

Alkynes

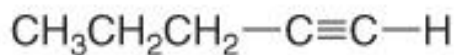
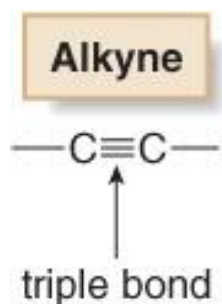
Chapter 9

Organic Chemistry, *8th Edition*

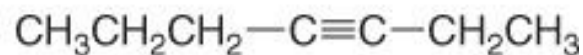
John E. McMurry

Structure and Bonding

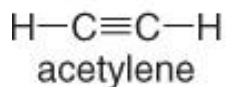
- general molecular formula C_nH_{2n-2} , Thus, the triple bond introduces two degrees of unsaturation.



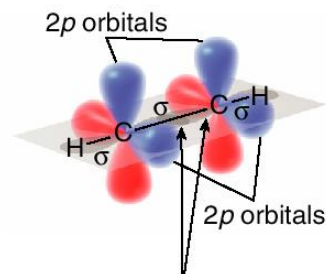
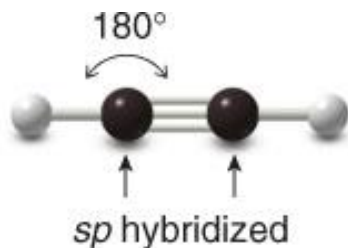
terminal alkyne



internal alkyne

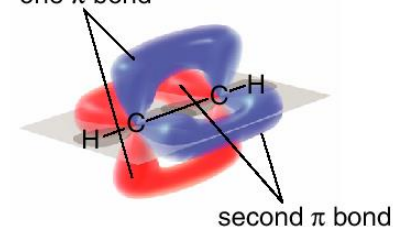


=



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

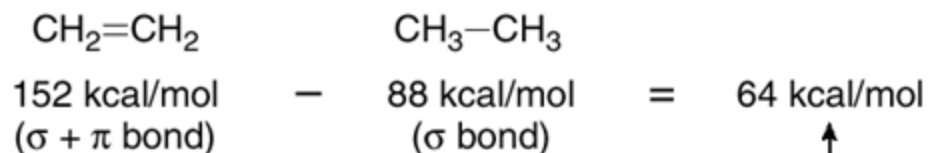
Two π bonds extend out from the axis of the linear molecule.
one π bond



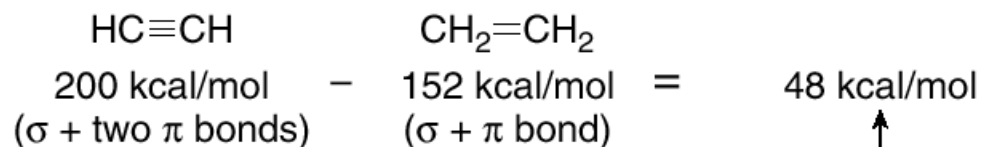
Overlap of two sets of two $2p$ orbitals forms two C—C π bonds.

- 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 $2p$ orbitals.

Structure and Bonding



↑
π bond only

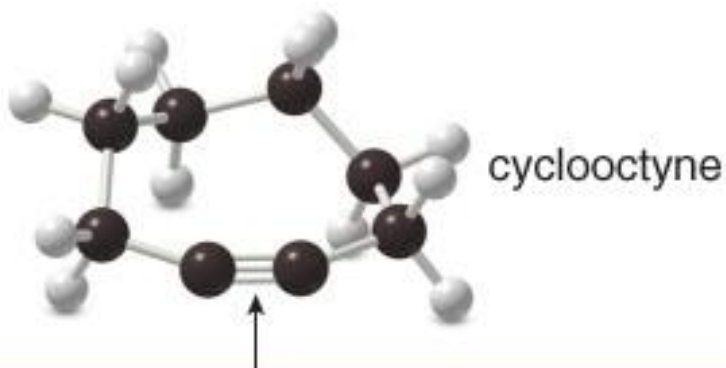


↑
second π bond

- 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.

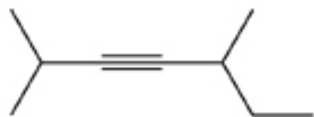
Nomenclature



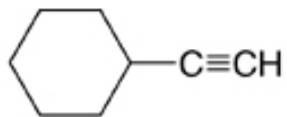
ethyne (acetylene)



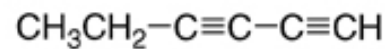
ethynyl



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.

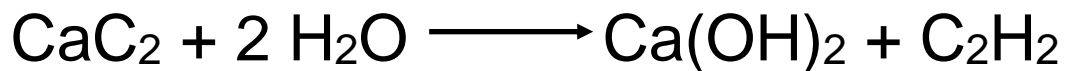
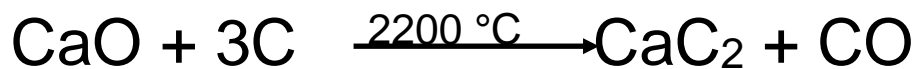
Acetylene

- 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.

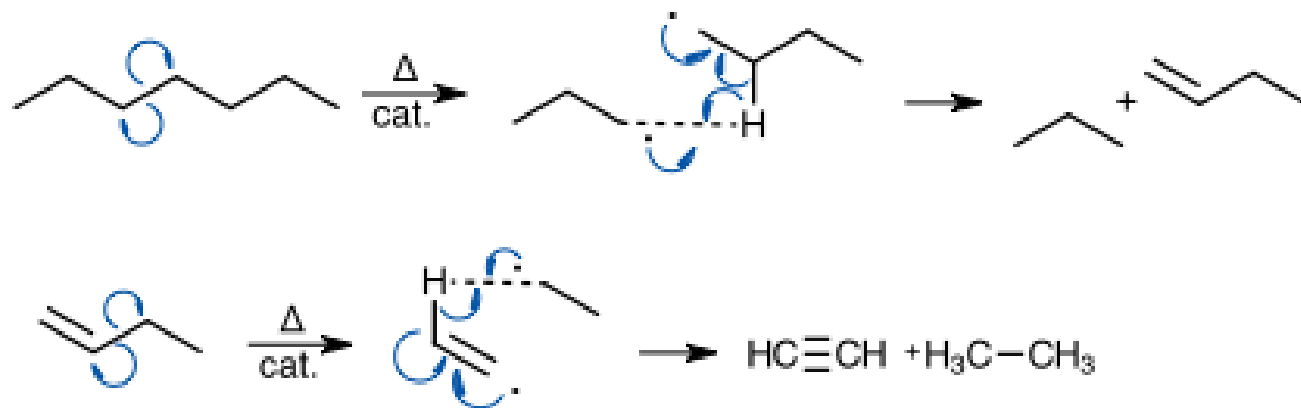
Reaction	ΔH (Kcal/mol)	$\Delta H/\text{mol O}_2$ (Kcal/mol)
$\text{H}_3\text{C}-\text{CH}_3 + 7/2 \text{O}_2 \longrightarrow 2 \text{CO}_2 + 3 \text{H}_2\text{O}$	-1550	-442
$\text{H}_2\text{C}=\text{CH}_2 + 3 \text{O}_2 \longrightarrow 2 \text{CO}_2 + 2 \text{H}_2\text{O}$	-1400	-467
$\text{HC}\equiv\text{CH} + 5/2 \text{O}_2 \longrightarrow 2 \text{CO}_2 + \text{H}_2\text{O}$	-1300	-520

Acetylene

- From coal:

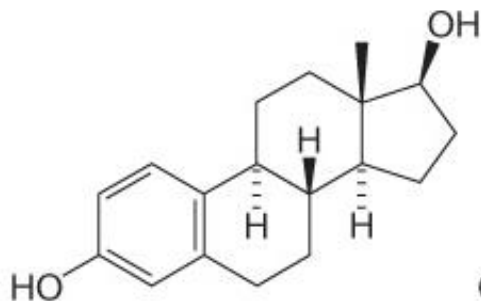


- From oil (cracking):

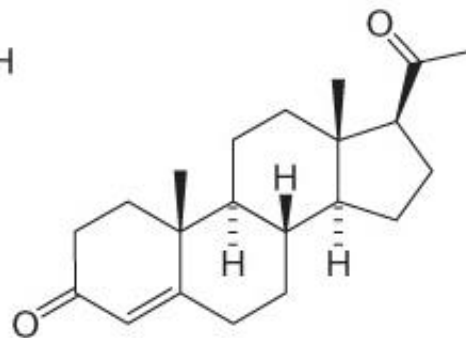


Other Interesting Alkynes

Naturally occurring female sex hormones

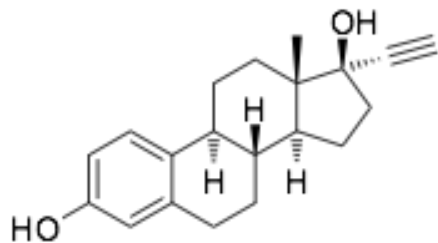


estradiol

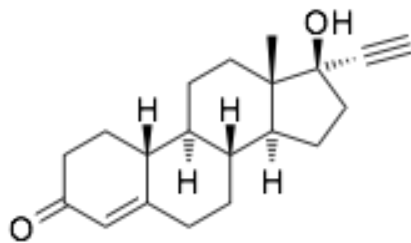


progesterone

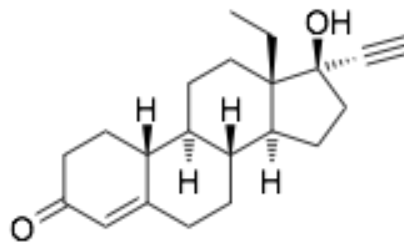
Contraceptives



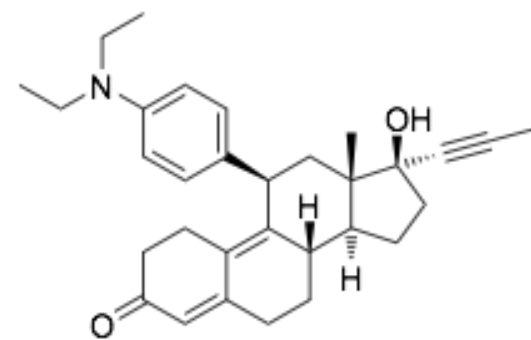
ethynylestradiol



norethindrone



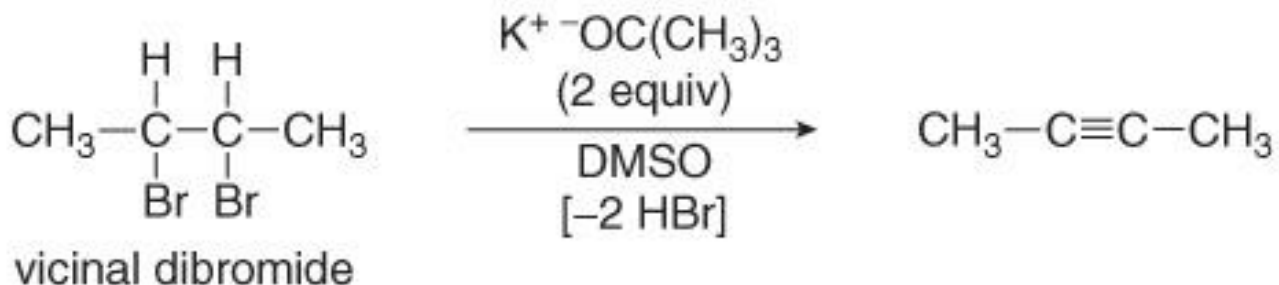
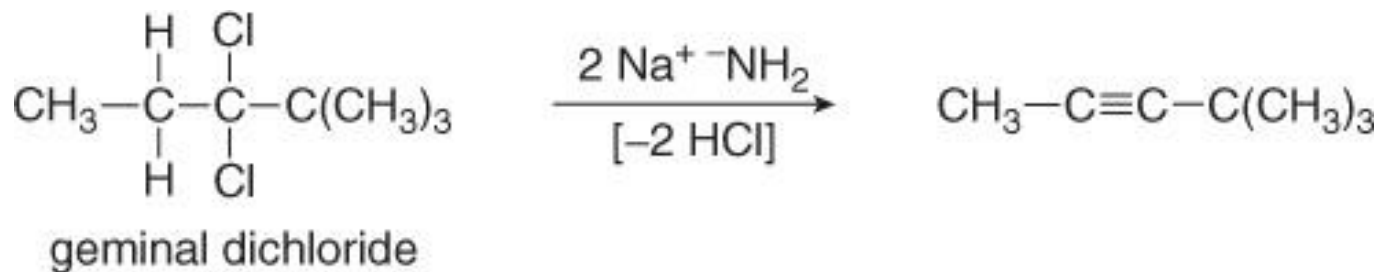
levonorgestrel



RU-486

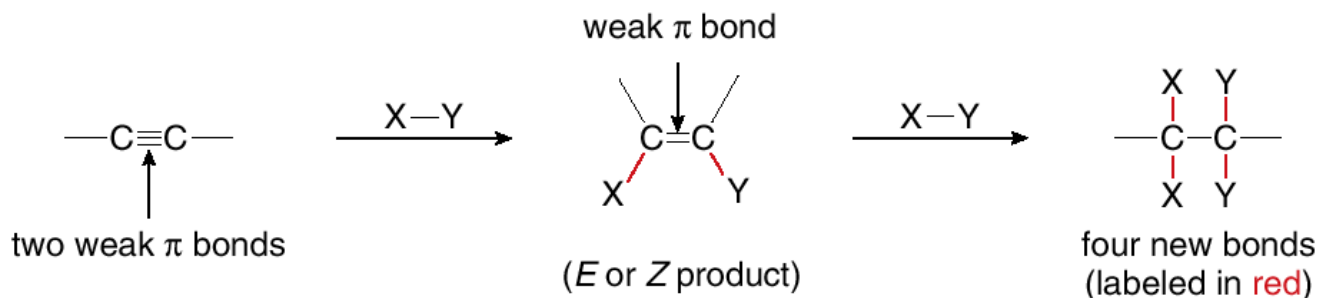
Preparation of Alkynes

- Alkynes are prepared by elimination reactions.



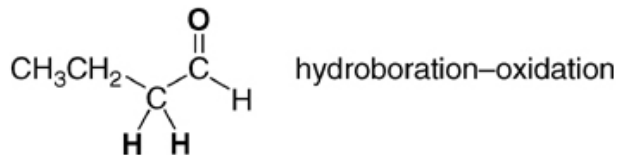
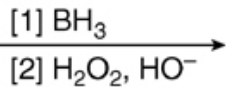
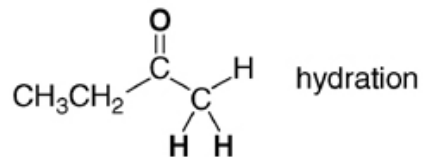
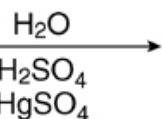
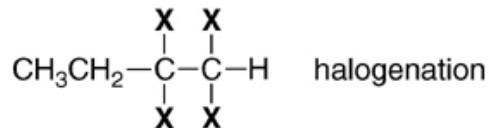
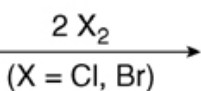
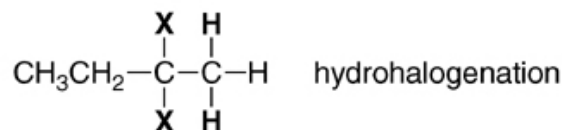
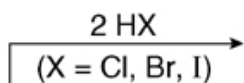
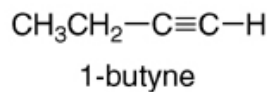
Alkyne Reactions—Additions

Addition reaction



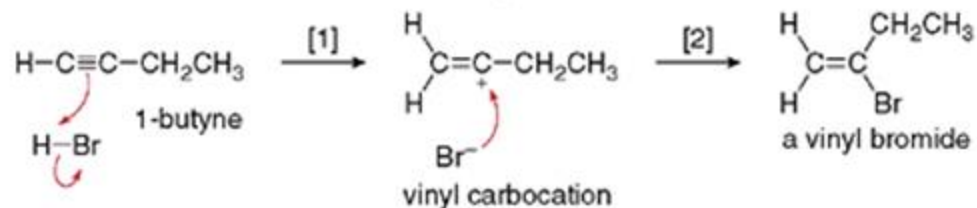
Four new bonds are formed.

Both π bonds are broken.



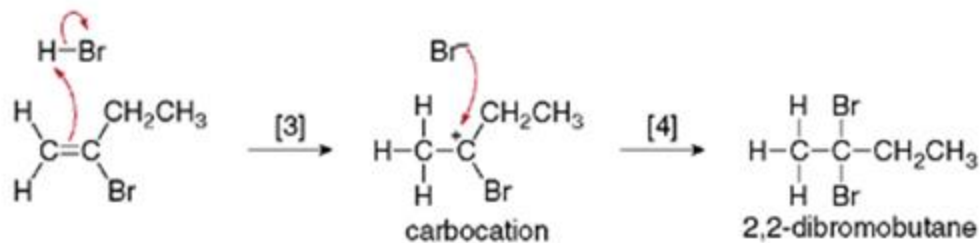
Hydrohalogenation

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

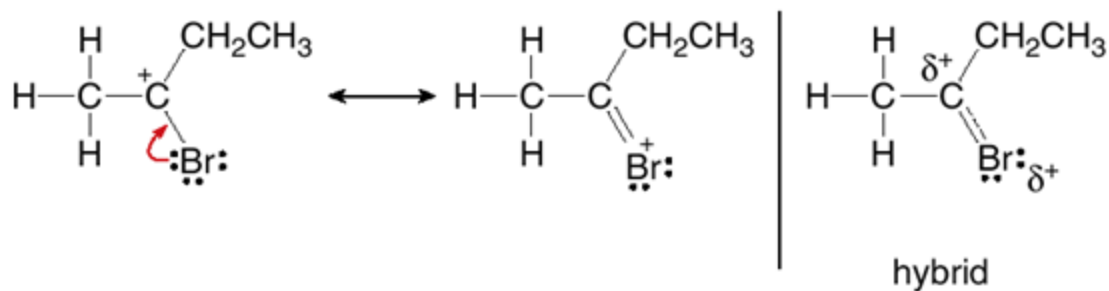


slower
(less stable vinyl cation)

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

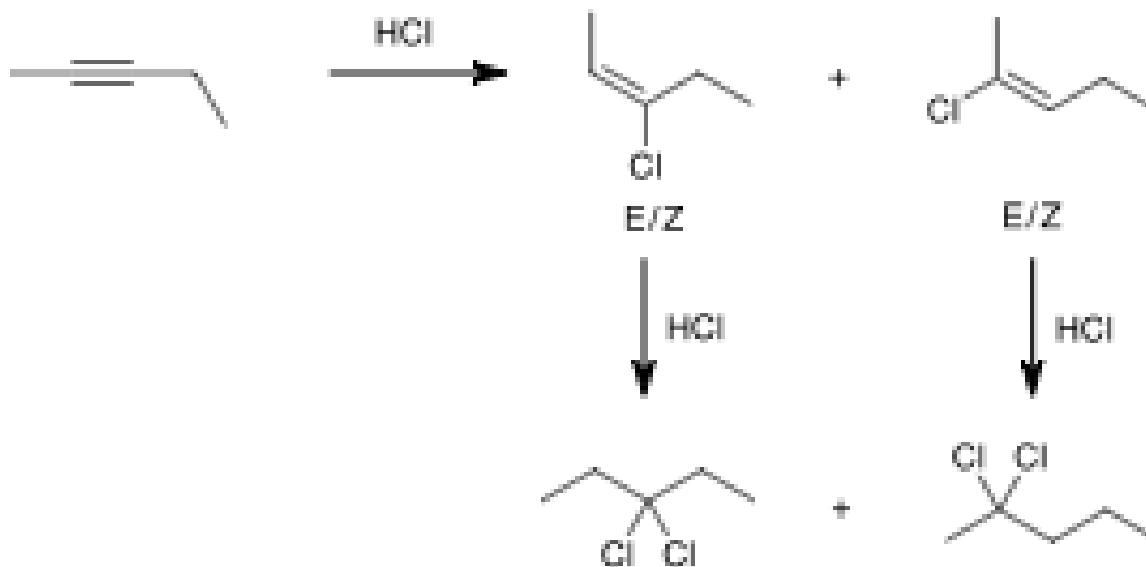


faster
(more stable alkyl cation)



The positive charge is delocalized.

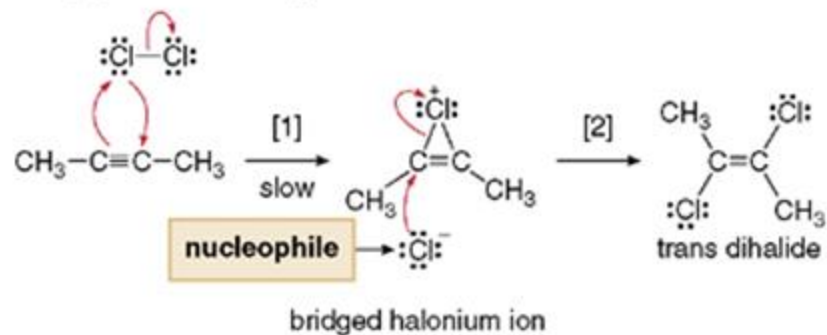
Hydrohalogenation



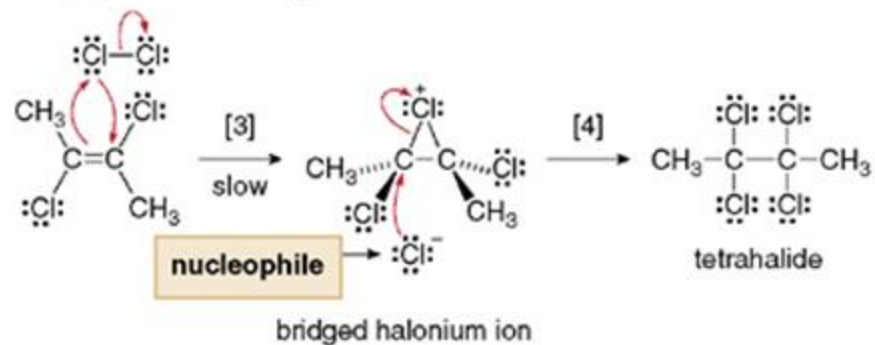
Not regioselective with internal alkynes

Halogenation

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

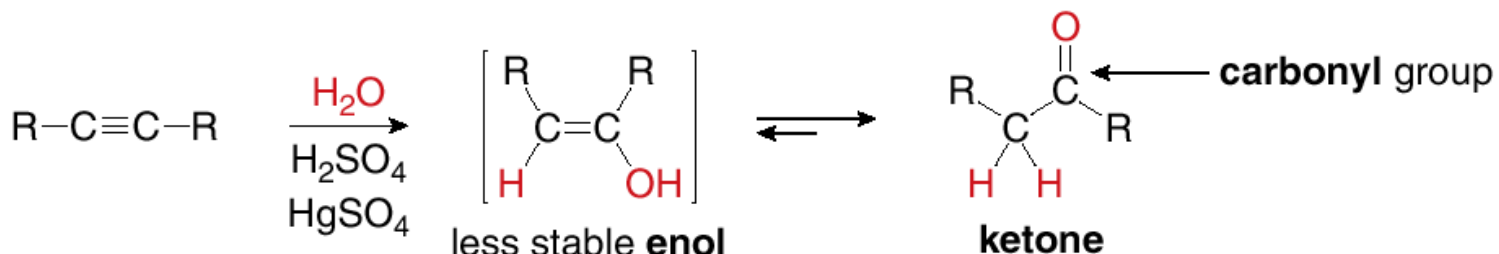


Part [2] Addition of X_2 to form a tetrahalide



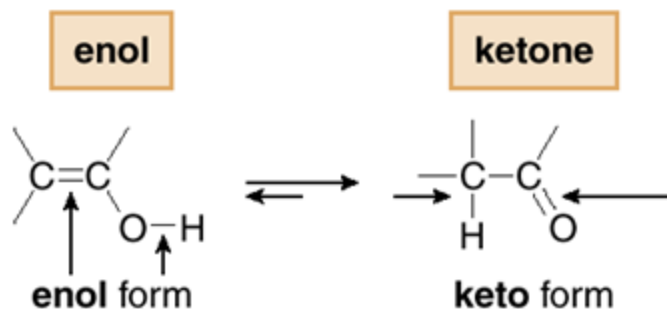
Hydration

Hydration



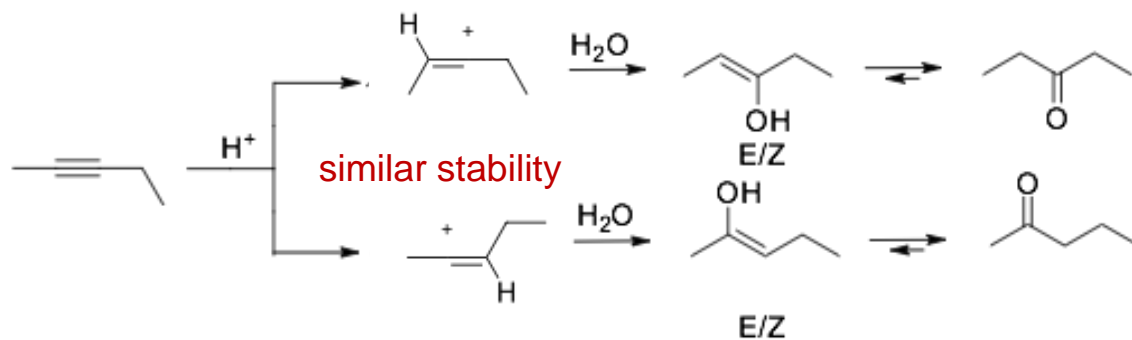
H_2O has been added.

- *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.

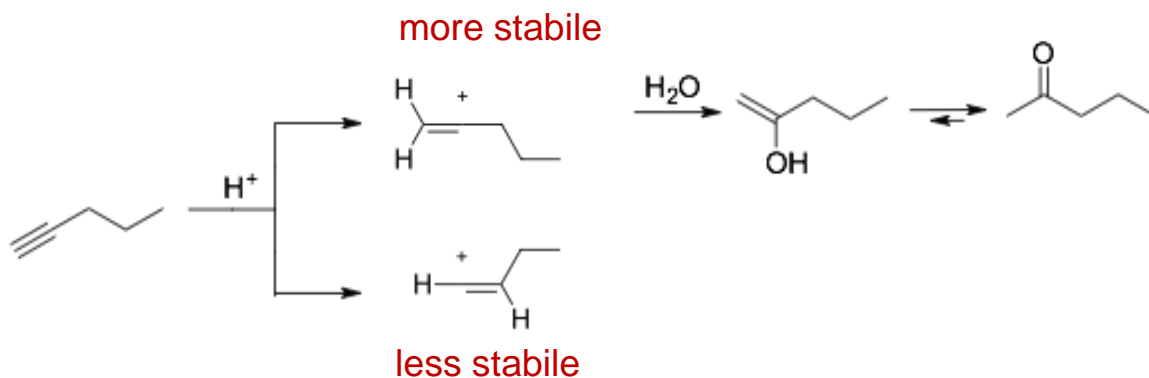


- Equilibrium favors the keto form largely because the C=O is much stronger than a C=C.

Hydration



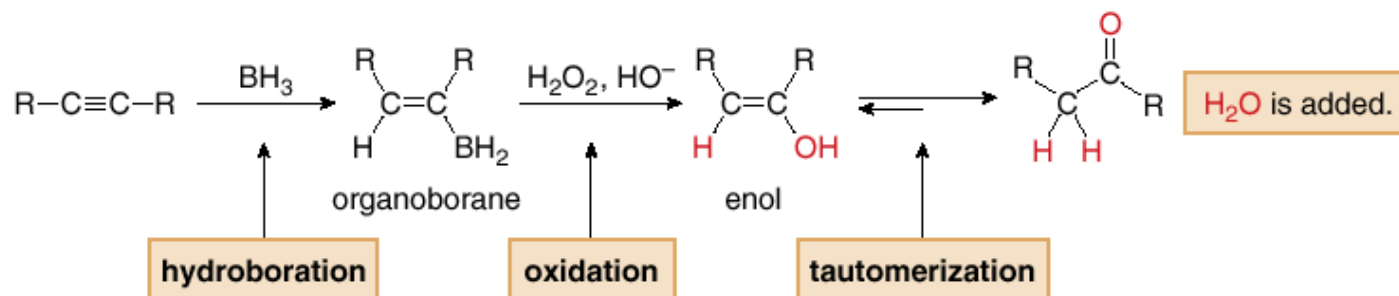
not regioselective



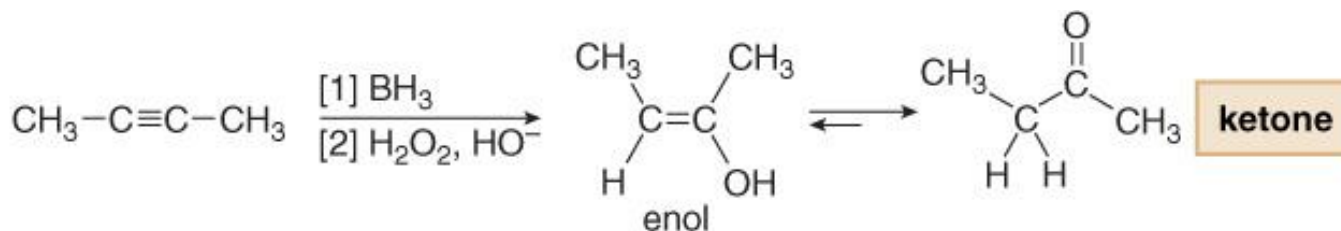
regioselective

Hydroboration—Oxidation

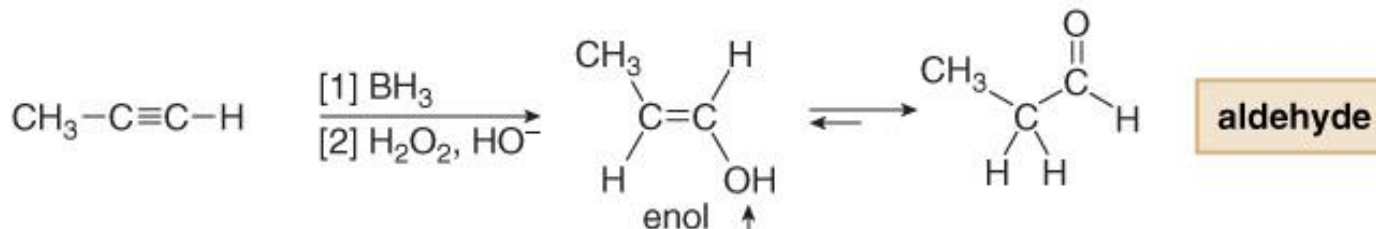
Hydroboration—oxidation



Internal alkyne



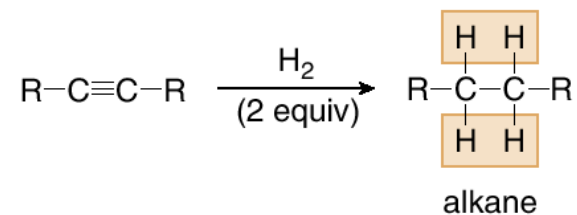
Terminal alkyne



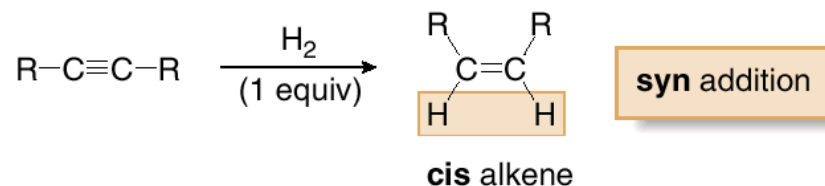
The OH group is bonded to the **less substituted C**.

Reduction of Alkynes

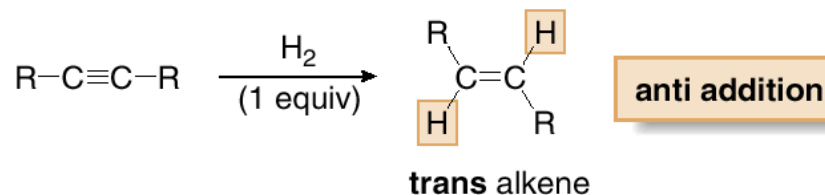
- Adding two equivalents of H_2 forms an alkane.



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

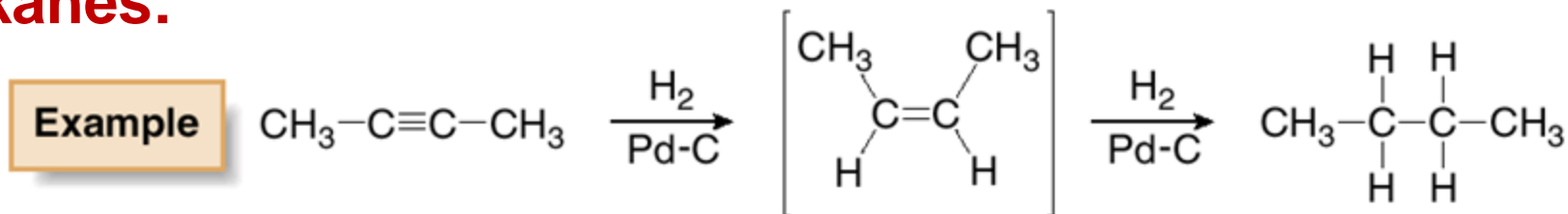


- Adding one equivalent of H_2 in an anti fashion forms a trans alkene.



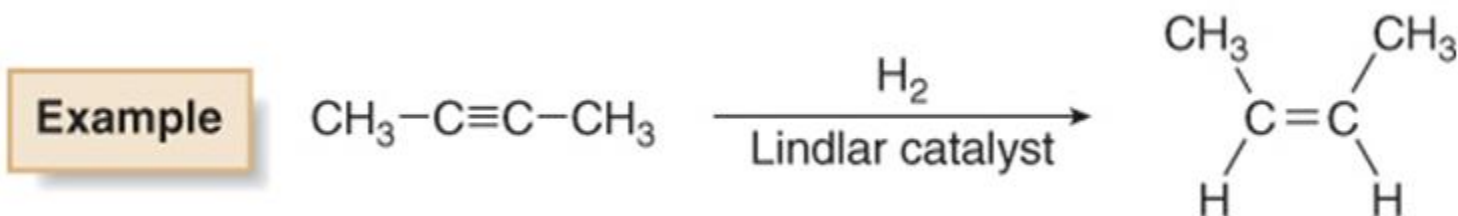
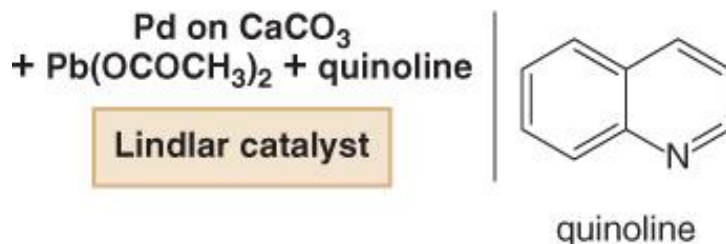
Catalytic Hydrogenation

Alkanes:



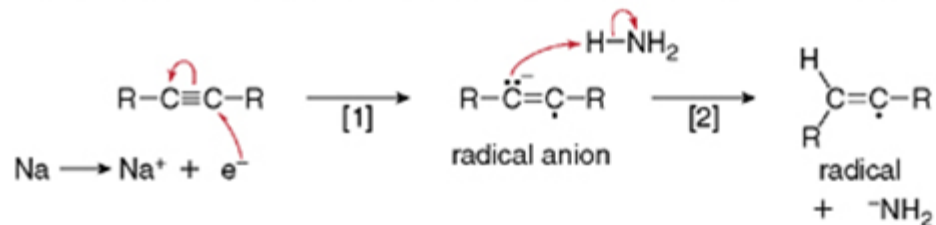
Cis-Alkenes:

- 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**.

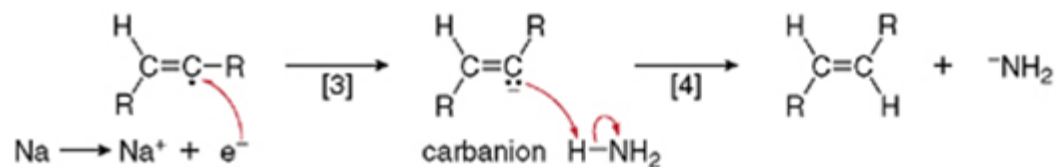


Dissolving Metal Reduction

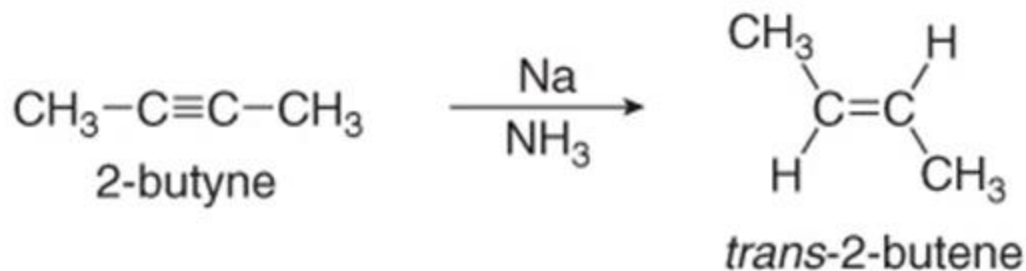
Steps [1] and [2] Addition of one electron and one proton to form a radical



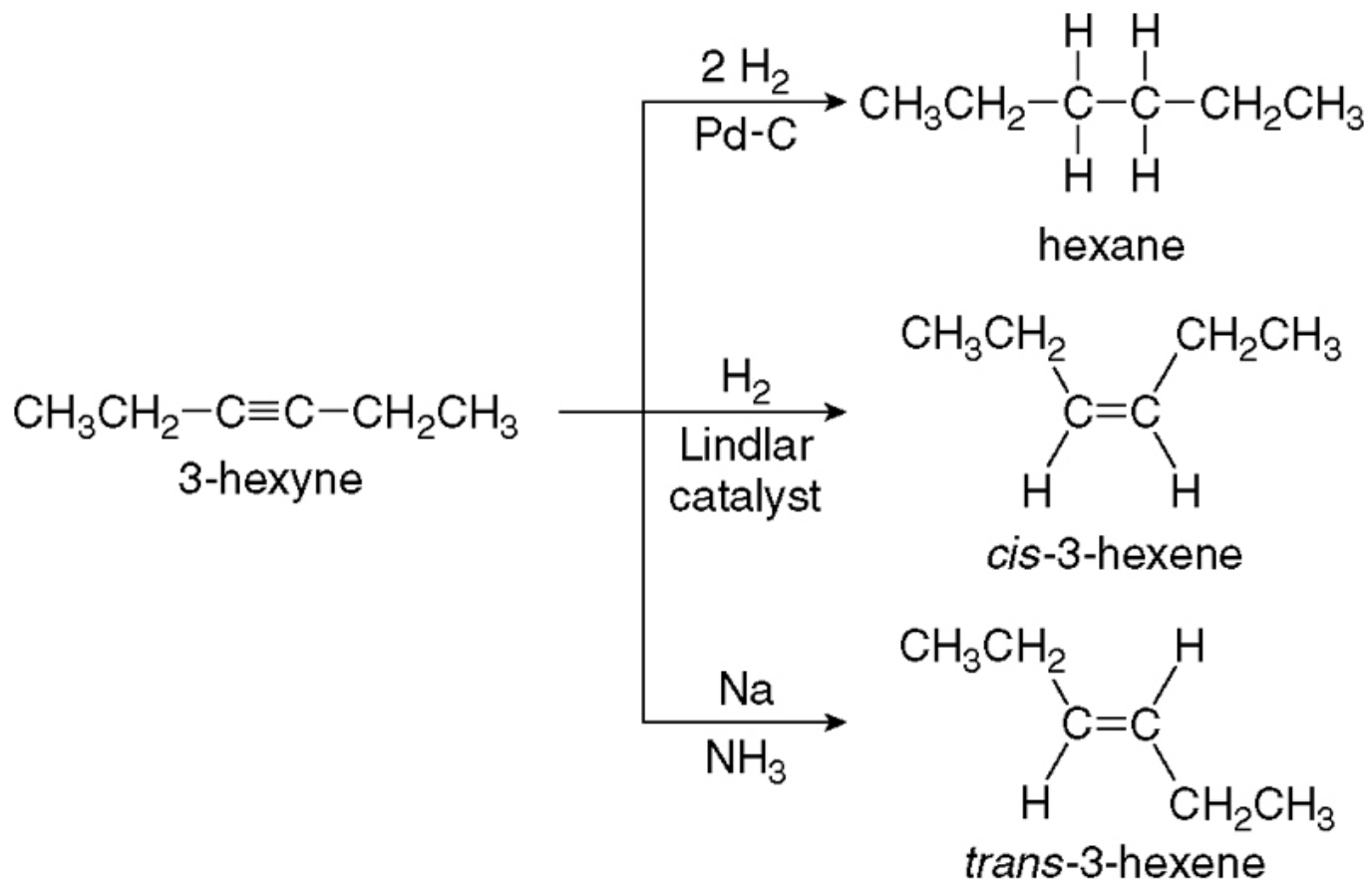
Steps [3] and [4] Addition of one electron and one proton to form the trans alkene



Example



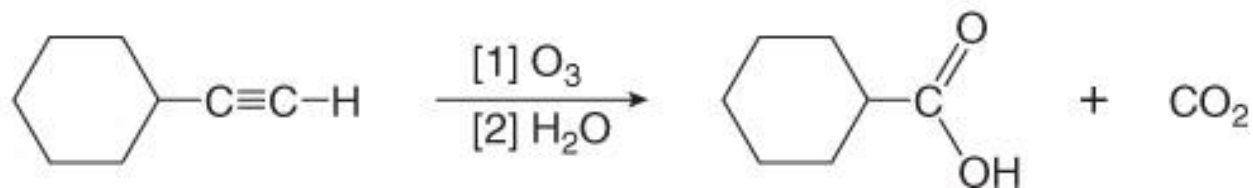
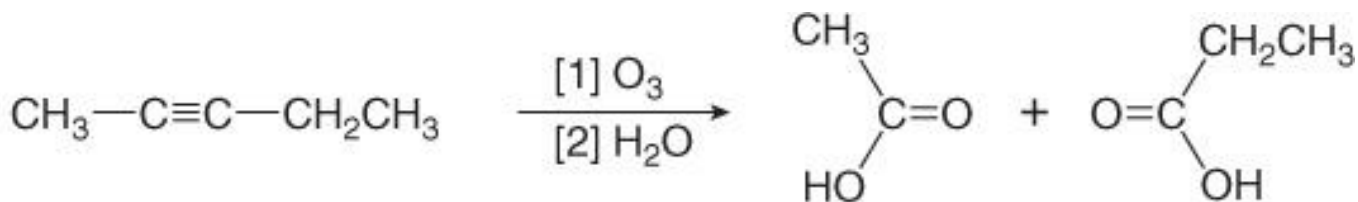
Summary of Alkyne Reductions



Oxidative Cleavage of Alkynes

- Internal alkynes are oxidized to carboxylic acids (RCOOH).
- Terminal alkynes afford a carboxylic acid and CO₂ from the *sp* hybridized C—H bond.

Examples



Acetylide anions



	Base	$\text{p}K_{\text{a}}$ of the conjugate acid
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These bases are **strong** enough to deprotonate an alkyne.

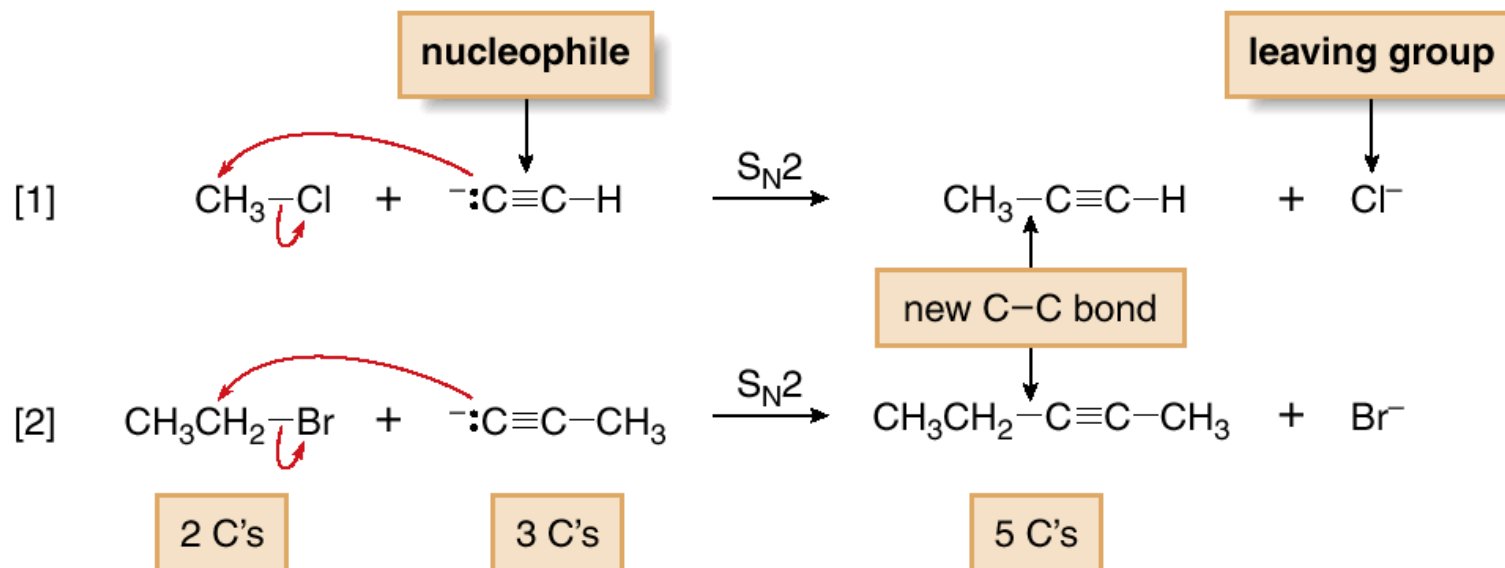
{	^-NH_2	38
	H^-	35

These bases are **not** strong enough to deprotonate an alkyne.

{	^-OH	15.7
	^-OR	15.5–18

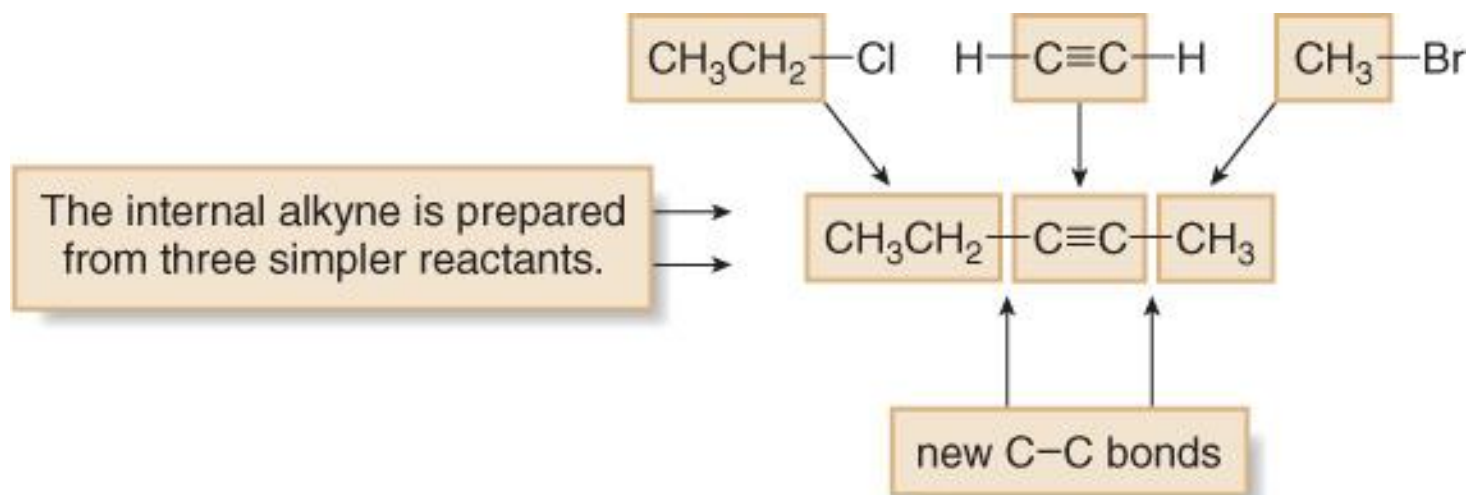
Acetylide Anions

- 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.

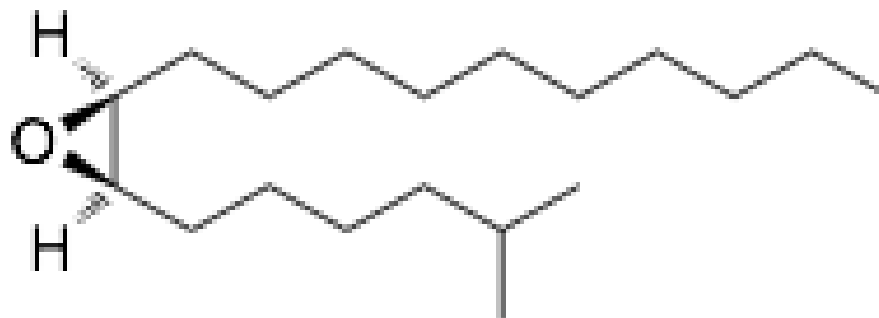


- Nucleophilic substitution with acetylide anions forms new carbon-carbon bonds.

Acetylide anions

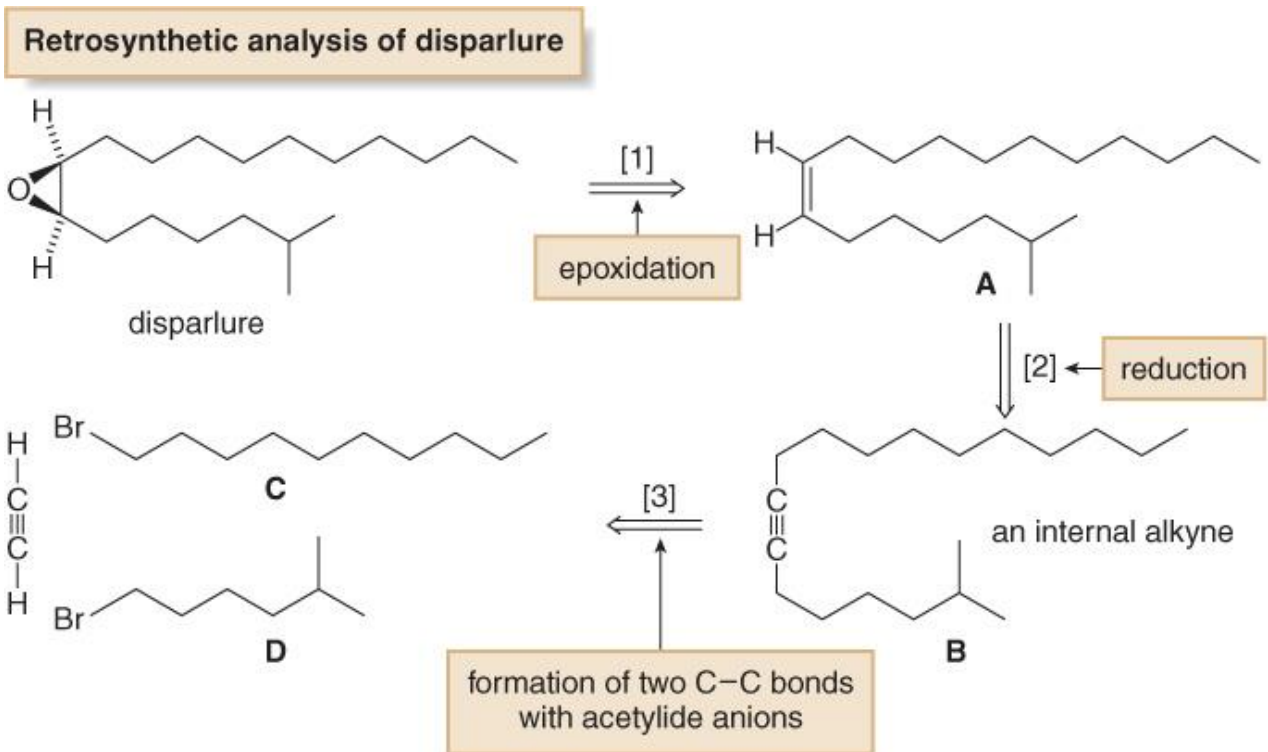


Synthesis



Disparlure – a pheromone

Synthesis



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.