Ch. 29

3 types of organic rxns.

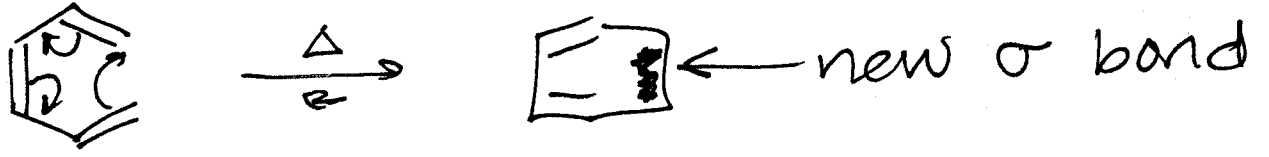
1. Polar rxns. Electrophile + Nucleophile - both e's for new bond come from nucl.

2. Radical rxns. New bond formed using one e' from each reactant.

3. Pericyclic rxns - the e's in one or more reactants are reorganized in a cyclic manner.

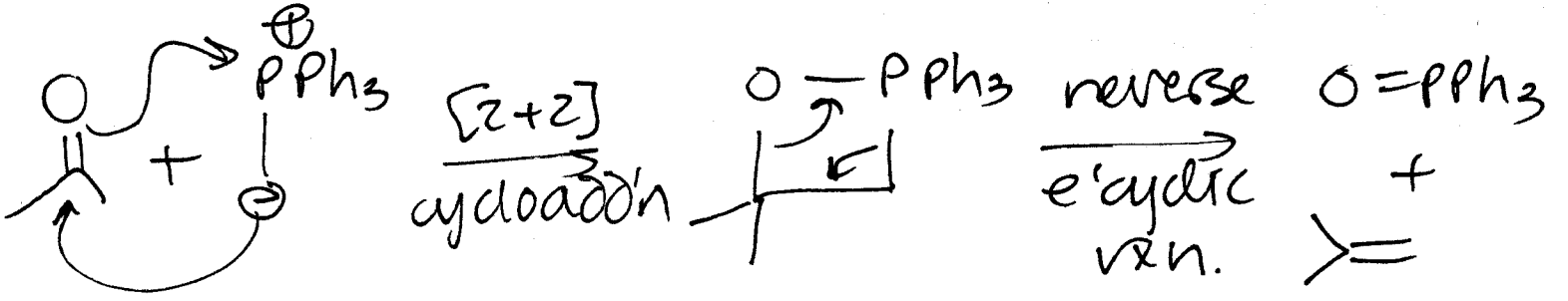
Types of pericyclic rxns:

a. electrocyclic - intramolecular rxn in which a new σ bond is formed between the ends of a conjugated π system. (These are reversible.)



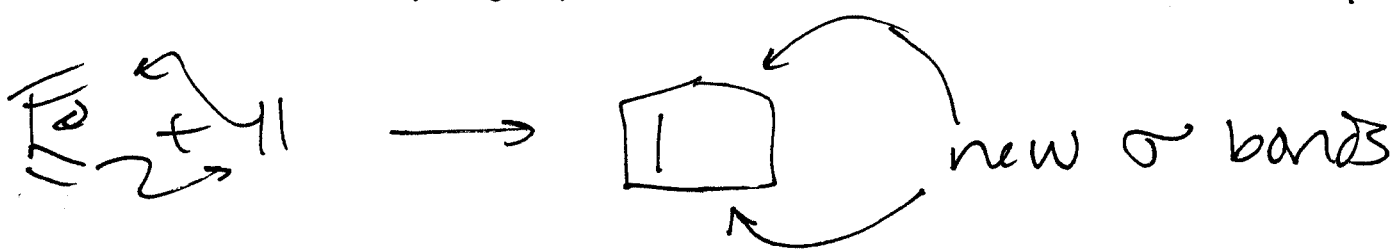
3 π bonds

2 π bonds
1 ring



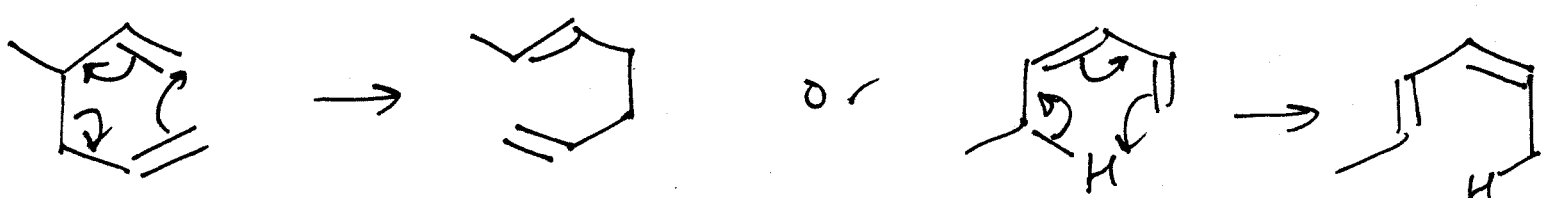
b. cycloadditions - 2 separate molecules each w/ at least one π bond, react to form a cyclic compound.

Diels-Alder is a classic example.



c. sigmatropic rearrangement.

A σ bond is broken, a new σ bond is formed, π bonds rearrange.



General features:

* concerted rxns. A single transition state, no intermediates.
* highly stereoselective
* generally not affected by catalysts or solvent changes.

The configuration of the product is determined by:

* configuration of reactant(s).
* # of π e's - conjugated π bonds or lone pairs
* thermal vs. photochemical

↑ reactant does not absorb light

↑ reactant absorbs light hν

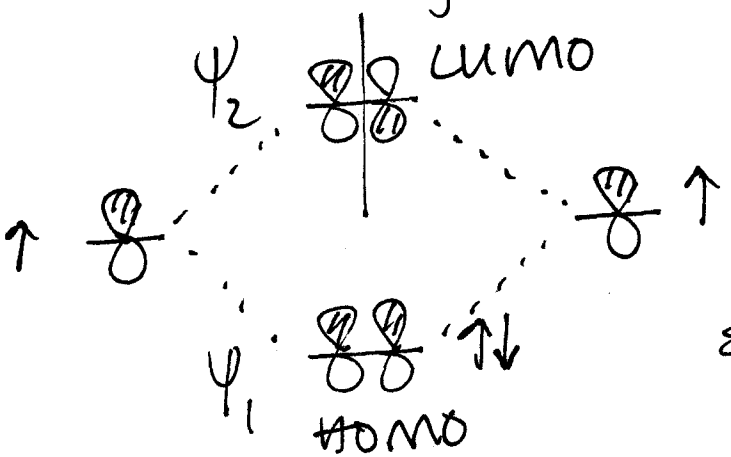
Basic M.O. Theory - focus on π system.

- because the p-orbitals / π system are ⊥ to the σ framework, we can treat the π system independently.

- two lobes of the p-orb. have opposite phases. If the lobes overlap in-phase, form a bonding M.O.

- for every A.O. in, you get one M.O. out
- describe M.O. as LCAO.
- M.O. fill according to Hund's Rule, Pauli Exclusion Principle + aufbau principle.

M.O. diagram for $CH_2=CH_2$.

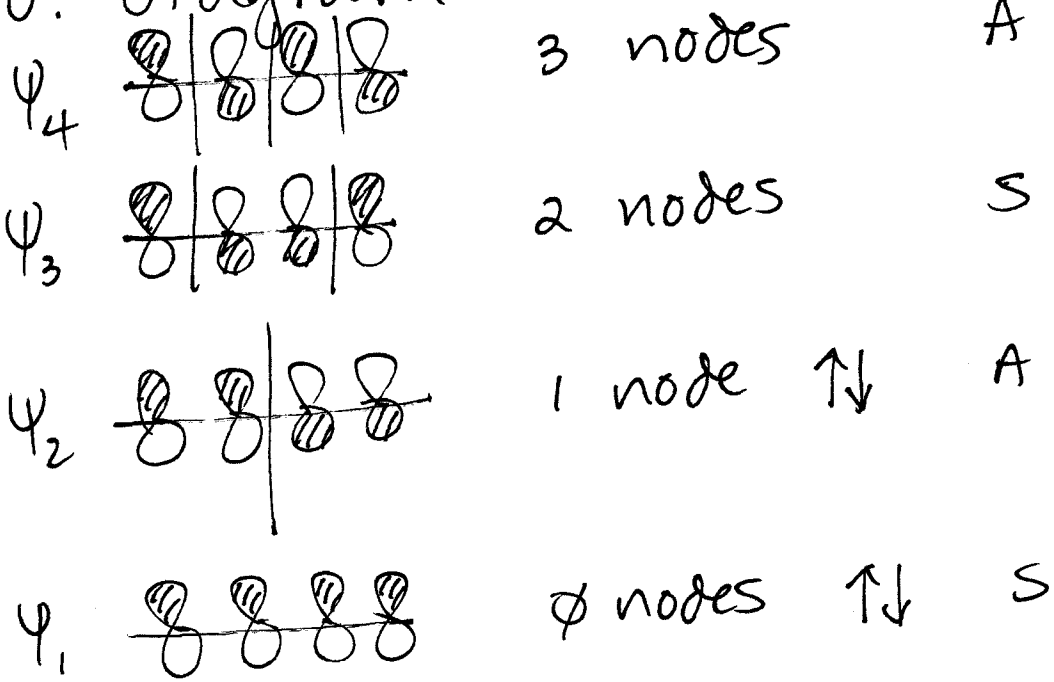


unsymmetrical
one node

symmetrical
no nodes

node = place where M.O. changes sign (phase)

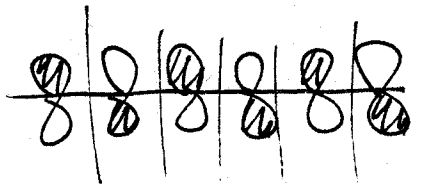
M.O. diagram for 



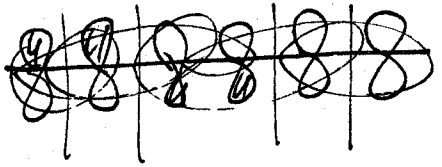
S = symmetric
A = asymmetric

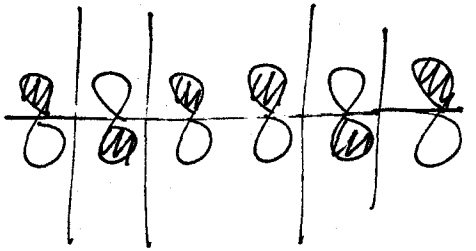
M.O. Diagram for 

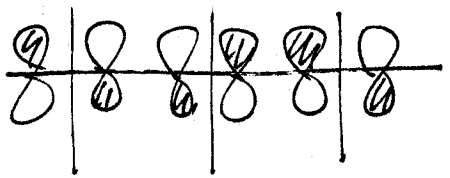
HOMO + LUMO are the "Frontier" molecular orbitals



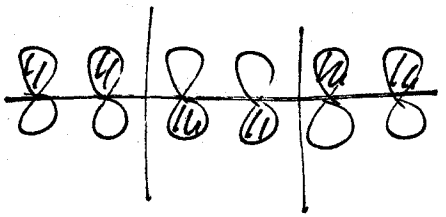
ψ_6 5 A



ψ_5 4 S  — LUMO*

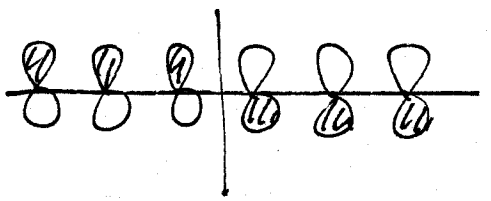


ψ_4 3 A — LUMO ↑ HOMO*

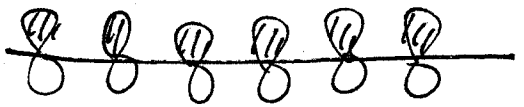


ψ_3 2 S ↑↓ HOMO ↑

$h\nu \rightarrow$



ψ_2 1 A ↑↓ ↑↓



ψ_1 ∅ S ↑↓ ↑↓

nodes ground state excited state

Thermal rxns use the ground state MO configuration.

Photochemical rxns use the excited state MO configuration.