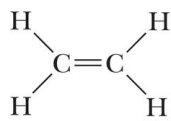
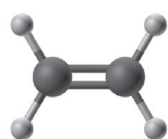


Chapter 4 Table of Content

- * Unsaturated Hydrocarbons
- * Introduction and hybridization
- * Alkenes and Alkynes
- * Benzene and Phenyl groups
- * Structure of Alkenes, cis-trans Isomerism
- * Nomenclature of Alkenes and Alkynes
- * Configuration cis/trans, and cis/trans Isomerism
- * Configuration E/Z
- * Physical Properties of Hydrocarbons
- * Acid-Base Reactions of Hydrocarbons
- * pka and Hybridizations

Unsaturated Hydrocarbons

- **Unsaturated Hydrocarbon**: A hydrocarbon that contains one or more carbon-carbon double or triple bonds or benzene-like rings.
 - **Alkene**: contains a carbon-carbon double bond and has the general formula C_nH_{2n} .
 - **Alkyne**: contains a carbon-carbon triple bond and has the general formula C_nH_{2n-2} .



Ethene
(an alkene)

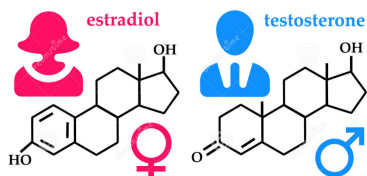
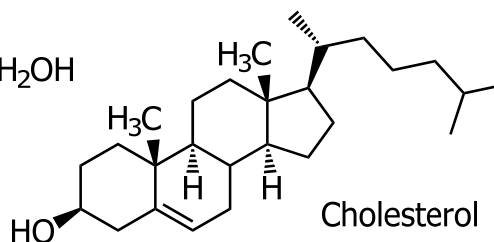
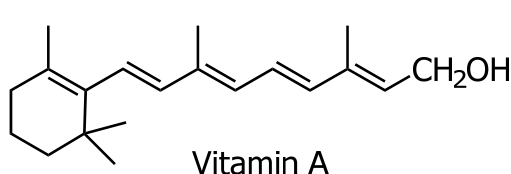


Ethyne
(an alkyne)

Introduction

❖ Alkenes

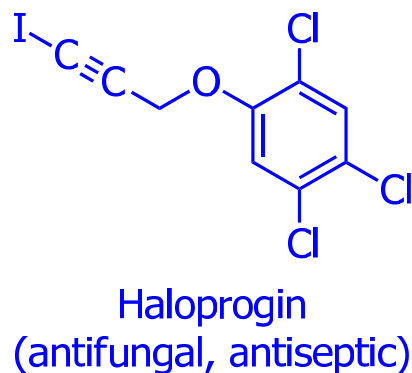
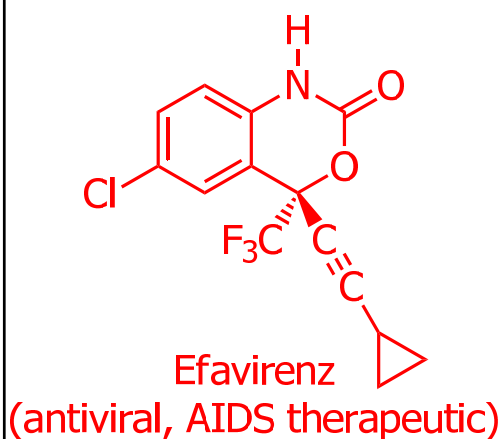
- Hydrocarbons containing $C=C$
- Old name: olefins



- Steroids
- Hormones
- Biochemical regulators

- Alkynes

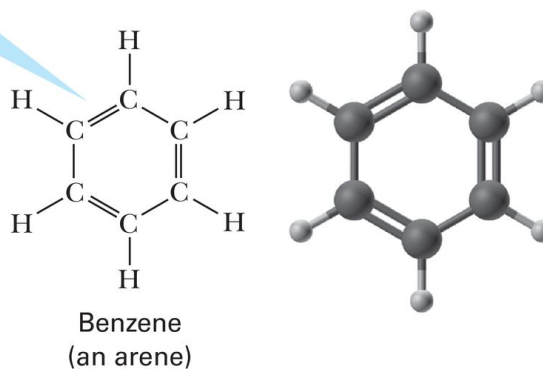
- Hydrocarbons containing $\text{C}\equiv\text{C}$
- Common name: acetylenes



Unsaturated Hydrocarbons

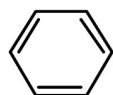
- Arene:** benzene and its derivatives (Ch 9)

although benzene and other arenes contain C–C double bonds, we must remember that their double bonds are not reactive in the ways we will describe in Chapters 4–8 (i.e., we will leave them unreacted in reactions that we cover in these chapters)

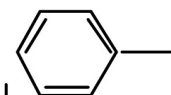


Benzene and Phenyl Groups

- We do not study benzene and its derivatives until Chapter 9.
 - However, we show structural formulas of compounds containing a phenyl group before that time.
 - The phenyl group is not reactive under any of the conditions we describe in chapters 5-8.



Benzene

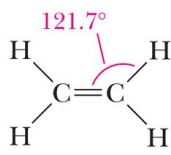
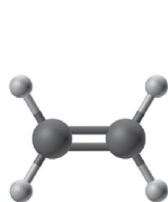
 C_6H_5-

Ph

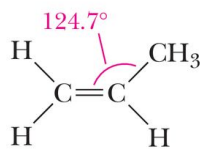
Alternative representations
for the phenyl group

Structure of Alkenes

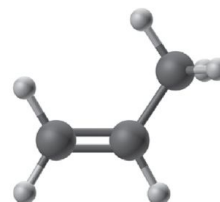
- The two carbon atoms of a double bond and the four atoms bonded to them lie in a plane, with bond angles of approximately 120° .



Ethylene

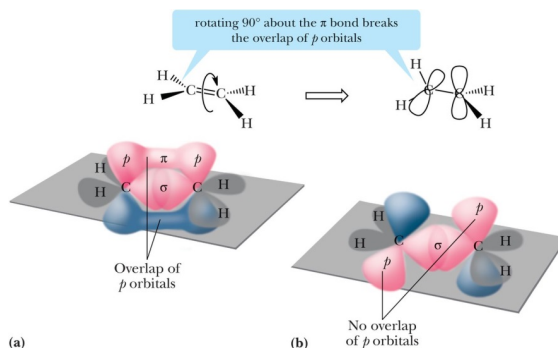


Propene



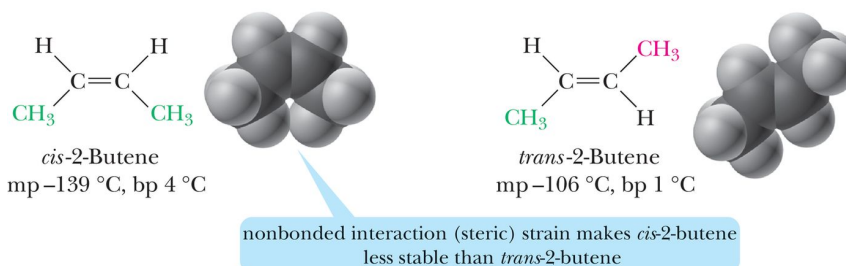
Structure of Alkenes

- **Figure 4.1** According to the orbital overlap model, a double bond consists of one σ bond formed by overlap of sp^2 hybrid orbitals and one π bond formed by overlap of parallel $2p$ orbitals.
- **Rotating by 90° breaks the pi bond. (Not allowed)**



Cis-Trans Isomerism

- Because of restricted rotation about a C–C double bond, groups on the carbons of a double bond are either *cis* or *trans* to each other.
 - Because of nonbonded interaction strain between alkyl substituents on the same side of the double bond, a *trans* alkene is more stable than an isomeric *cis* alkene.



Structure of Alkynes

- The functional group of an alkyne is a carbon-carbon triple bond.
- A triple bond consists of:
 - One σ bond formed by the overlap of sp hybrid orbitals.
 - Two π bonds formed by the overlap of sets of parallel $2p$ orbitals.

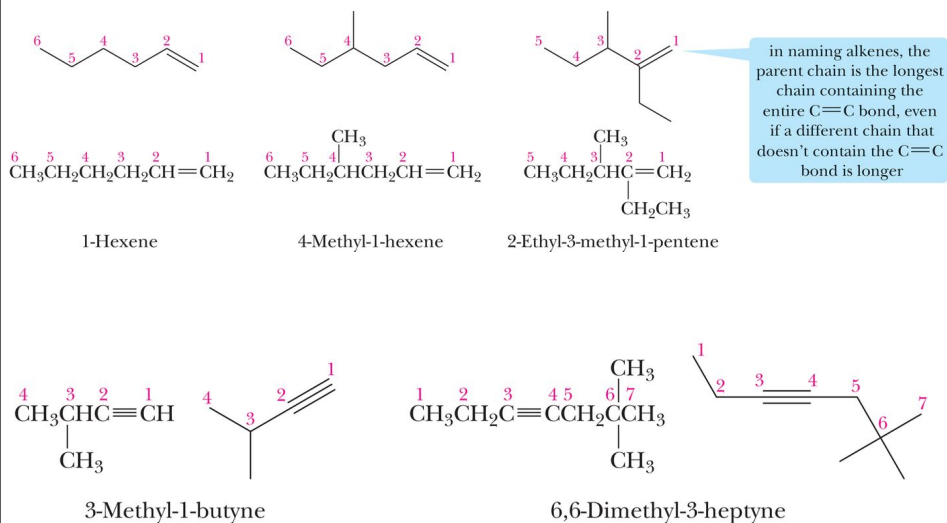


Nomenclature of Alkenes

- IUPAC Nomenclature of alkenes
 - Use the infix **-en-** to show the presence of a carbon-carbon double bond.
 - Number the parent chain to give the first carbon of the double bond the lower number.
 - Follow IUPAC rules for numbering and naming substituents.
 - For a cycloalkene, number the atoms of the ring beginning with the two carbons of the double bond.

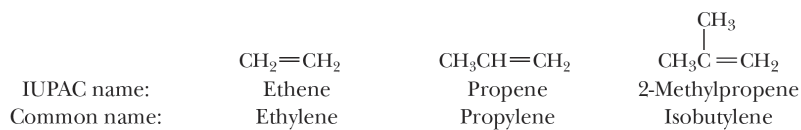
Nomenclature of Alkenes

- IUPAC nomenclature of alkenes



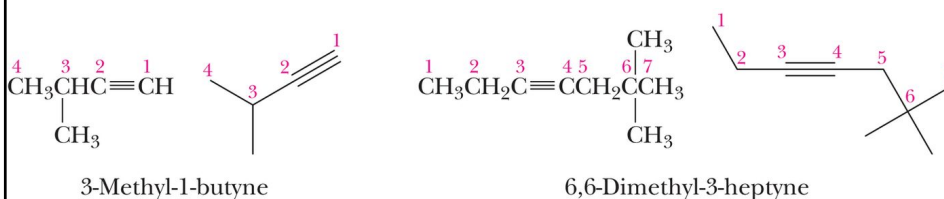
Nomenclature of Alkenes

- Some alkenes, particularly low-molecular-weight alkenes, are known almost exclusively by their common names.



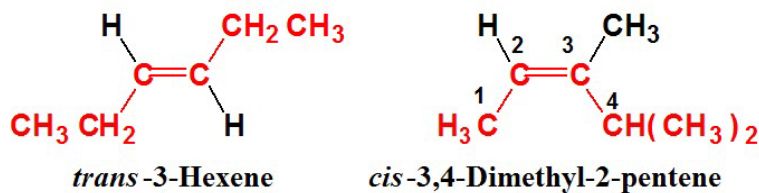
Nomenclature of Alkynes

- IUPAC nomenclature of alkynes
 - Use the infix **-yne** to show the presence of a carbon-carbon triple bond.
 - Number the parent chain to give the first carbon of the triple bond the lower number.
 - Follow IUPAC rules for numbering and naming substituents.



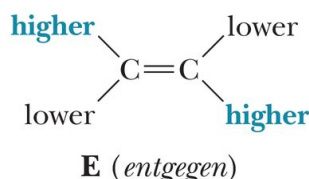
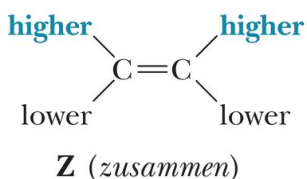
Configuration: *Cis-Trans*

- The *cis-trans* system:** Configuration is determined by the orientation of atoms of the main chain.



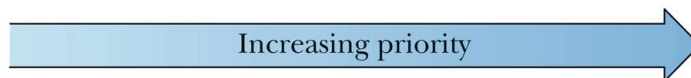
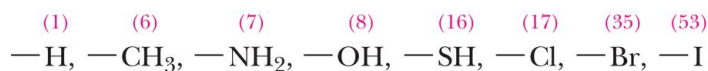
Configuration: *E,Z*

- To Assign an *E,Z* configuration, first assign a priority to the substituents on each carbon of the double bond.
 - If the groups of higher priority are on the same side of the double bond, the configuration is **Z** (German: *zusammen*, together).
 - If the groups of higher priority are on opposite sides of the double bond, the configuration is **E** (German: *entgegen*, opposite).

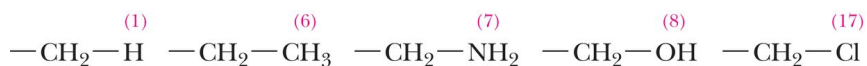


Configuration: *E,Z*

- Priority rules
 - Priority is based on atomic number; **the higher the atomic number, the higher the priority.**

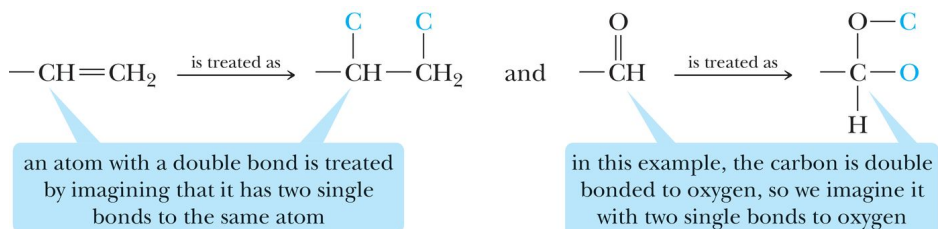


- If priority cannot be assigned on the basis of the atoms bonded directly to the double bond, look to the next set of atoms; **priority is assigned at the first point of difference.**



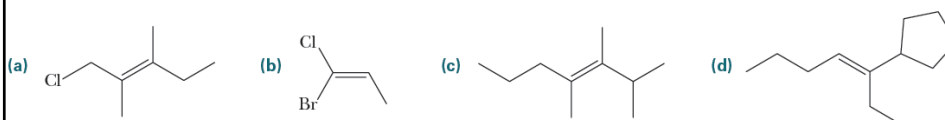
Configuration - *E,Z*

3. Atoms participating in a double or triple bond are considered to be bonded to an equivalent number of similar atoms by single bonds.



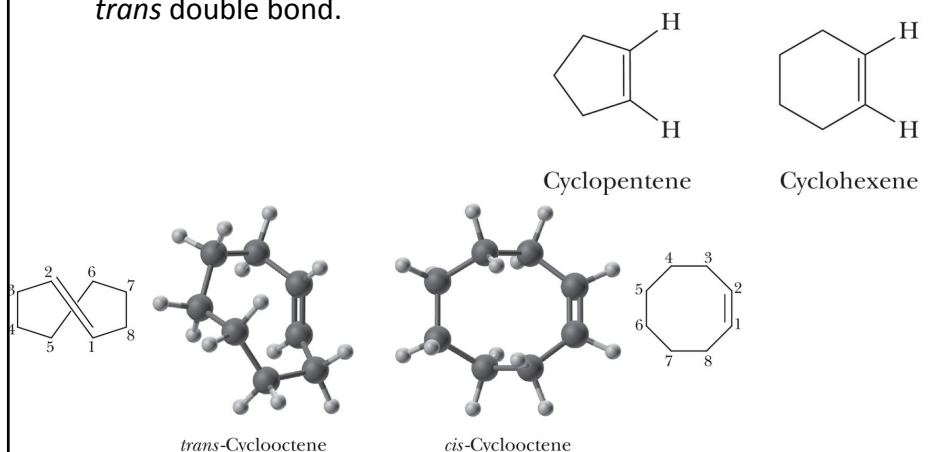
Configuration - *E,Z*

- Example:** Name each alkene by the *E,Z* system and specify its configuration.



Cis-Trans Isomerism

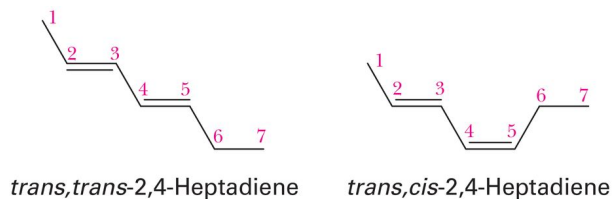
- The configuration of the double bond in cyclopropene through cycloheptene must be *cis*. These rings are not large enough to accommodate a *trans* double bond.
- Cyclooctene is the smallest cycloalkene that can accommodate a *trans* double bond.



Cis-Trans Isomerism

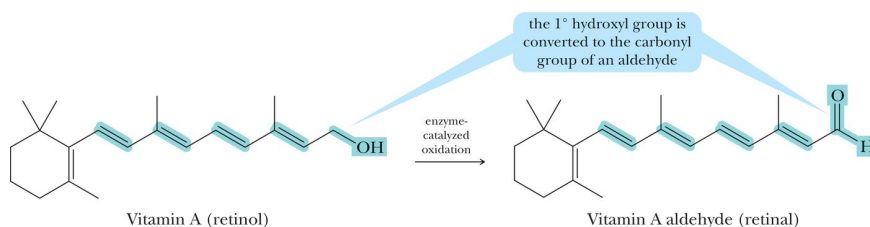
- Dienes, trienes, and polyenes
 - For an alkene with n carbon-carbon double bonds, each of which can show *cis-trans* isomerism, 2^n *cis-trans* isomers are possible.
 - Consider 2,4-heptadiene; it has four *cis-trans* isomers, two of which are drawn here.

Double bond	
C_2-C_3	C_4-C_5
<i>trans</i>	<i>trans</i>
<i>trans</i>	<i>cis</i>
<i>cis</i>	<i>trans</i>
<i>cis</i>	<i>cis</i>



Cis-Trans Isomerism

- Vitamin A has five C-C double bonds, four of which can show *cis-trans* isomerism.
- Vitamin A is the all-*trans* isomer.

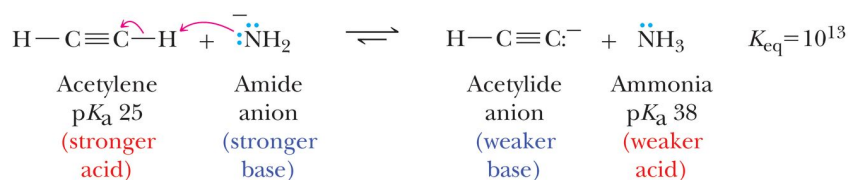


Physical Properties

- Alkenes and alkynes are nonpolar compounds.
 - The only attractive forces between their molecules are **dispersion forces**.
- The physical properties of alkenes and alkynes are similar to those of alkanes with similar carbon skeletons.
 - Those that are liquid at room temperature are less dense than water (1.0 g/mL).
 - They dissolve in each other and in nonpolar organic solvents.
 - They are insoluble in water.

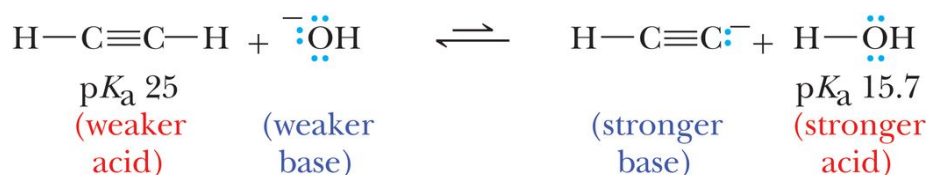
The Acidity of Terminal Alkynes

- One of the major differences between the chemistry of alkenes and alkynes is that the hydrogen atom of a terminal alkyne is sufficiently acidic (pK_a 25) that it can be removed by a strong base such as sodium amide, NaNH_2 , to give an alkyne anion.



The Acidity of Terminal Alkynes

- Because water (pK_a 15.7) is a stronger acid than acetylene or a terminal alkyne, hydroxide ion is not a strong enough base for an acid-base reaction with a terminal alkyne.



The Acidity of Terminal Alkynes

- The pK_a values for alkane and alkene hydrogens are so large that no base is strong enough to remove a hydrogen from either of these classes of compounds.

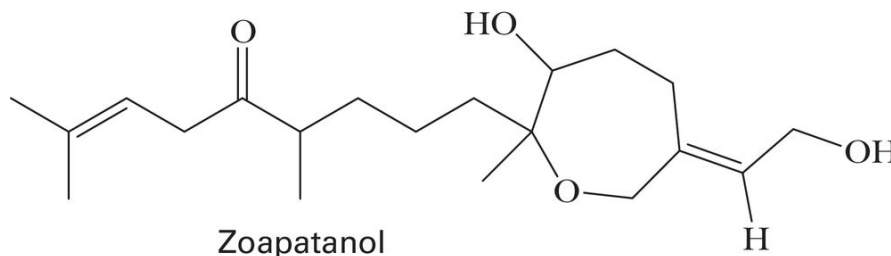
TABLE 4.1 Acidity of Alkanes, Alkenes, and Alkynes

Weak Acid		Conjugate Base	pK_a
Water	$\text{HO}-\text{H}$	HO^-	15.7
Alkyne	$\text{HC}\equiv\text{C}-\text{H}$	$\text{HC}\equiv\text{C}^-$	25
Alkene	$\text{CH}_2=\text{CH}-\text{H}$	$\text{CH}_2=\text{CH}^-$	44
Alkane	$\text{CH}_3\text{CH}_2-\text{H}$	CH_3CH_2^-	51

↑
Increasing acidity

- Zoapatanol is found in the leaves and twigs of *Montanoa tomentosa*.

- Specify the configuration of each carbon-carbon double bond.
- How many *cis-trans* isomers are possible for this compound.

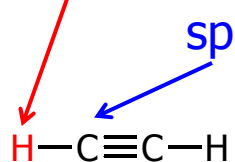


The Acidity of Terminal Alkynes

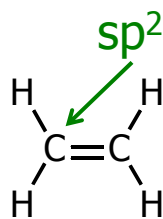
- How do we account for the acidity of a terminal alkyne compared to an alkane or alkene?
- To answer this question, we must focus on the stability of the anion derived from each class of hydrocarbon.
- The lone pair of electrons of an alkane anion lies in an sp^3 hybrid orbital, which has 25% s character.
- For an alkene anion, the lone pair lies in an sp^2 hybrid orbital, which has 33% s character.
- For a terminal alkyne anion, the lone pair lies in an sp hybrid orbital, which has 50% s character.

The Acidity of Terminal Alkynes

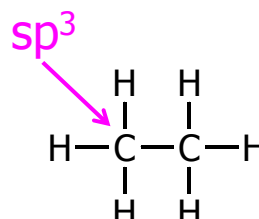
Acetylenic hydrogen



$$\text{p}K_a = 25$$

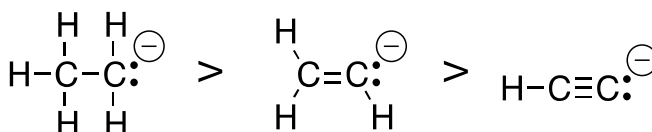


$$\text{p}K_a = 44$$

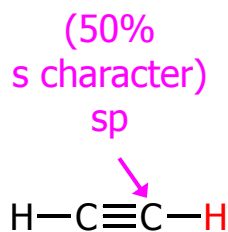


$$\text{p}K_a = 50$$

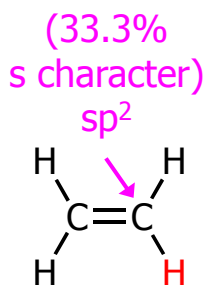
❖ Relative basicity of the conjugate base



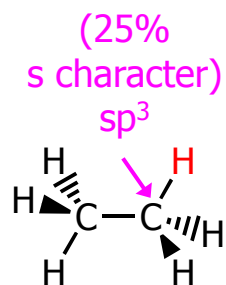
The Effect of Hybridization



$$pK_a = 25$$



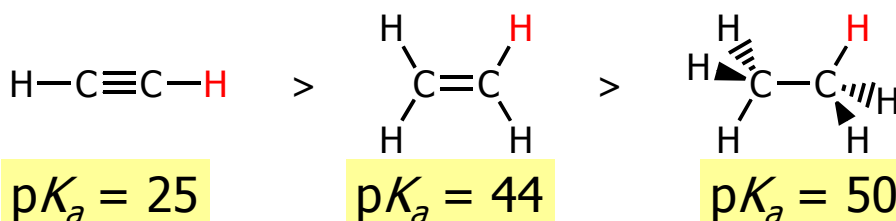
$$pK_a = 44$$



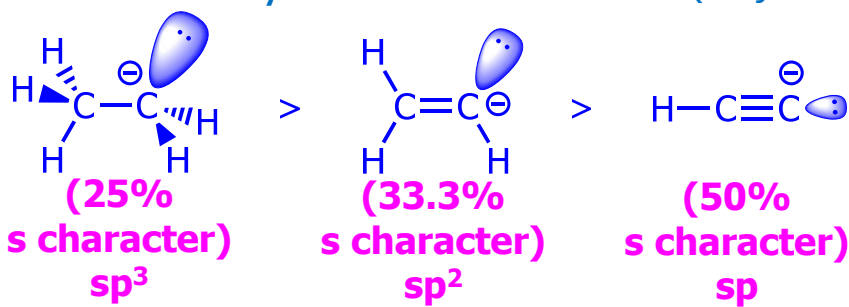
$$pK_a = 50$$

- ❖ Having more s character means that the electrons of the anion will, on the average, be lower in energy, and the anion will be more stable

Relative Acidity of the Hydrocarbons



Relative Basicity of the Carbanions (conj. Base)



The Acidity of Terminal Alkynes

- The greater the s character of the orbital bearing the negative charge, the greater the stability of the anion, and thus the greater acidic the hydrogen removed.
- Of the series of compounds alkane, alkene, and alkyne, the carbon of a terminal alkyne has the most s character (50%). Therefore, a terminal alkyne anion is the most stable of the series, and a terminal alkyne is the most acidic.