

Massachusetts Institute of Technology

5.13: Organic Chemistry II

Dr. Sarah A. Tabacco

Hour Exam #4
December 5, 2003

Printed Name Key Signature _____
MIT ID # _____ Recitation TA _____

General Instructions:

- **This is a closed book exam.** No books, notes, or calculators allowed. You are allowed to use molecular models.
- Make sure that your exam has **12 pages** (including cover, a blank page for extra work, and a periodic table).
- Write your name on each page.
- Write answers in the spaces provided. If you run out of room, use the blank page and **indicate this for your grader.**
- Show all of your work if you wish to receive partial credit.
- Read the instructions **carefully**, and budget your time.

• **GOOD LUCK!!**

1 _____/5 _____

2 _____/9 _____

3 _____/12 _____

4 _____/10 _____

5 _____/10 _____

6 _____/10 _____

7 _____/10 _____

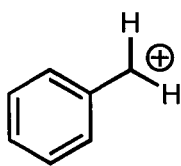
8 _____/10 _____

9 _____/12 _____

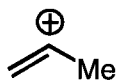
10 _____/12 _____

Total _____
(out of 100 points)

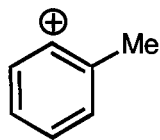
1. (5 points, all or nothing) Please rank the following species by carbocation stability.
(1 = most stable, 2 = least stable)



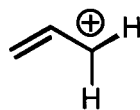
1



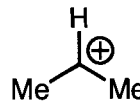
4



5



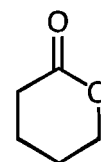
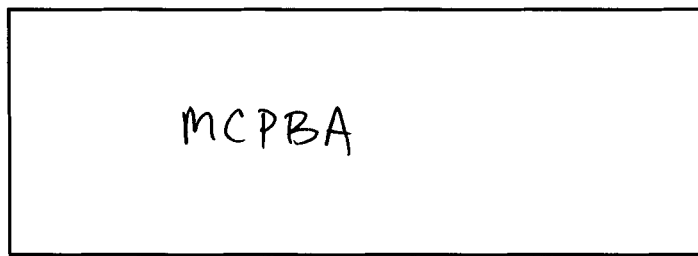
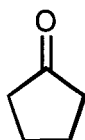
2



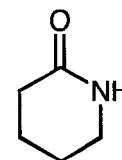
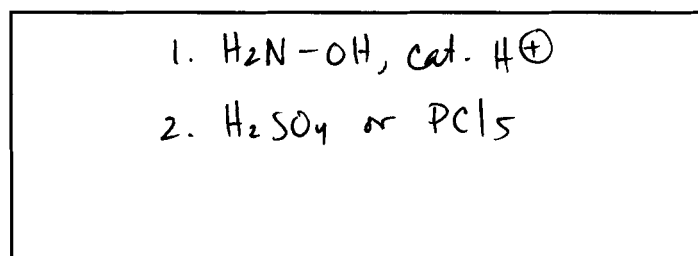
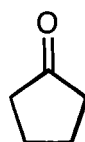
3

2. (3 points each, 9 points total) In the boxes, please provide the reagents for the illustrated transformations. More than one step may be required.

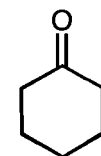
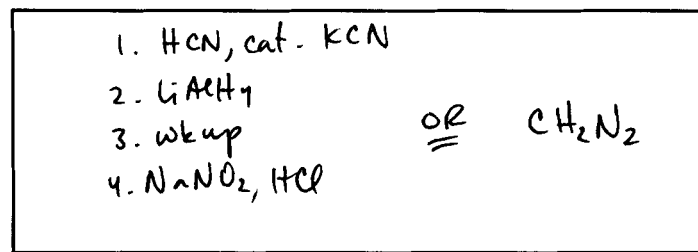
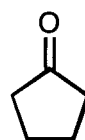
a)



b)



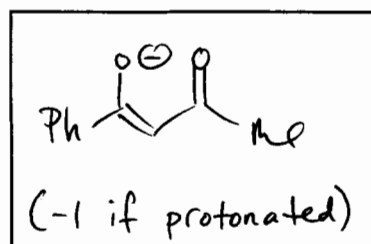
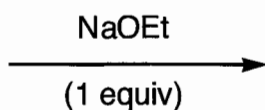
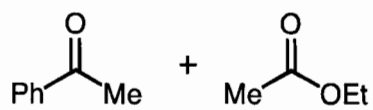
c)



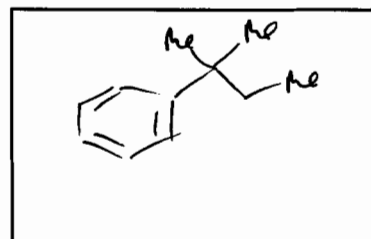
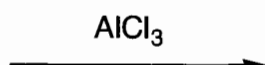
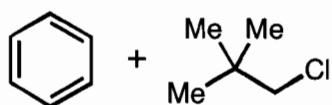
Name Key

3. (2 points each, 12 points total) Please provide the products of the following reactions. If no reaction is expected, write "NR".

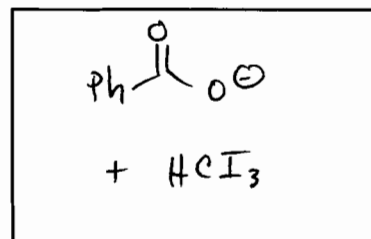
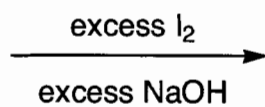
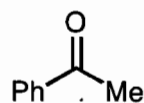
a)



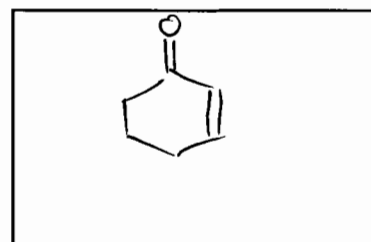
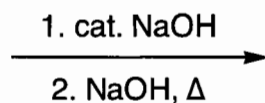
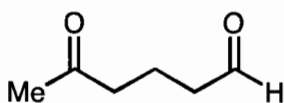
b)



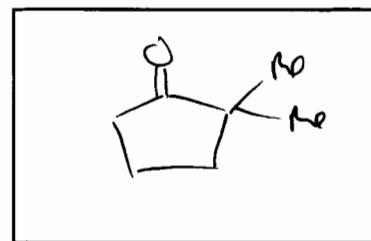
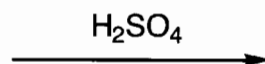
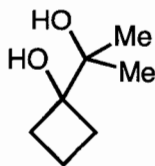
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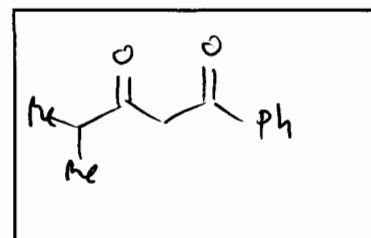
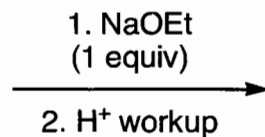
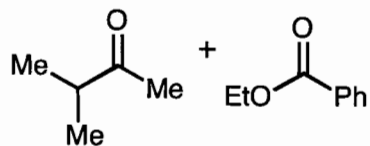
d)



e)



f)



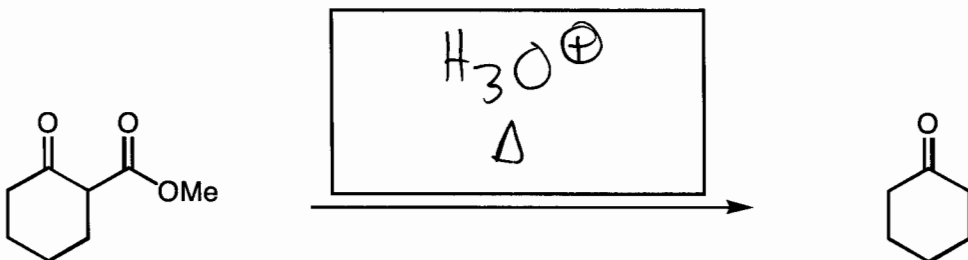
Name Key

4. (2 points each, 10 points total) Please provide the reagents for the following transformations. Be specific about quantities of reagents where relevant.

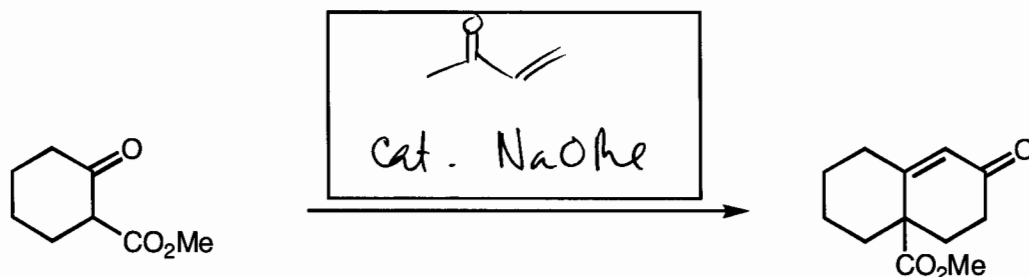
a)



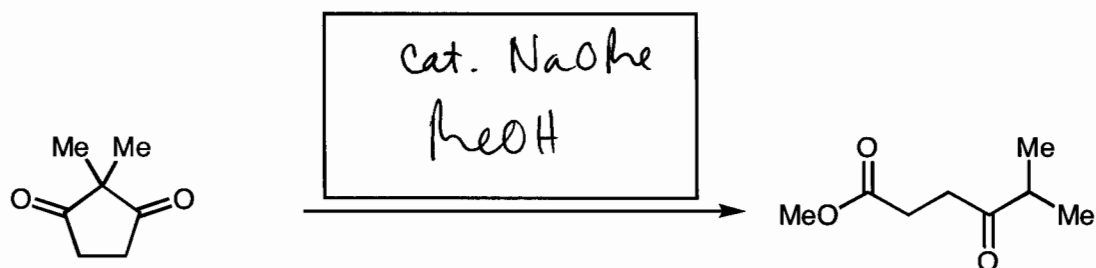
b)



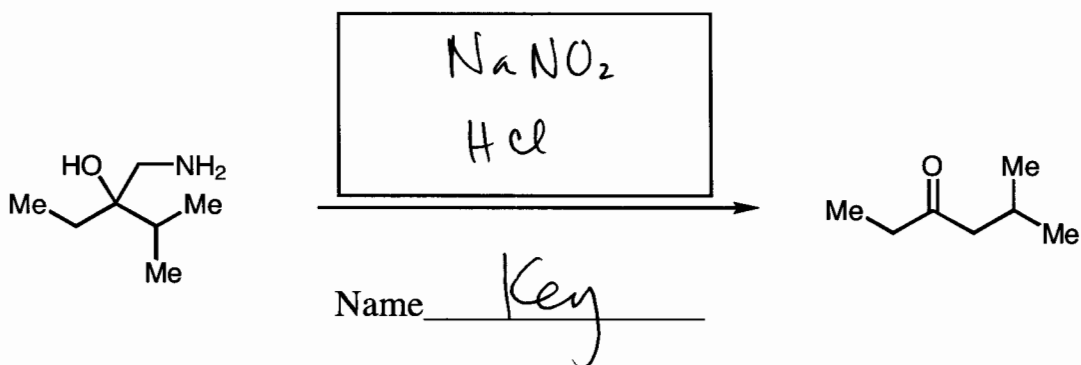
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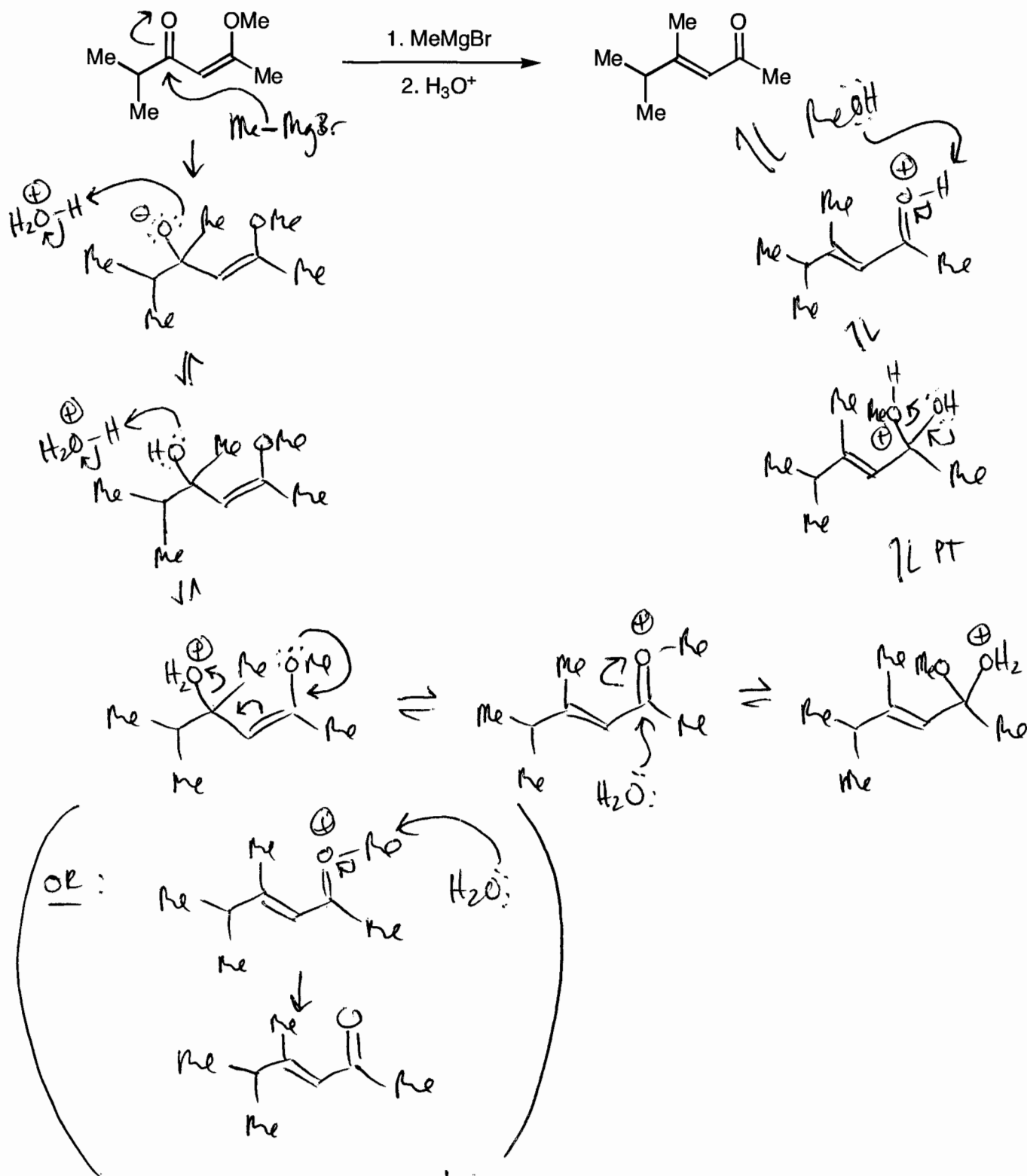
d)



e)

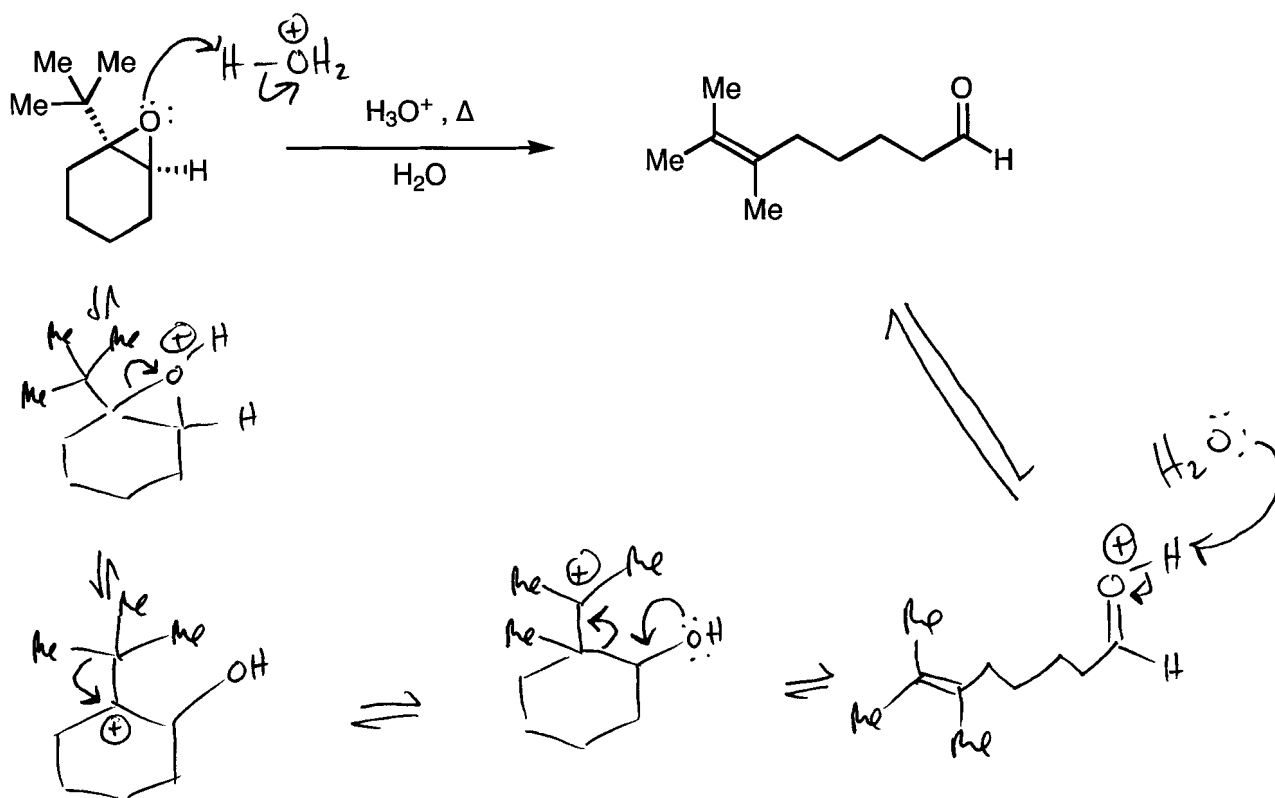


5. (10 points) Please provide a detailed mechanism for the following transformation. Show all arrow pushing.



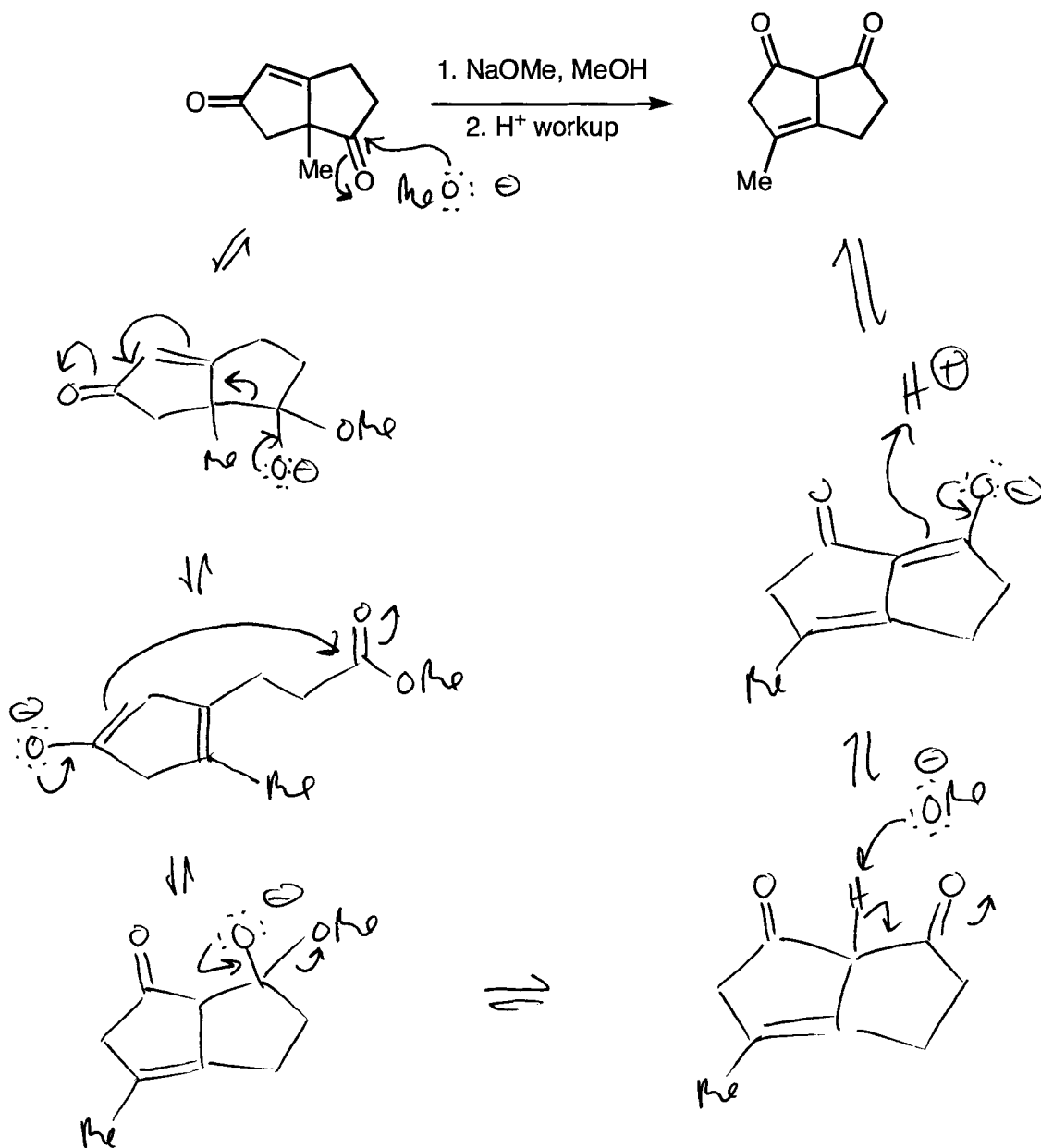
Name Key

6. (10 points) Please provide a detailed mechanism for the following transformation. Show all arrow pushing.



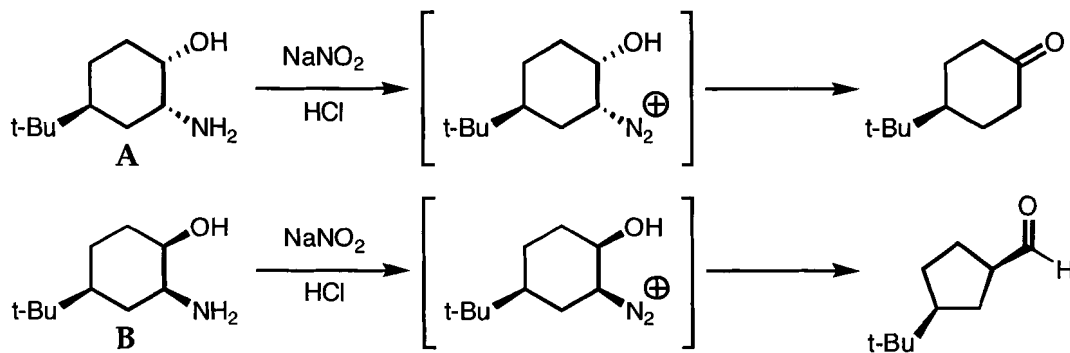
Name Key

7. (10 points) Please provide a detailed mechanism for the following transformation. Show all arrow pushing. Hint: This mechanism is from problem set 6.

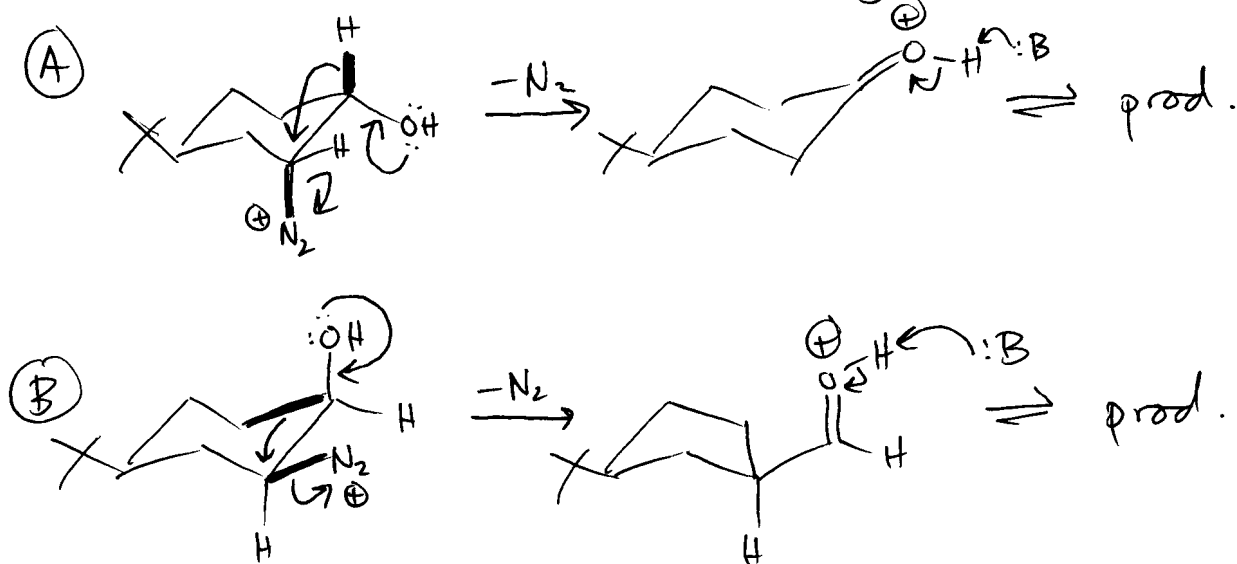


Name Key

8. (10 points) Diastereomers **A** and **B** provide different products upon diazotization. Please explain why only one product is formed selectively in each reaction. Your explanation should include a **3-dimensional** mechanism for the formation of each product from the corresponding diazonium salt.



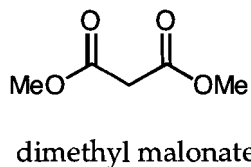
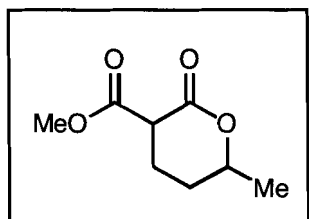
In the concerted Tiffeneau-Desjardos rearrangement, the migrating bond must be antiperiplanar to the leaving group.



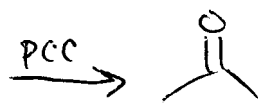
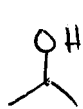
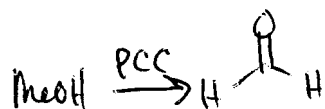
(Bolded bonds are antiperiplanar.)

Name Key

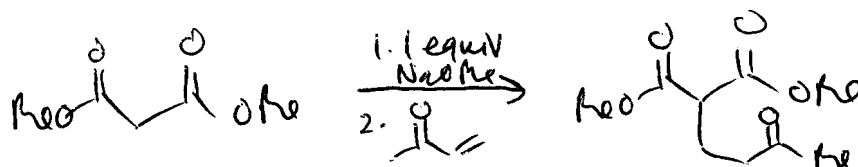
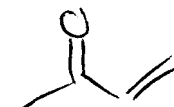
9. (12 points) Please provide a synthesis of the indicated compound. All of the carbon atoms should be derived from **dimethyl malonate** and **alcohols containing three or fewer carbons**. You will receive partial credit for a complete retrosynthesis.



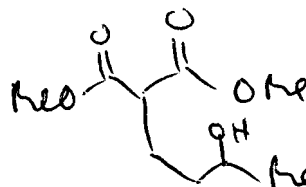
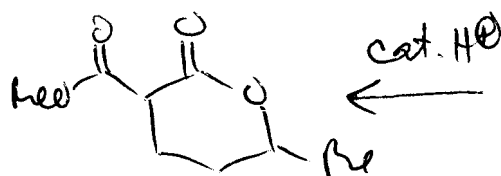
R-OH
 alcohols containing
 three or fewer carbons



1. excess
CC=O, cat. H^+
 2. H^+ , Δ

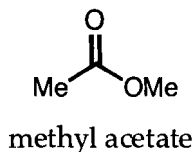
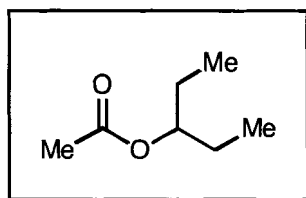


1. NaBH₄
 2. workup

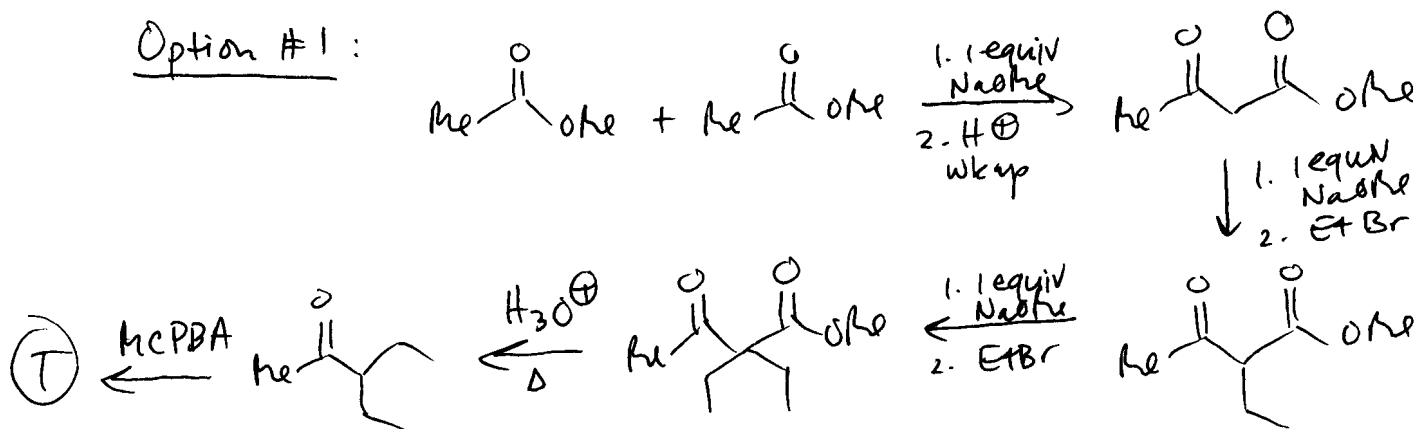


Name Key

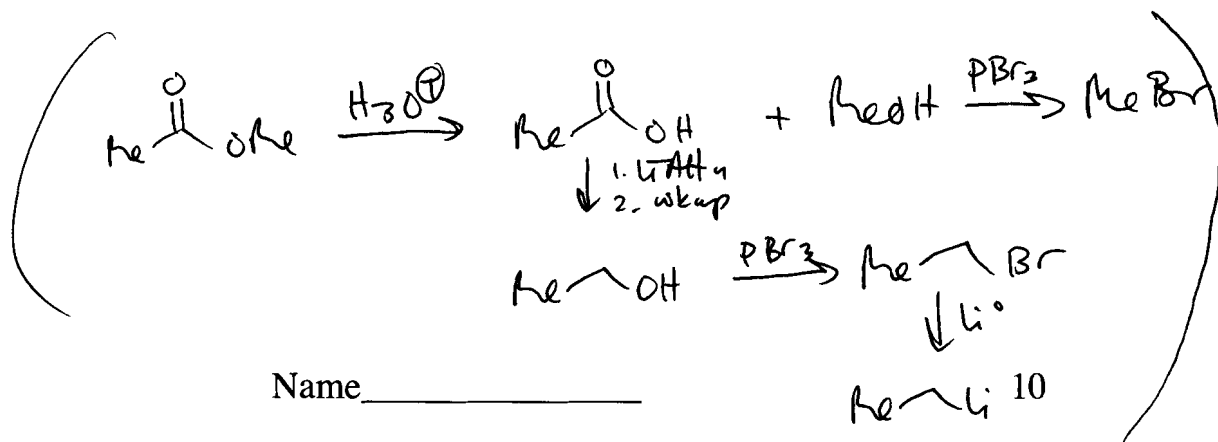
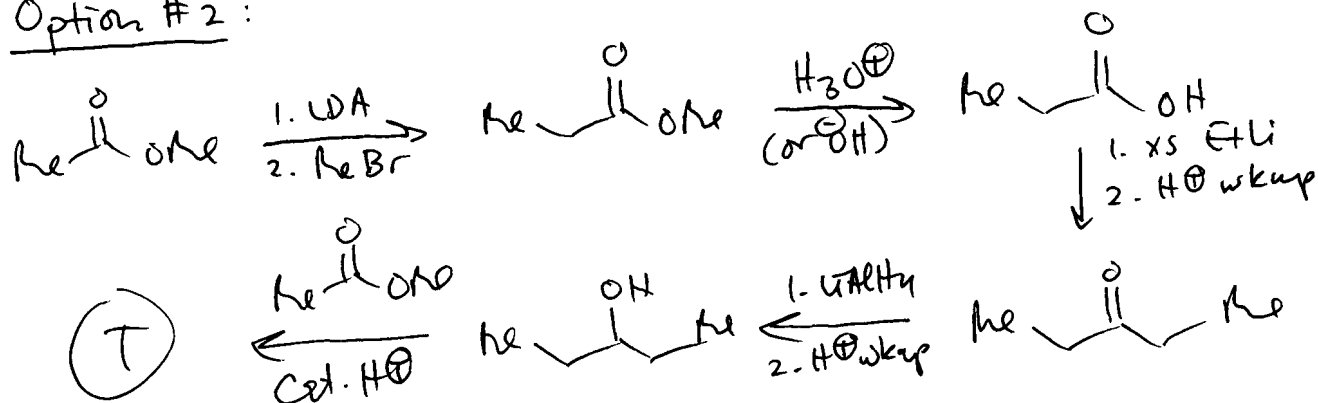
10. (12 points) Please provide a synthesis of the indicated compound. All of the carbon atoms should be derived from **methyl acetate**. You will receive partial credit for a complete retrosynthesis.



Option #1:



Option #2:



Name _____

MeLi 10