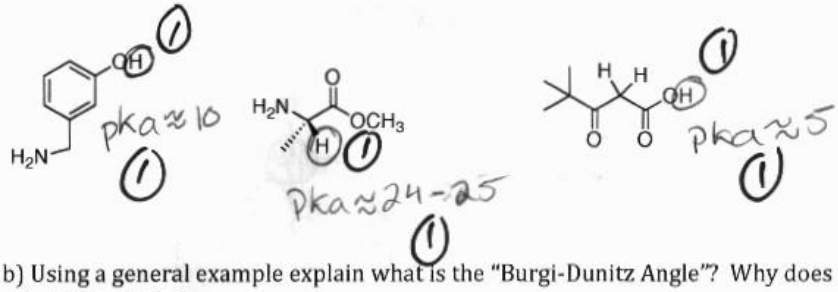
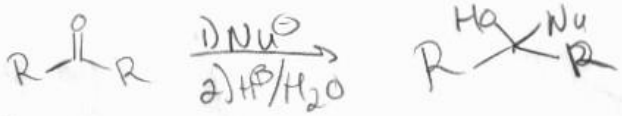
CHM 3120 (Fall 2010)
Midterm #1 – Saturday, October 2

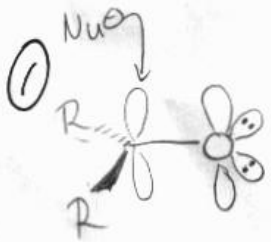
Instructions: Please write all of your answers on the following pages. If you require additional space, you may write on the back pages of the exam. The last page of the exam has been intentionally left blank. Assume aqueous work ups in all questions. Clearly denote stereochemistry where appropriate. Molecular model kits are permitted. **Good luck!**

1. a) Identify the **most** acidic proton in each of the following molecules and give its pKa value. **(6 points)**

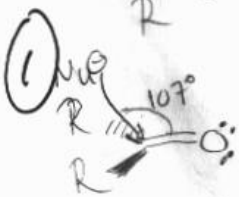


b) Using a general example explain what is the "Burgi-Dunitz Angle"? Why does it arise? **(4 points)**





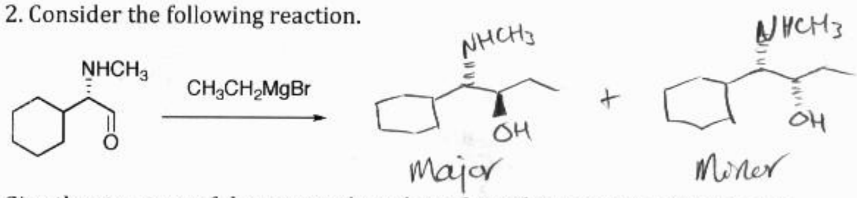
Nu⊖ would prefer to attack 90° to C=O for best orbital overlap.



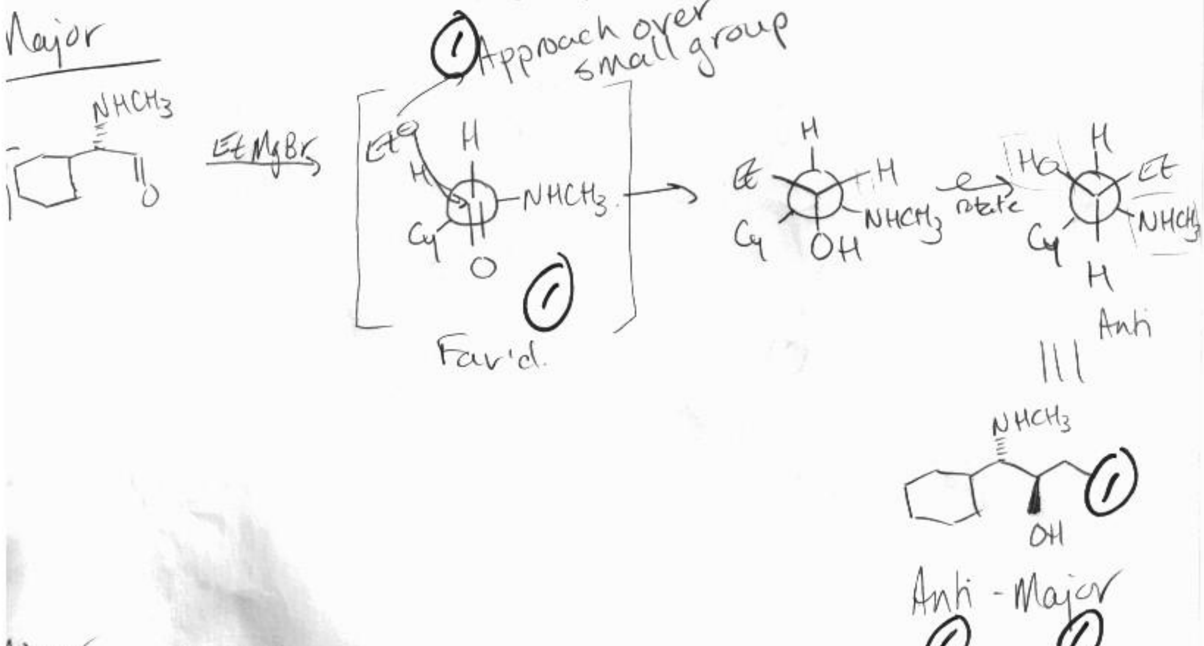
Because of lone pair on oxygen the Nu⊖ can only approach at 107°.

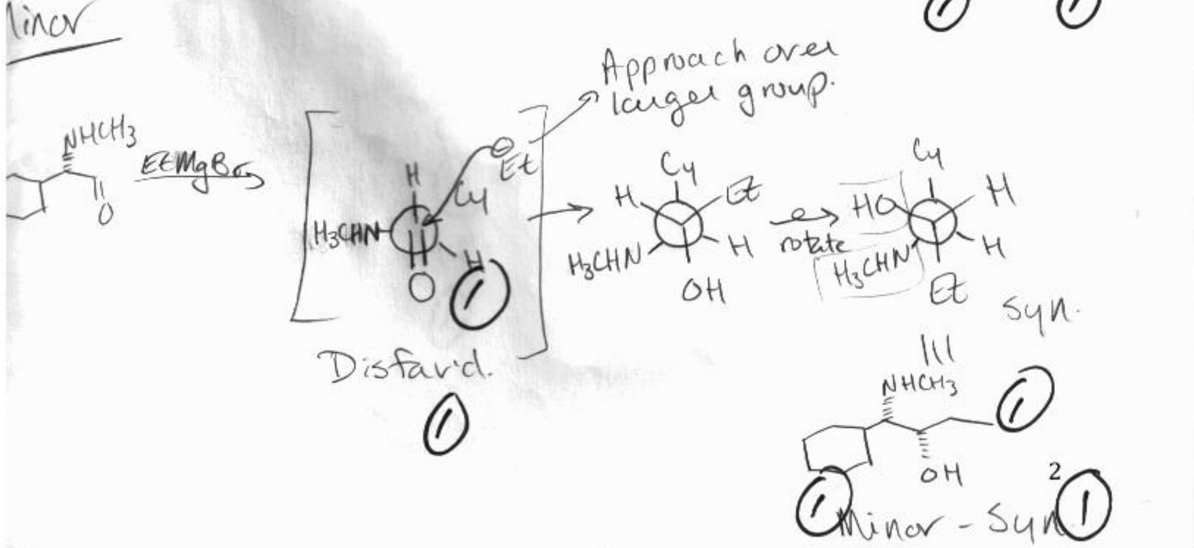
Burgi-Dunitz Angle = 107°

2. Consider the following reaction.

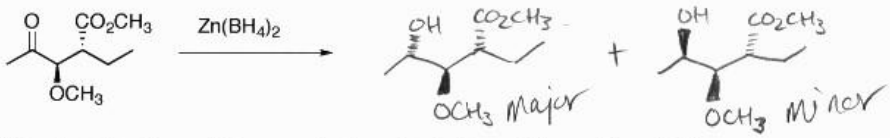


Give the structure of the expected products from this reaction. Is there any selectivity in this reaction and if so, what is the major product? Justify your answer using appropriate models. **(10 points)**



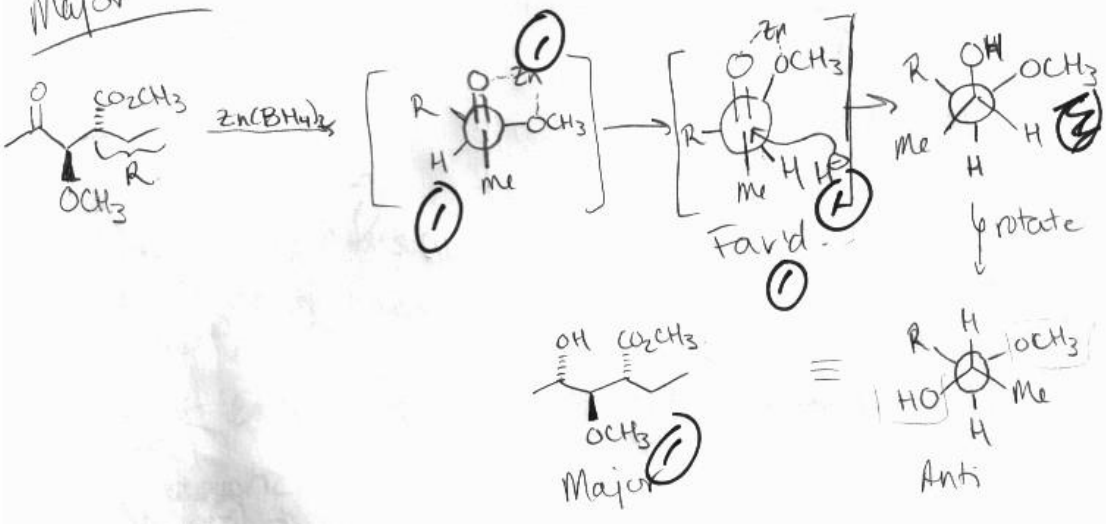


3. Consider the following reaction.

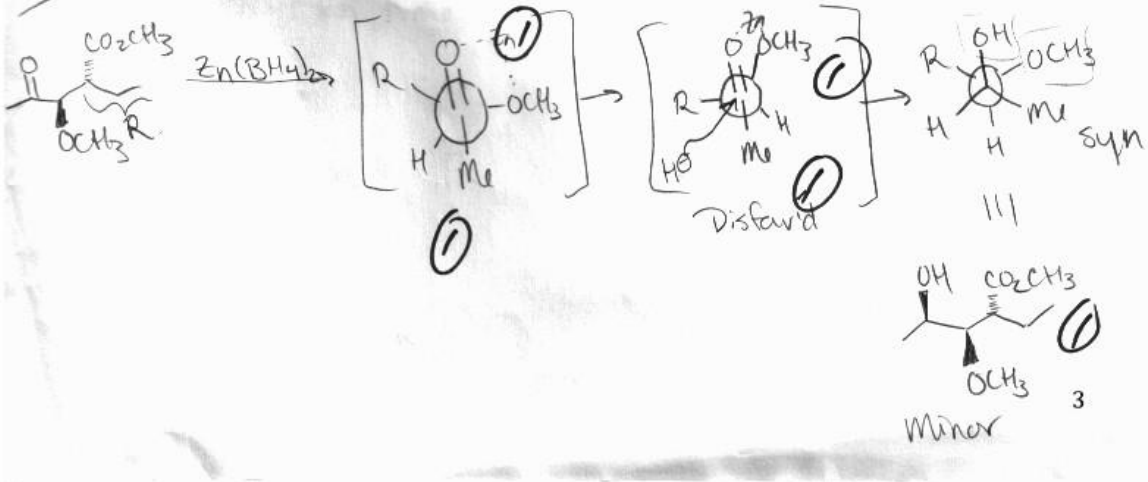


Give the structure of the expected products from this reaction. Is there any selectivity in this reaction and if so, what is the major product? Justify your answer using appropriate models. **(10 marks)**

Major

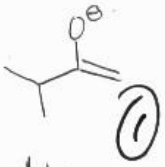


Minor



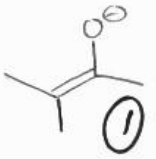
4. Consider the following unsymmetrical ketone.

Draw the structures of the "kinetic" and "thermodynamic" enolates. Provide the reagents and conditions necessary to form each of these enolates selectively. **(10 marks)**



kinetic

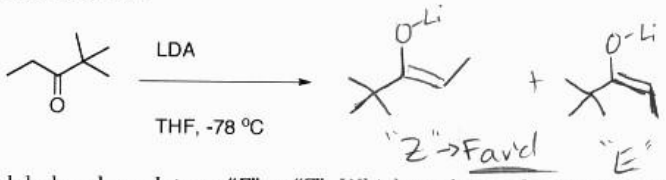
- Irreversible conditions. (1)
- → Strong, hindered base (1) (eg. LDA)
- → Slight excess of base (1)
- → Use aprotic solvent (1) (ex. THF)
- → Lower temperature, Decreased rxn time.



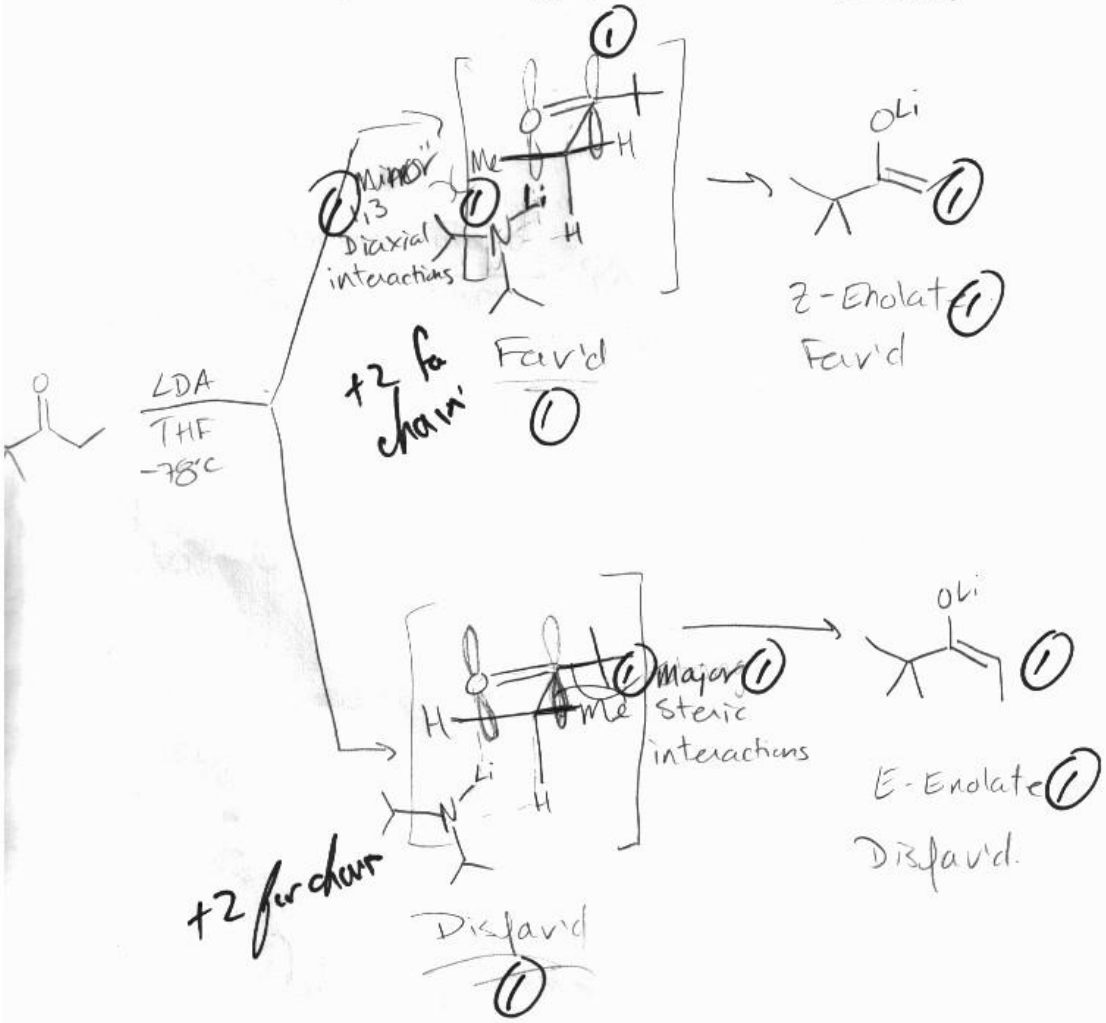
Thermodynamic

- → Reversible conditions (1)
- → Use base with similar pka as ketone (1)
- → Use protic solvent (1)
- → Have slight excess of ketone (1)
- → Higher temperature, longer rxn time

5. Provide the structures of the two enolates that result from deprotonation of the ketone shown below.

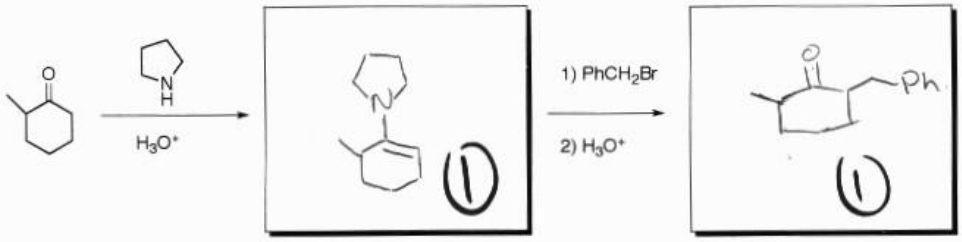


Clearly label each enolate as "*E*" or "*Z*". Which enolate is favored? Why? As part of your discussion you should draw appropriate transition states. **(15 marks)**

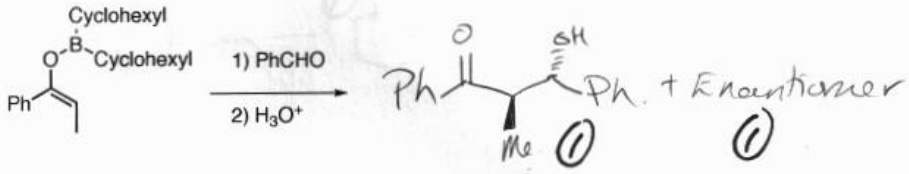


6. Consider the following reactions. What is the structure of the **major** product in each case? What are the transition states for the major and minor products in (b)? Clearly illustrate why the transition state for the minor product is disfavored. **(10 marks)**

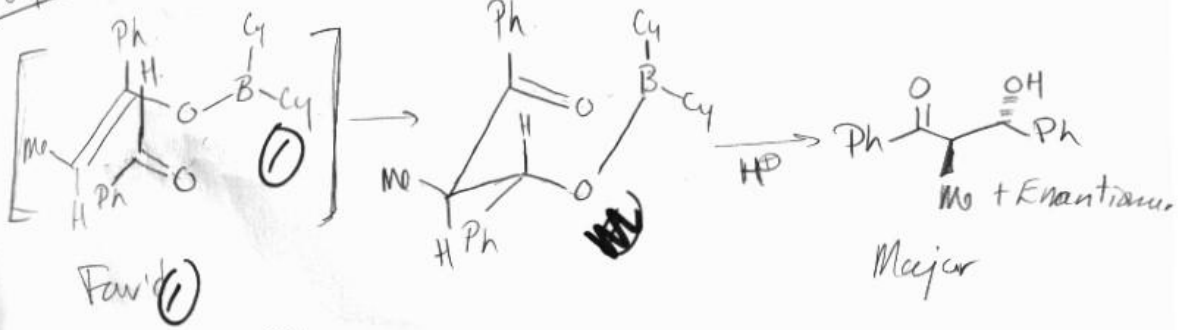
a)



b)



Major



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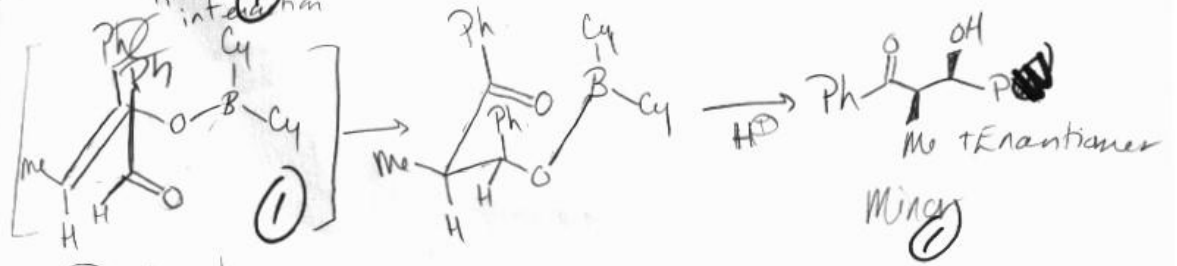
Major

Minor

1,3 Diaxial interaction



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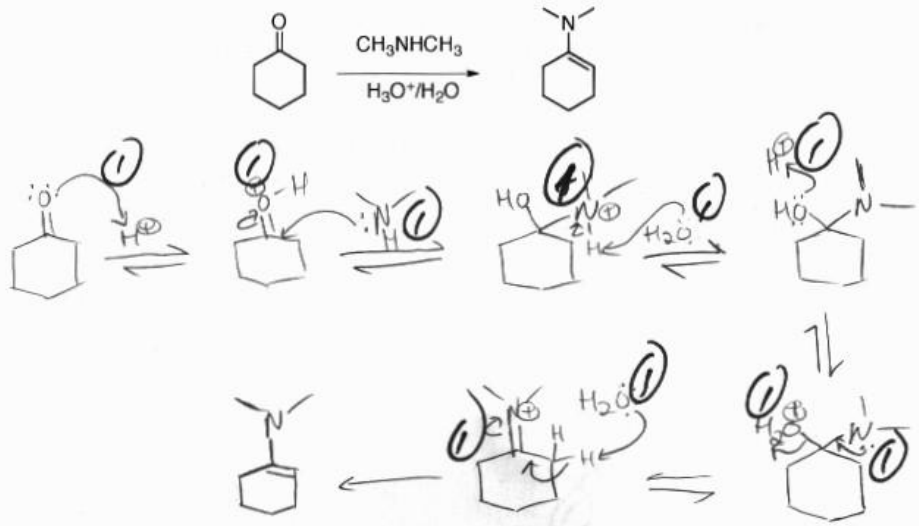
Minor

7. Provide a <u>detailed</u> mechanism for the following reaction. **(10 marks)**



(-1) if no Reversible Arrows

8. Consider the following reaction. What is the structure of the enolate formed under these conditions? Why is only <u>one</u> enolate formed? How is the starting material prepared? **(10 points)**