Lecture 6: More on Bonding Theories

Note Title 2/25/2014

Today:
- Cyclopropyl carbinyl cation & Walsh orbitals of cyclopropane
- Baldwin's Rules for Ring Closure
- Hard-Soft Acid-Base Theory

Wed 2:30 – 3:30

Thurs 10 – 11

Announcements:
- Problem Set 2 due on Thurs, 9/22 at the beginning of lecture.
- Extra Office Hours tomorrow: Fri, 9/16, 2:30-3:30pm, 201 LDL.

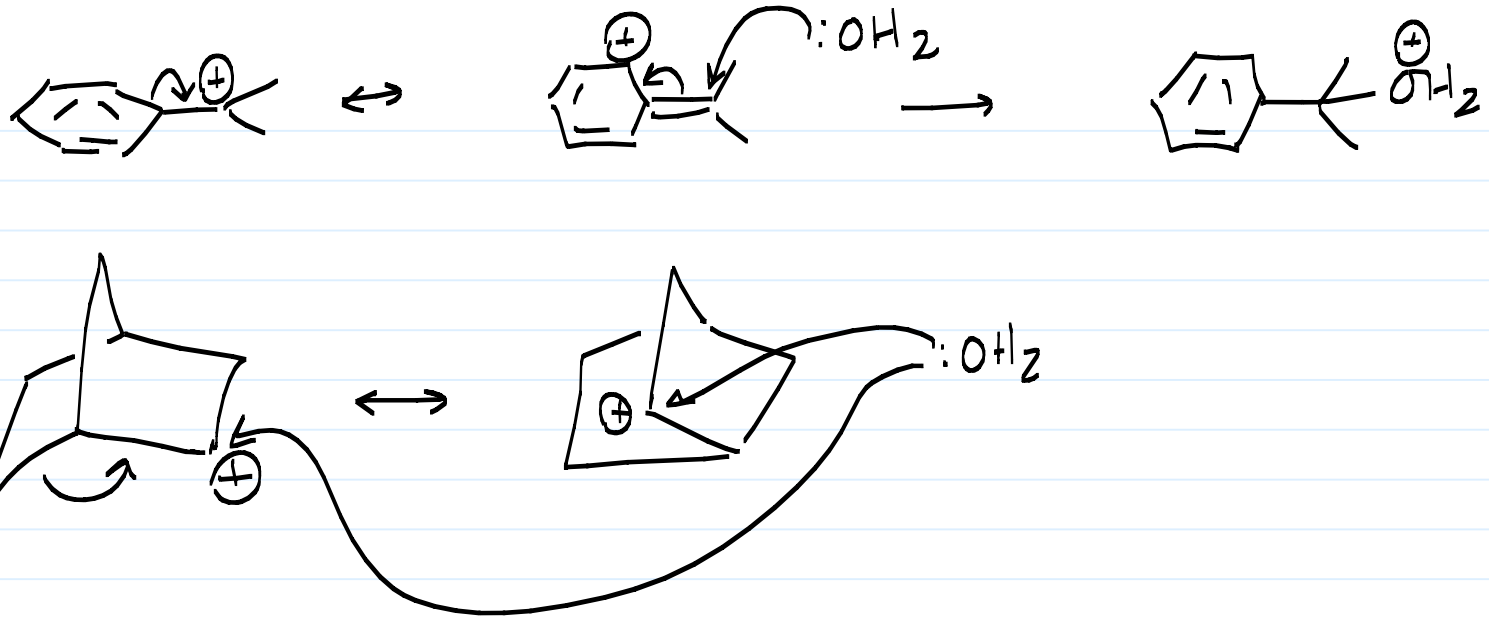
Is this a good time for those with conflicts for my Wed office hour? Is Monday better 1:30-2:30 better?

- Organic Jounal Club TODAY, 12:30pm, 219 BRL.

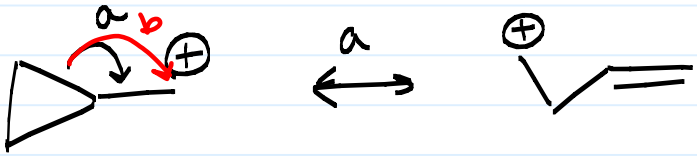
Mon 1:30 - 2:30 *

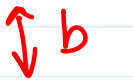
or

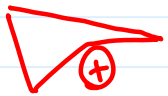
Fri 1:30 - 2:30

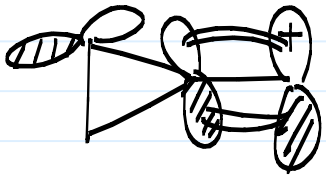

:OH2
:OH2

Cyclopropylcarbinyl Cation



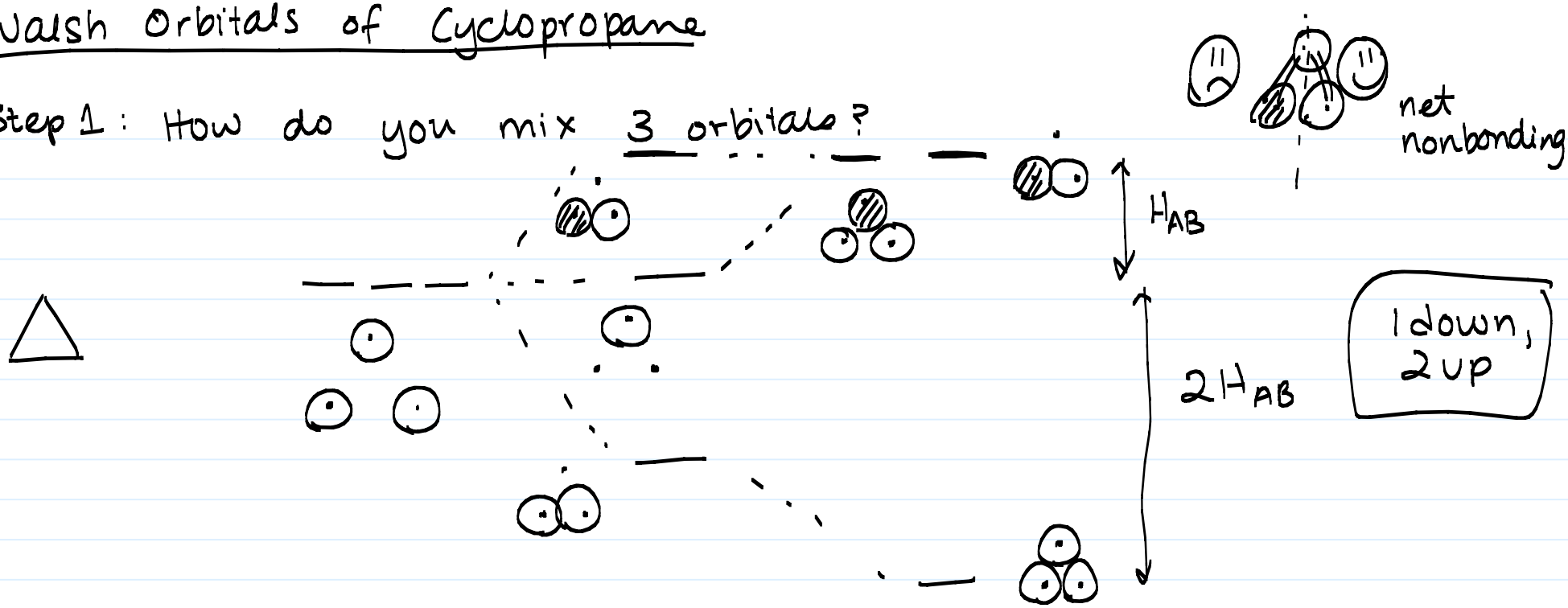




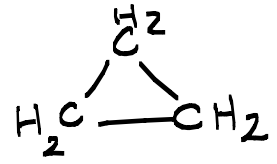


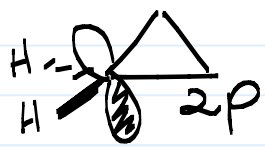
Walsh Orbitals of Cyclopropane

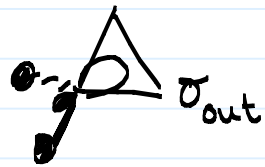
Step 1: How do you mix 3 orbitals?

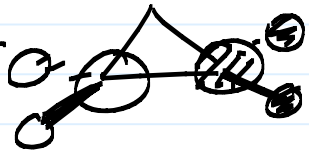


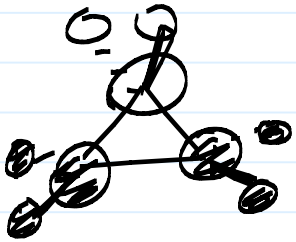
Step 2 :

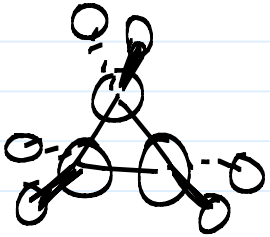


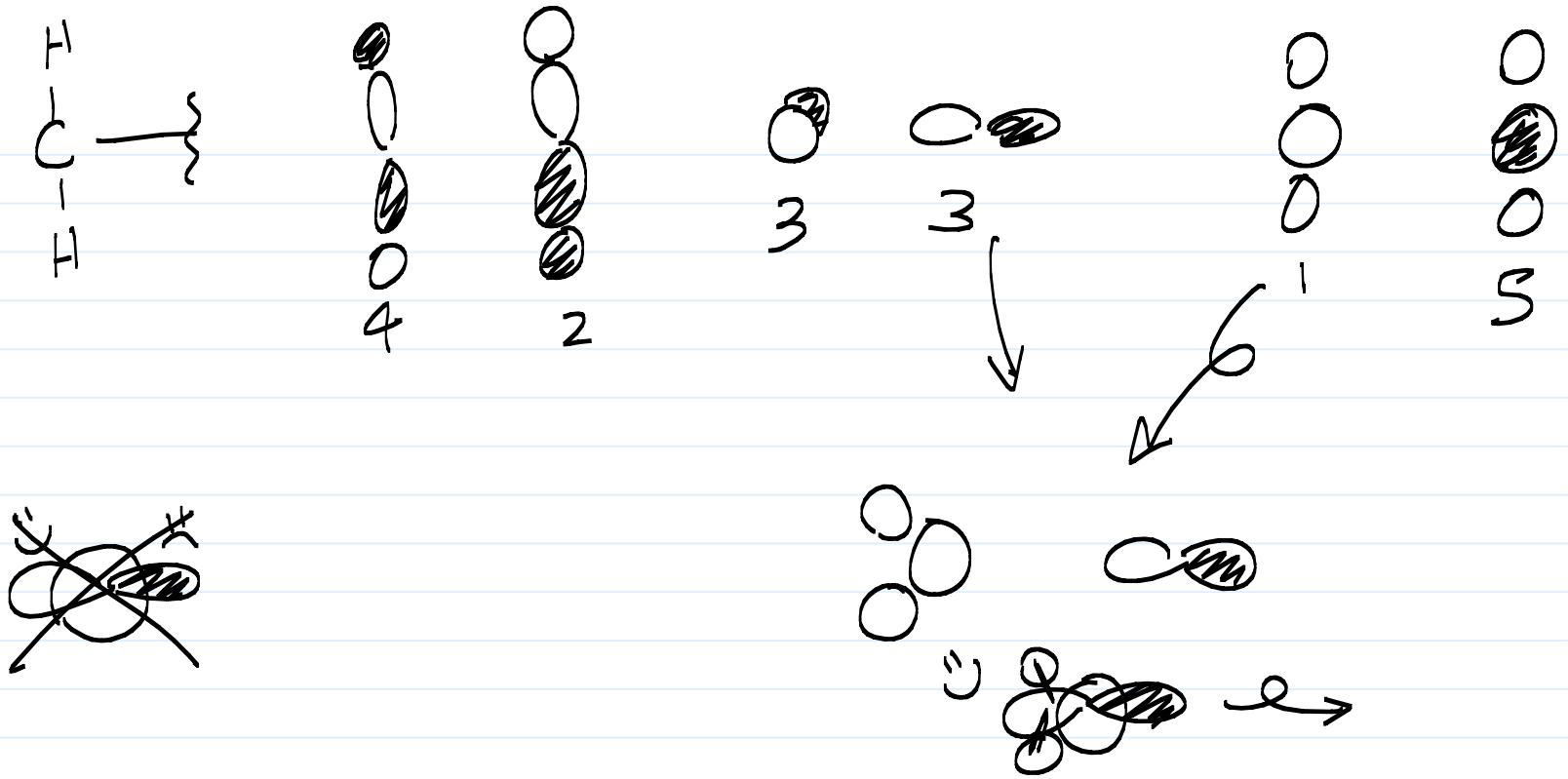











H
H
H
4
2
3
3
1
5
6

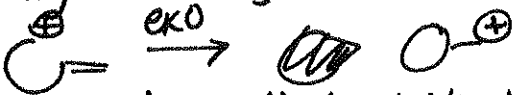
① LECTURE 4: Baldwin's Rules
HSAB

② Baldwin's Rules for Ring Closure → "Guidelines"

- b/c of Burgi-Dünitz angle.
- predicts relative reactivity trends
- true for nucleophilic, radical & cationic ring closures.

3 variables matter:

1. Ring size
   5 > 6 > 3 > 7 > 4 > 8-10
2. Regiochemistry of the attack



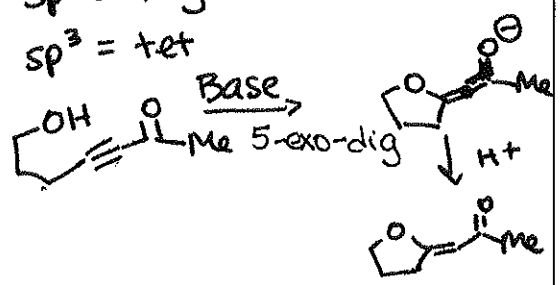
(cation, anion, radical outside ring)

③

(cation, anion, radical inside ring)

3. Hybridization of C under attack.
   sp = dig
   sp^2 = trig
   sp^3 = tet

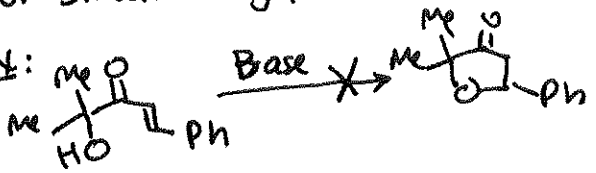
ex:



④ For larger rings, (ring size ≥ 6), endo vs. exo, dig vs. trig vs. tet DOES NOT MATTER.

For small rings, it does matter.

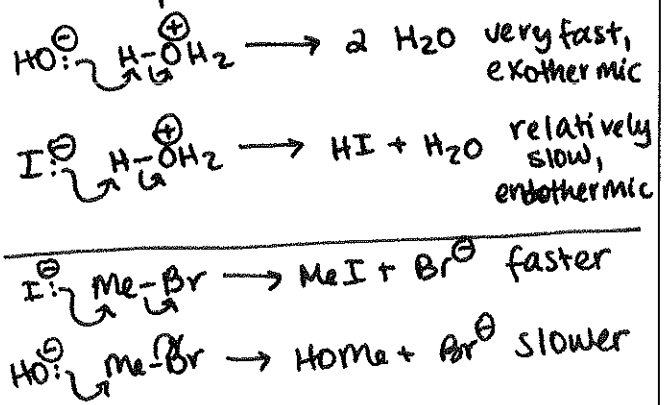
ex:



Nuc cannot achieve Burgi-Dünitz angle!

See Table 10.5 (p. 569) in AE, D for Baldwin's Rules.

⑤ A Complication:



Why?

FMO doesn't explain everything.

⑥ Hard-Soft Acid-Base Theory

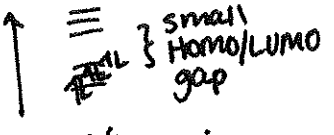
Electrostatics matter.

HARD ← ionic Bonds (ELECTROSTATICS) — SOFT → Covalent Bonds (FMO)

Rxns fall somewhere on the continuum → some form more ionic bonds, some more covalent.

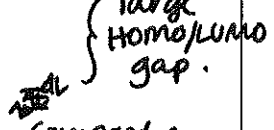
Relates to Homo/Lumo gap:

Soft Species



Large atom or ion w/ small effective nuclear charge. Easily polarized.

Hard Species



Compact e- distribution. High net nuclear charge.

(7)

Hard anions: Small, e⁻s held close to nucleus — LOW HOMO

Hardness increases w/ EN & ⊖ charge:

$F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$

$F^{\ominus} > H^{\ominus} > {}^{\ominus}OH > {}^{\ominus}NH_2 > {}^{\ominus}CH_3$

Hard cations: Small, HIGH LUMO

Hardness ↓ w/ size & ↑ w/ ⊕ charge

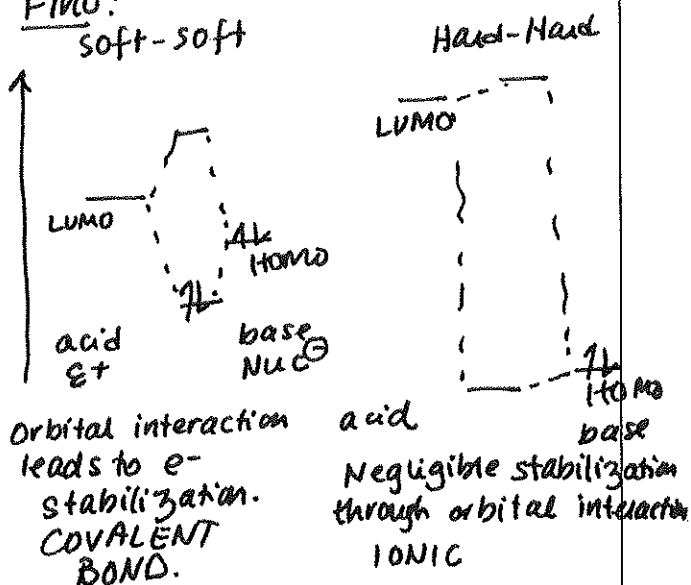
$H^{\oplus} > Li^{\oplus} > Na^{\oplus} > K^{\oplus}$

$H^{\oplus}$: infinitely hard (no e⁻ or neutrons!)

Metal ion hardness increases w/ oxid state (e⁻ cloud shrinks)

(8)

FMO:



Orbital interaction leads to e⁻ stabilization. COVALENT BOND.

Negligible stabilization through orbital interaction. IONIC

(9)

Generalities:

1) Hard-Hard interactions are dominated by electrostatics.
2) Softer cmpds are usually more reactive & more nucleophilic (want to donate e⁻ to Et)

Nucleophilicity:

${}^{\ominus}CH_3 > {}^{\ominus}NH_2 > {}^{\ominus}OH > {}^{\ominus}H > {}^{\ominus}F$

* 3) Hard prefers Hard. Soft prefers soft.

$H\text{-}S + S\text{-}H \rightleftharpoons H\text{-}H + S\text{-}S$

(10)

HSAB & Polarizability

C-X: I < Br < Cl < F

I: Easily polarizable

F: Most polar/hardest bond.

Polarizability & Hybridization

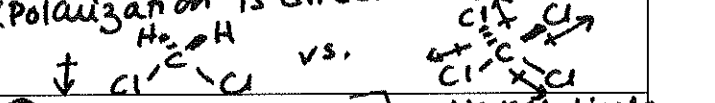
$sp^3 > sp^2 > sp$

SOFTEST, most polarizable

HARDEST, less polarizable

lower energy, closer to nucleus.

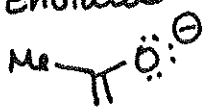
(Polarization is directional.)



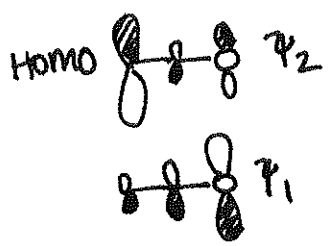
(11)

Ambident Nucleophiles → 2 different nucleophilic centers.

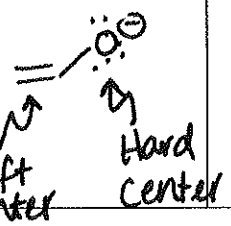
ex: Enolates



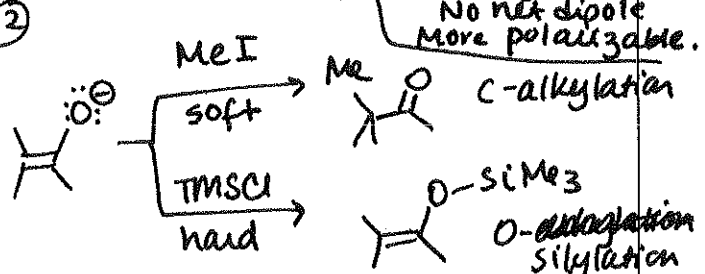
MO's:



But... charge on O = 0.98, on C = 0.52



(12)



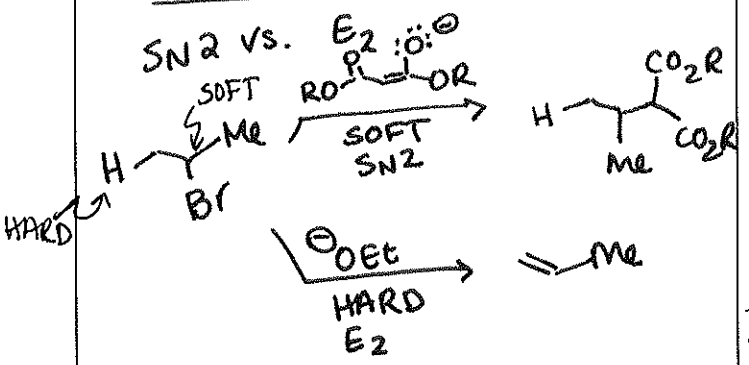
Complication: Solvent.

Solvent "gathers" around site w/ higher charge → Shields ⊖

(In gas phase, often see alkylation on O.)

(13) Ambident Electrophiles

SN2 vs. E2



(14)

Disclaimer: HSAB ~~doesn't~~ doesn't always predict the right pdts. But it can be helpful.

Typical Hard & Soft Nuc & El+

	Nuc (Lewis Base)	El (Lewis Acid)
HARD	H_2O, HO^-, F^- all oxyanions (eg CO_3^{2-})	H_3O^+, Li^+, Na^+, K^+, Mg^{2+}, Al^{3+} BF_3, $AlCl_3$, AlH_3, AlR_3
SOFT	I^-, Br^-, RS^-, SCN^-, $S_2O_3^{2-}$, RSH, RSR', R_3P, $(RO)_3P$, CN^- RO^-, benzene	Ag^+, Pd^{2+} I_2, Br_2

(15)

(16)

(17)

(18)