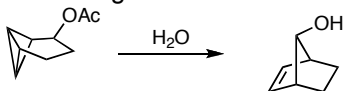


**CHEM 633: Advanced Organic Chem: Physical**

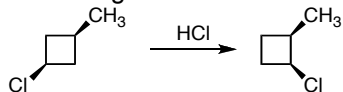
**Problem Set 4**

**Due on 9/29/09**

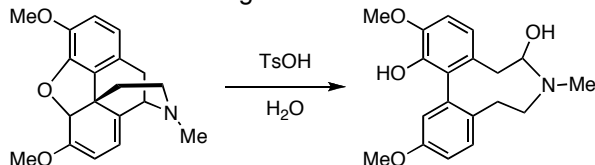
1. Provide an arrow-pushing mechanism for the following transformation. Do not concern yourself with stereochemistry.



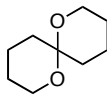
2. Provide an arrow-pushing mechanism for the following transformation. Do not concern yourself with stereochemistry.



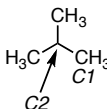
3. Provide an arrow-pushing mechanism for the following transformation. Do not concern yourself with stereochemistry.



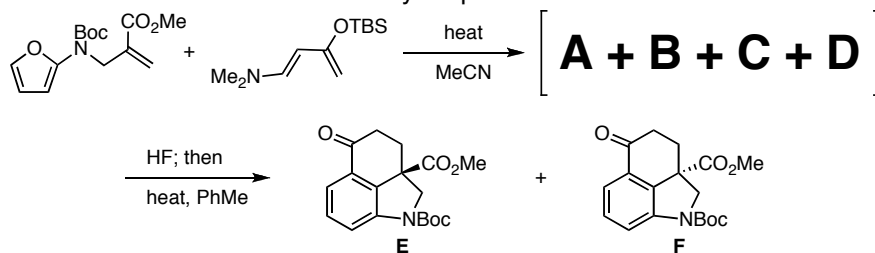
4. Predict the most stable conformation of this dioxospiran. Please show the less stable conformations and explain why they are higher in energy.



5. Calculate the rotational barrier about the C1–C2 bond in isobutene. Please draw a torsional energy profile, labeling the energies and structures of the different conformations.

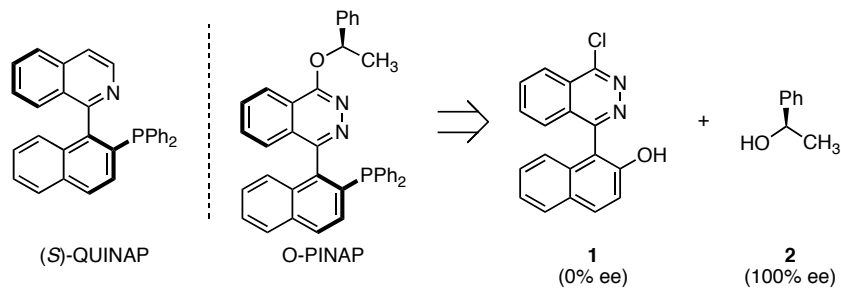


6. A Diels–Alder cyclization is used in the formation of tricyclic products **E** and **F**.

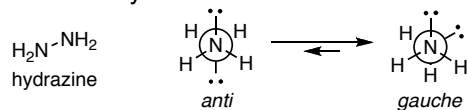


- What four products **A – D**, are formed in the Diels–Alder cyclization?
- Please describe the relationship between these products (isomers, regioisomers, enantiomers, diastereomers, etc).
- Please propose an arrow-pushing mechanism for the formation of intermediates **A – D**.
- Please propose an arrow-pushing mechanism for the formation of tricycles **E** and **F**.
- Predict the relative ratio of **E:F** that will be formed in this sequence.

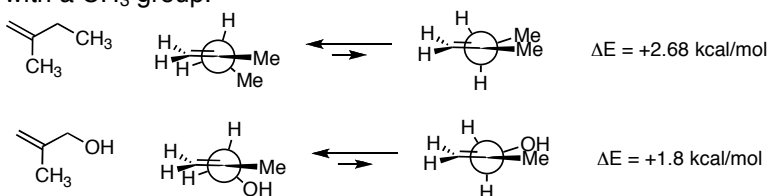
7. Enantiopure QUINAP is a useful ligand for enantioselective metal-catalyzed transformations. The Carreira group designed a similar ligand, O-PINAP, because they anticipated it would have similar reactivity but would be easier to isolate in enantiopure form. Why is O-PINAP easier to isolate in 100% ee than QUINAP? Hint: O-PINAP is synthesized by combination of **1** and **2**, as shown below.



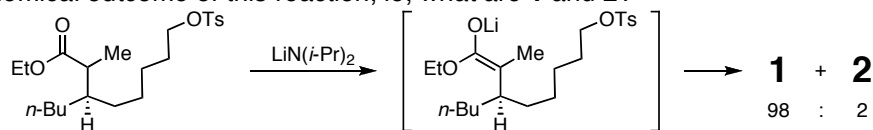
8. Please explain why the gauche conformation of hydrazine is favored.



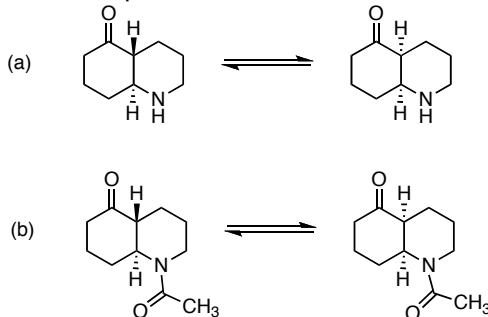
9. Please propose an explanation for the observation that an eclipsing interaction with an OH group is less destabilizing than an eclipsing interaction with a CH<sub>3</sub> group.



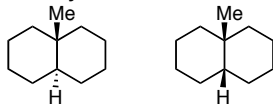
10. Predict the stereochemical outcome of this reaction, ie, what are **1** and **2**?



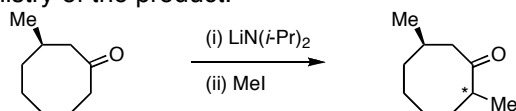
11. Predict and explain which conformation will be preferred.



12. Estimate the energy difference between the 2 methyl-substituted decalins shown below.



13. Predict and explain the stereochemistry of the product.



14. What is the more stable C=C isomer in the two THC structures?

