Alkynes

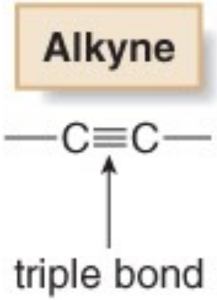
Chapter 9

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

$CH_3CH_2CH_2-C\equiv C-H$

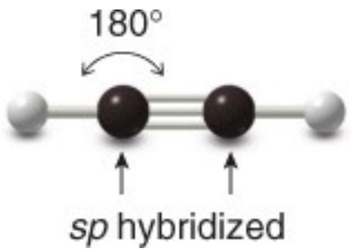
terminal alkyne

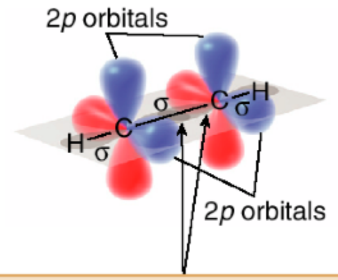
$CH_3CH_2CH_2-C\equiv C-CH_2CH_3$

internal alkyne

$H-C\equiv C-H$ =

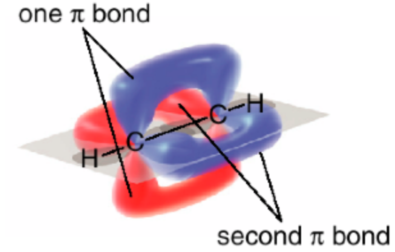
acetylene





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

Two π bonds extend out from the axis of the linear molecule.



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

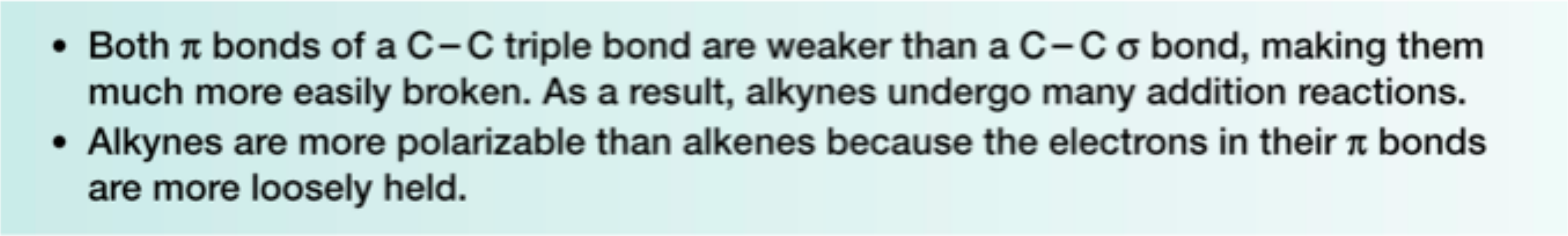
Alkynes are more reactive than alkenes

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

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

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

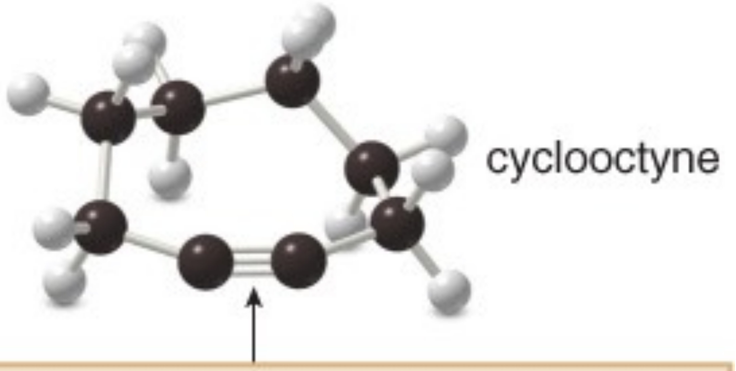
200 Kcal/mol - 152 Kcal/mol. = 48 Kcal/mol



- 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.



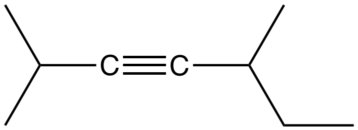
To accommodate the triple bond in a ring, bending occurs around the *sp* hybridized C's, destabilizing the molecule.

modelli 3D

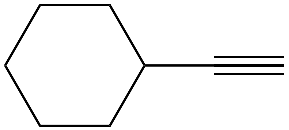
Nomenclature

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

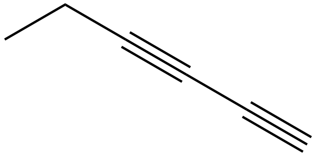
$H-C\equiv C-$ ethynyl



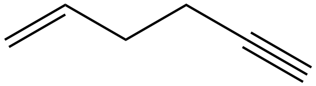
2,5-dimethyl-3-heptyne



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.

Acetylene

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

Reaction	**ΔH** (Kcal/mol)	**ΔH/mol O_2** (Kcal/mol)
$H_3C{-}CH_3 + 7/2\ O_2 \longrightarrow 2\ CO_2 + 3\ H_2O$	***-1550***	***-442***
$H_2C{=}CH_2 + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O$	***-1400***	***-467***
$HC{\equiv}CH + 5/2\ O_2 \longrightarrow 2\ CO_2 + H_2O$	***-1300***	***-520***

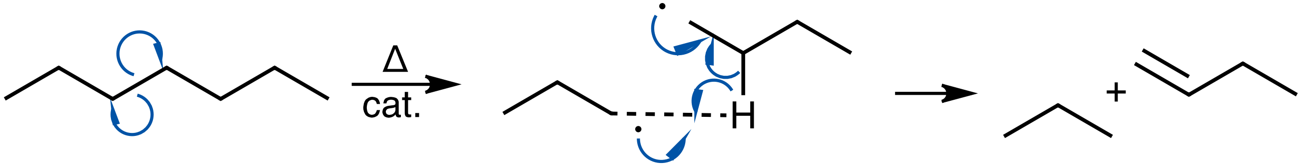
Acetylene

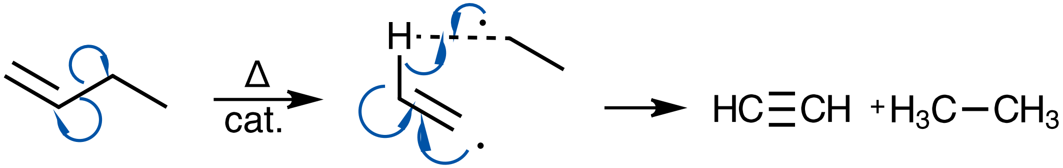
- From coal:

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

$$CaC_2 + 2\ H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

- From oil (cracking):

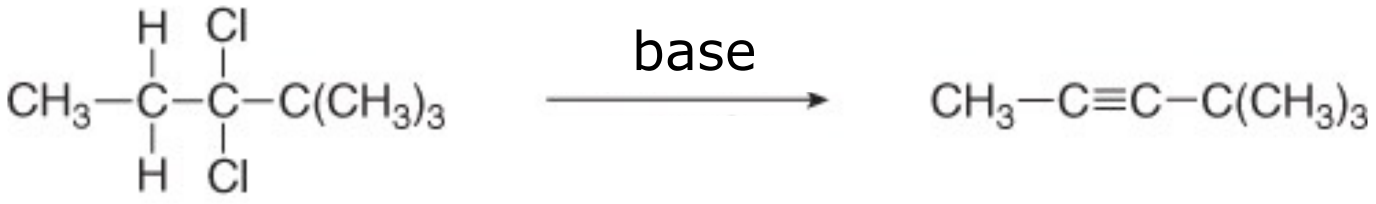




$HC{\equiv}CH + H_3C{-}CH_3$

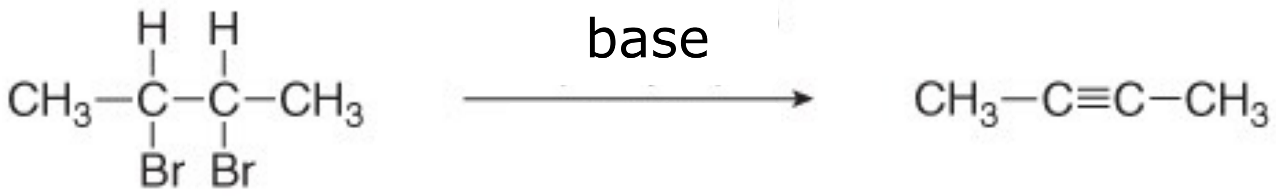
Preparation of Alkynes

Alkynes are prepared by elimination reactions.



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

geminal dichloride

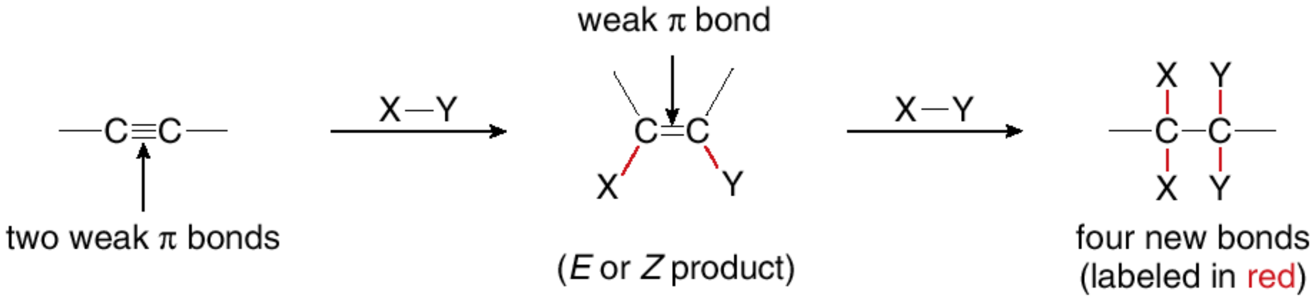


$$\mathrm{CH_3-\overset{H}{\underset{Br}{C}}-\overset{H}{\underset{Br}{C}}-CH_3 \xrightarrow{\text{base}} CH_3-C\equiv C-CH_3}$$

vicinal dibromide

Alkyne Reactions—Additions

Addition reaction



two weak π bonds

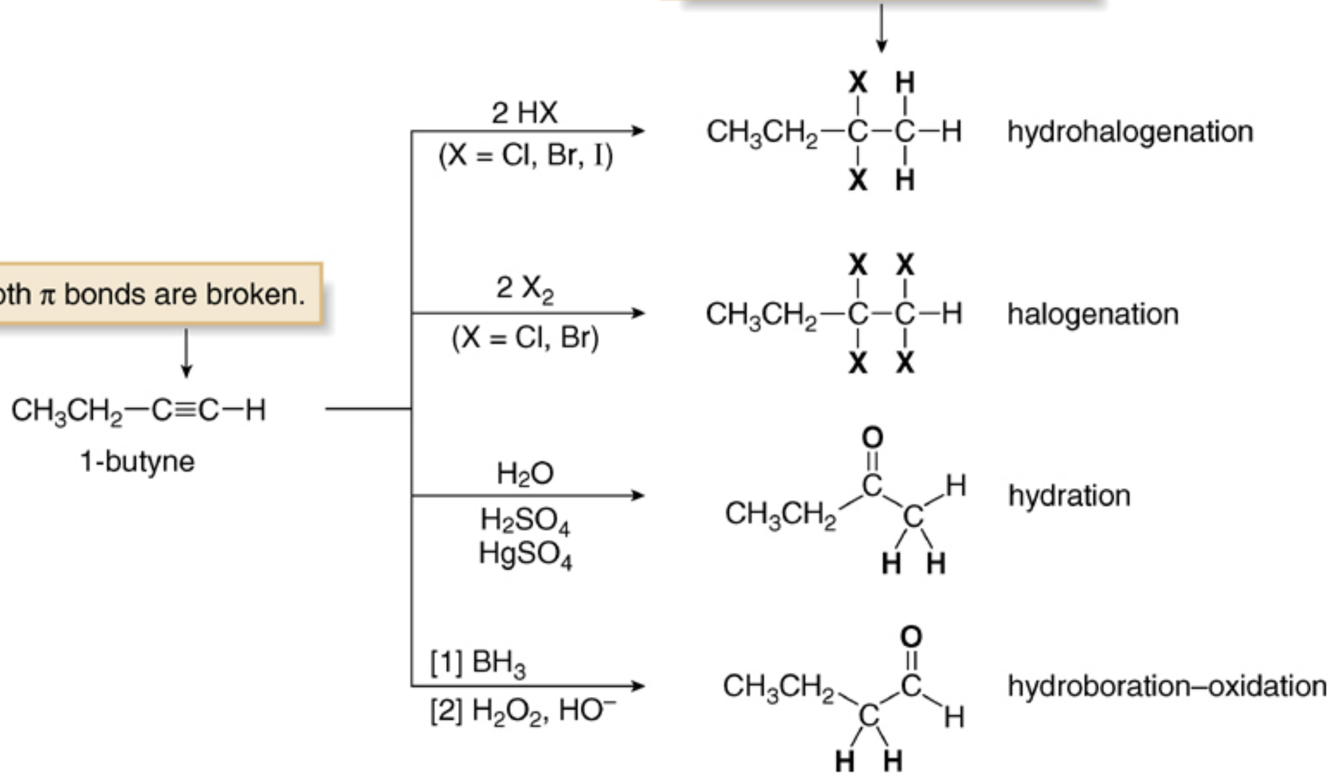
weak π bond

(*E* or *Z* product)

four new bonds (labeled in red)

Four new bonds are formed.

Both π bonds are broken.



1-butyne

hydrohalogenation

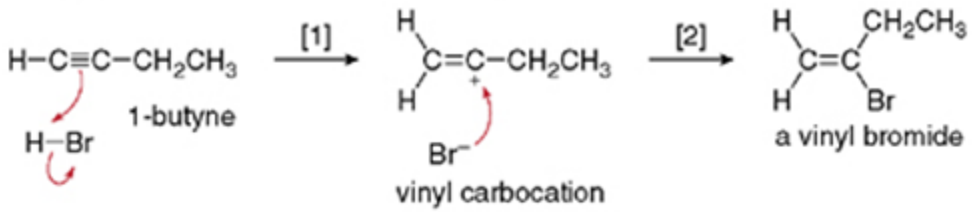
halogenation

hydration

hydroboration–oxidation

Hydrohalogenation

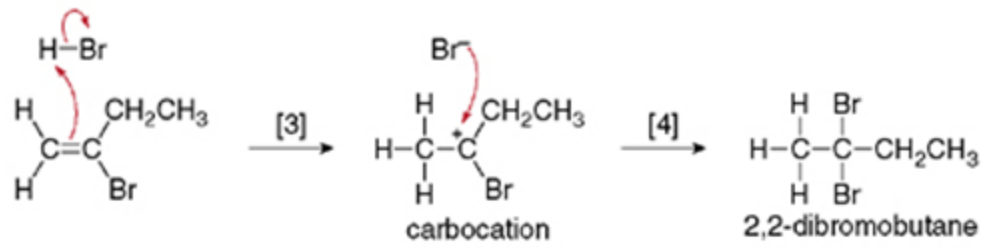
Part [1] Addition of HBr to form a vinyl halide



slower

(less stable vinyl cation)

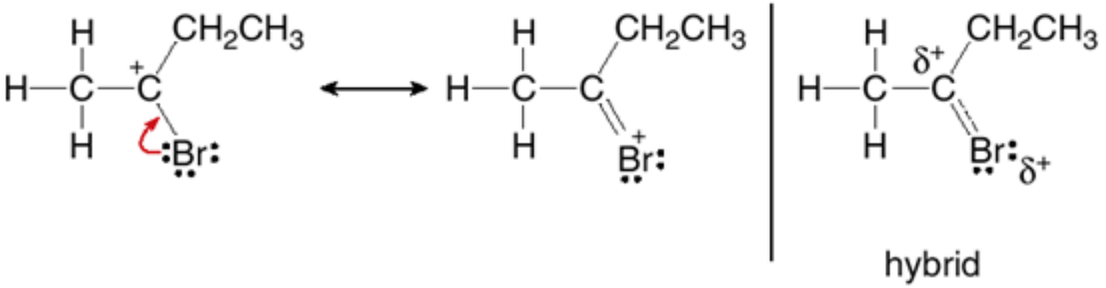
Part [2] Addition of HBr to form a geminal dihalide



faster

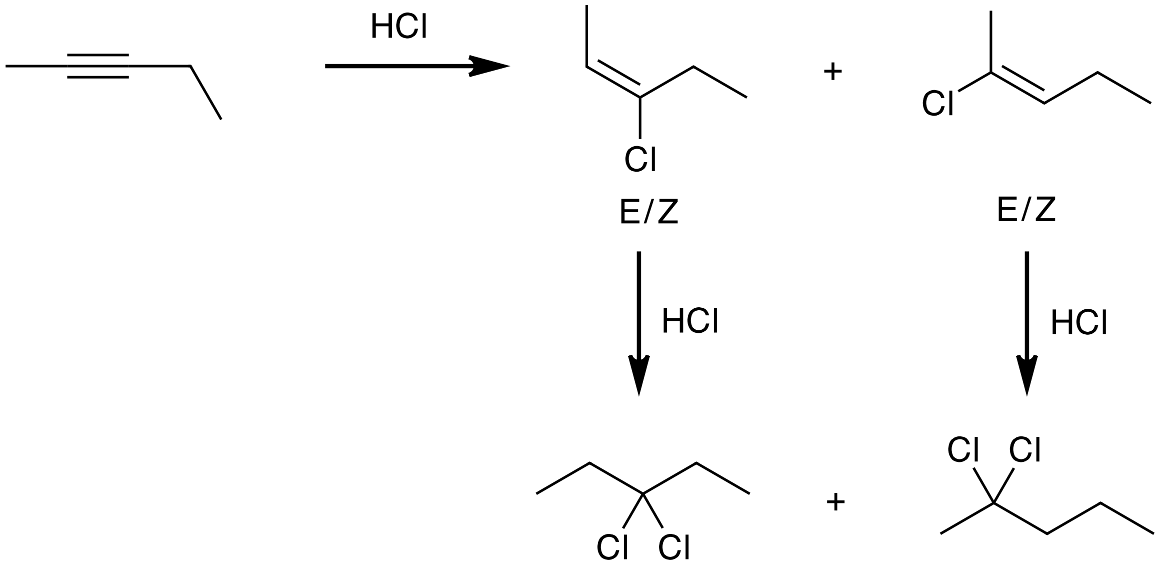
(more stable,

tertiary alkyl cation)



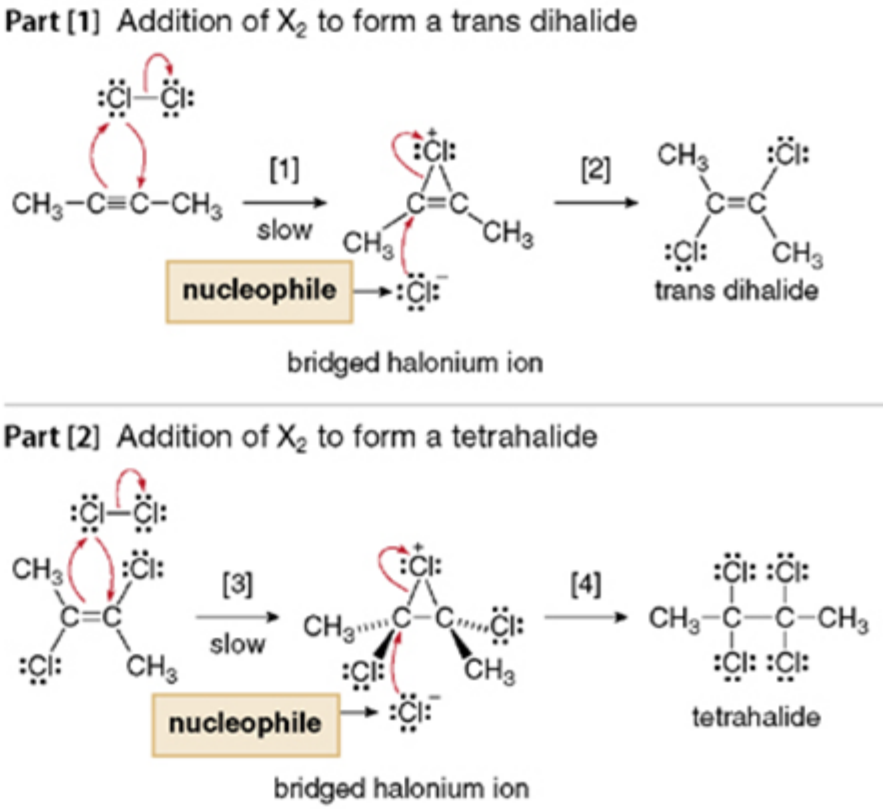
The positive charge is delocalized.

Hydrohalogenation



Not regioselective with internal alkynes

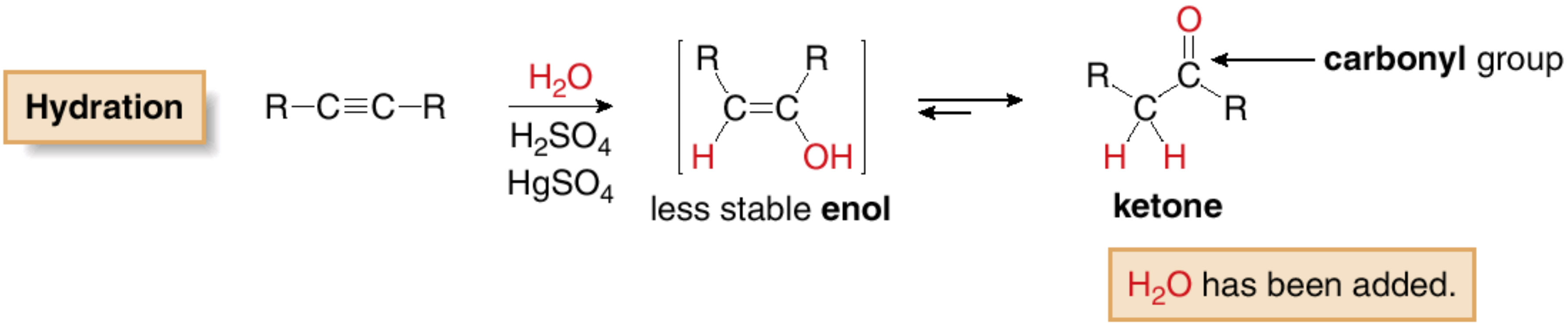
Halogenation



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

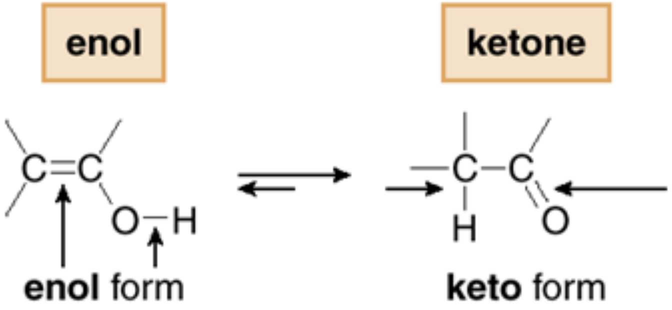
Part [2] Addition of X_2 to form a tetrahalide

Hydration

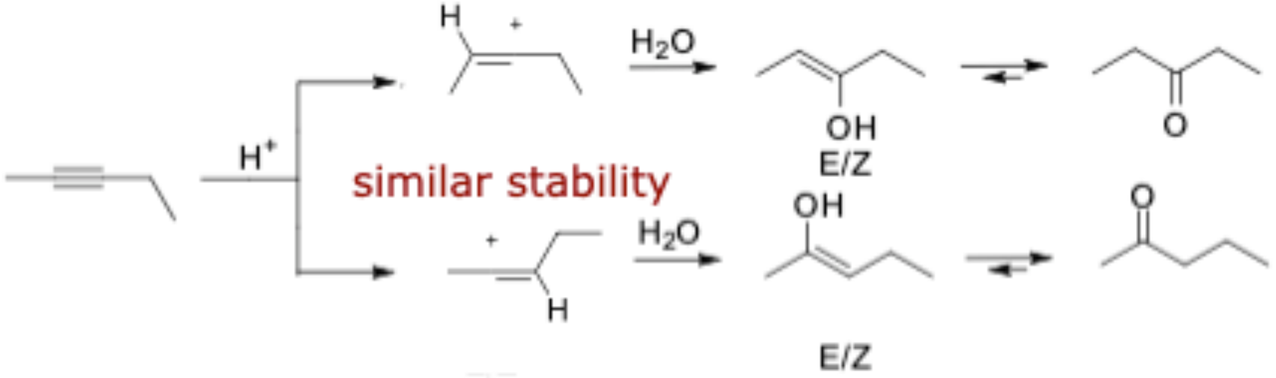


Equilibrium favors the keto form largely because the C=O is much stronger than a C=C.

- *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.



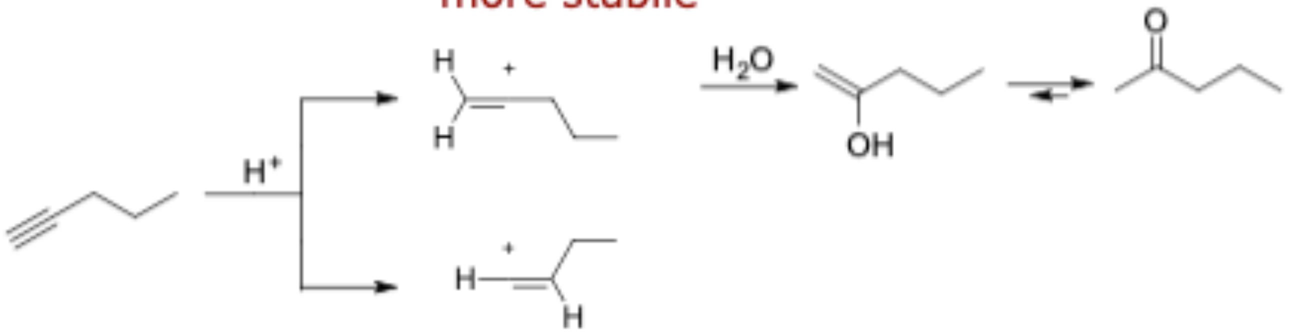
Hydration



similar stability

not regioselective

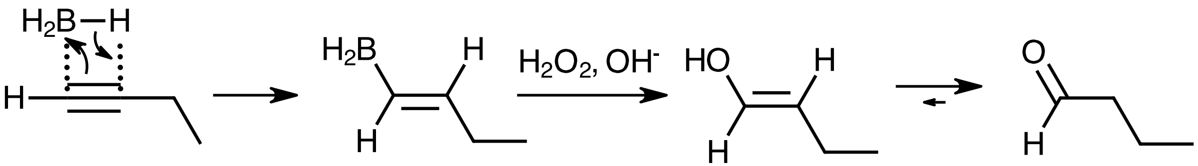
more stabile



less stabile

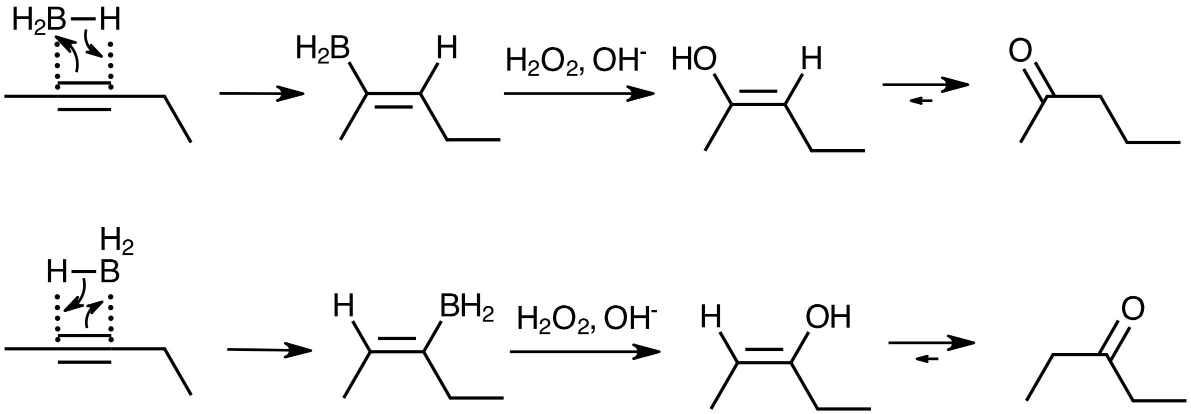
regioselective

Hydroboration—Oxidation



terminal
alkyne

aldehyde

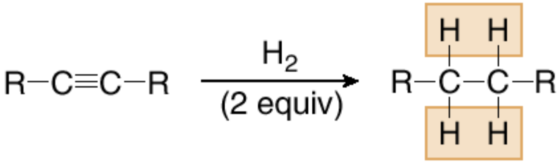


internal
alkyne

isomeric
Ketones

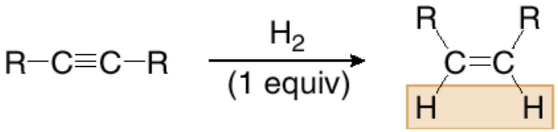
Reduction of Alkynes

- Adding two equivalents of H_2 forms an alkane.



alkane

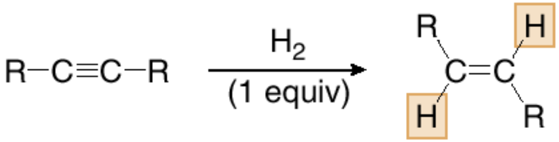
- Adding one equivalent of H_2 in a syn fashion forms a cis alkene.



cis alkene

syn addition

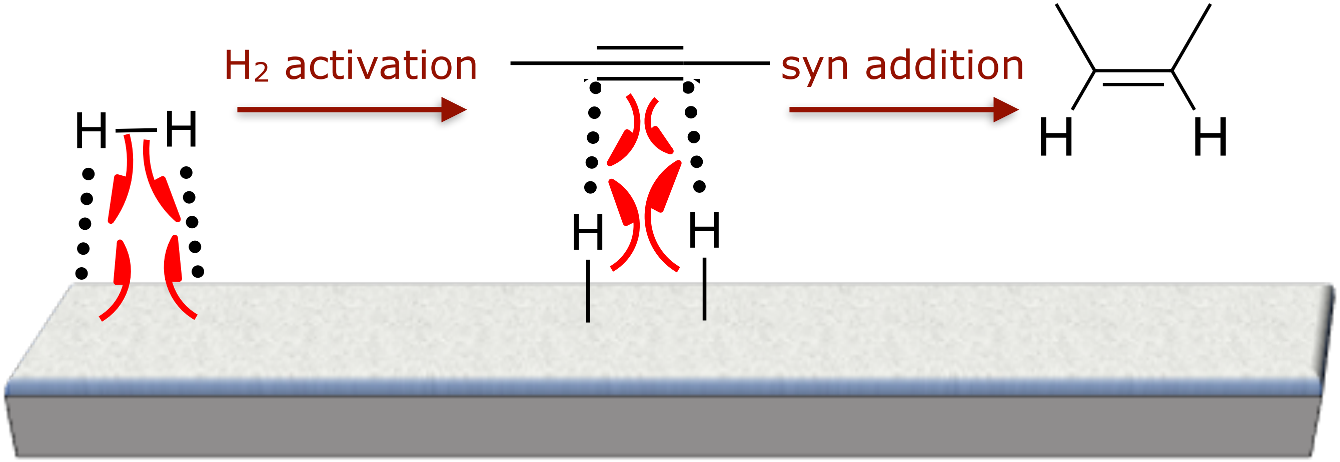
- Adding one equivalent of H_2 in an anti fashion forms a trans alkene.



trans alkene

anti addition

Catalytic Hydrogenation



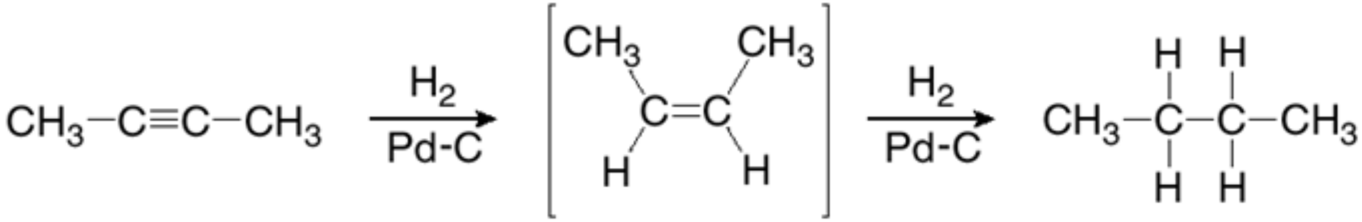
H_2 activation

syn addition

Catalytic Hydrogenation

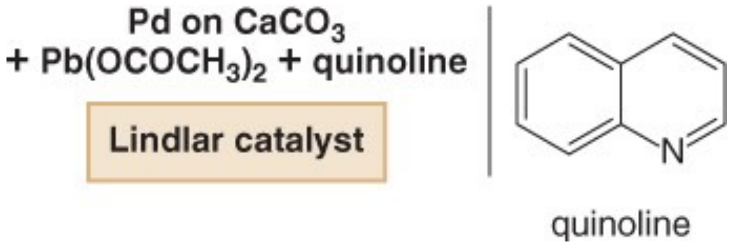
Alkanes:

Example



Cis-Alkenes:

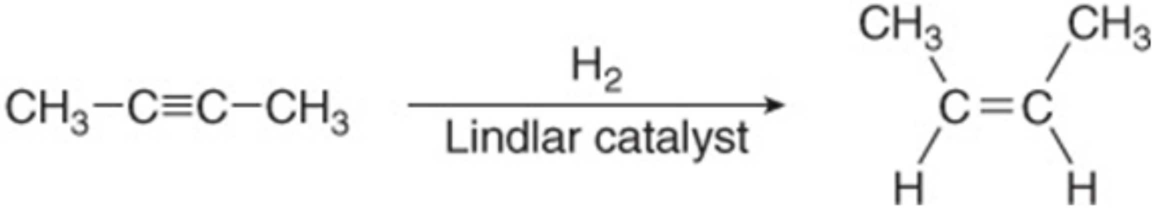
- Palladium metal is too reactive to allow hydrogenation of an alkyne to stop after one equivalent of H_2 adds.
- To stop at a cis alkene, a less active Pd catalyst is used - Pd adsorbed onto $CaCO_3$ with added lead(II) acetate and quinoline. This is called Lindlar's catalyst.



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

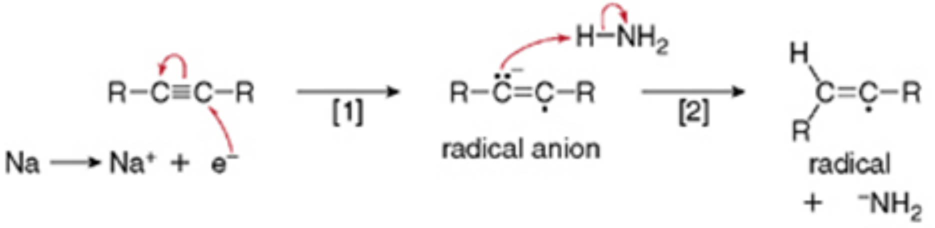
Lindlar catalyst

Example

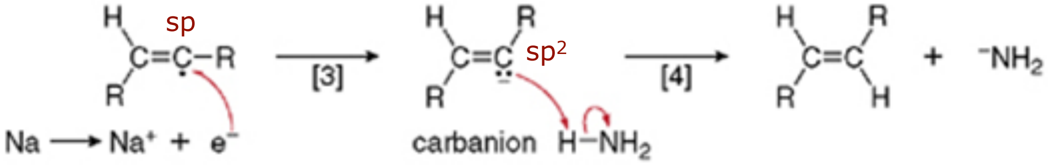


Dissolving Metal Reduction

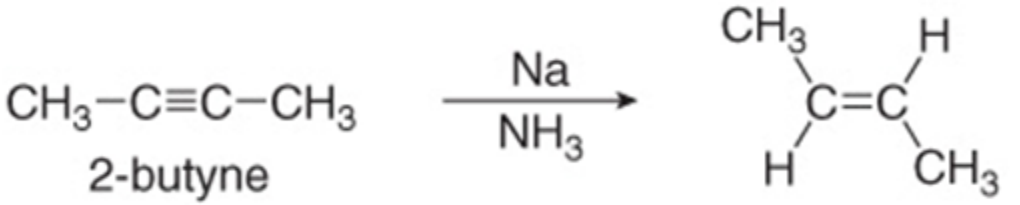
Steps [1] and [2] Addition of one electron and one proton to form a radical



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



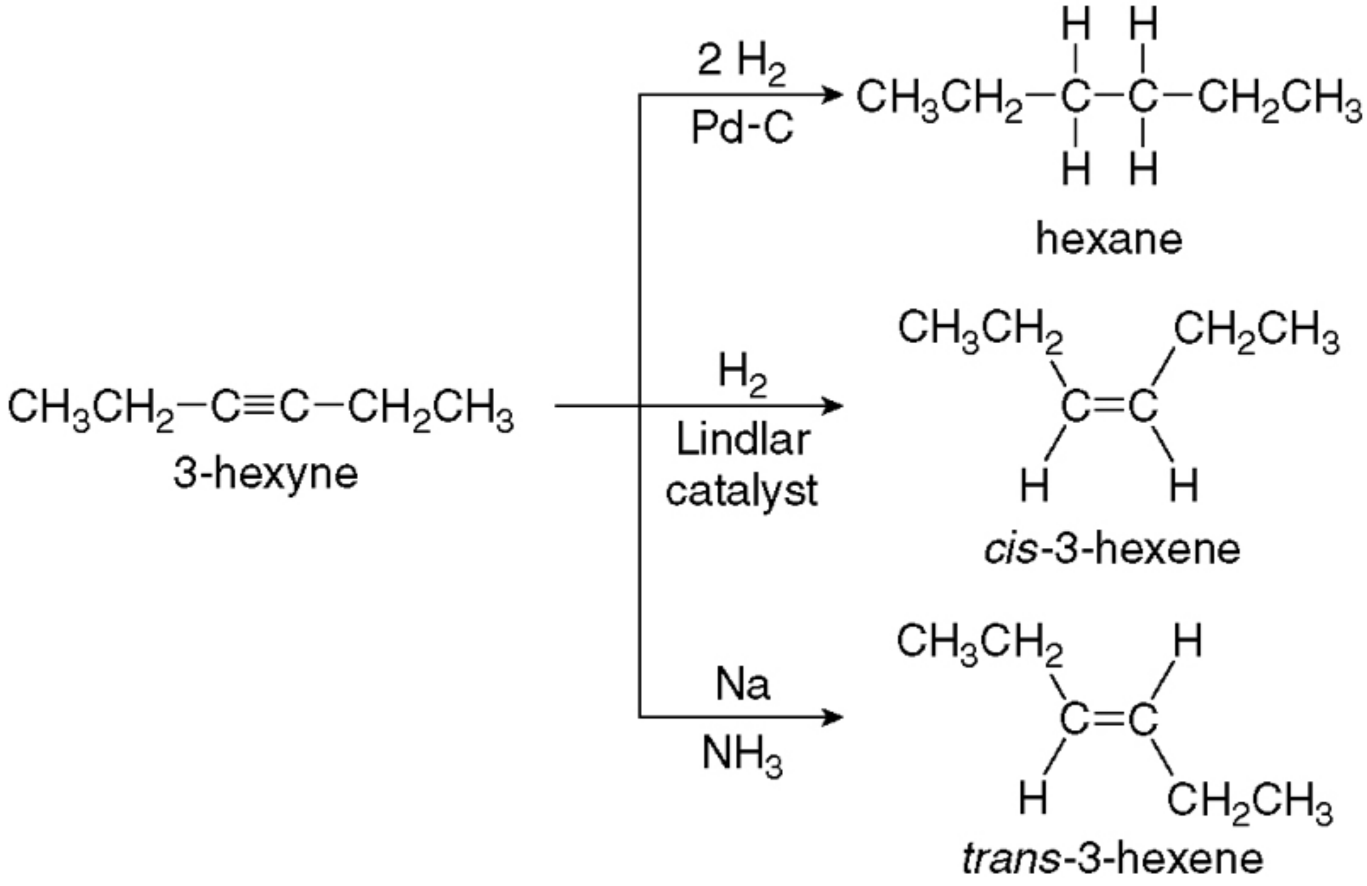
Example



2-butyne

trans-2-butene

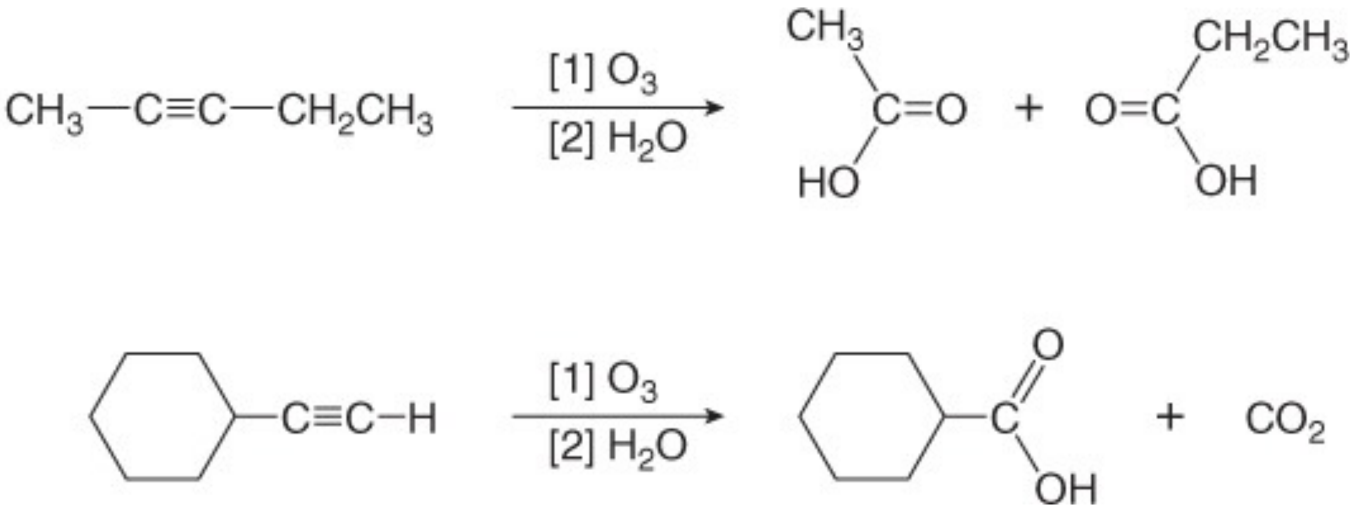
Summary of Alkyne Reductions



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

terminal alkyne
$pK_a \approx 25$

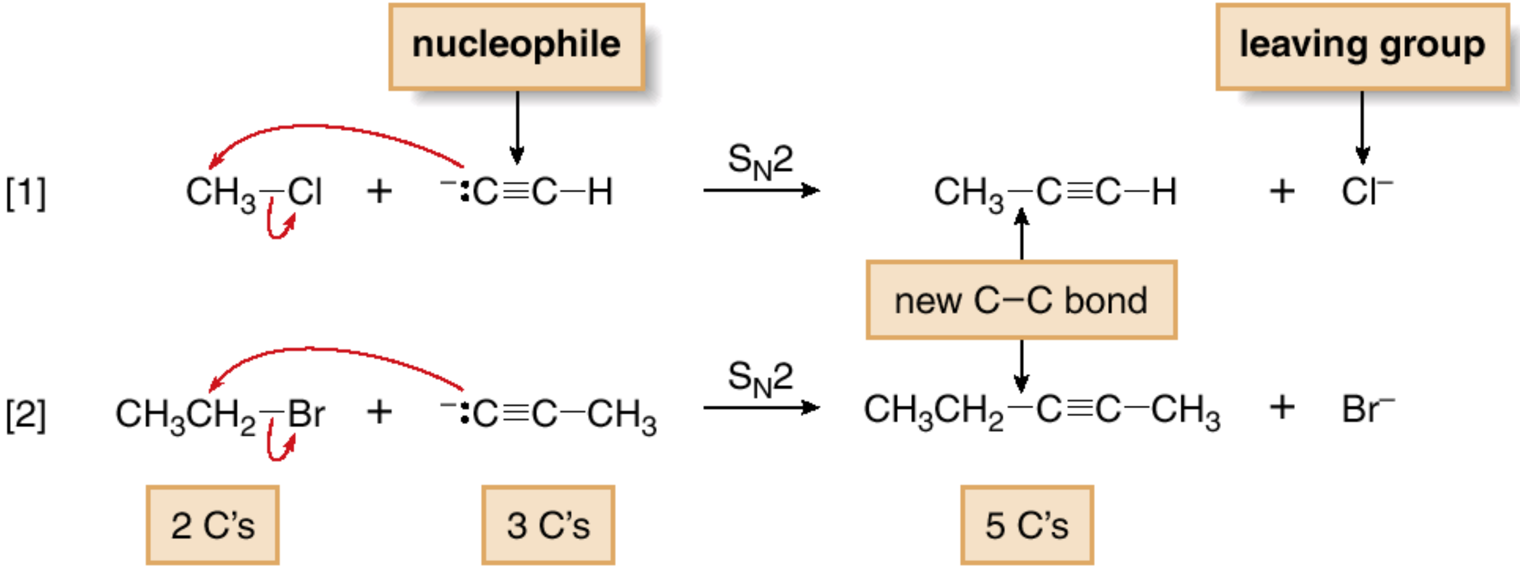
acetylide anion

	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

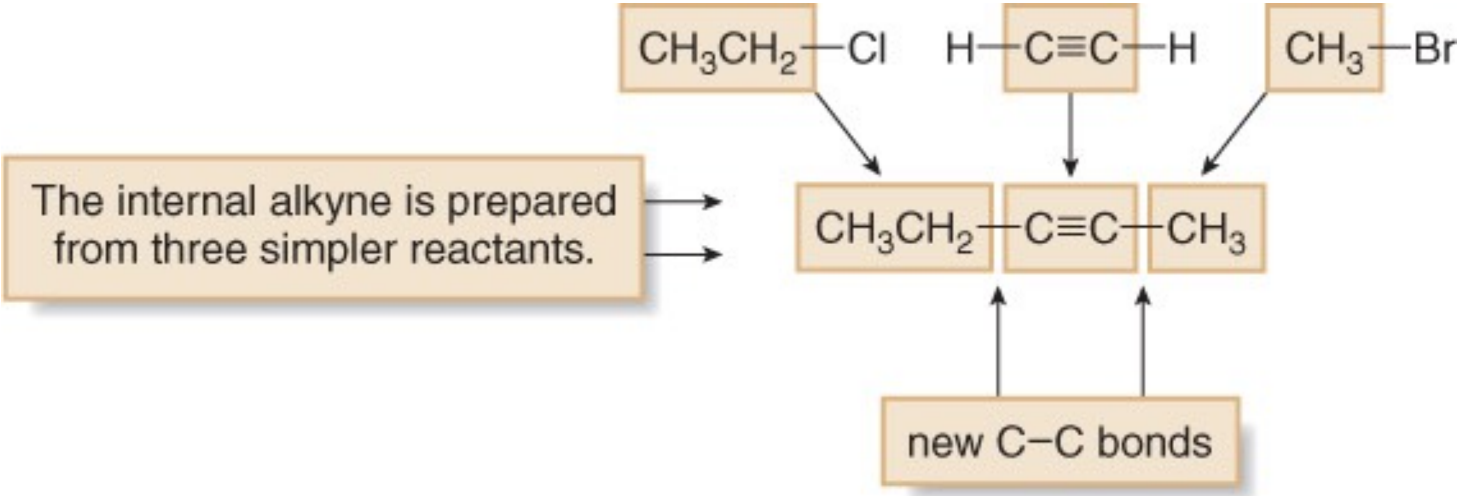
- Acetylide anions are strong nucleophiles and react with methyl and 1° alkyl halides to yield products of nucleophilic substitution.

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



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

Acetylide anions



CH_3CH_2-Cl

$H-C\equiv C-H$

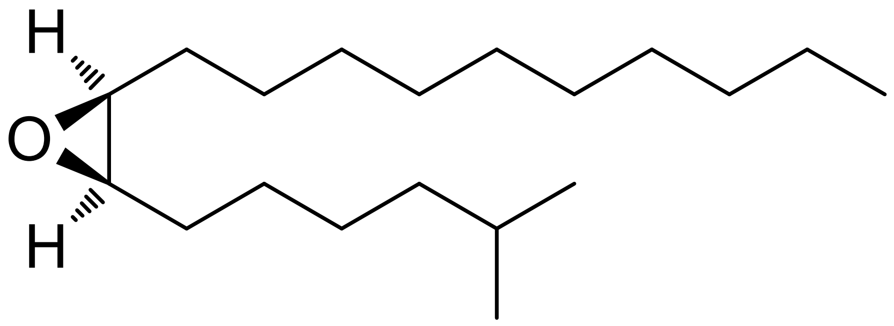
CH_3-Br

The internal alkyne is prepared from three simpler reactants.

$CH_3CH_2-C\equiv C-CH_3$

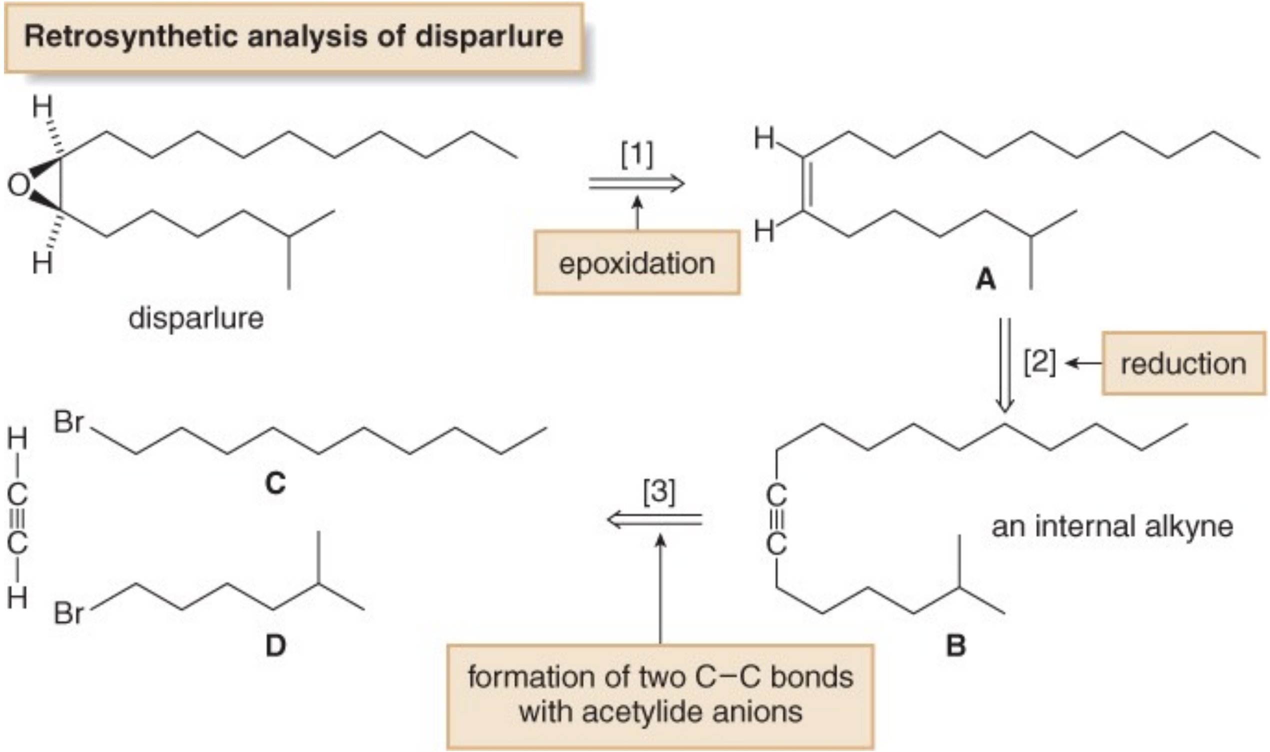
new C–C bonds

Synthesis

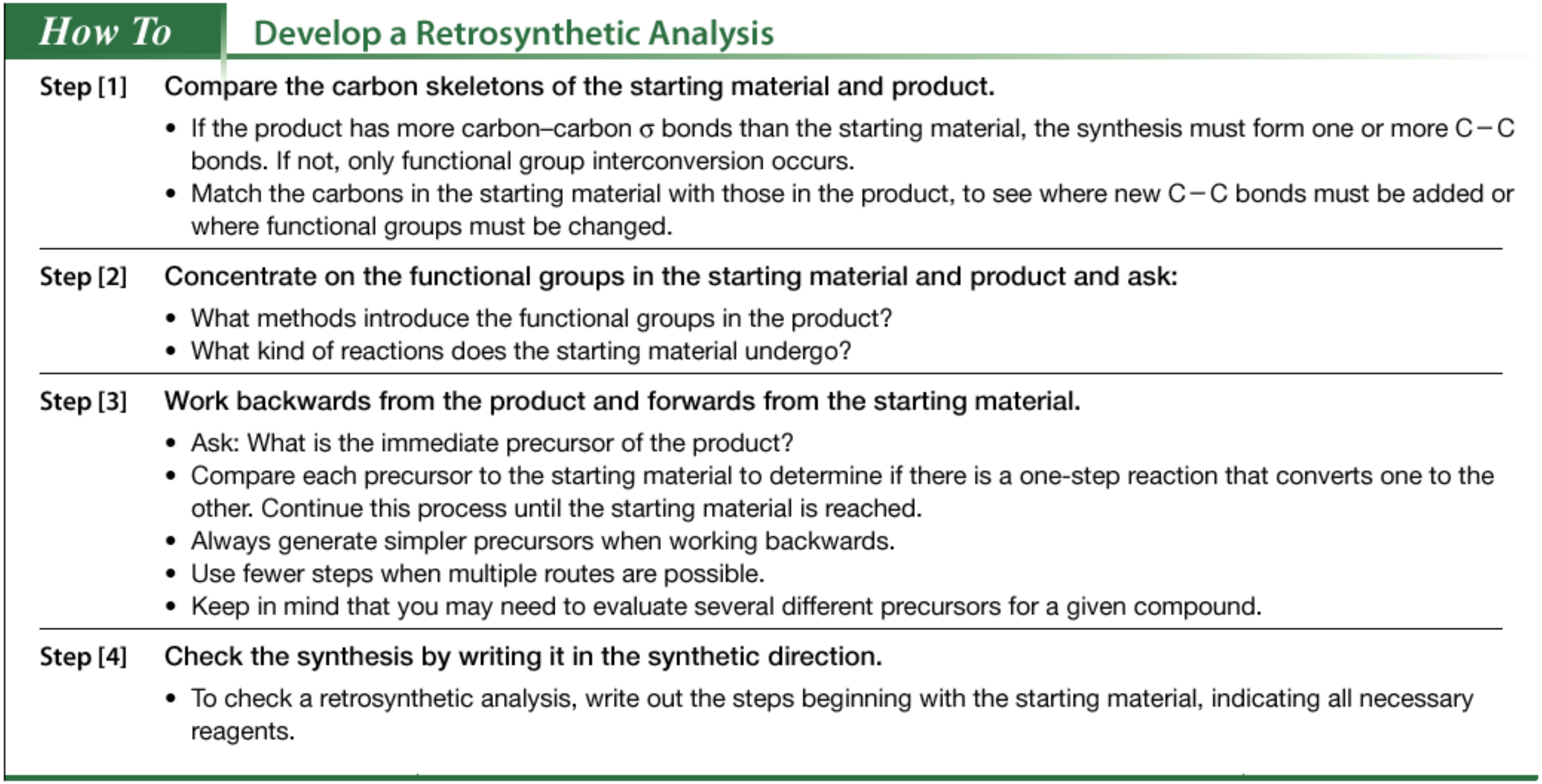


Disparlure – a pheromone

Synthesis


Retrosynthetic analysis of disparlure
H
O
H
disparlure
[1]
epoxidation
H
H
A
[2]
reduction
C
C
B
an internal alkyne
[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.