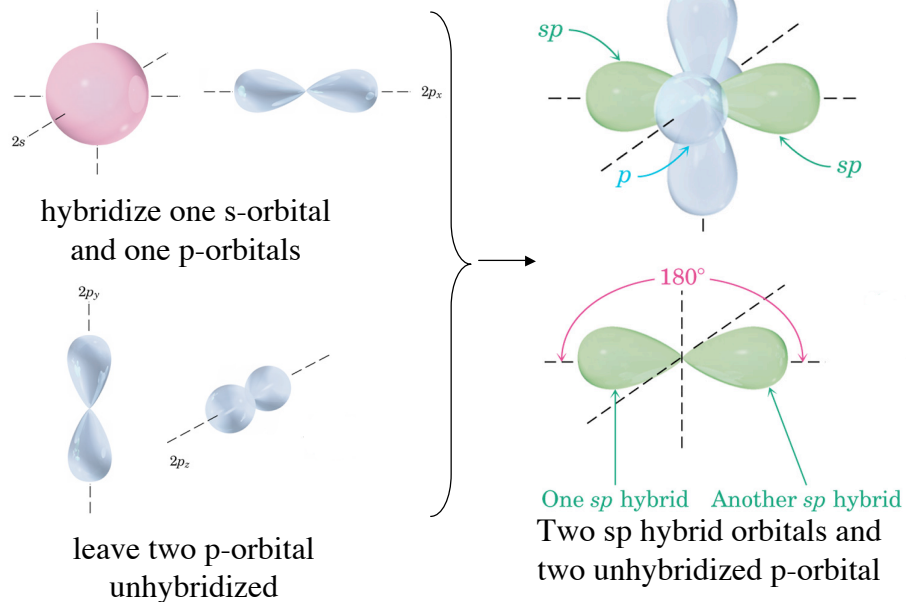
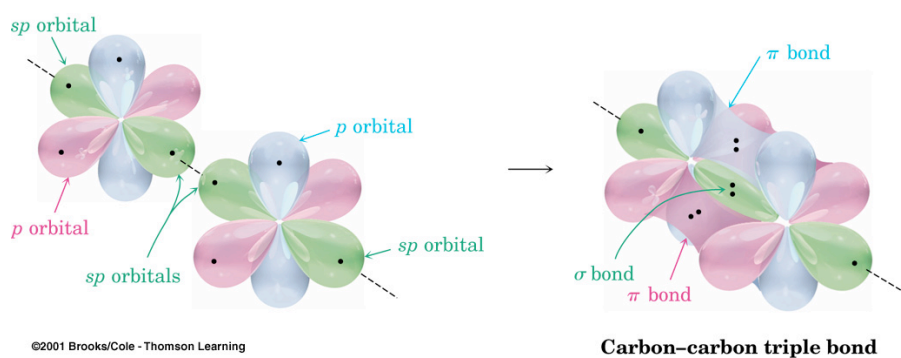


## Chapter 8: Alkynes

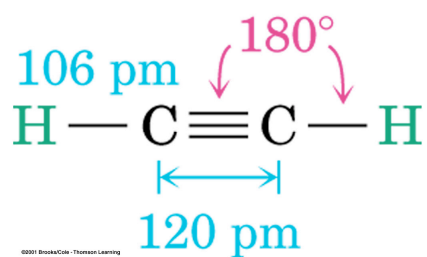
### sp Hybridized Orbitals



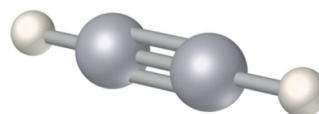
### $\text{C}\equiv\text{C}$ triple bonds- acetylene ( $\text{C}_2\text{H}_2$ )



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## Alkyne Nomenclature

### Systematic Nomenclature (IUPAC System)

Prefix-Parent-Suffix

### Naming Alkynes

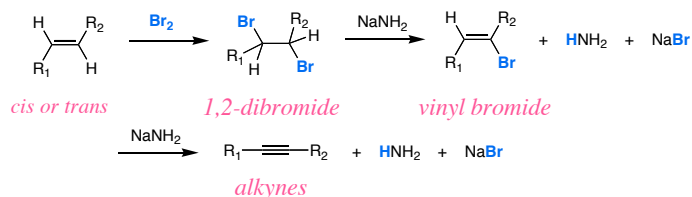
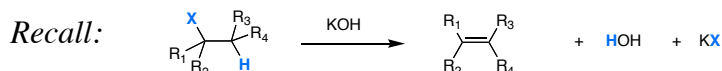
Suffix: -yne

Many of the same rules for alkanes apply to alkenes

1. Number the carbon chain from the end of the carbon nearest the triple bond
2. The alkyne position is indicated by the number of the alkyne carbon in the chain
3. Compounds with two triple bonds are referred to as diynes, three triple bonds as triynes, etc

## Preparation of Alkynes

### a. Elimination reactions of 1,2-dihalides



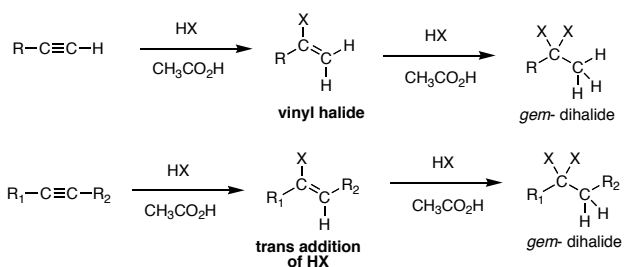
### b. From other alkynes. *Section 8.8 - 8.10*

$\text{R}_1-\text{C}\equiv\text{C}-\text{H}$       Terminal Alkyne: triple bond is at the end of the carbon chain

$\text{R}_1-\text{C}\equiv\text{C}-\text{R}_2$       Internal Alkyne: triple bond is not at the end of the carbon chain

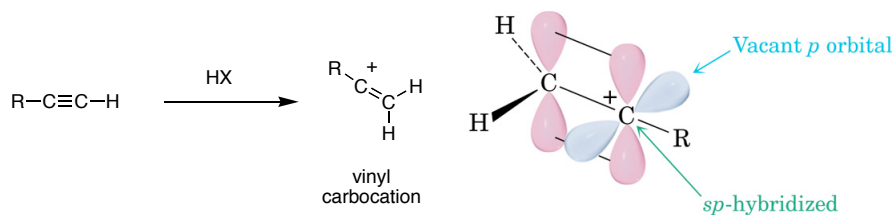
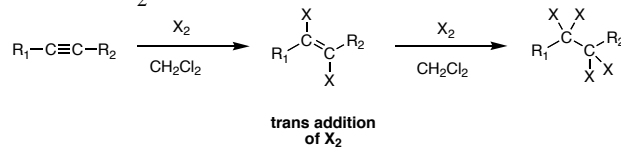
## Reactions of Alkynes:

### Addition of HX- Markovnikov addition



only useful if  $\text{R}_1 = \text{R}_2$  or if  $\text{R}_2 = \text{H}$

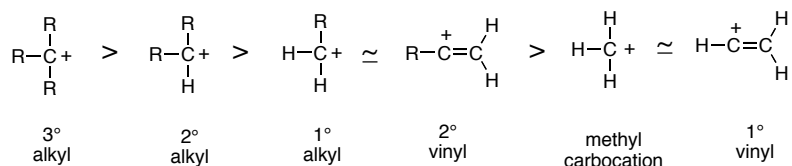
### Addition of $\text{X}_2$



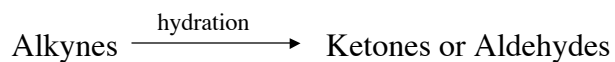
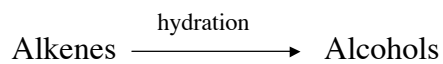
### A 2° vinylic carbocation

Vinyl carbocations are generally less stable than the corresponding alkyl carbocation

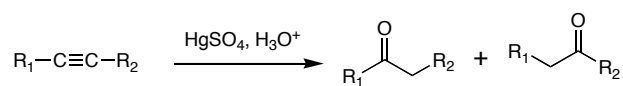
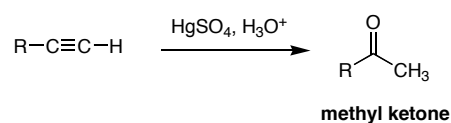
### Carbocation Stability



## Hydration of Alkenes

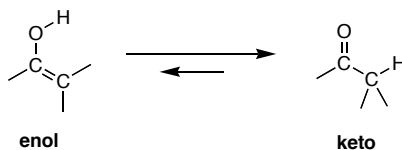


Mercury (II) Catalyzed Hydration: similar to oxymercuration  
- Markovnikov Addition



## Keto-enol tautomerization

tautomer: constitutional isomers that interconvert

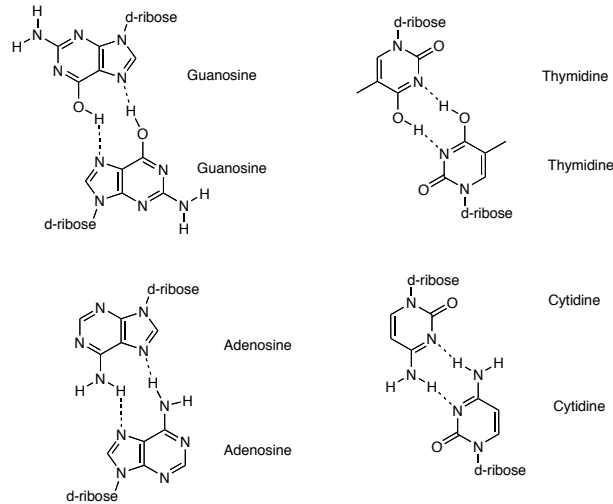


C=C	$\Delta H^\circ = 611 \text{ KJ/mol}$	C=O	$\Delta H^\circ = 735 \text{ KJ/mol}$
C-O	380	C-C	376
O-H	436	C-H	420

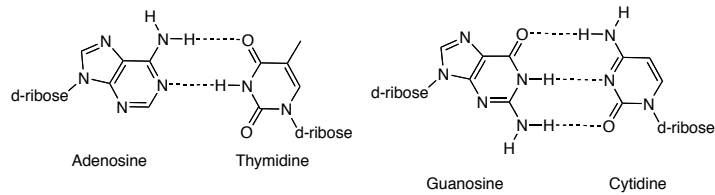
$$\Delta H^\circ = -104 \text{ KJ/mol}$$

## Keto-Enol Tautomerization and the Structure of DNA

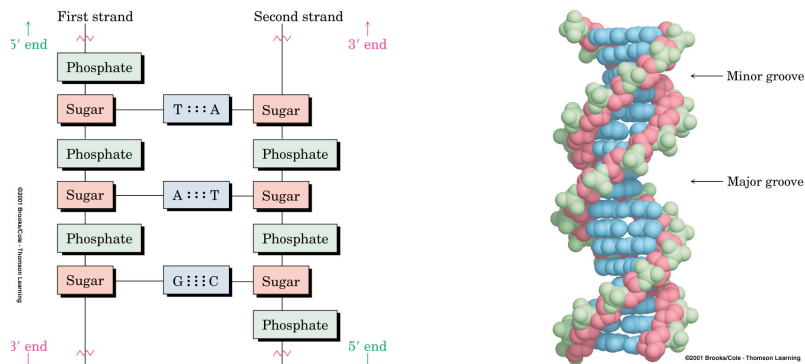
Proposed structure:



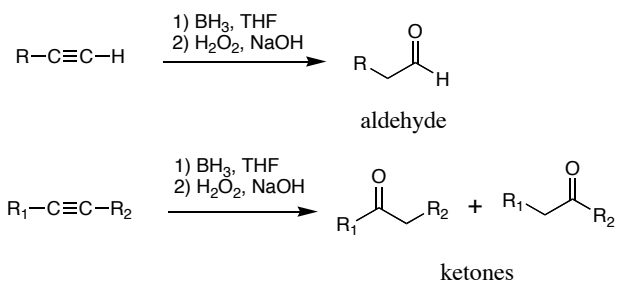
Proposal inconsistent with Chargaff's Rule



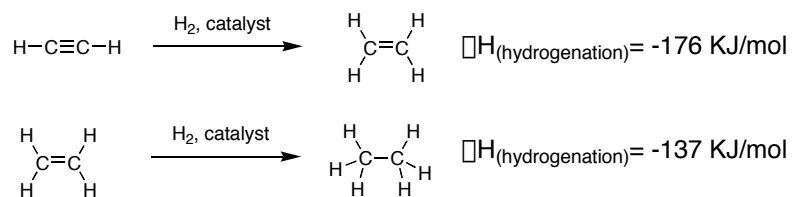
### Watson-Crick (-Donohue) Base Pairing



## Hydroboration of Alkynes

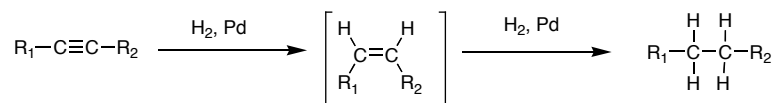


## Hydrogenation of Alkynes



The second  $\pi$ -bond of an alkyne is slightly more reactive toward hydrogenation

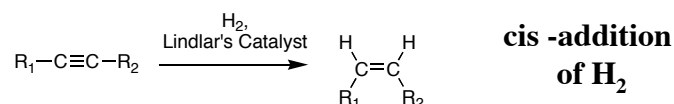
Under normal hydrogenation conditions, hydrogenation of an alkyne ***can not*** be stopped at the alkene stage



Lindlar's catalyst: "poisoned" palladium catalyst

Pd on  $\text{CaCO}_3$  +  $\text{Pb}(\text{OAc})_4$  + quinoline (amine)

"poisons" reduce the catalysts activity so only the most reactive functional groups are hydrogenated

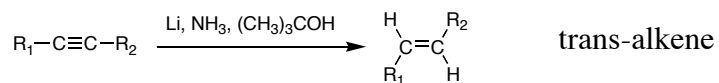


Reaction can be stopped at the cis-alkene stage

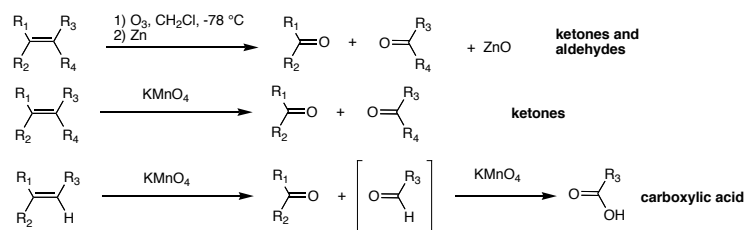
Dissolving Metal Reduction:

Li(0) metal in liquid ammonia ( $\text{NH}_3$ )

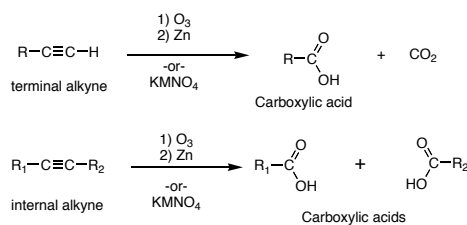
$\text{Li(0) in NH}_3 \longrightarrow \text{e}^\bullet$  (solvated electron)



### Oxidative cleavage of alkenes (sect. 7.8):

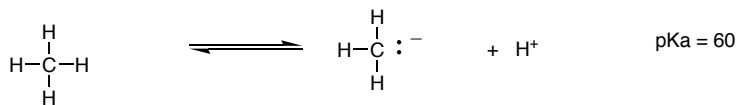
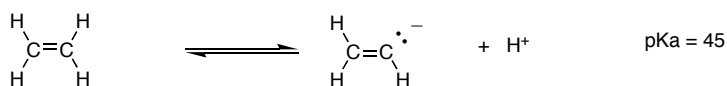
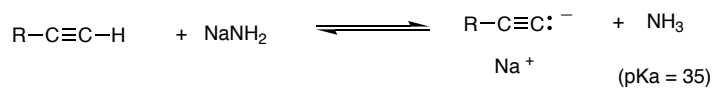
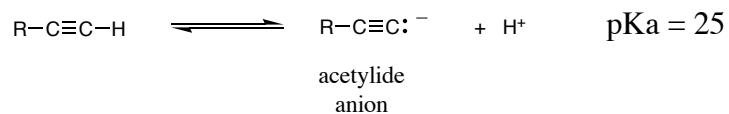


### Oxidative Cleavage of Alkynes (sect.8.7)



Alkynes are less reactive toward oxidative cleavage than alkenes.  
Alkenes can be oxidatively cleaved in the presence of alkynes

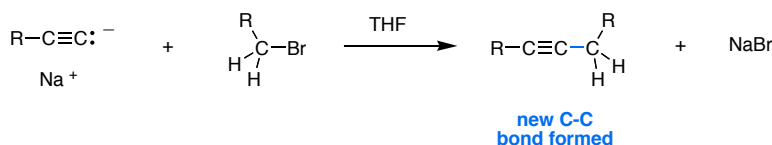
### Acidity of Terminal Alkynes





**Alkylation of the acetylide anion:** formation of C-C bonds  
a substitution reaction between a nucleophile and alkyl halide

Acetylide anions are strong nucleophiles and will undergo substitution reactions with alkyl halides



The acetylide anion displaces bromide from the alkyl bromide forming a new C-C bond.

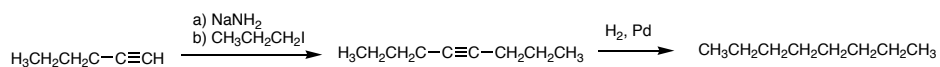
Alkylation is a general method of making alkynes from simpler alkynes.

Alkylation of acetylide anions is generally limited to primary alkyl bromides and iodide

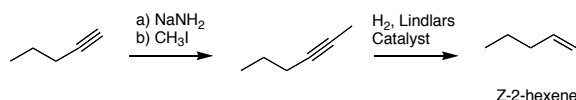
## Organic Synthesis

Synthesis: making larger, more complex molecules out of smaller ones using known and reliable reactions

Prepare octane from 1-pentyne



Prepare Z-2-butene from 1-pentyne



work the problem backwards