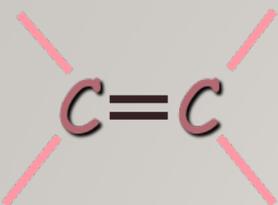


CHM-134 ORGANIC CHEMISTRY

CHAPTER-2: ALKENES & ALKYNES



Double bond
Names: ending **-ane** → **-ene**

Naming follows the rules for hydrocarbons (functional groups —OH and —SH override these rules):

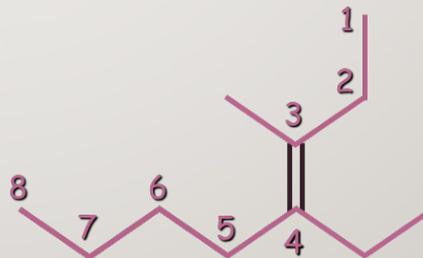
General guidelines:

Rings have priority, regardless of the presence of double (or triple) bonds.

If there are no rings: the longest chain has priority, regardless of the presence of double (or triple) bonds.

Names in the absence of rings;

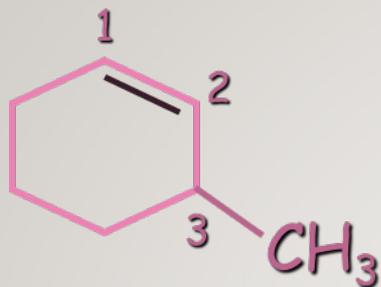
1. Find longest chain. If it contains both C_{sp^2} carbons → alkene. If not → alkenylalkane
2. Number the chain with C=C close to terminus
3. Name and # substituents, in alphabetical order



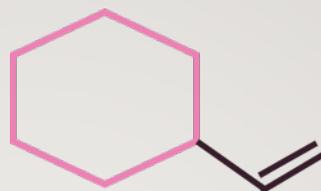
4-Ethyl-3-methyl-3-octene

3.1 NOMENCLATURE RULES

4. Find largest ring. If it contains both C_{sp^2} carbons \rightarrow cycloalkene. If not \rightarrow alkenylcycloalkane

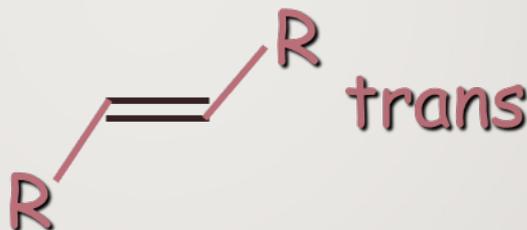


3-Methylcyclohexene



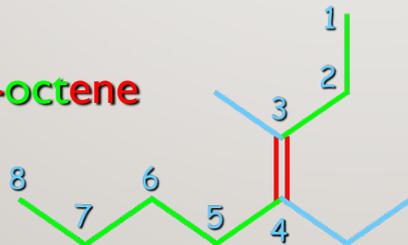
Ethenylcyclohexane

5. Stereoisomers:



6. For tri- and tetrasubstituted alkenes: E, Z naming

E-4-Ethyl-3-methyl-3-octene



Respective higher priority groups on:
Opposite sides: E
Same side: Z

3.1 NOMENCLATURE RULES



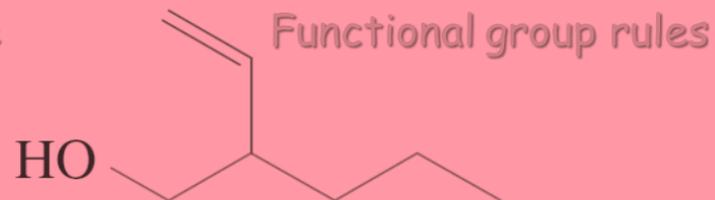
4-Ethenylnonane



(3-Ethenylhexyl)cyclohexane



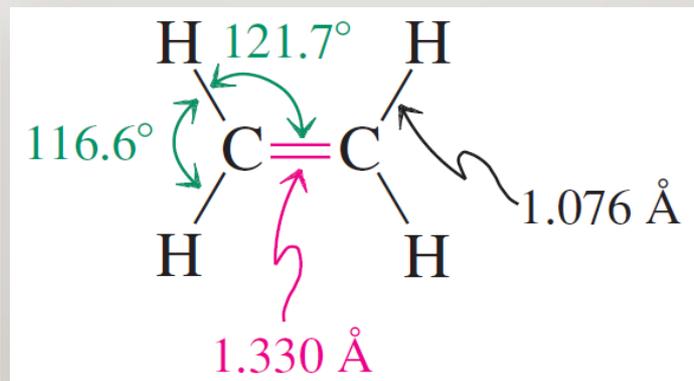
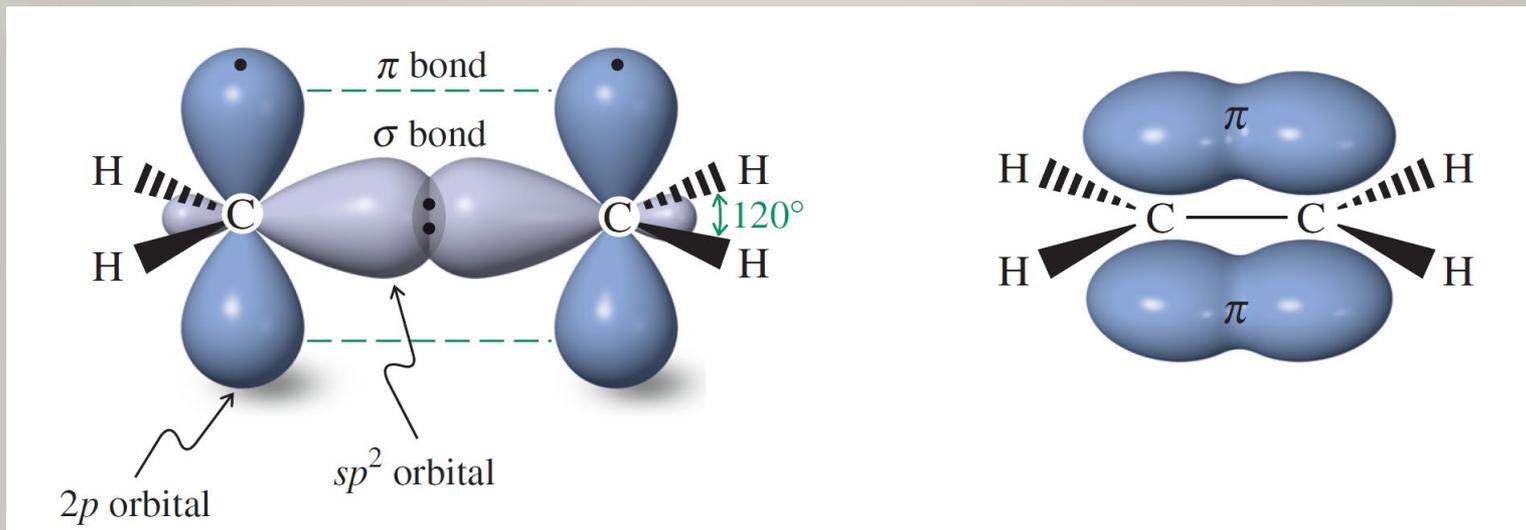
3-Methyl-1-hexene



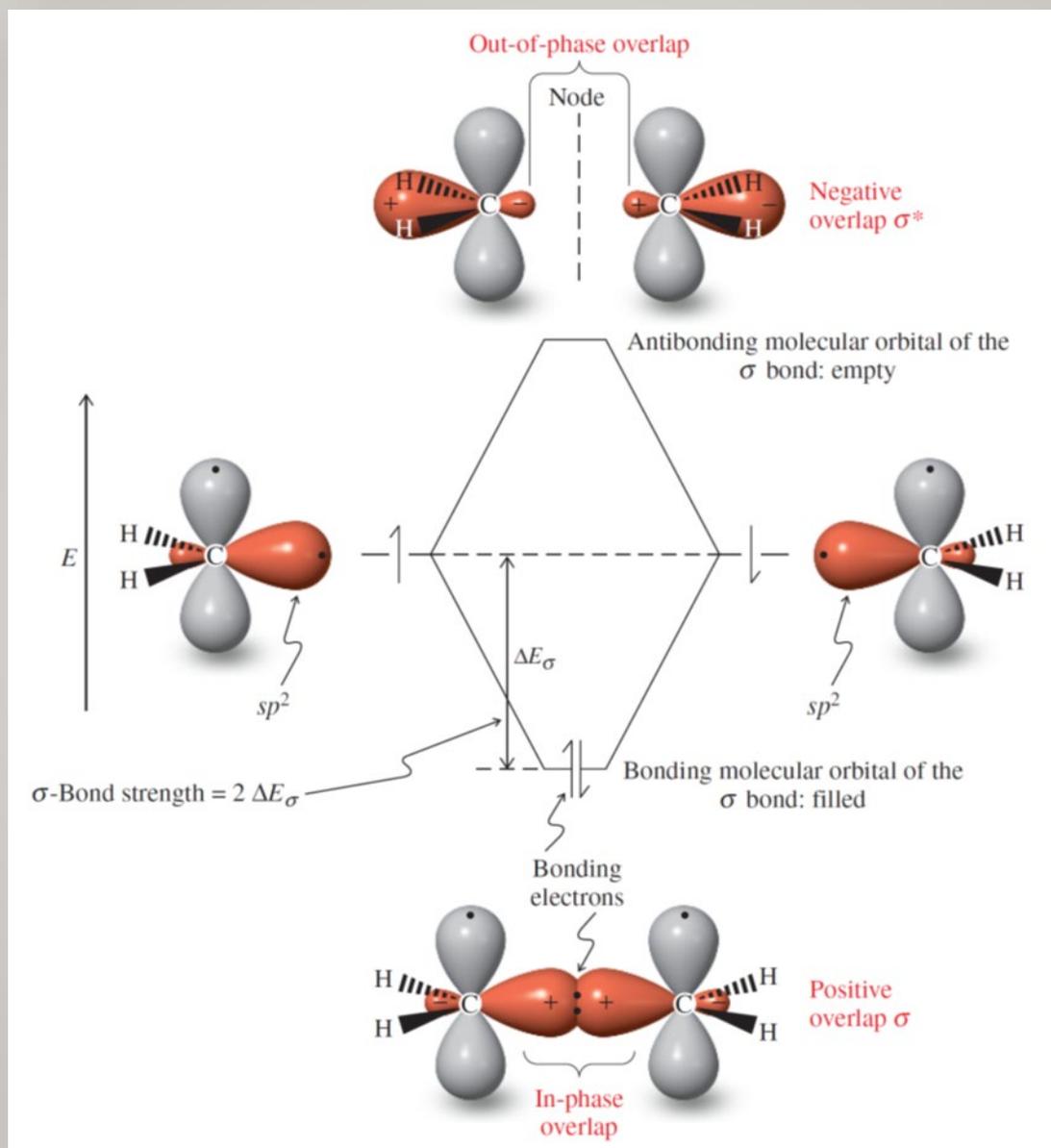
2-Ethenyl-1-pentanol

3.2 STRUCTURE OF THE DOUBLE BOND

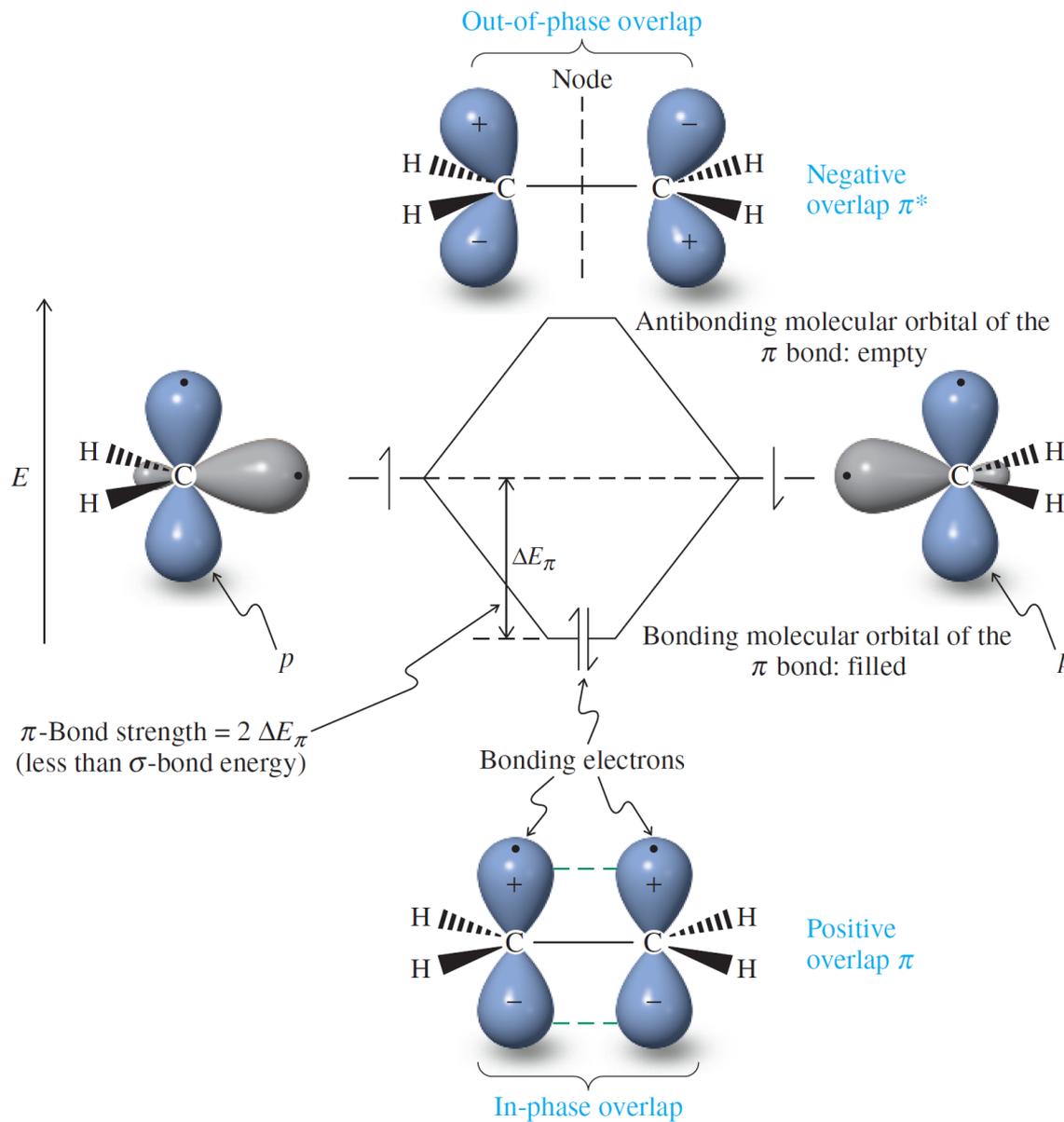
Two components: the σ -bond and the π -bond



3.2 STRUCTURE OF THE DOUBLE BOND

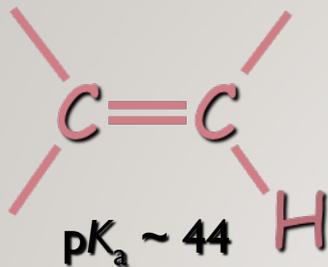


3.2 STRUCTURE OF THE DOUBLE BOND

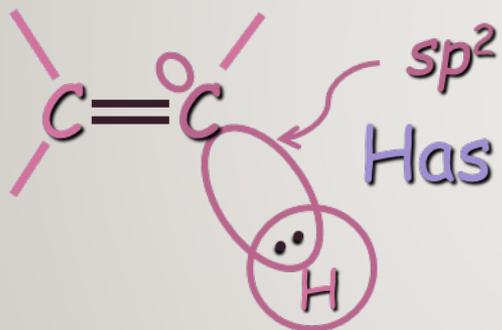


3.2 STRUCTURE OF THE DOUBLE BOND

Alkenyl Hydrogens Are Relatively Acidic



Compare to $\text{CH}_3\text{CH}_2\text{-H}$ $\text{p}K_a \sim 50$



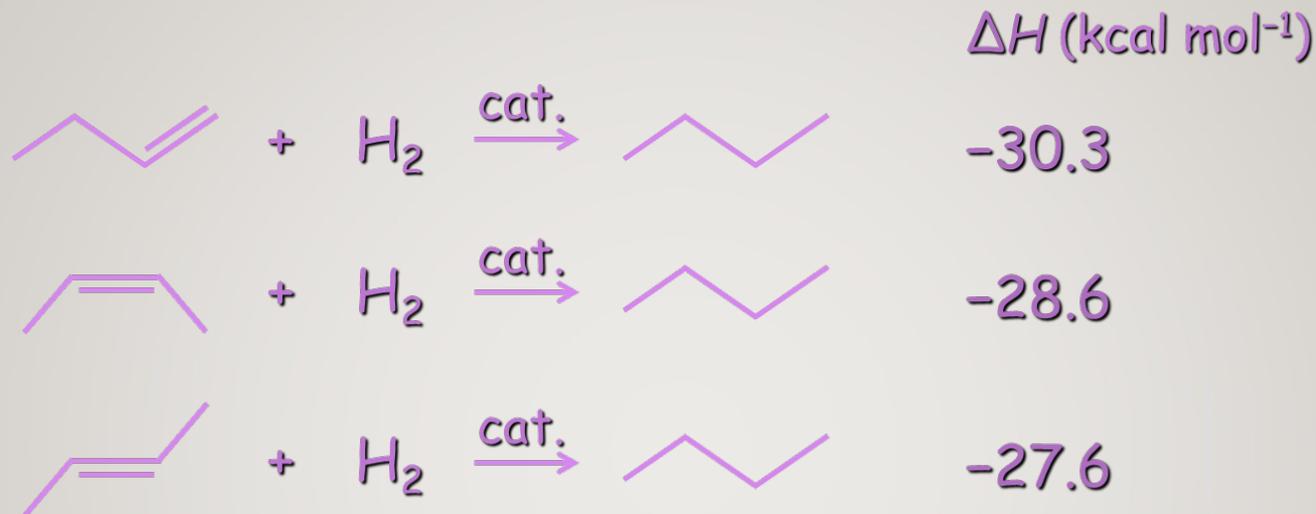
Has 33% s character.

In contrast:

sp^3 has 25% s character.

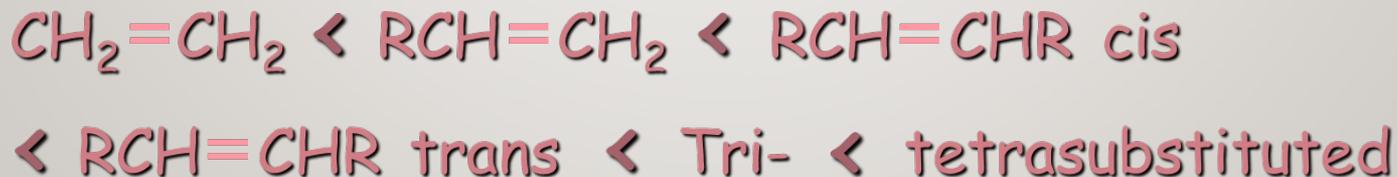
3.3 RELATIVE STABILITY OF ALKENES

Measure heat of hydrogenation, $\Delta H_{\text{Hydrogenation}}$, of isomers, e.g., of butenes:

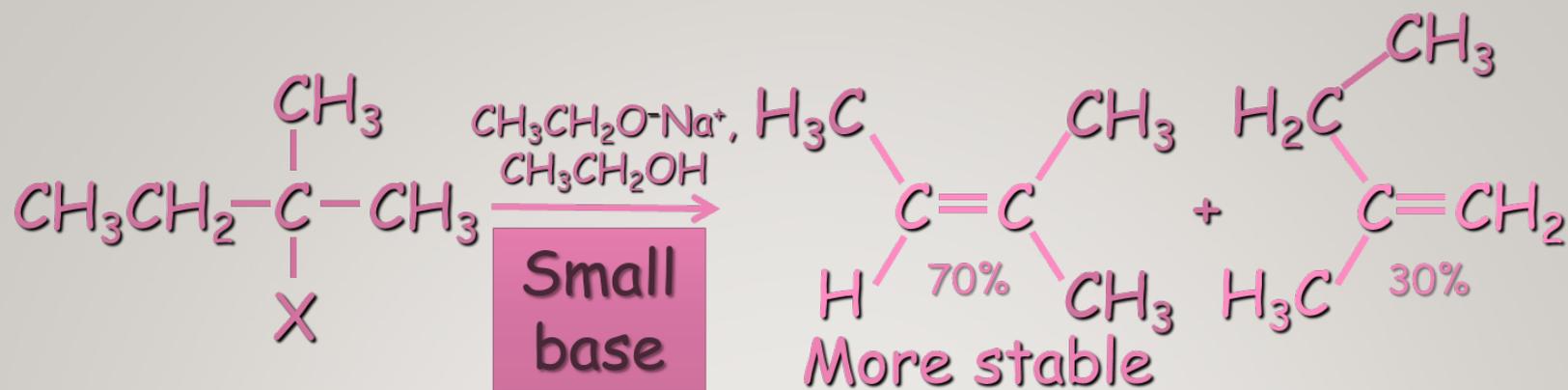


Relative stability: Internal > terminal trans > cis

General order of stability:

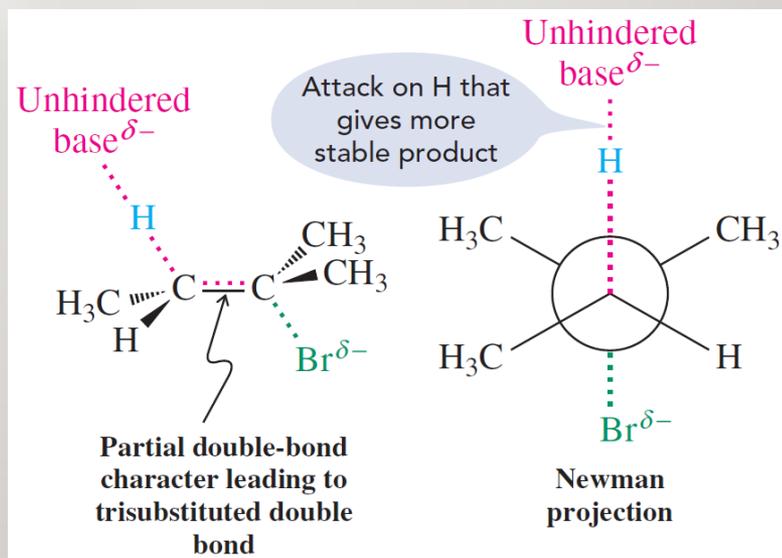


3.4 SYNTHESIS OF ALKENES



Saytzev-Rule:

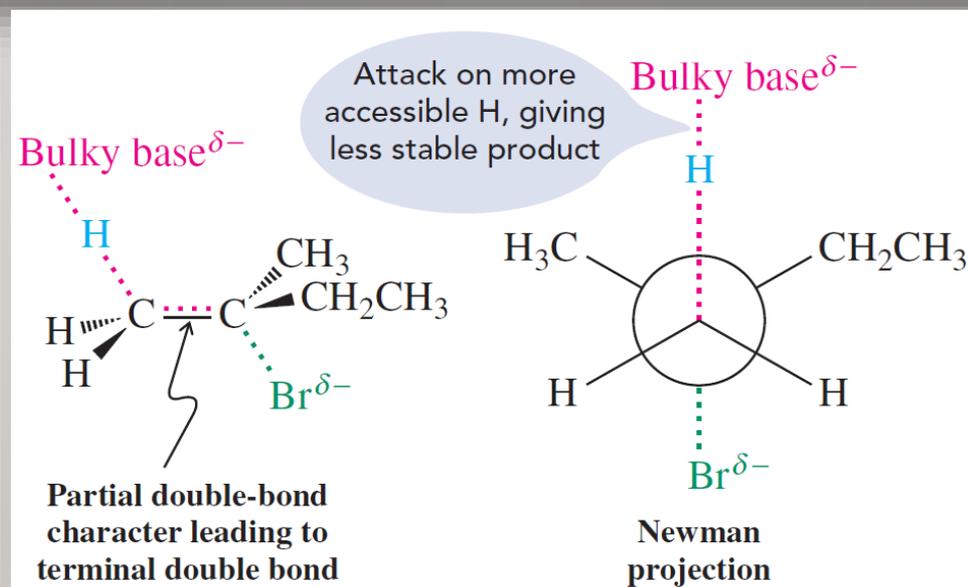
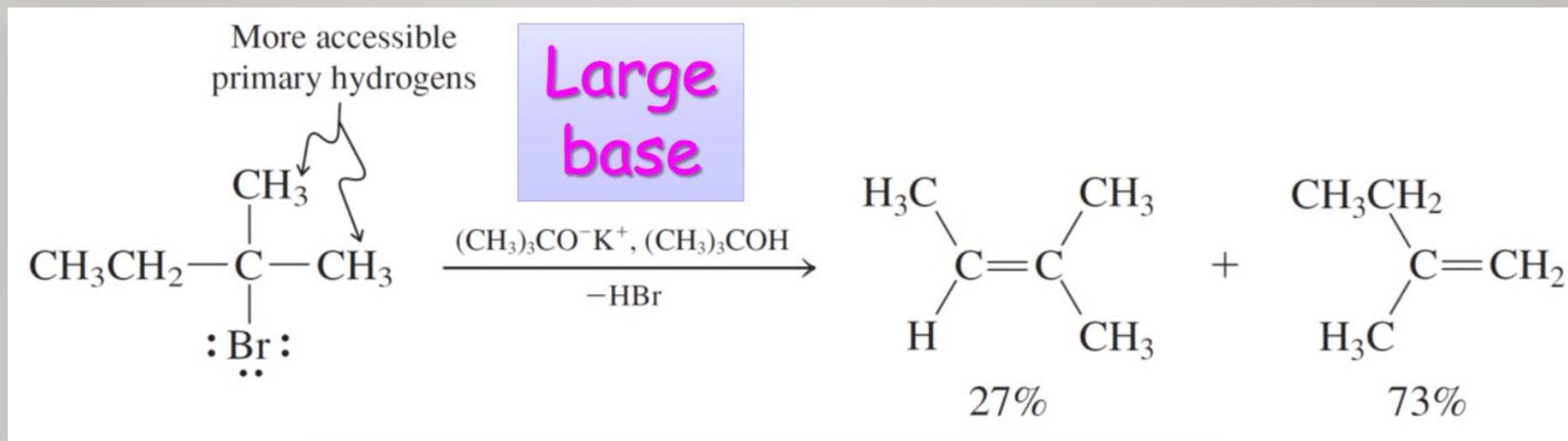
Non-bulky base leads to more stable internal double bond.



3.4 SYNTHESIS OF ALKENES

Hofmann Rule

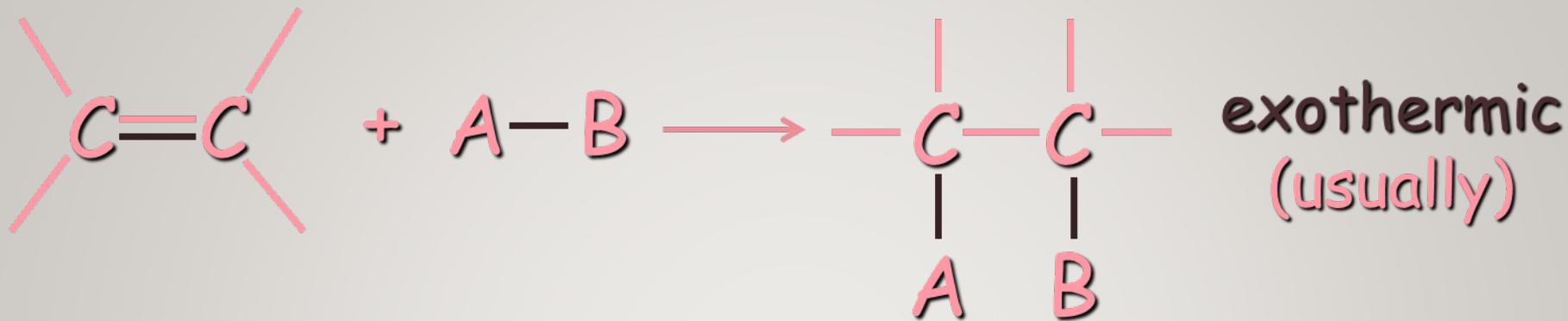
Bulky base leads to less stable terminal double bond



3.4 REACTIONS OF ALKENES

Addition Reactions Of Alkenes

π Bond is unsaturated: Reacts by addition.



IMPORTANT REACTIONS

1. Catalytic Hydrogenation
2. Electrophilic Additions
3. Hydroboration-Oxidation
4. Electrophilic Carbene Additions
5. Electrophilic Oxidation
6. Radical Hydrobromination
7. Alkene Polymerization

3.5 ALKYNES

C≡C Triple Bond

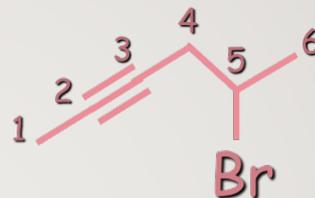
Naming: Same rules as for alkenes. When triple bond is in longest chain: ending -ene turns into -yne.



Ethyne



1-Pentyne
(or pent-1-yne)



5-Bromo-2-hexyne

Priority:

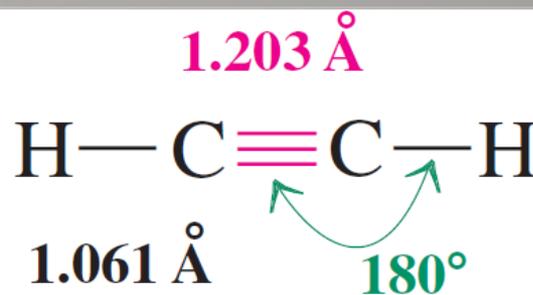
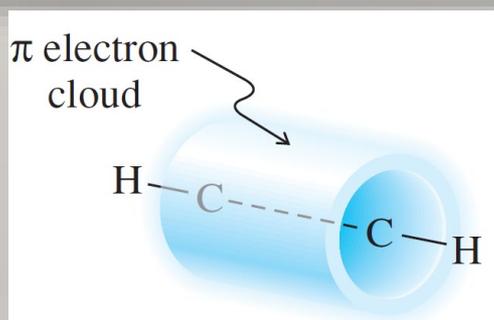
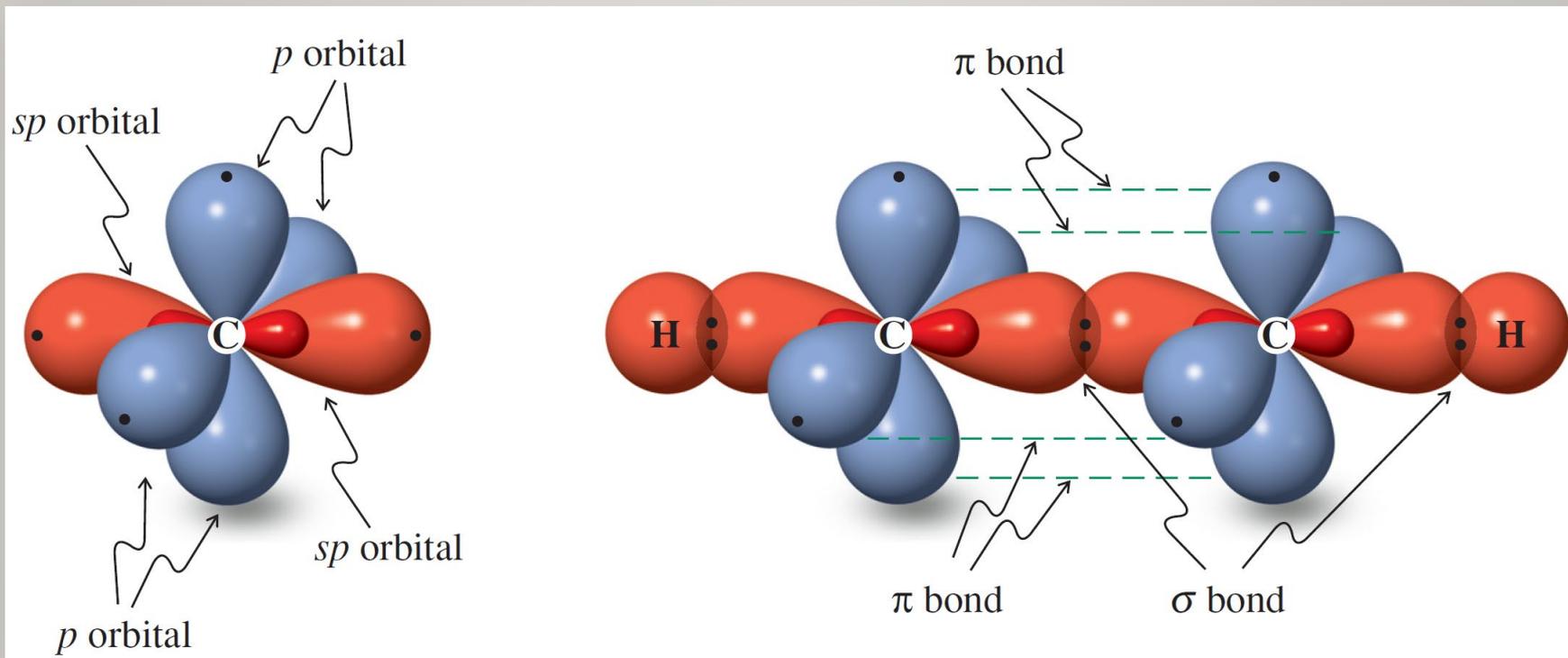
-ol > -thiol > -yne



2-Propyn-1-ol

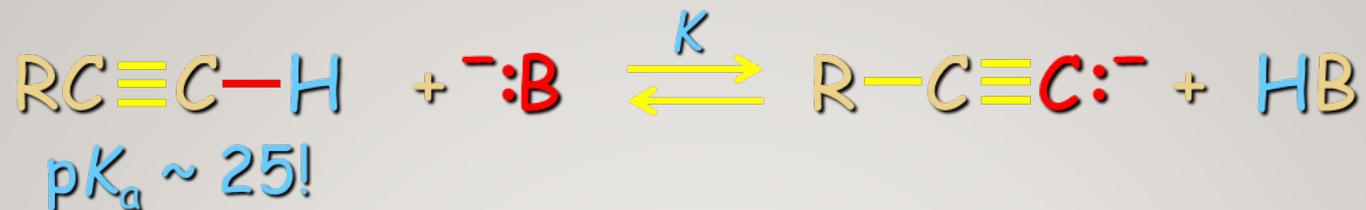
3.6 STRUCTURES OF ALKYNES

Two perpendicular π bonds; sp hybrids



3.6 STRUCTURES OF ALKYNES

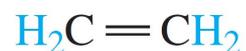
Alkynes Are Relatively Acidic



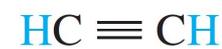
Hybridization:
 $\text{p}K_a$:



<



<



sp^3

50

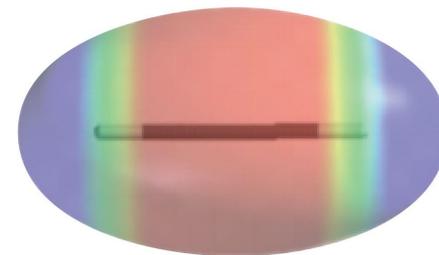
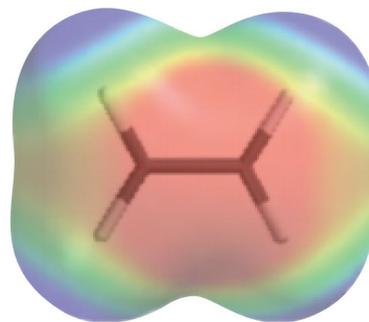
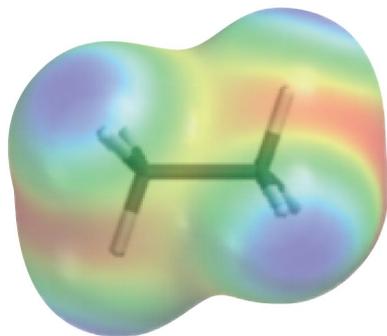
sp^2

44

sp

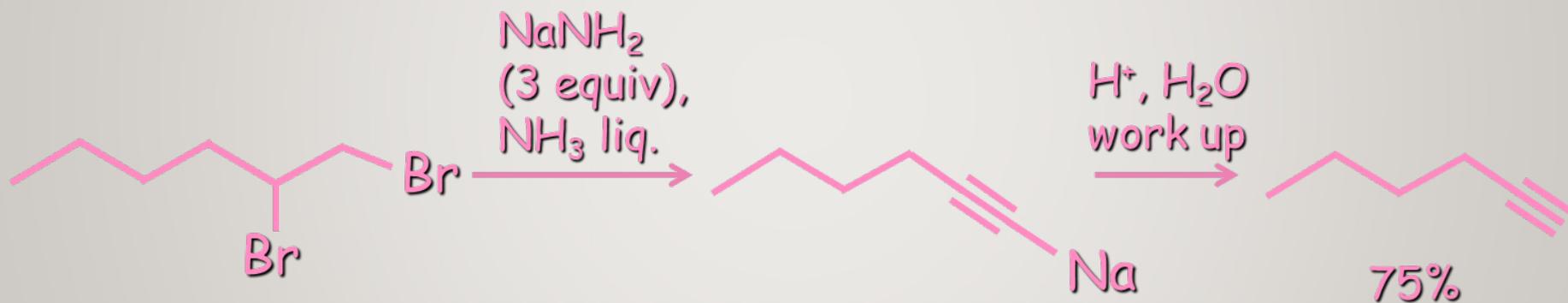
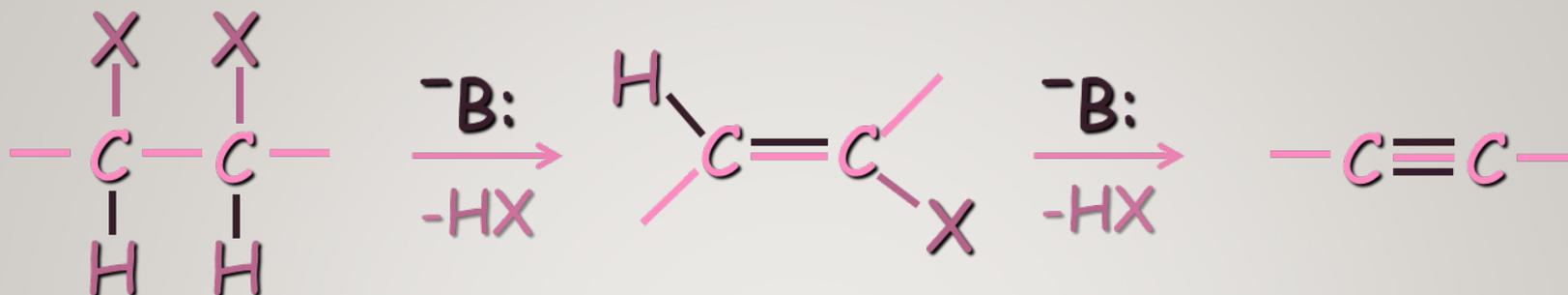
25

Increasing acidity



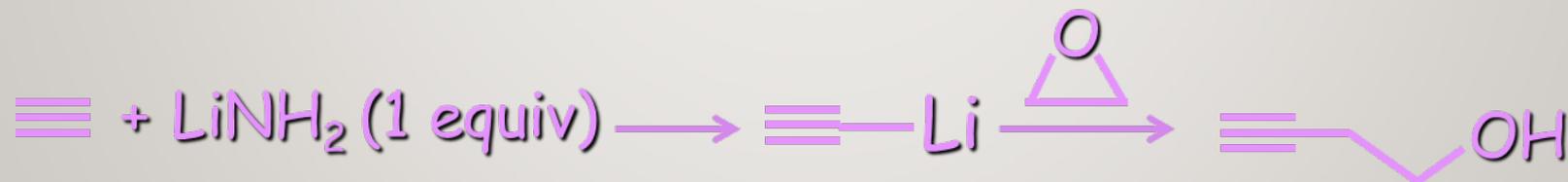
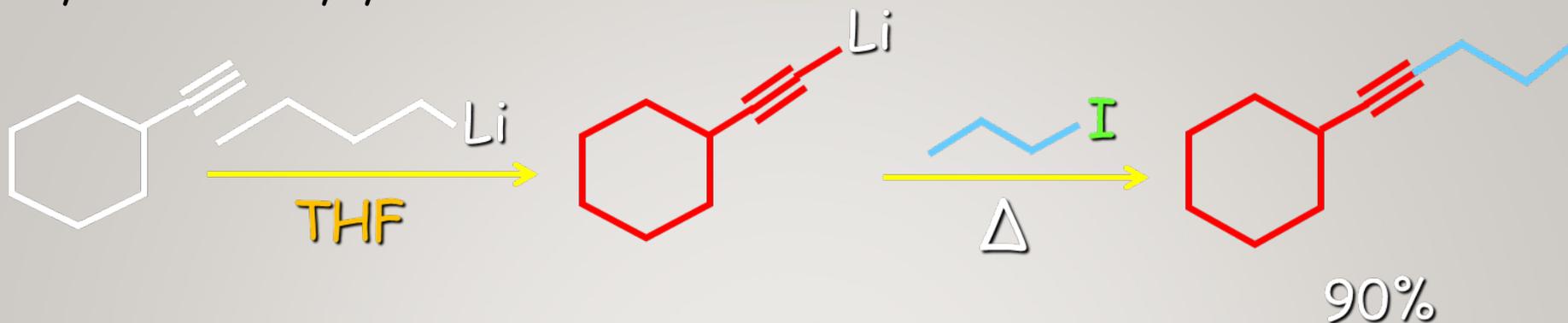
3.7 SYNTHESIS OF ALKYNES

Elimination E2 from dihaloalkanes



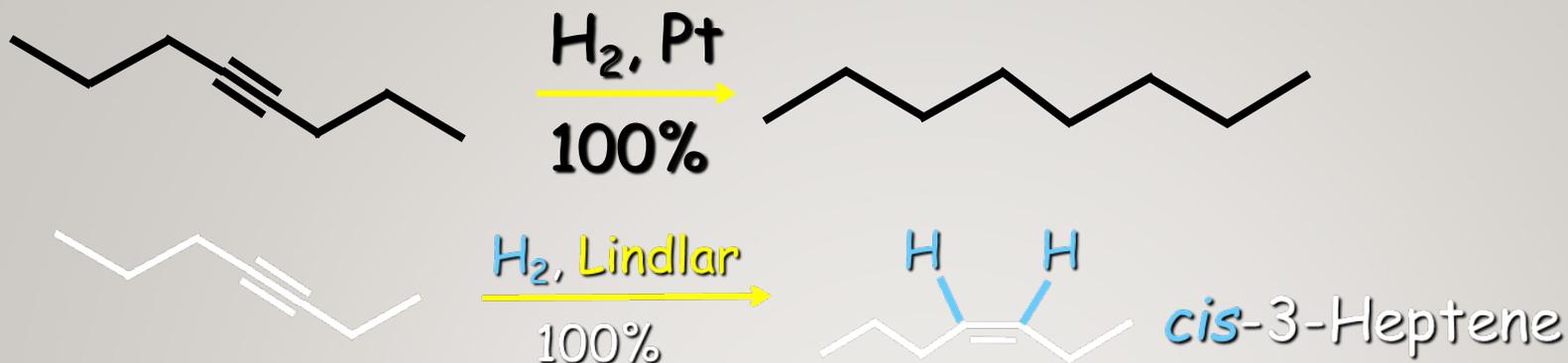
3.7 SYNTHESIS OF ALKYNES

Alkylation of Alkynyl Metals



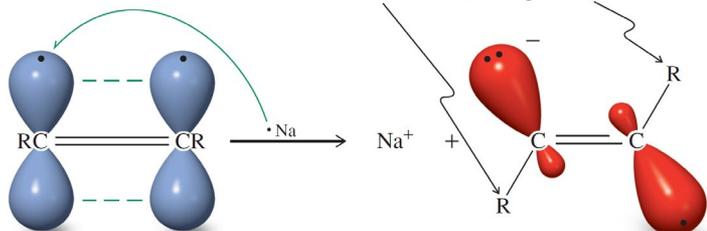
3.8 REACTIONS OF ALKYNES

Reductions



Step 1. One-electron transfer

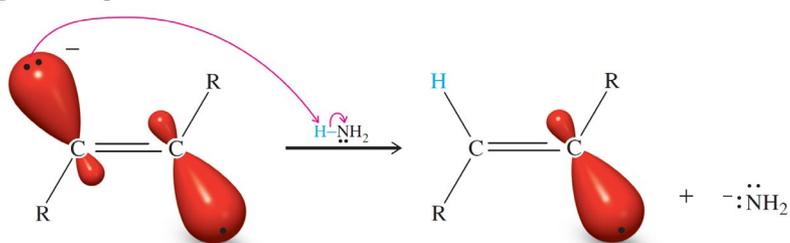
R groups adopt trans-like geometry to minimize steric repulsion



A

Alkyne radical anion

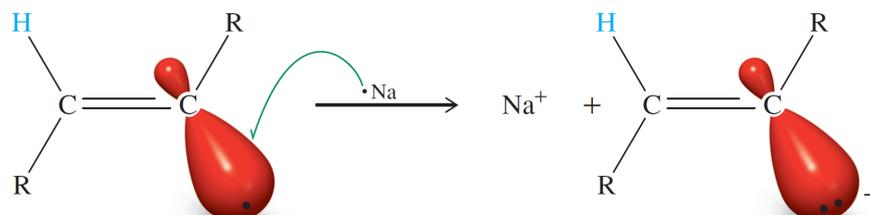
Step 2. First protonation



B

Alkenyl radical

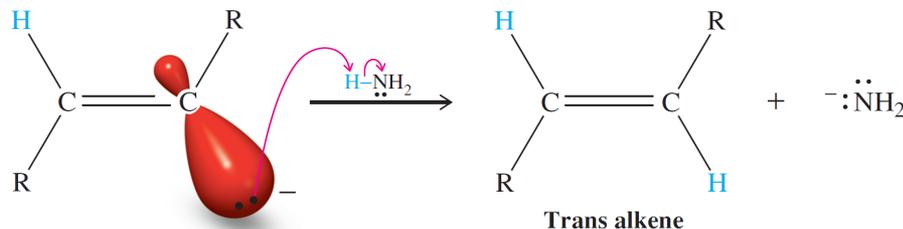
Step 3. Second one-electron transfer



C

Alkenyl anion

Step 4. Second protonation



Trans alkene