Cheat Sheet Bundle

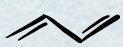
For Organic Chemistry II

(First 5 Pages)

By Organic Chemistry Simplified

How to draw a molecular orbital energy level diagram:

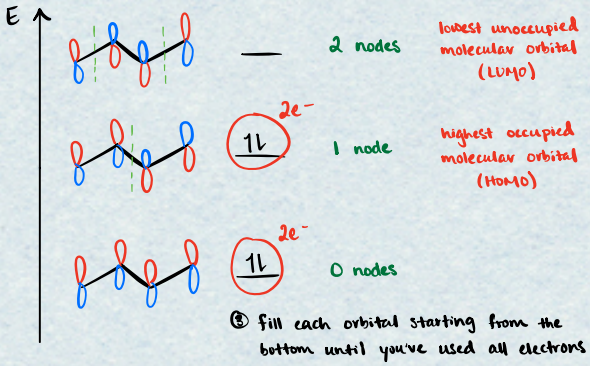
Say you're given this:



① count the number of e⁻ in the pi system

2 in each bond
4 total

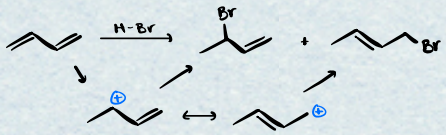
② draw a basic 4-carbon energy level diagram (since our example has 4 carbons)



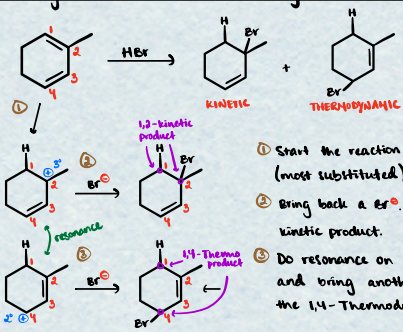
③ fill each orbital starting from the bottom until you've used all electrons

longest λ absorption = most conjugation

HBr reaction:



Finding the Kinetic & Thermodynamic Products



① Start the reaction from the most stable (most substituted) double bond.

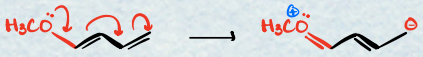
② Bring back a Br⊖. This is the 1,2-kinetic product.

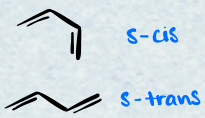
③ Do resonance on the intermediate and bring another Br⊖ in. This is the 1,4-Thermodynamic product.

Electron Donating Groups (EDG's)

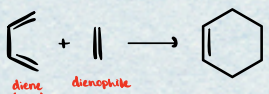
- Alkyl Groups (weak): Donate through hyperconjugation.

- Substituents with O or N atoms that contain lone pairs (strong): Donate through resonance.





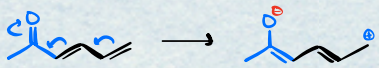
Basic Diels Alder Setup



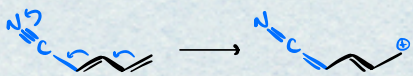
Electron Withdrawing Groups (EWG's)

- Halogens (weak): Take through the inductive effect.

- Carbonyls (strong): Take through resonance and the inductive effect.

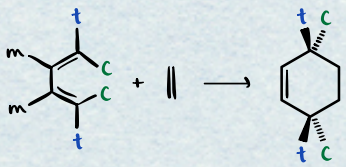


- Cyano substituents (strong): Take through resonance and the inductive effect.

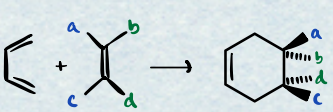


Diels Alder Stereochemistry Guide

Diene

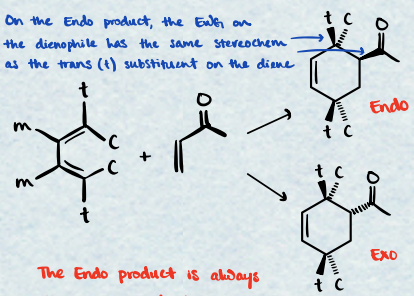


Dienophile



Endo/Exo

On the Endo product, the EWG on the dienophile has the same stereochem as the trans (t) substituent on the diene

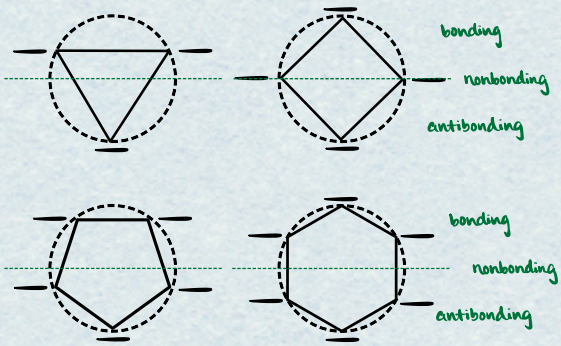


The Endo product is always the major product

Frost Circles

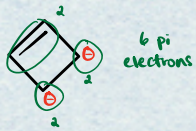
Basic Templates

*Tip: Always draw upside down

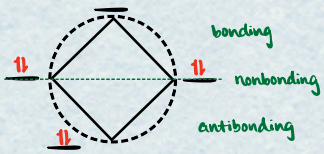


Example Problem:

① count pi electrons



② Draw Frost Circle and fill it in from the bottom up

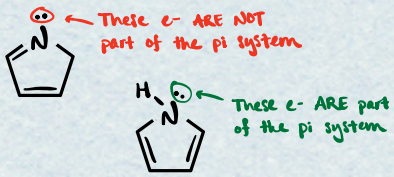


Aromaticity

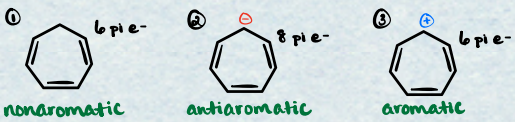
Aromatic: $(4n + 2)e^-$ (2, 6, 10, 14, ...)

Antiaromatic: $4n$ e- (4, 8, 12, ...)

Nonaromatic: noncyclic pi systems



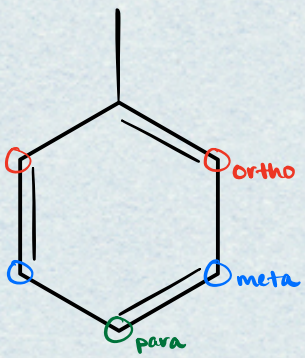
Example Problem: Arrange in order of increasing stability



2 < 1 < 3

STABILITY RULE

anti-aromatic < nonaromatic < aromatic



Ortho-Para Directors

*Always add para first, then ortho

Electron Donating Groups

- **Strongly Activating**
  - NH_2, OH
  - NHR, O^-
  - NR_2
- **Moderately Activating**
  - $NHCOCH_3$, OCH_3
  - $NHCOR$, OR
- **Weakly Activating**
  - Alkyl groups
- **Weakly Deactivating**
  - halogens

Meta Directors

- **Moderately Deactivating**
  - $C\equiv N$, CHO
  - SO_3H, CO_2R
  - CO_2H, COR
- **Strongly Deactivating**
  - NO_2, NR_3^+
  - NH_3^+, CCl_3
  - CF_3
- **Acyl groups**

Electron Withdrawing Groups

Electrophilic Aromatic Substitution

Halogenation — Br_2, $FeBr_3$ → Br

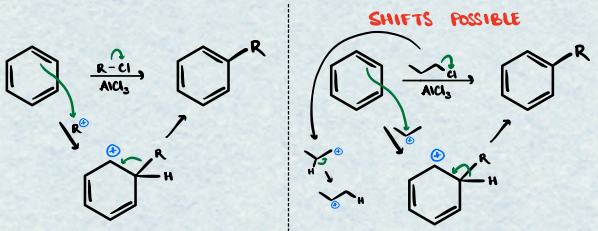
Halogenation — Cl_2, $FeCl_3$ → Cl

Nitration — HNO_3, H_2SO_4 → NO_2

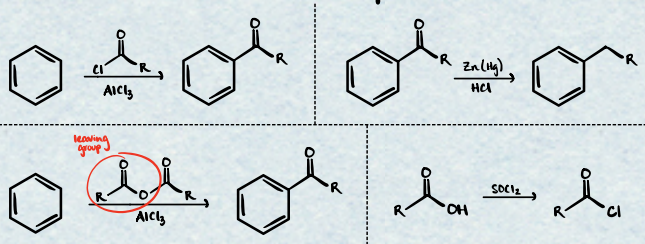
Sulfonation — SO_3, H_2SO_4 → SO_3H

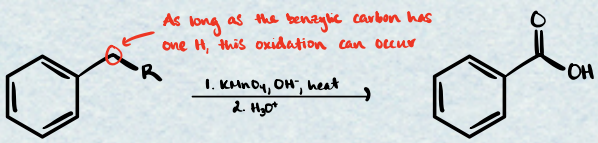
Dil. H_2SO_4 — SO_3H + H_2SO_4 (dilute) →

Friedel Crafts Alkylation

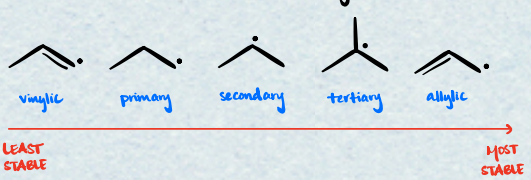


Friedel Crafts Acylation

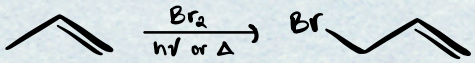




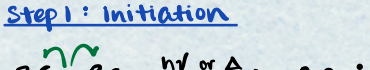
Radical Stability



Allylic Substitution

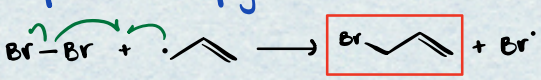


Step 1 : Initiation

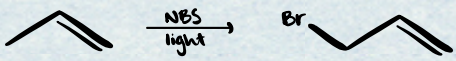


Step 2 : 1st Propogation

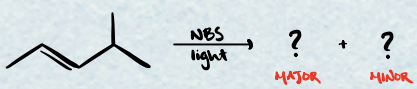
Step 3 : 2nd Propogation



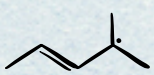
Allylic Halogenation



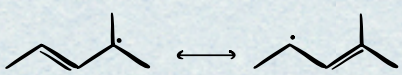
Example:



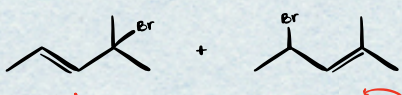
Step 1 : Put a radical on the more substituted side



Step 2 : Do resonance



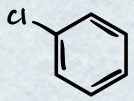
Step 3 : Add Br where the radicals are



* the major product has the more stable double bond

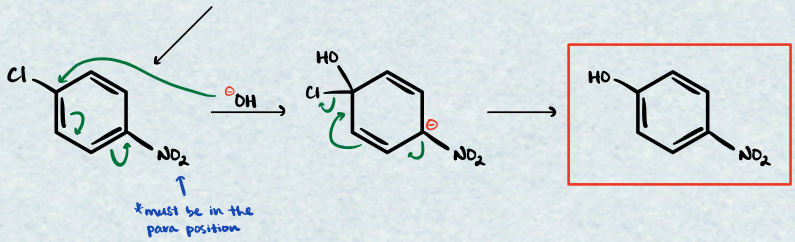
Nucleophilic Aromatic Substitution

Addition - Elimination



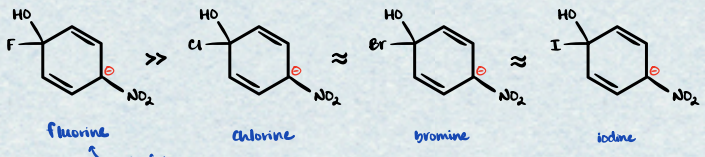
$^{\ominus}OH$ → NO REACTION

A strong electron withdrawing group (EWG) will make an aryl halide more reactive (ex: NO_2)



*must be in the para position

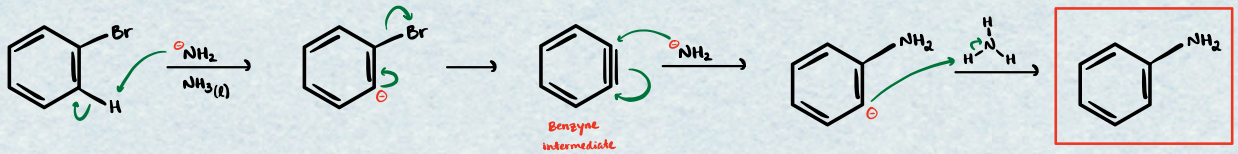
Halogen Anion Stabilizing Ability



Fluorine (By far the best) >> Chlorine ≈ Bromine ≈ Iodine

Elimination - Addition

* only works with very strong bases

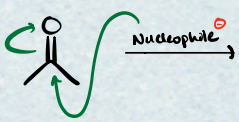


NH_2 / $NH_{3(l)}$

Benzyne intermediate

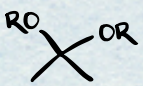
Carbonyl Additions

Keep in mind: All carbonyls are highly susceptible to nucleophilic attack.



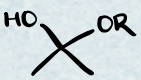
Acetals & Hemiacetals

Acetals



Stable

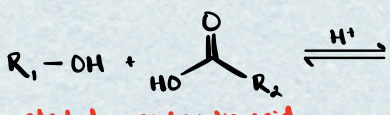
Hemiacetals



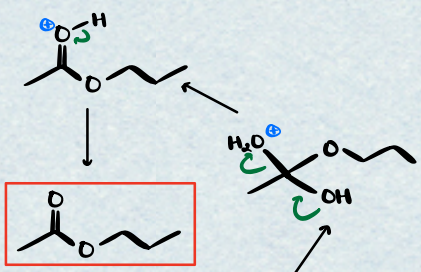
unstable

*Hemiacetals can be stable if they are in the form of a ring.

Fischer Esterification



alcohol + carboxylic acid ⇌ ester + water



Mechanism