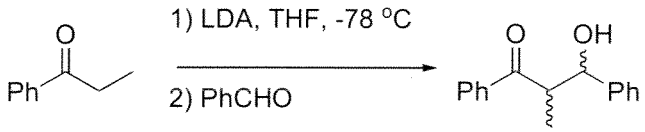
ANSER KEY

Name:
Student #:

CHM 3120
Intermediate Organic Chemistry (Fall 2011)
EXAM #1 Version A

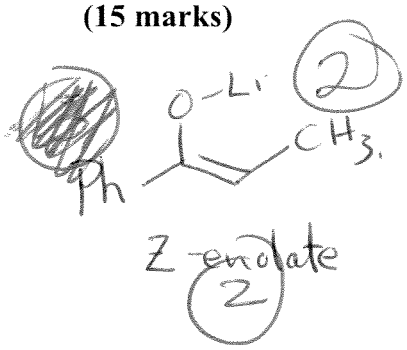
Instructions: Please answer all questions in the space provided. If you require additional space you may use the back pages. The last page of the exam has been intentionally left blank. Model kits are permitted. There are 11 pages and 90 marks in total.
Time allotted: 2 hours

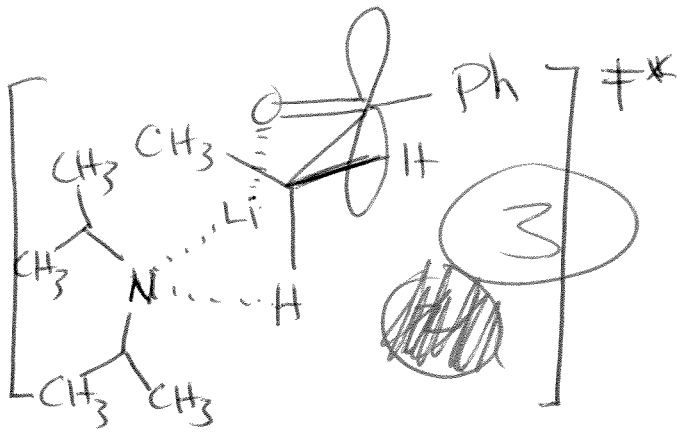
1. Consider the following reaction.

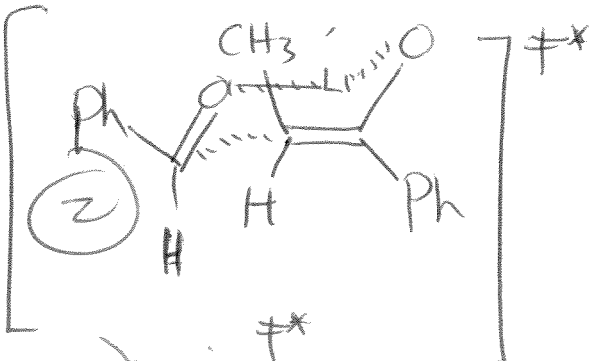


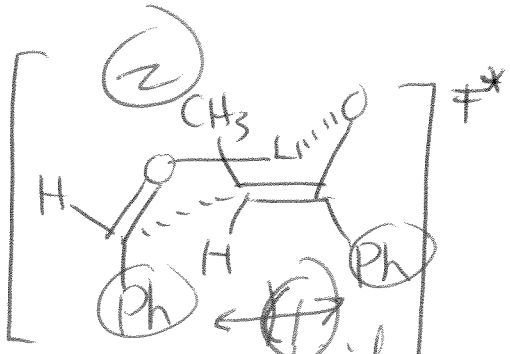
a) Draw the structure of the enolate generated under these conditions. What is the configuration of this enolate?
b) Clearly illustrate the favored transition state for deprotonation of this ketone (show all steric interactions and the p orbitals of the ketone).
c) Draw the structure of the major diastereomer produced in this reaction.
d) Draw the 3D Zimmerman-Traxler transition states for the major and minor diastereomers and indicate the key steric interactions that result in high stereoselectivity.

(15 marks)

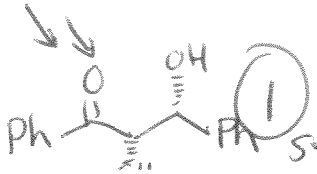








1 major ‡* (favored)



minor ‡*

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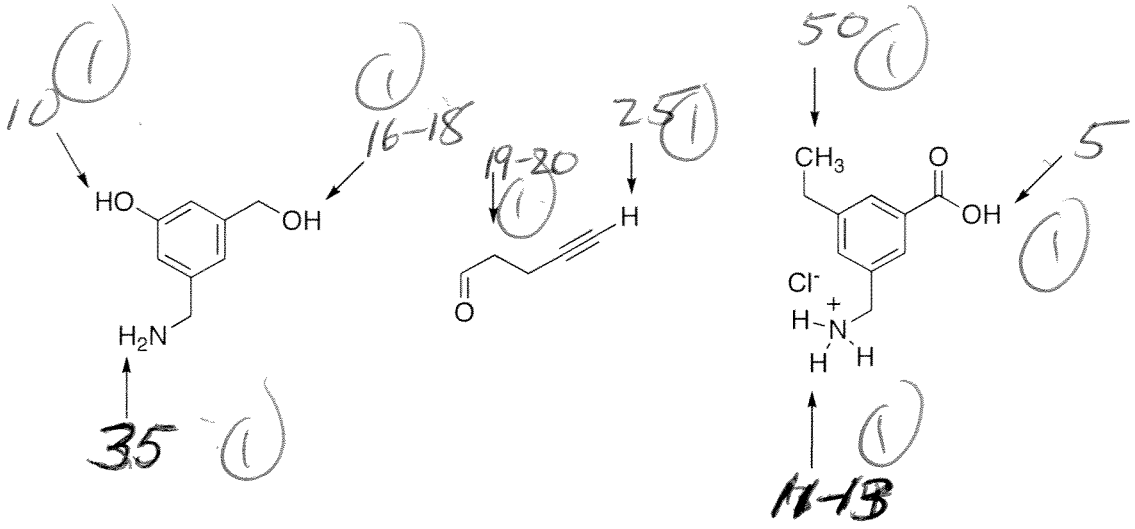
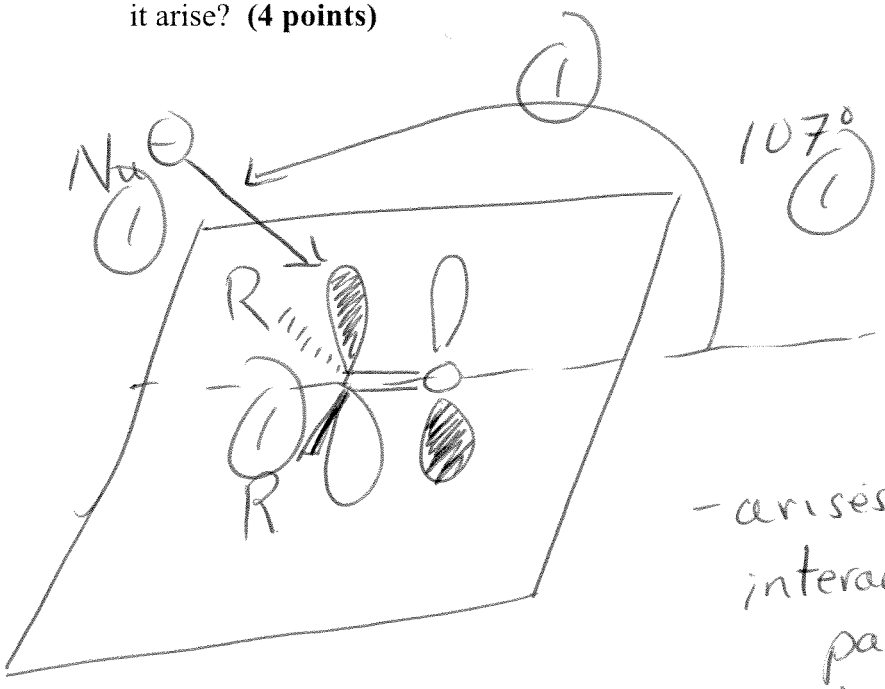
2. a) Provide a pKa value for the indicated proton(s) in the following molecules. **(8 points)**



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



- arises b/c Nuc⊖ interacts with lone pairs on oxygen ⇒ trajectory is "pushed" closer to the R-groups

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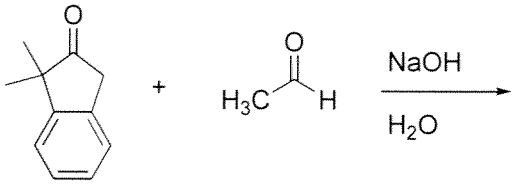
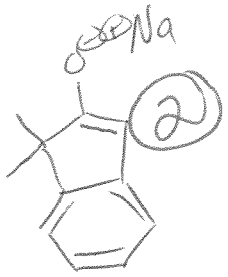
3. What are the products that result from the following reaction? You do not need to show enantiomers. Draw the structures of the enolate(s) that are involved and denote the configuration where appropriate. **(10 marks)**

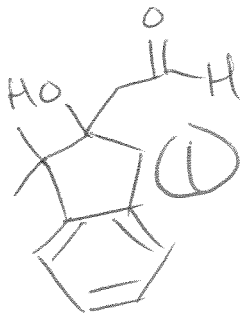


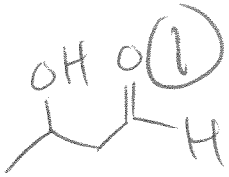
Enolates

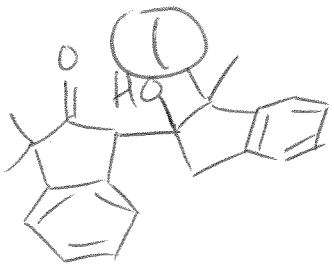


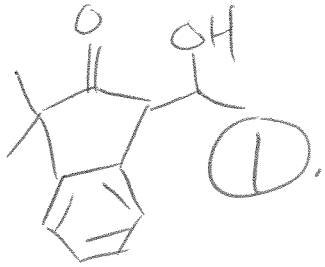
"E"-enolate (2)

Products.

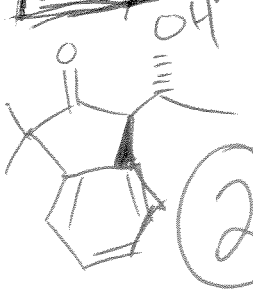






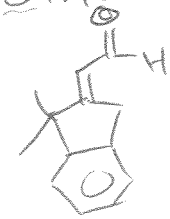


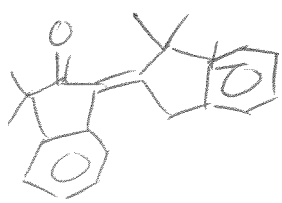
and/or

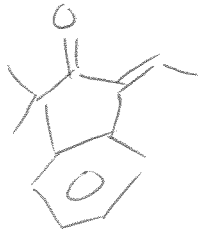


anti (major)
(+ syn minor)

other possible products.







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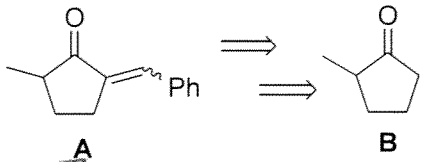
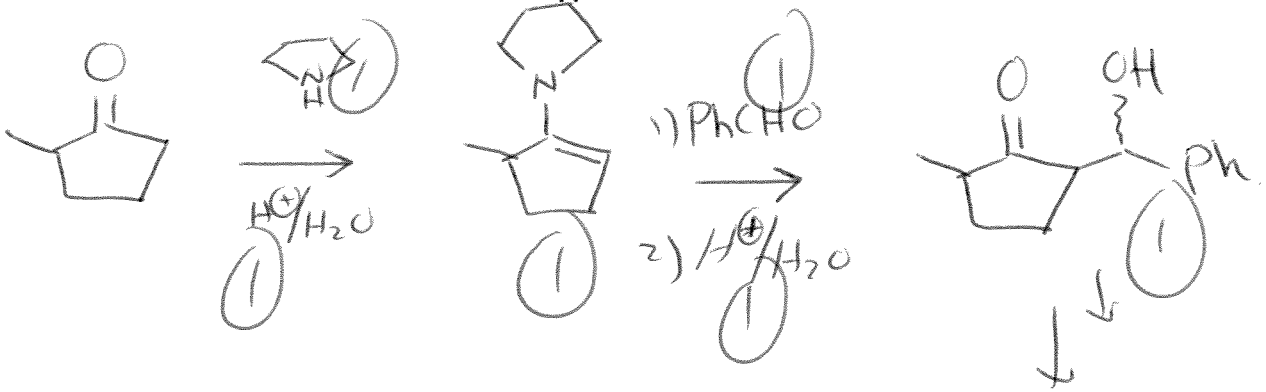
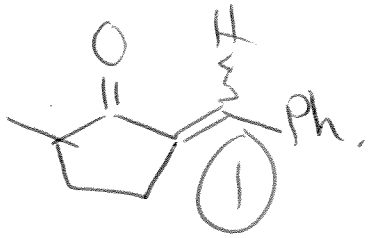
4. How would you prepare **A** starting from **B** using a strategy that **does not** involve formation of a kinetic enolate? You many use any reagents and solvents that you require. Your synthesis must be an efficient one. For full credit you must show a detailed retrosynthesis in addition to your synthesis. **(10 marks)**

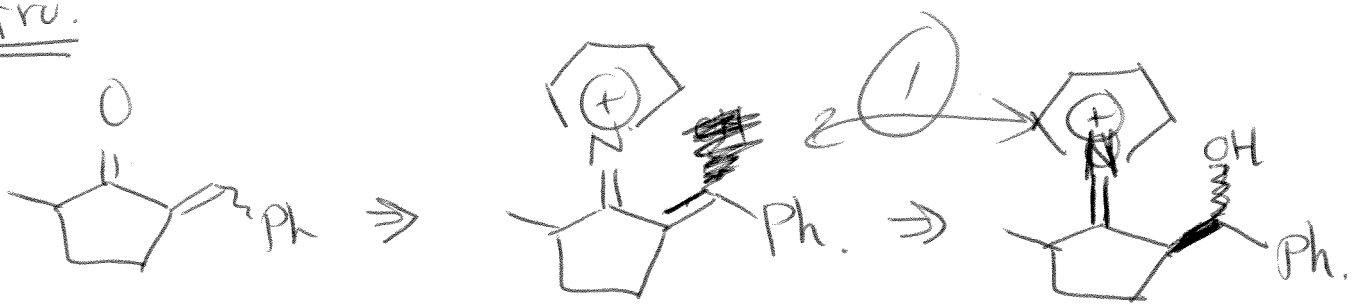


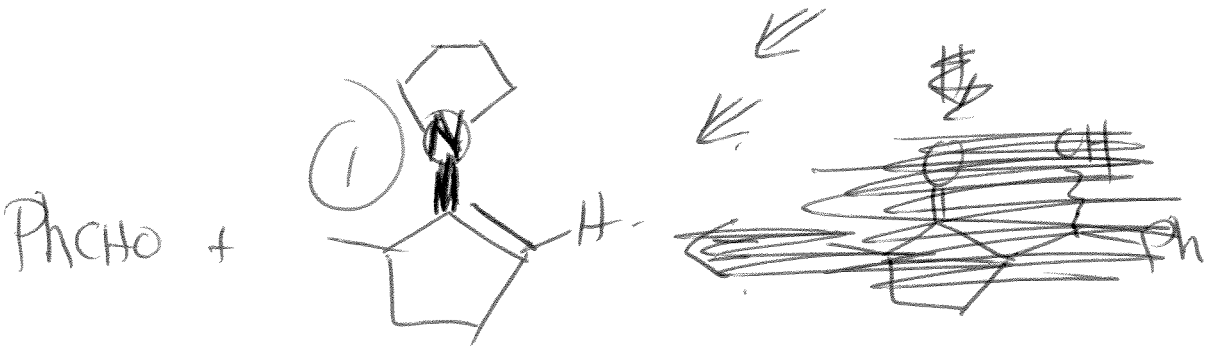
A B

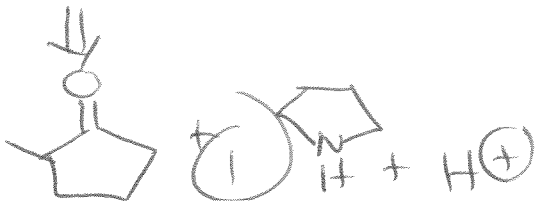




Retro:

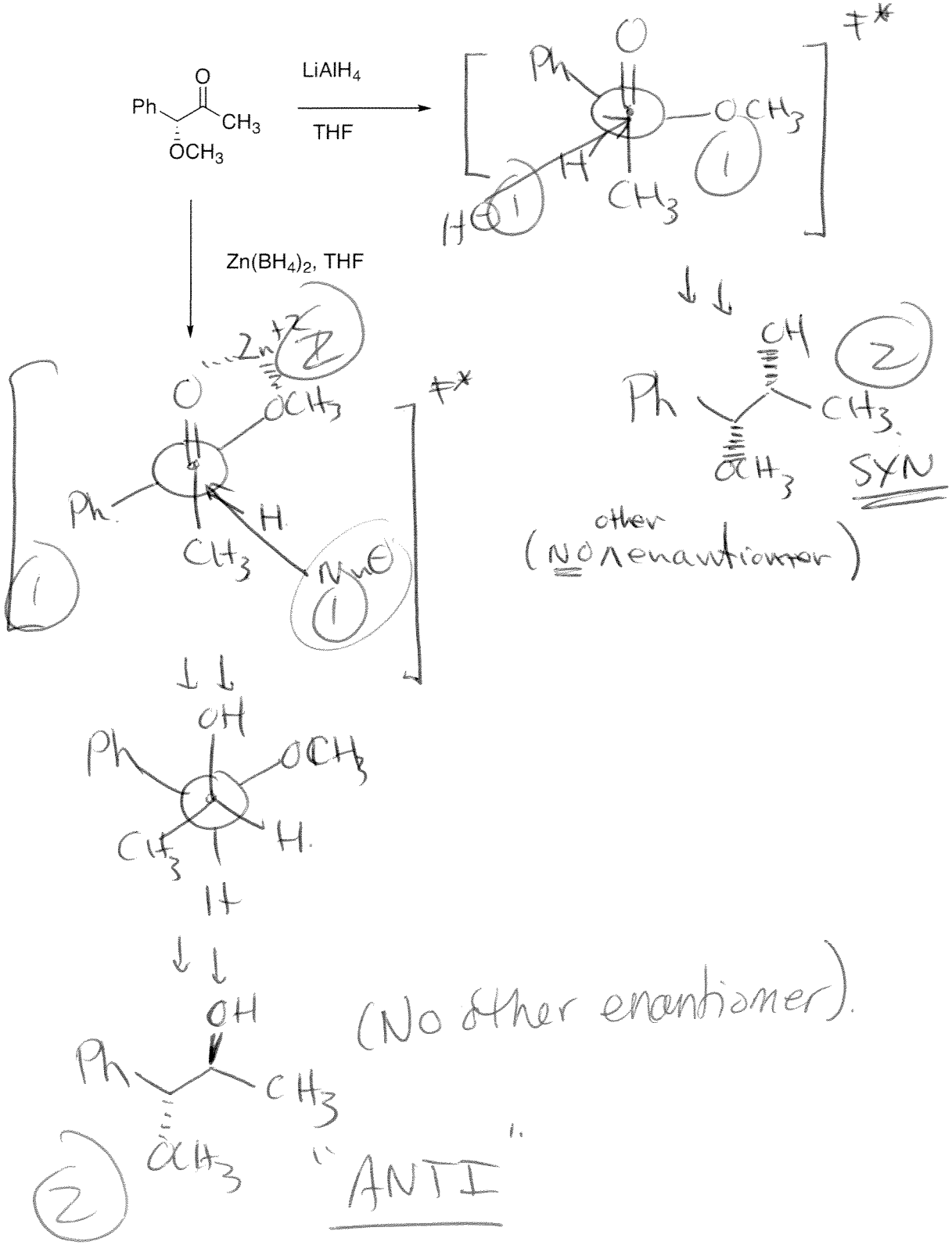






Name:
Student #:

5. Provide the structure of the major product(s) formed under the following two different reaction conditions (include appropriate stereochemistry). Show the appropriate transition state that rationalizes the formation of each product. **(10 marks)**



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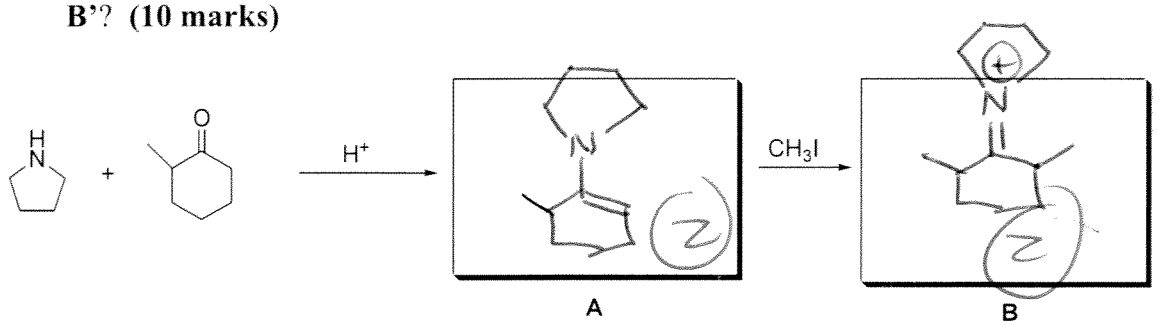
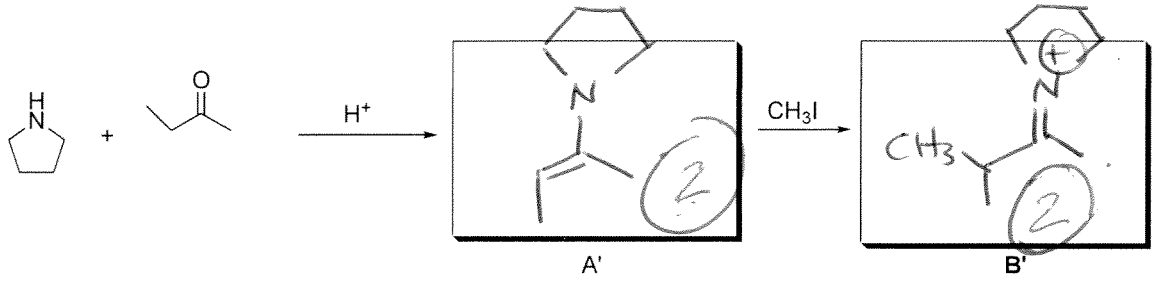
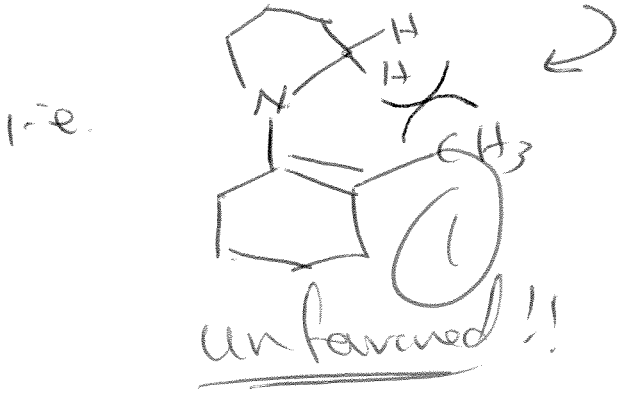
6. Consider the following reaction sequences. What are the structures of **A, A'** and **B, B'**? **(10 marks)**





At first glance the formation of **A** appears to violate several "rules". Explain why **A** is formed in the first reaction but **A'** is formed in the second.

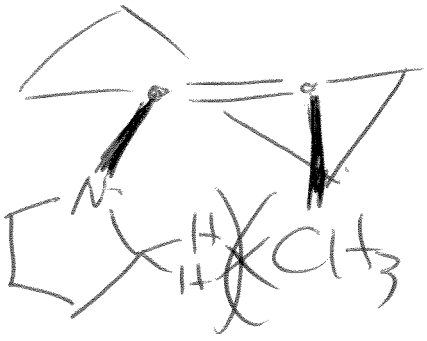
- Steric Interactions (1)



i.e.

unfavored !! (1)

or



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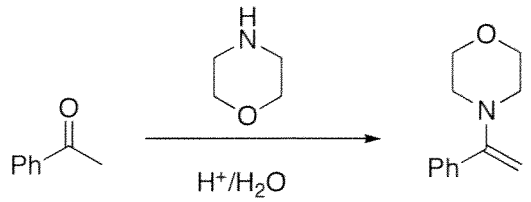
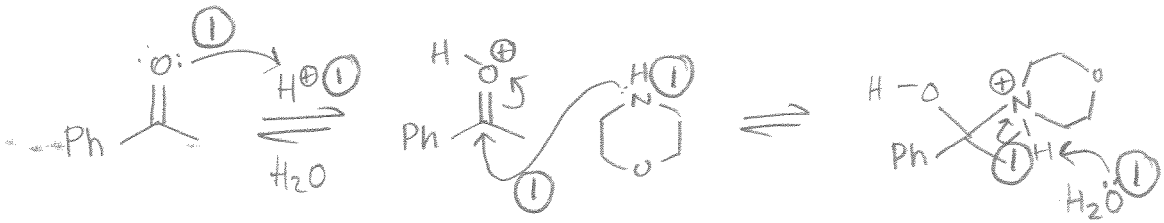
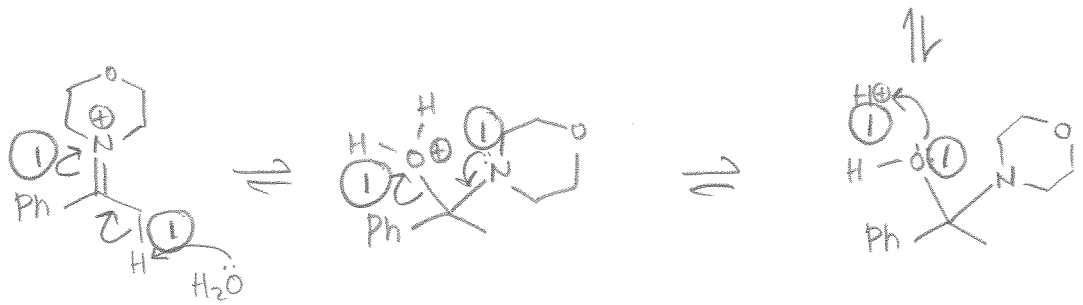
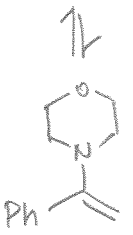
7. Provide a detailed reaction mechanism (i.e. stepwise with arrows) for the following reaction. You must show all proton transfers for full credit. **(13 marks)**









(1) reversable arrows

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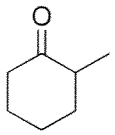
8. Consider the following unsymmetrical ketone. Draw the structures of the thermodynamic and kinetic enolates that are derived from this ketone. What are the reaction conditions and factors that ensure the selective formation of each? **(10 marks)**



Thermodynamic Enolate

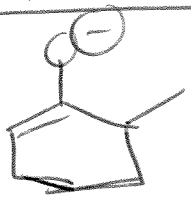
(2)

Requirements:

- base with similar pKa to α-H's
- Slightly more carbonyl gp present (2)
- protic solvents
- ↑er temps.

* Reversible!! (1)

Kinetic Enolate



(2)

Requirements:

- strong, hindred base
- low temps
- Slight Xs of base (2)
- add Ketone dropwise to base.
- aprotic solvents

Irreversible (1)