

5.12 Lecture 8

VII. Overview of Chemical Reactions

- A. Chemical Reactions
- B. Classifications
- C. Radical Mechanism
- D. Polar Mechanism
 - 1. Nuts and Bolts
 - 2. Nucleophile
 - 3. Electrophile
 - 4. Describing Polar Reactions
 - a. Arrow Pushing
 - b. Molecular Orbital
 - 5. Example

Suggested Reading: Chapter 5

Suggested Problems: 5.24-5.33, 5.39-5.47

A. Chemical Reactions

What: Changes in electron configuration

Bonds broken/bonds formed

Why: Attain a stable state

High energy structures spontaneously react

Lower energy structures need external energy to react

How: Collisions (between atoms, molecules, ions)

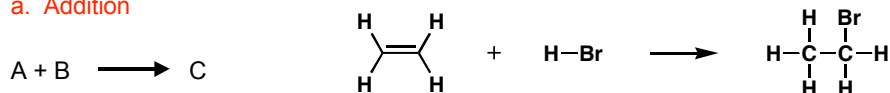
For a collision to result in a reaction, the molecule must have:

- 1) sufficient kinetic energy
- 2) proper orientation

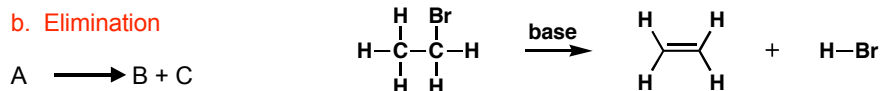
B. Classifications of Reactions

1. Overall Transformation (relationship of reactant to product)

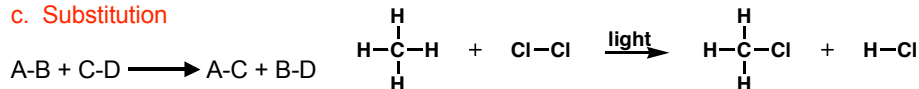
a. Addition



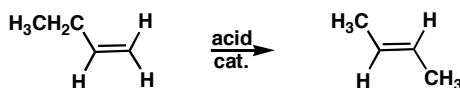
b. Elimination



c. Substitution



d. Rearrangement



B. Classification of Reactions

2. Mechanism

- overall description of how a reaction occurs (changes in elec. configuration)
- which bonds are broken and formed

a. Free Radical

Movement of one electron, usually proceeds by chain reaction

b. Polar

Movement of electron pairs from areas of high electron density (nucleophile) to areas of low electron density (electrophile)

c. Pericyclic

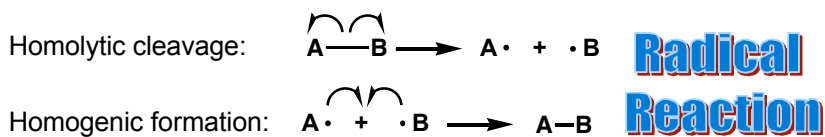
Movement of electrons in a cyclic fashion

d. Metal-mediated and Metal-catalyzed (need transition metal)

(If the transition metal complexes act only as Lewis acids or 1 electron transfer agents, the reactions are better classified as polar, pericyclic or radical)

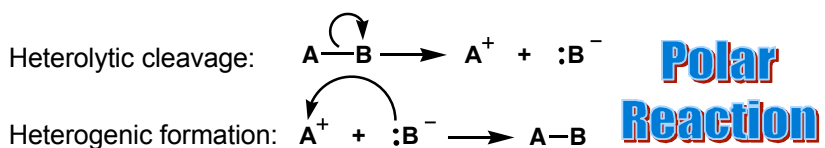
Ways to Form and Break Covalent Bonds:

1. **Symmetrical** - 1 electron goes to each atom in bond



Use fishhook arrows!

2. **Unsymmetrical** - Both electrons go to one of the atoms in the bond

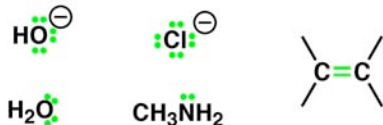


Use double-headed arrows!

Nucleophiles and Electrophiles

Involved in polar reaction bond formation

Nucleophiles **donate** electrons.

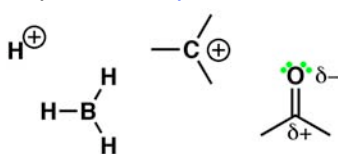


Nucleophilic atom either starts neutral and becomes positive, or starts negative and becomes neutral

Identifying nucleophiles

- Lone pairs
- (-) charges
- π bonds

Electrophiles **accept** electrons.



Electrophilic atom either starts neutral and becomes negative, or starts positive and becomes neutral

Identifying electrophiles

- Empty orbitals (incomplete octet)
- (+) charges
- π bonds (polarized)

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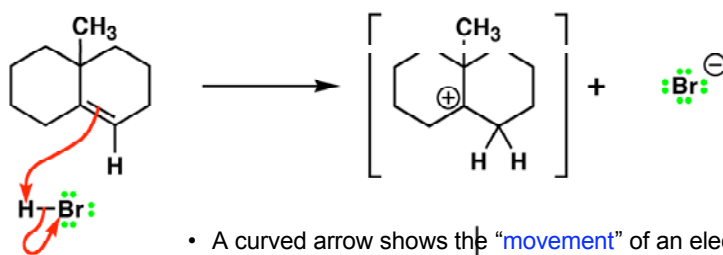
Still Having Trouble Identifying Nu: and E+?

1. Look for regions of electron density and electron deficiency
2. Draw in all lone pairs
3. Draw as many resonance structures as you can
(often, the 2nd best resonance structure shows the electrophilic and nucleophilic sites in a molecule)

The terms “nucleophile” and “electrophile” can mean the entire molecule or specific atoms and functional groups.

Don't let the dual meaning confuse you!

A Few Notes About Electron Pushing

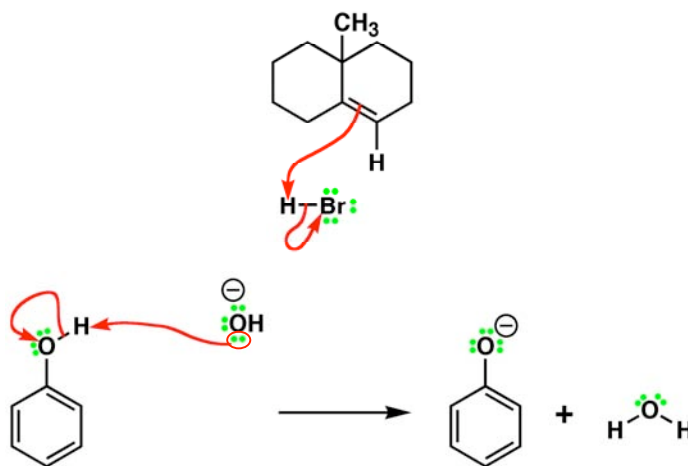


- A curved arrow shows the “movement” of an electron pair
- The tail of the arrow shows the source of the electron pair, which is a filled orbital. This will be a:
 - lone pair
 - π -bond
 - σ -bond
- The head of the arrow indicates the destination (sink) of the electron pair which will be:
 - An electronegative atom able to support negative charge
 - An empty orbital when a new bond is formed
- Overall charge is conserved. Check that your products obey this rule.

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Electron Pushing to Uncharged C, H, N, or O

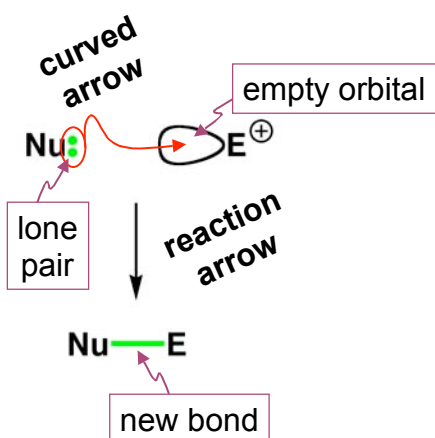
If you make a new bond by pushing an arrow to an uncharged C, H, N, or O, you must also break one of the existing bonds in the same step.



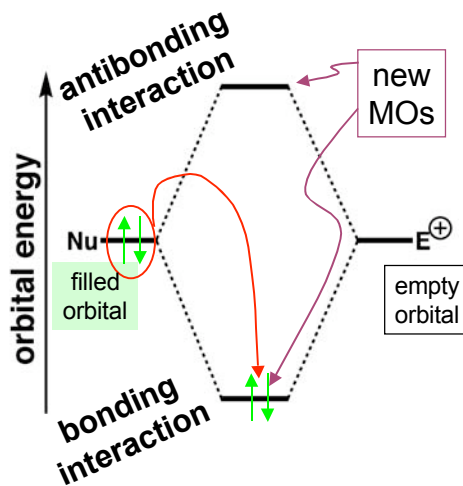
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Addition of Nucleophiles to Electrophiles

“Arrow Pushing” Description

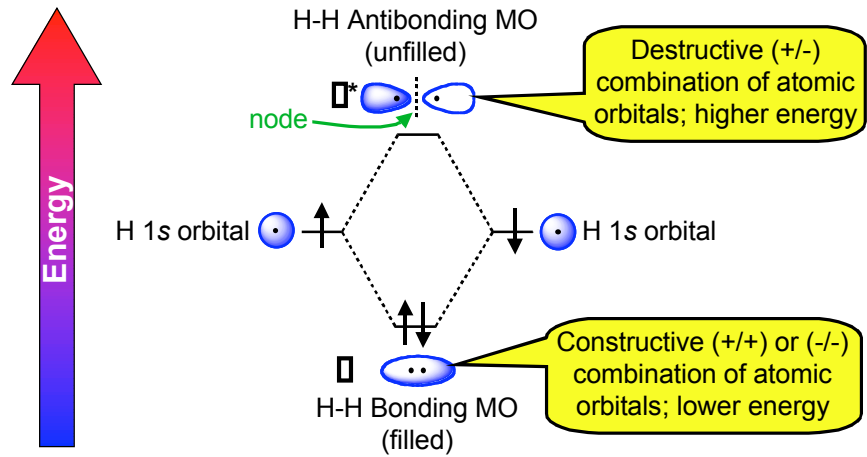


Molecular Orbital Description

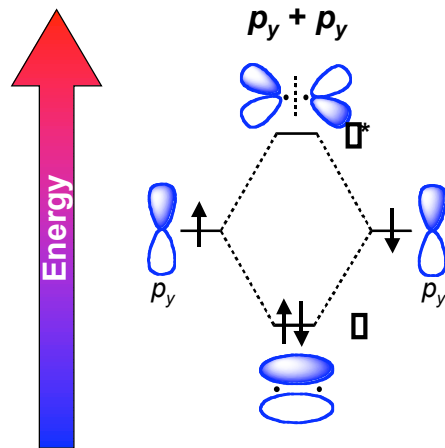


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Molecular Orbital Diagram: H₂



MO Diagrams: Pi Bonding (π)



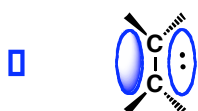
Orbitals of Nucleophiles and Electrophiles

Nucleophiles

1. Filled **nonbonding** orbital



2. Filled **π bonding** orbital



3. Filled **σ bonding** orbital

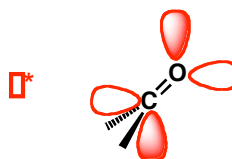


Electrophiles

1. Empty **nonbonding** atomic orbital



2. Empty pi **antibonding** orbital

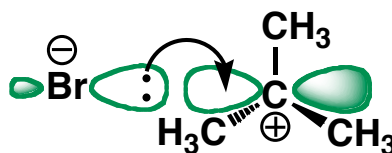
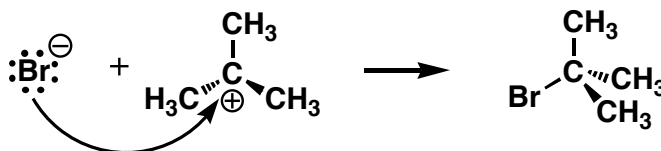


3. Empty sigma **antibonding** orbital



Filled Nonbonding + Empty Nonbonding

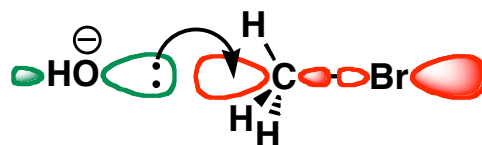
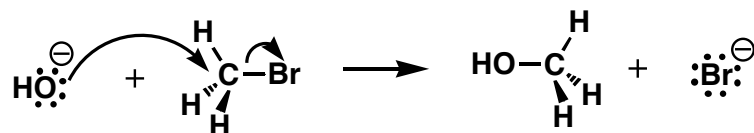
n + a



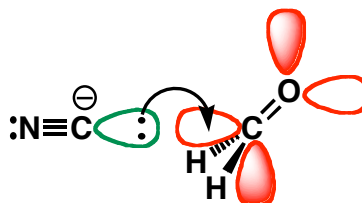
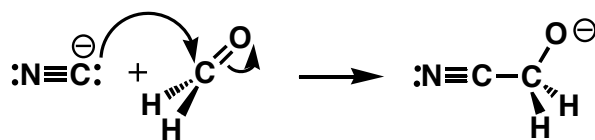
n

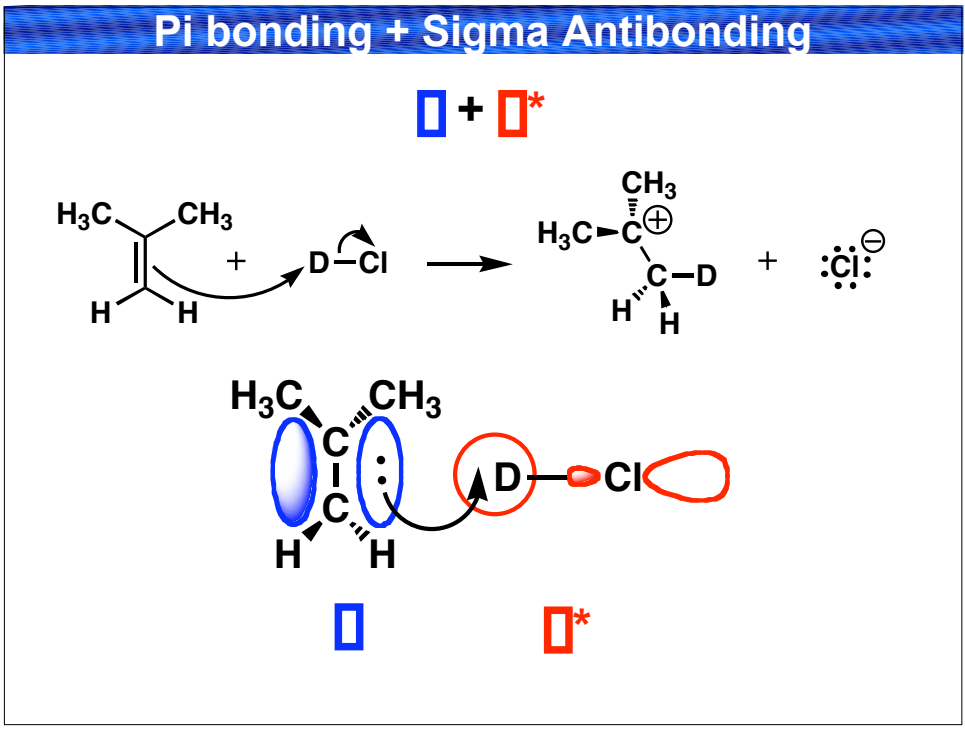
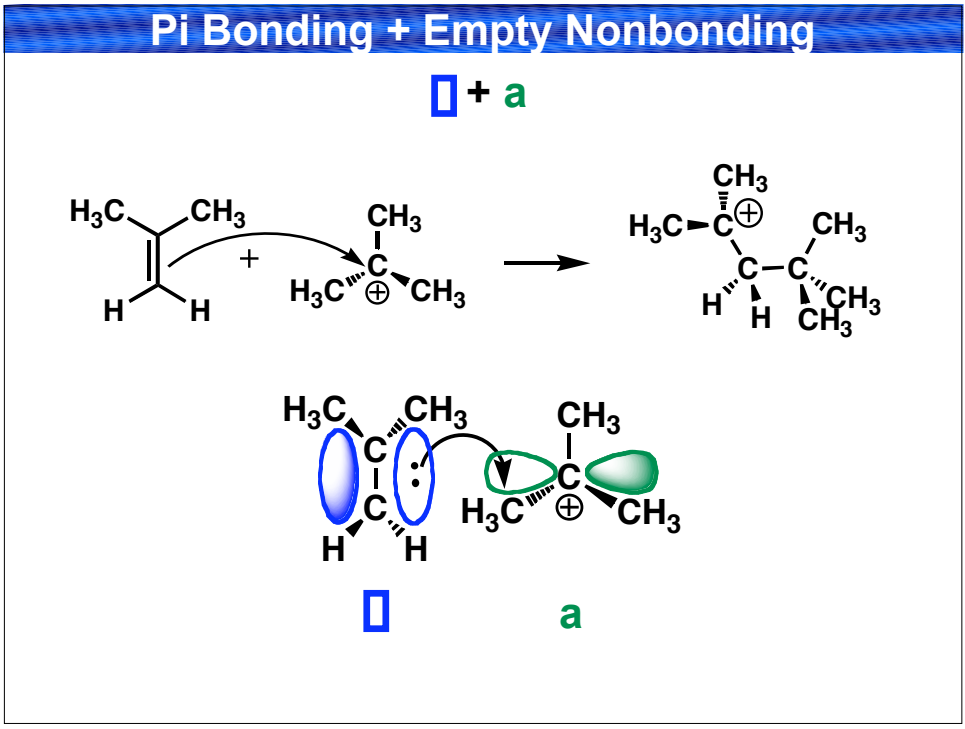
a

Filled Nonbonding + Sigma Antibonding

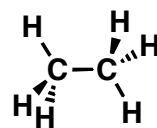
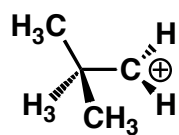


Filled Nonbonding + Pi Antibonding





Sigma Bonding + Empty Nonbonding and σ^*



hyperconjugation

