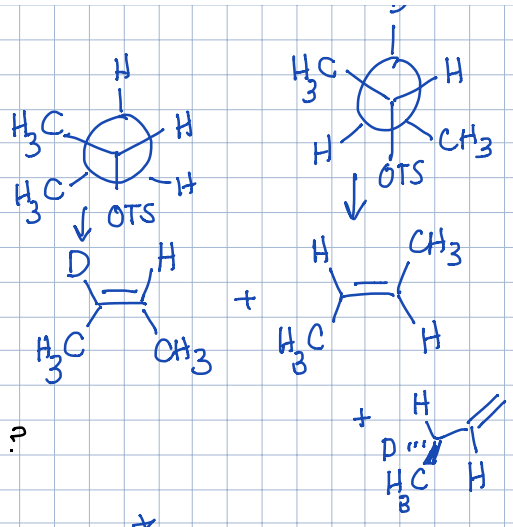
Lecture 6

Today:
- Stereoelectronic Effects (continued)
- Orbitals of Cyclopropane
- Baldwin's Rules
- Hard-Soft Acid-Base Theory (HSAB)

Announcements:
- Problem Set 2 is posted online. Due Thurs, 9/22/16.
- Problem Set 1 Answer Key is posted online. ***Please*** come see me if you have questions. Office hour: Wed 2:30-3:30pm.
- Seminar: Prof. Tim Warren, Wed, 4pm, 219 BRL
- Organic Journal Club (OJC): Thurs, 12:30, 219 BRL`````

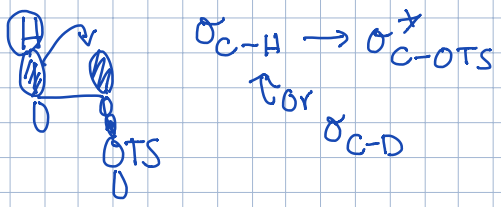
Problems from Last Time:

1) E2 Eliminations

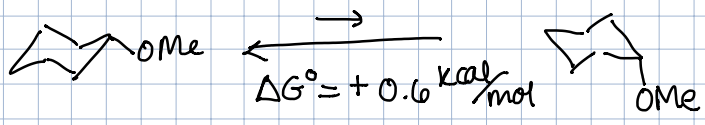


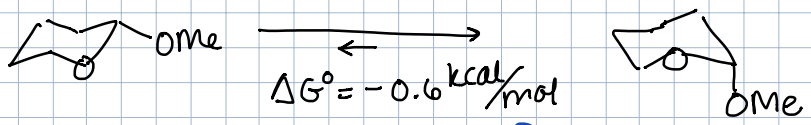
a) what are the products?

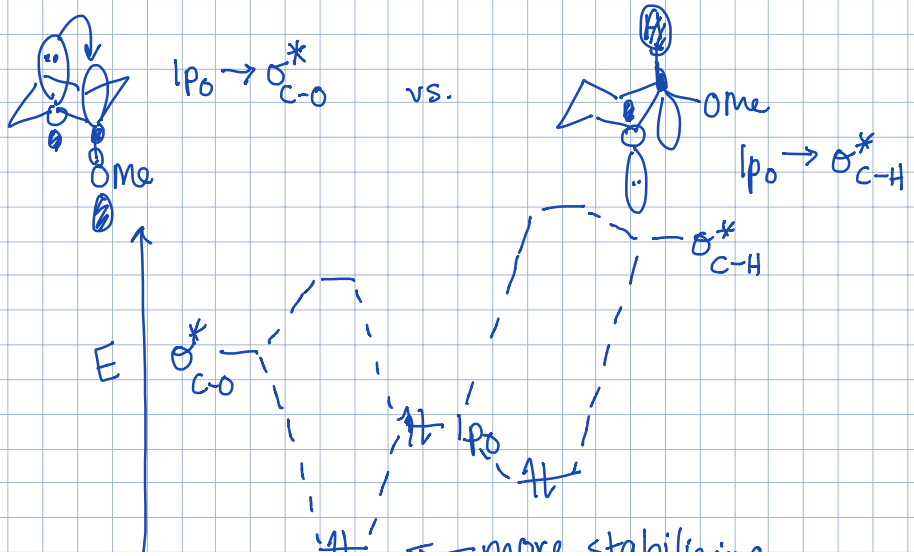
b) Why?

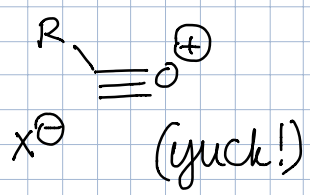


2) Anomeric Effect: Why?

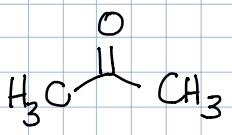


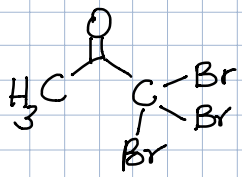


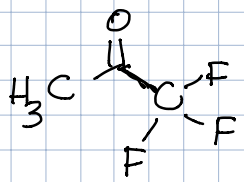




IR:

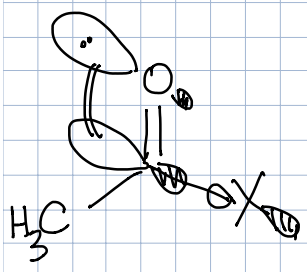


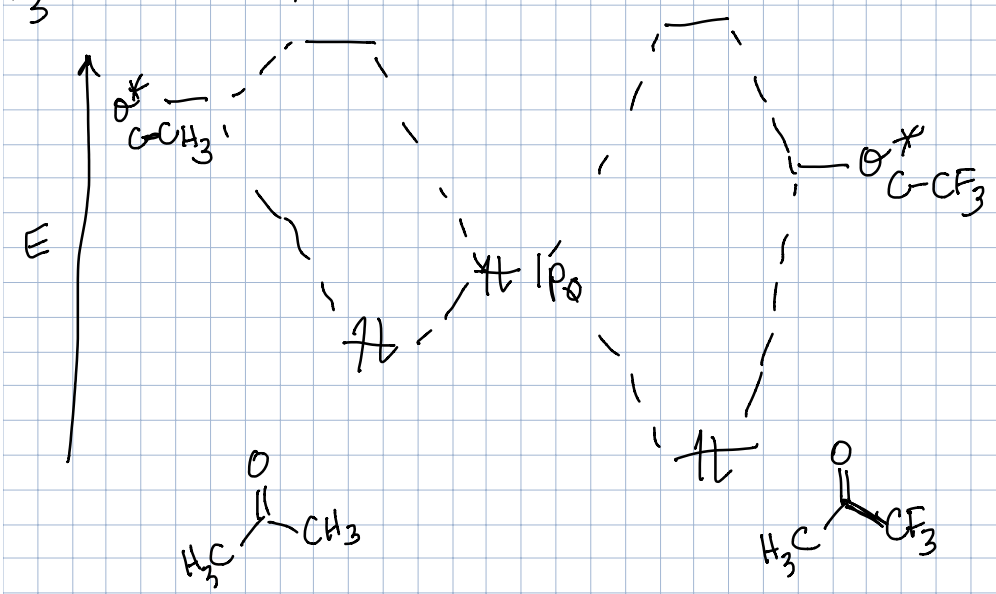




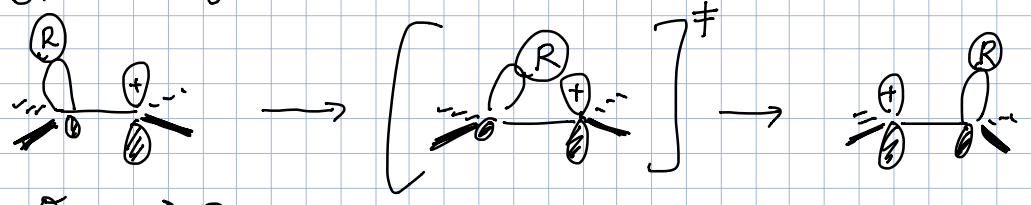
$\nu_{C=O}$ (cm^{-1})	1720	1750	1780

Stronger





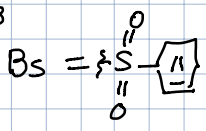
Hyperconjugation:



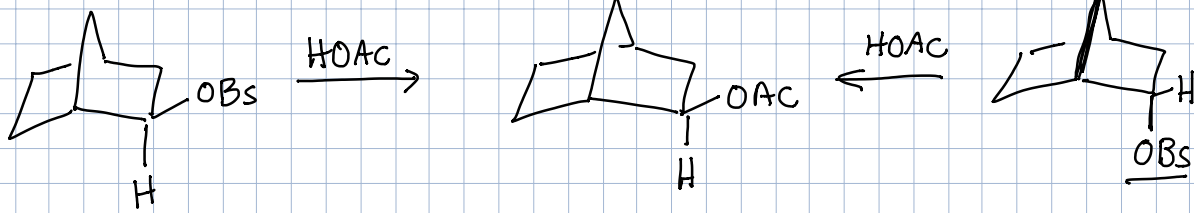
$\sigma_{C-R} \rightarrow p_C$

1,2-rearrangement!

R = H, CR_3

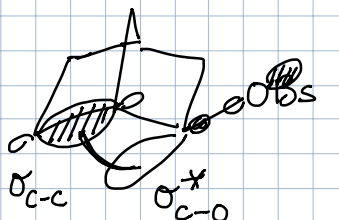
Bs = 

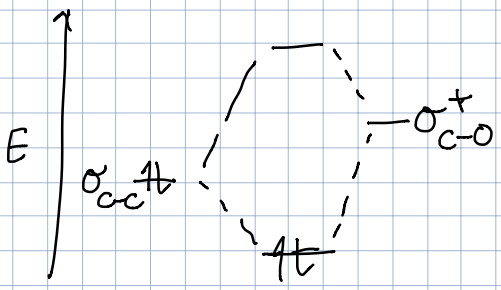
Nonclassical Carbonium Ions:



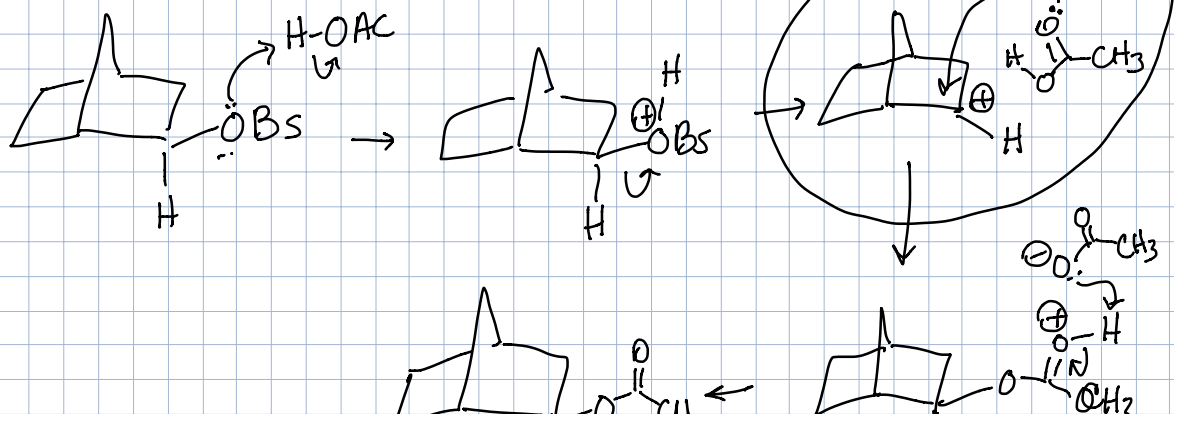
relative rates 350 : 1

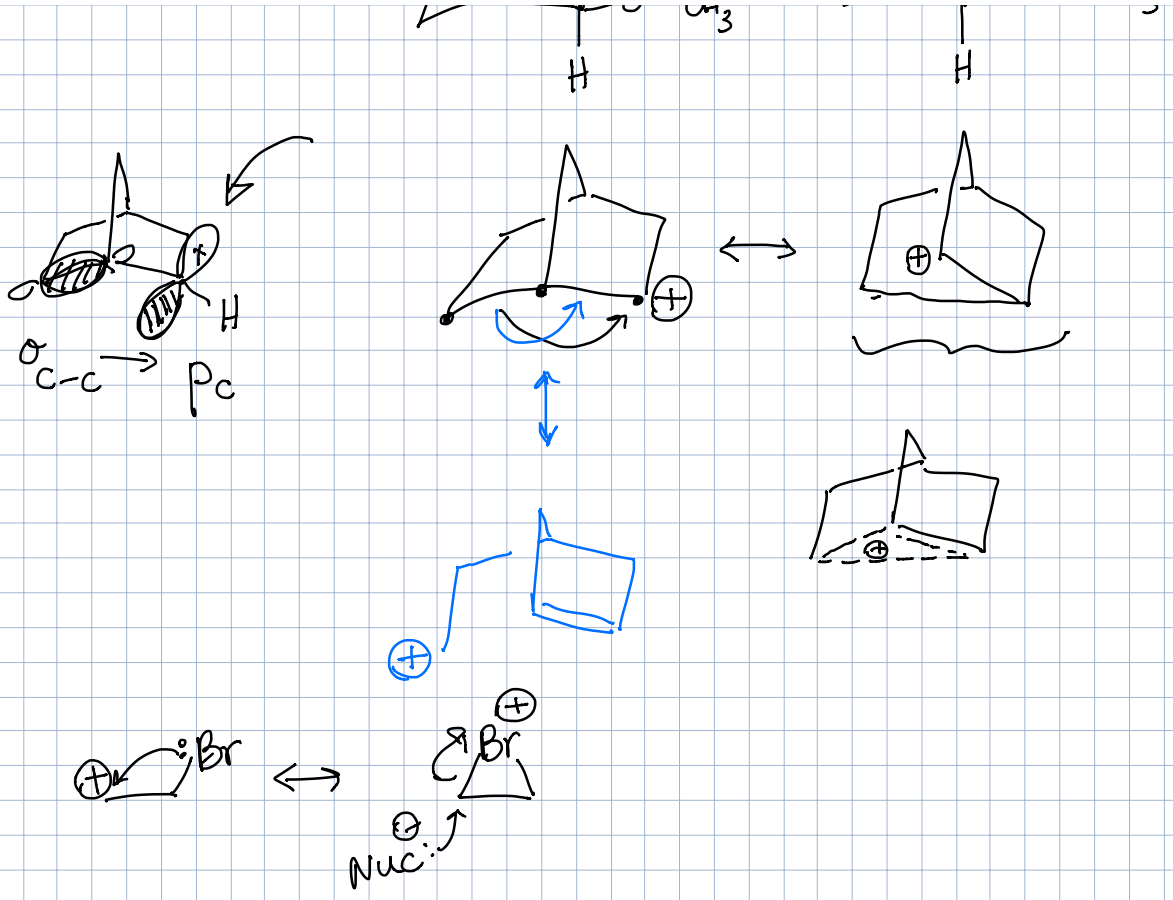
Why?





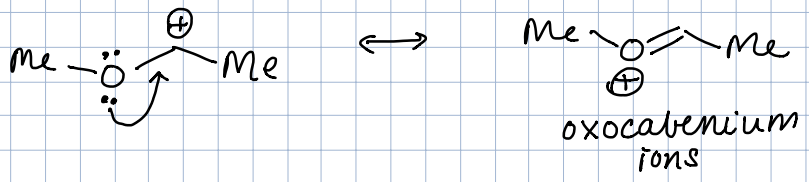
↑ weakens C-O bond

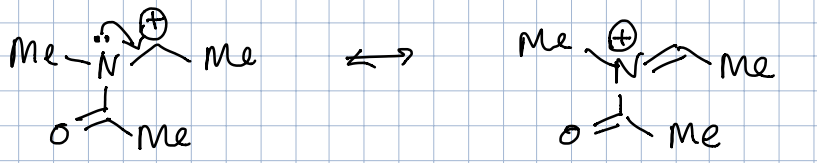



H
H
σ_{C-C}
p_C
Br
Br
Nuc:

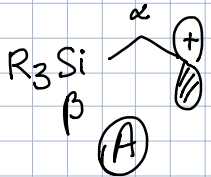
Other Ways to Stabilize Carbocations

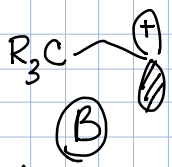
Heteroatoms:





β-silicon effect

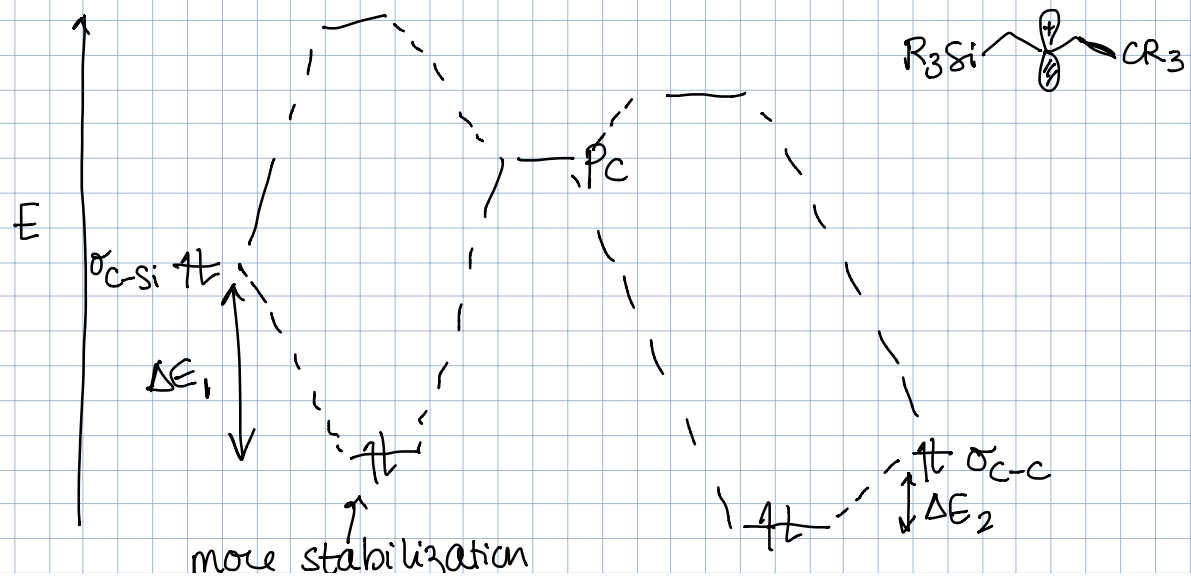




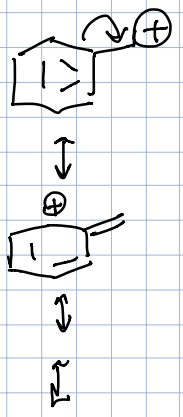
(A) calculated to 38 kcal/mol more stable than (B).

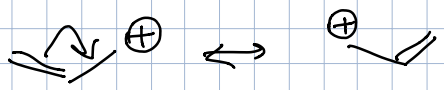
JACS 1985, 107, 1496.

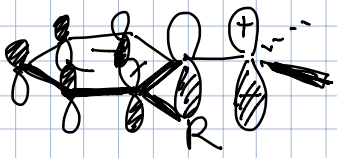
Why?



Benzylic & Allylic Cations







For Thurs: Read A & D p. 848-853
Walsh orbitals of Cyclopropane.