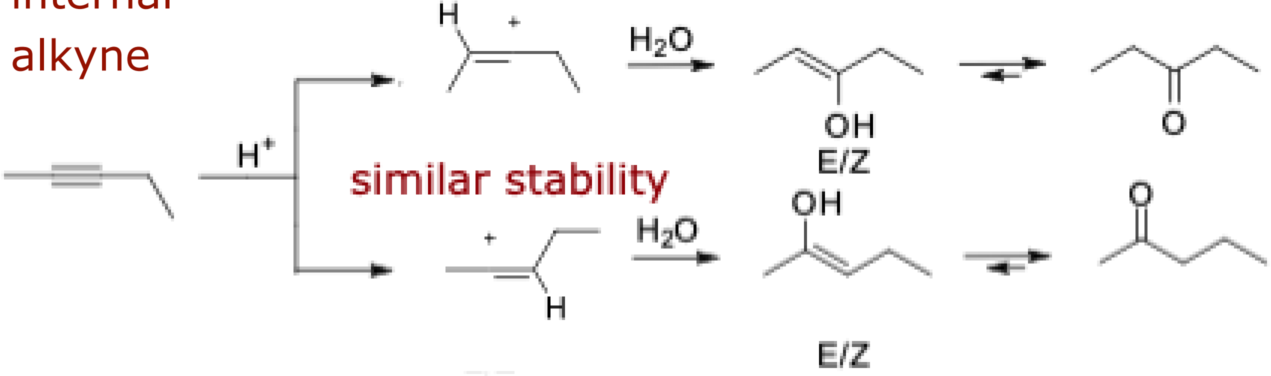


more stabile

less stabile

regioselective

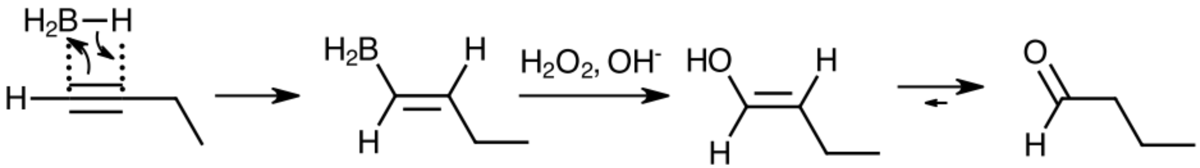
internal
alkyne



similar stability

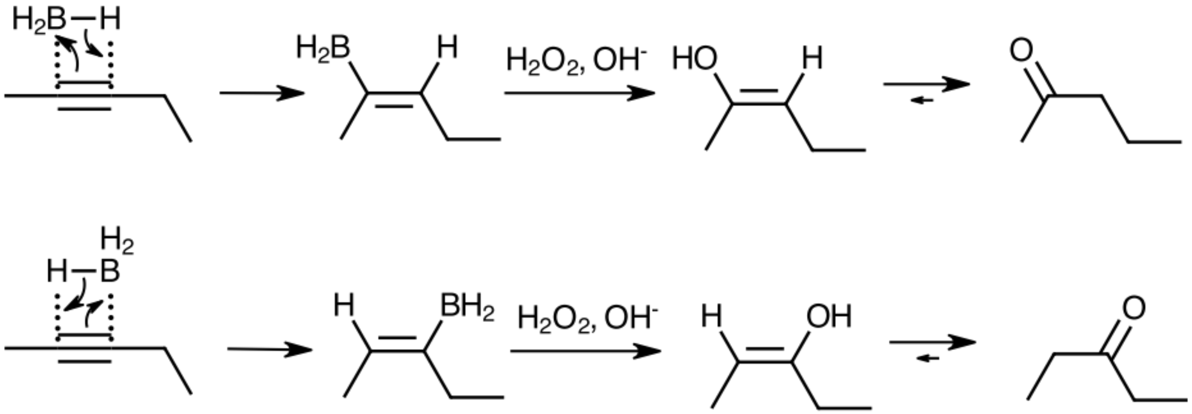
not regioselective

Hydroboration—Oxidation



terminal
alkyne

aldehyde

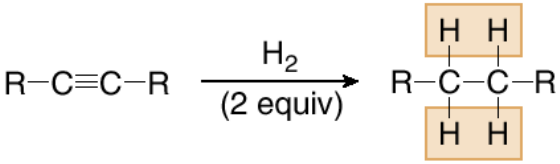


internal
alkyne

isomeric
Ketones

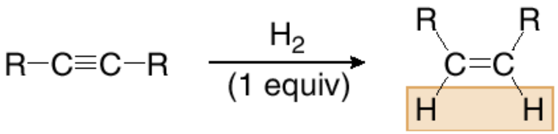
Reduction of Alkynes

- Adding two equivalents of H_2 forms an alkane.



alkane

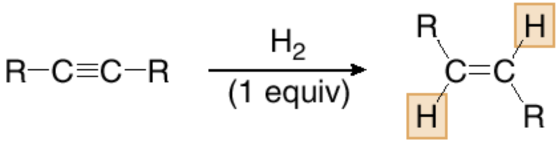
- Adding one equivalent of H_2 in a syn fashion forms a cis alkene.



cis alkene

syn addition

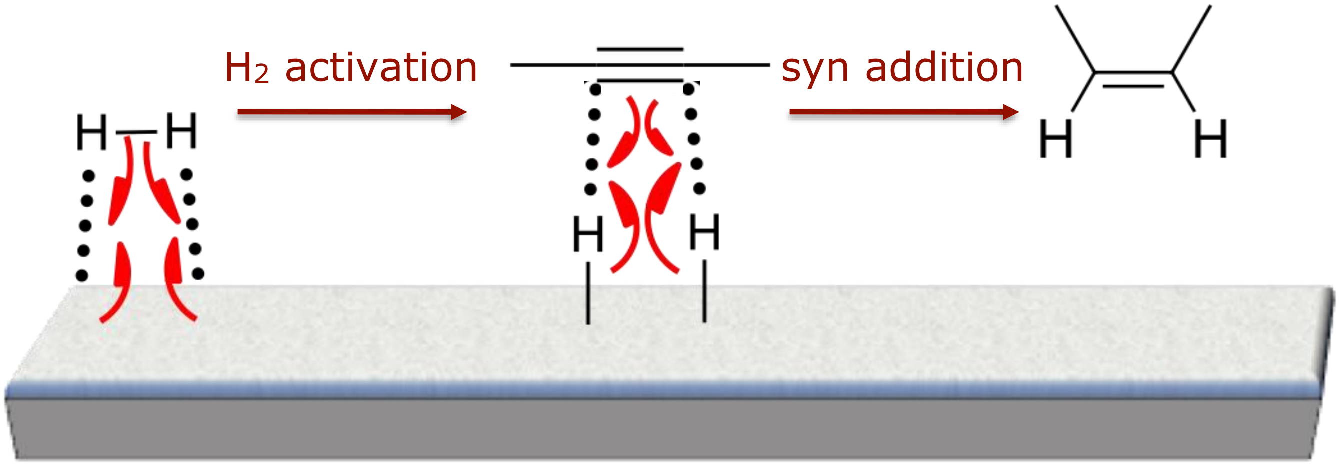
- Adding one equivalent of H_2 in an anti fashion forms a trans alkene.



trans alkene

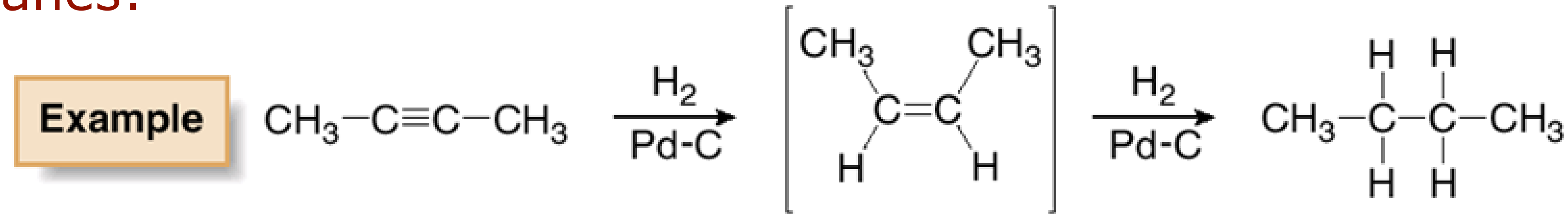
anti addition

Catalytic Hydrogenation



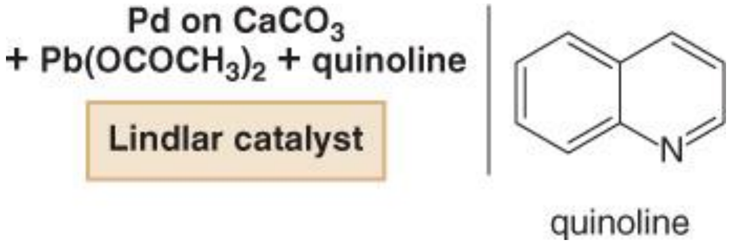
Catalytic Hydrogenation

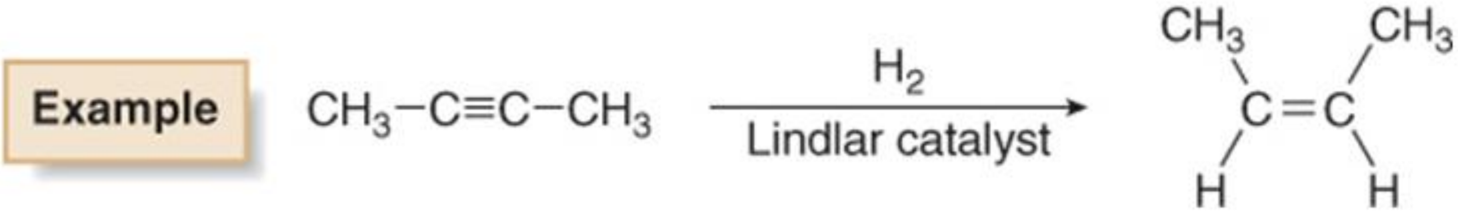
Alkanes:



Cis-Alkenes:

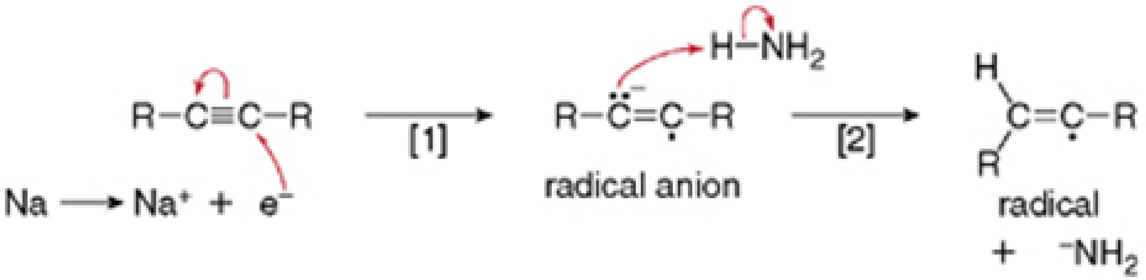
- Palladium metal is too reactive to allow hydrogenation of an alkyne to stop after one equivalent of H_2 adds.
- To stop at a cis alkene, a less active Pd catalyst is used - Pd adsorbed onto $CaCO_3$ with added lead(II) acetate and quinoline. This is called Lindlar's catalyst.





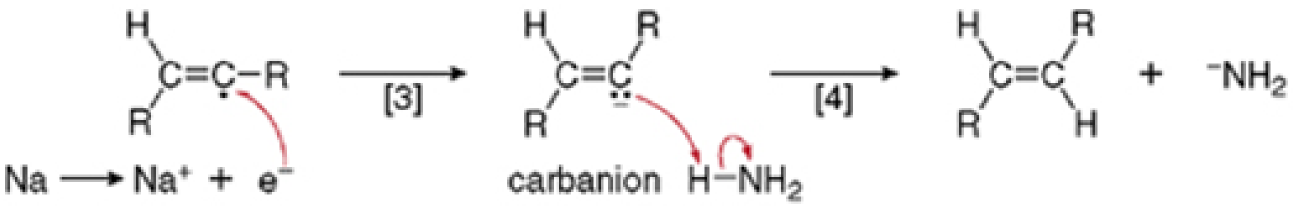
Dissolving Metal Reduction

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

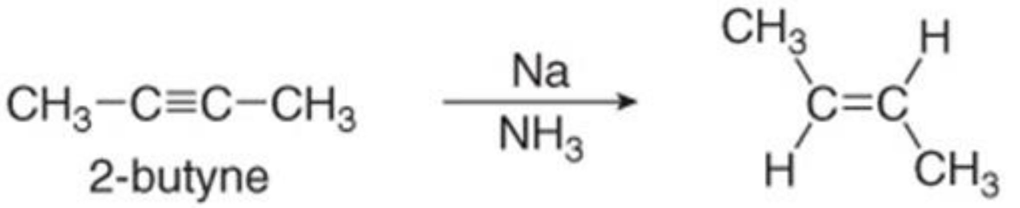


Steps [3] and [4] Addition of one electron and one proton to form the trans alkene

sp sp^2

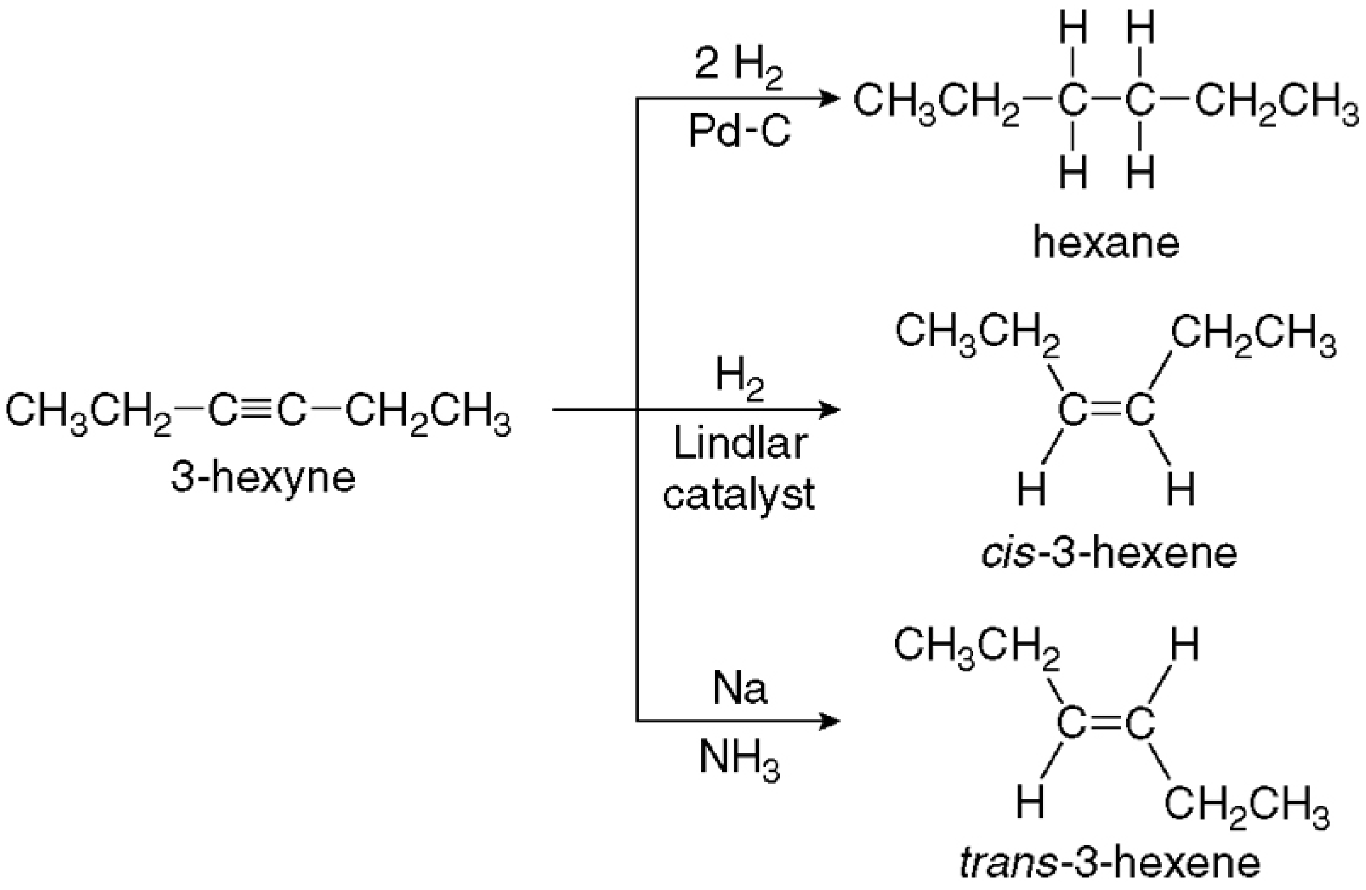


Example



trans-2-butene

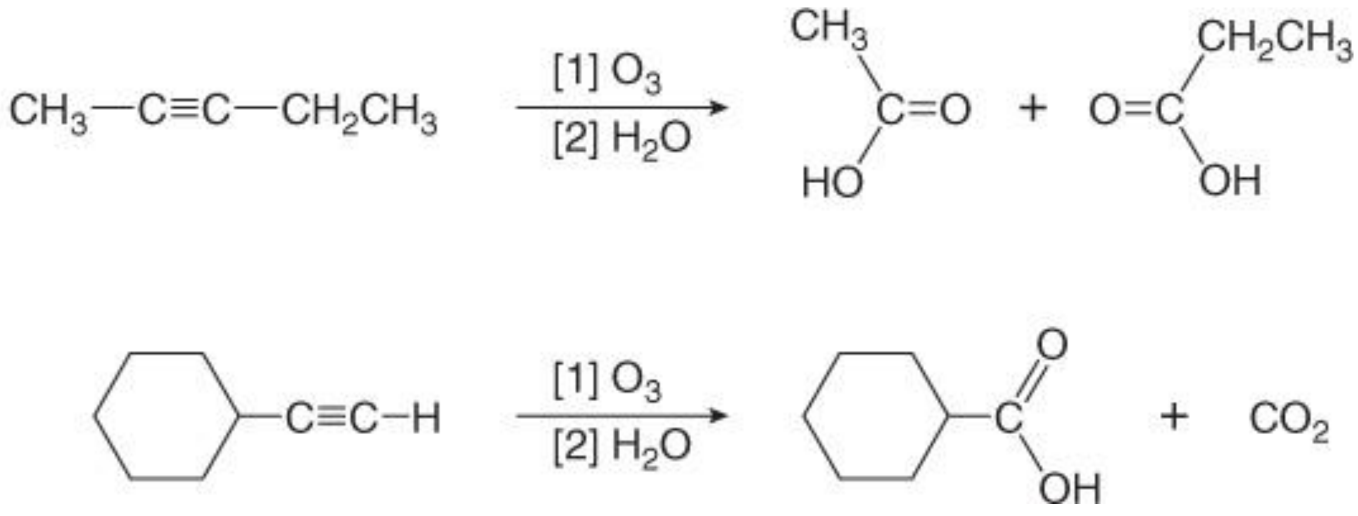
Summary of Alkyne Reductions



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.

Examples



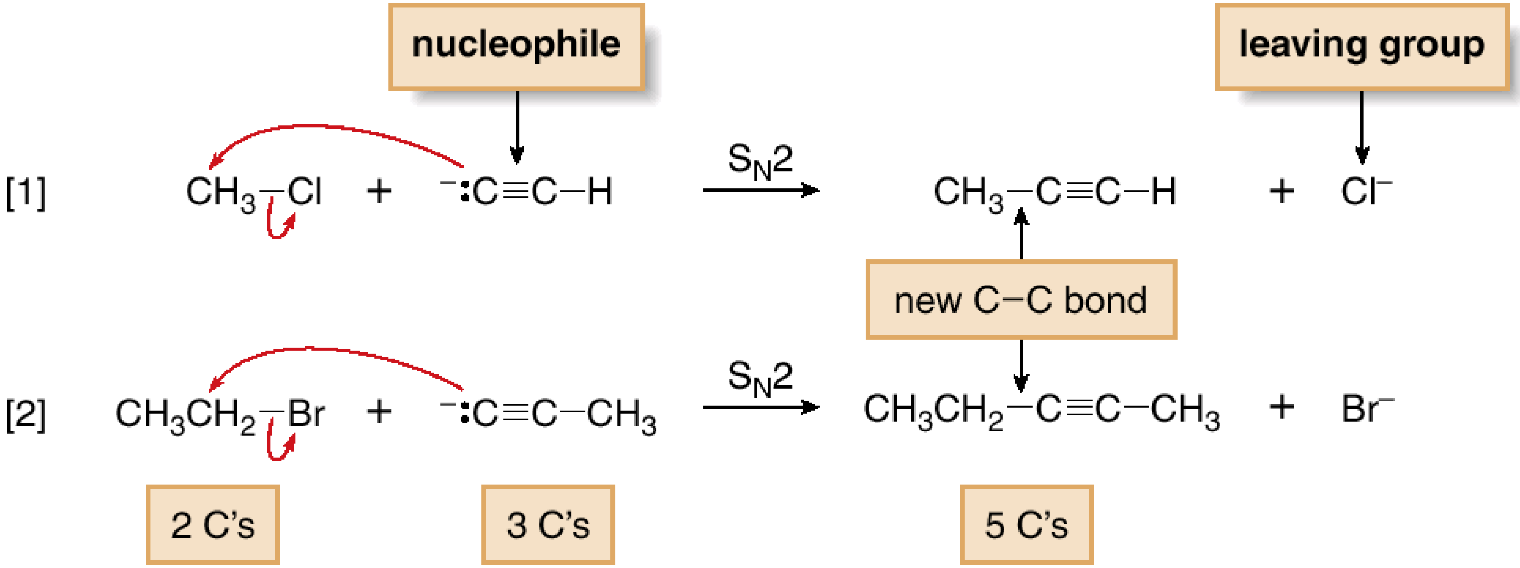
Acetylide anions

	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.

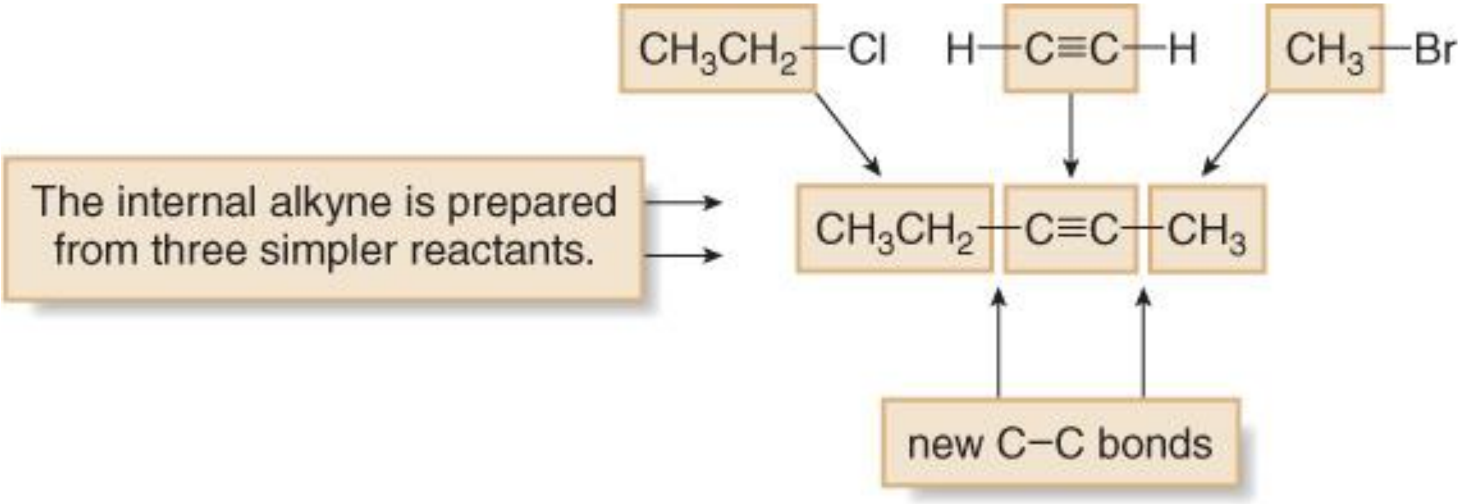


[1] $CH_3{-}Cl + {}^{-}{:}C{\equiv}C{-}H \xrightarrow{S_N2} CH_3{-}C{\equiv}C{-}H + Cl^{-}$

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

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

Acetylide anions



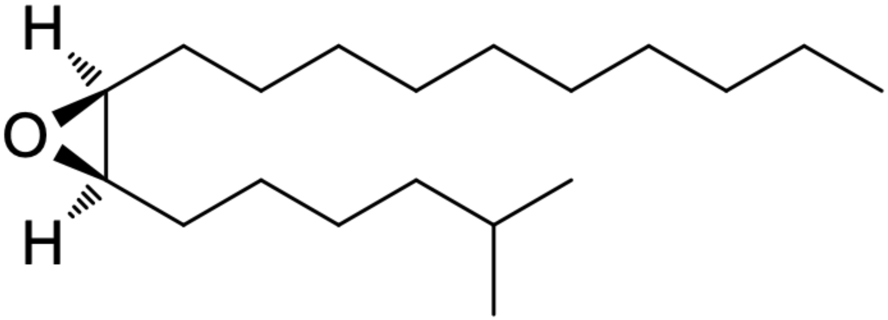
$CH_3CH_2{-}Cl$ $H{-}C{\equiv}C{-}H$ $CH_3{-}Br$

The internal alkyne is prepared from three simpler reactants.

$CH_3CH_2{-}C{\equiv}C{-}CH_3$

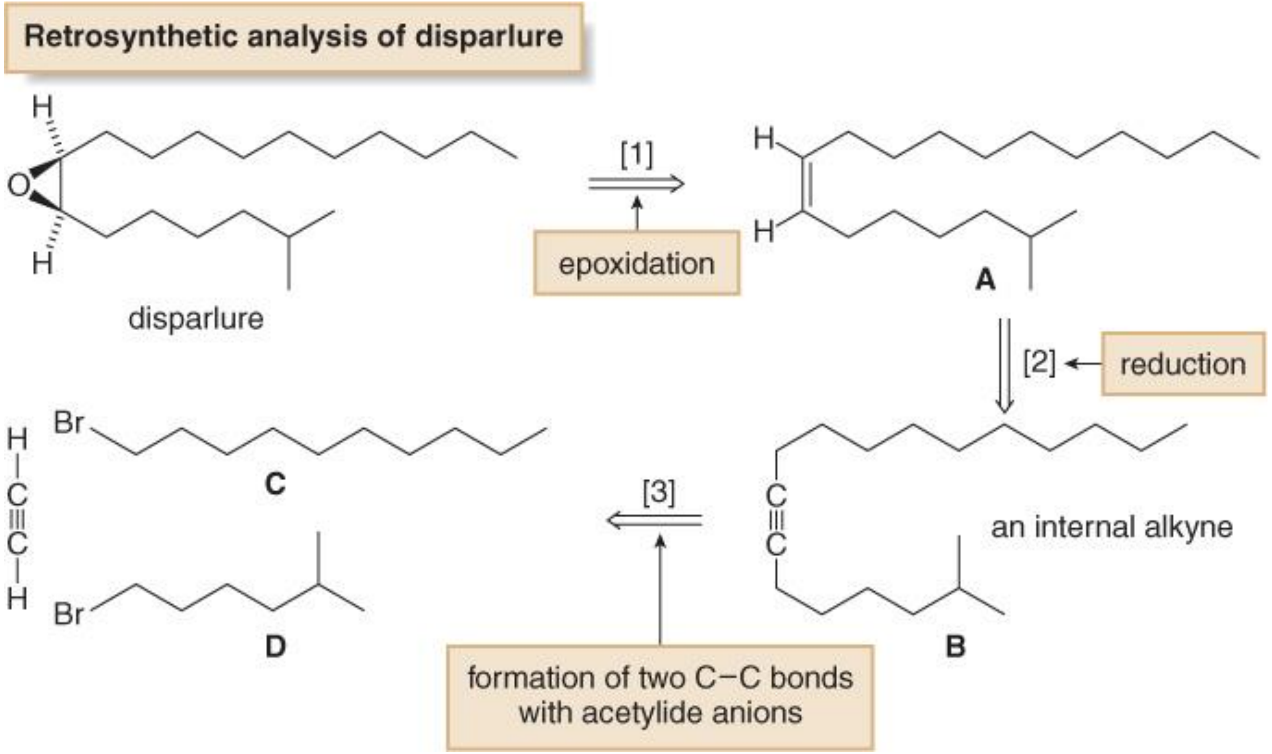
new C–C bonds

Synthesis



Disparlure – a pheromone

Synthesis


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