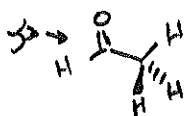


**Practice Problems for Midterm 1**  
 (This is not an inclusive list of the concepts!)

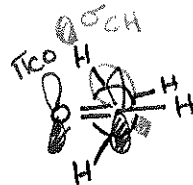
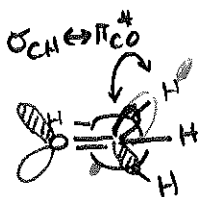
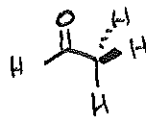
1. Predict the most stable conformation of acetaldehyde. Please use FMO arguments to support your prediction.



2 possible conformations:



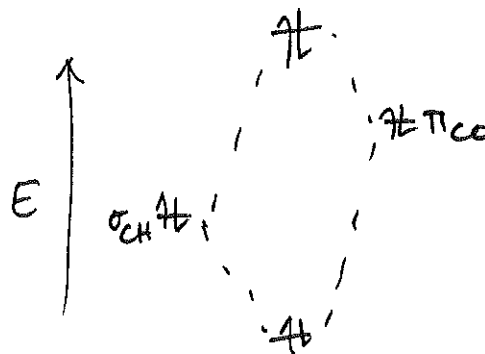
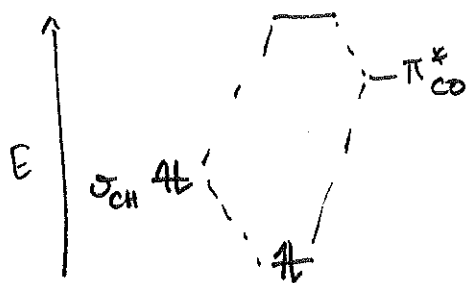
vs.



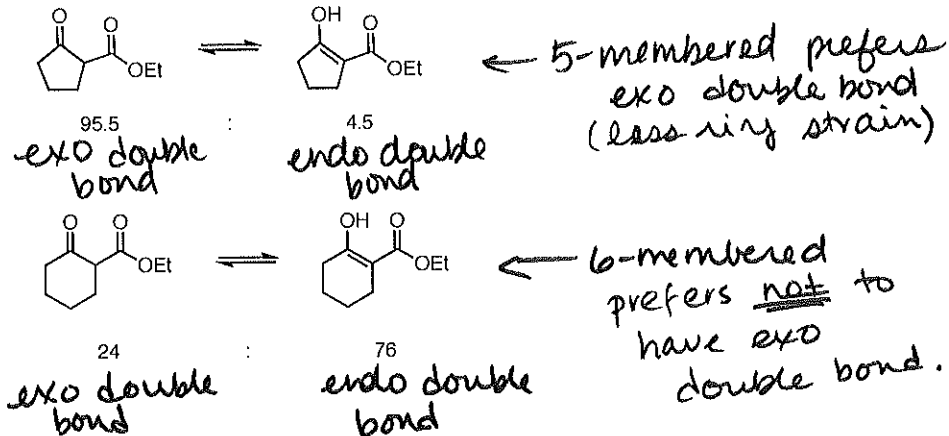
$\sigma_{CH} \leftrightarrow \pi^*_{CO}$   
 Filled/unfilled  
 ↓  
 Stabilizing

$\pi_{CO} \leftrightarrow \sigma_{CH}$   
 Filled/Filled  
 ↓  
 Destabilizing

↑  
 MORE STABLE



2. Please explain why ring size affects the position of the equilibria shown below (Brown et al. *JACS* 1954, 76, 467).



See Ref & Class Notes:

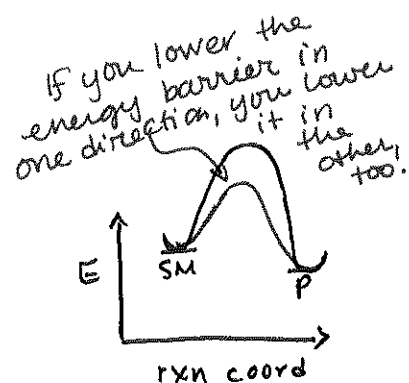
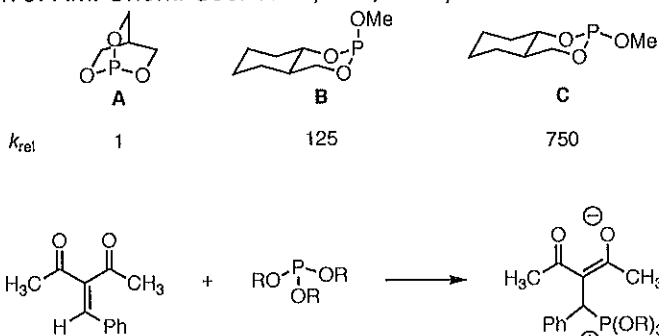
Exo double bonds in 5-membered rings  $\Rightarrow$  Relatively stable.

Exo double bonds in 6-membered rings  $\Rightarrow$  Relatively unstable.

Rxns of 5-membered rings  $\Rightarrow$  ~~5~~ exo double bonds.

Rxns of 6-membered rings  $\Rightarrow$  get rid of exo double bonds  
(endo dbl bond better)

3. Explain the relative reactivity of the following phosphites in the reaction with 3-benzylidene-2,4-pentanedione (Gorenstein *J. Am. Chem. Soc.* **1984**, *106*, 7831).



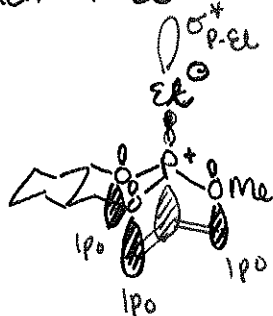
Consider microscopic reverse:



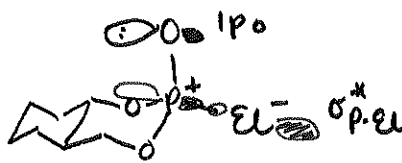
El = Electrophile

If something (like a stereoelectronic effect) lowers energy to bond cleavage, it also must lower energy barrier to bond formation.

Which P-El bonds are cleaved most easily?

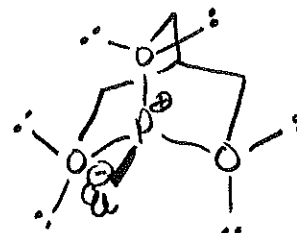


Great overlap  
 $3 \times \text{lpo} \leftrightarrow \sigma^*_{\text{P-El}}$



Some overlap

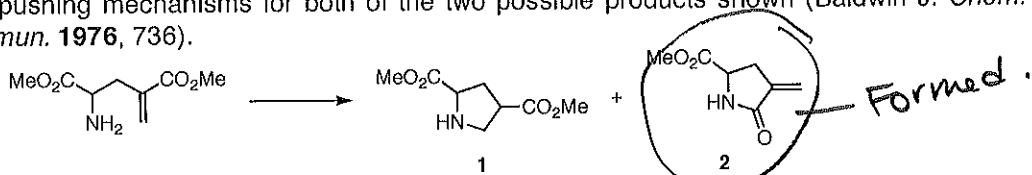
$1 \times \text{lpo} \leftrightarrow \sigma^*_{\text{P-El}}$



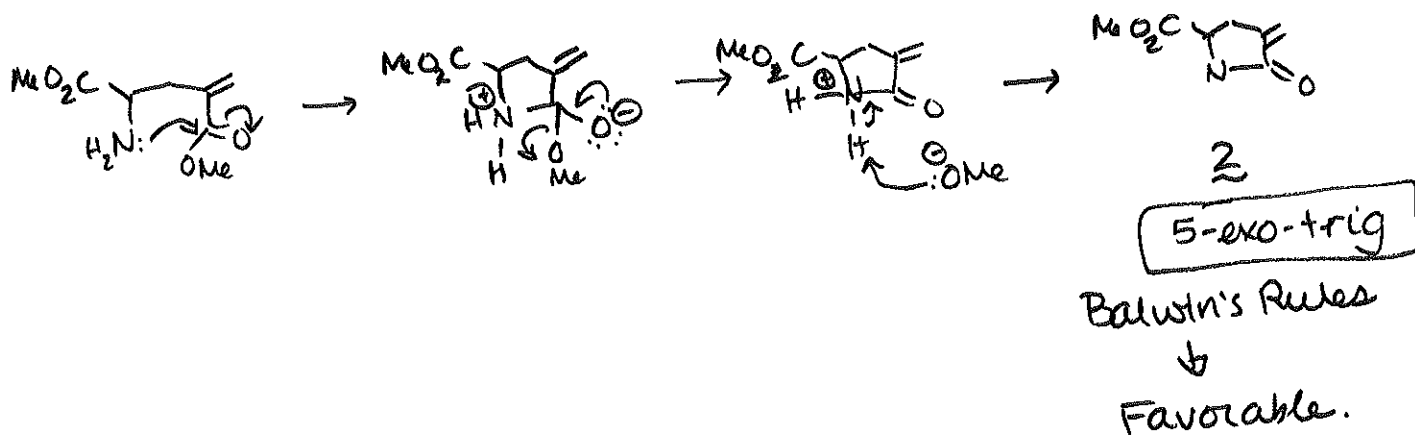
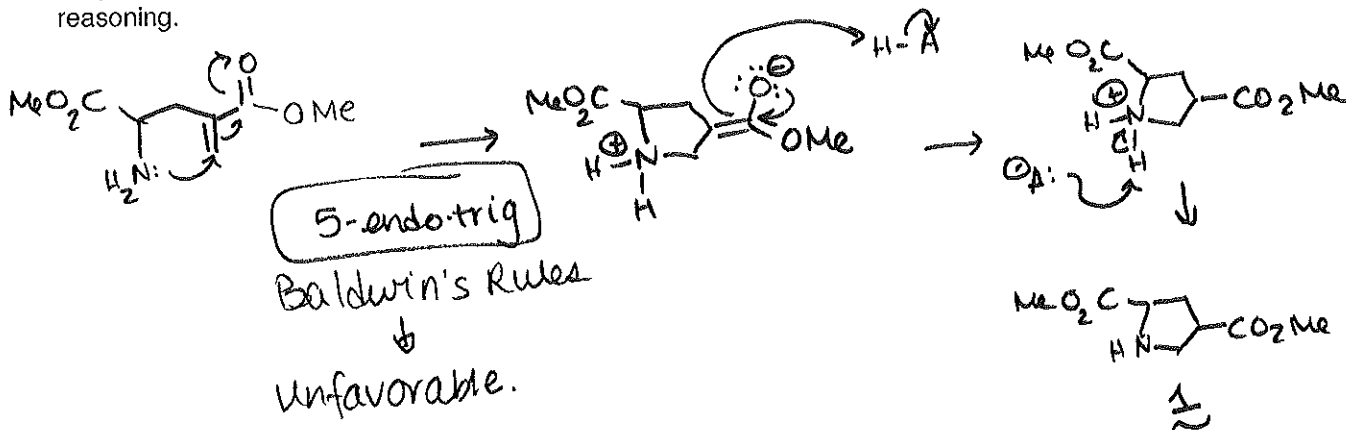
No overlap geometrically possible w/

$\text{lpo} \leftrightarrow \sigma^*_{\text{P-El}}$

4. Propose arrow-pushing mechanisms for both of the two possible products shown (Baldwin *J. Chem. Soc., Chem. Commun.* 1976, 736).



Only one of the two possible products is formed. Predict which product is formed and explain your reasoning.



5. Please propose an arrow-pushing mechanism for the following transformation (Pirung *J. Am. Chem. Soc.* **1979**, *101*, 7130).

