Dr. Carl Wagner Thursday August 3rd, 2006

Chemistry 3B
Midterm 2

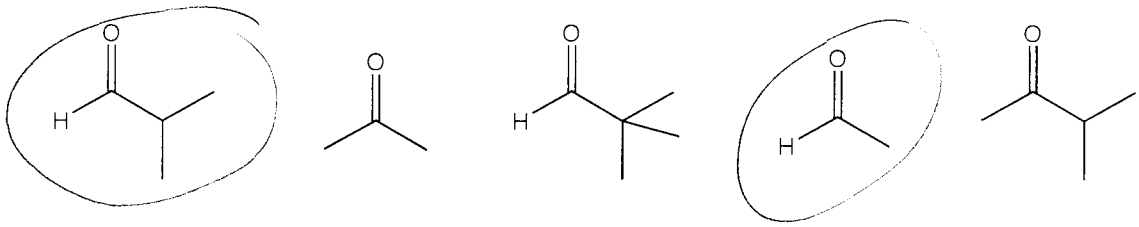
Student Name: Key
Student ID: _____
Write TA's full name (section number) or Lecture Only: _____

Problem 1	_____	(28 pts)
Problem 2	_____	(32 pts)
Problem 3	_____	(40 pts)
Problem 4	_____	(25 pts)
Problem 5	_____	(25 pts)
Problem 6	_____	(15 pts)
Problem 7	_____	(25 pts)
Problem 8	_____	(25 pts)
Problem 9	_____	(20 pts)
Problem 10	_____	(15 pts)
Total Points	_____	(250 pts)

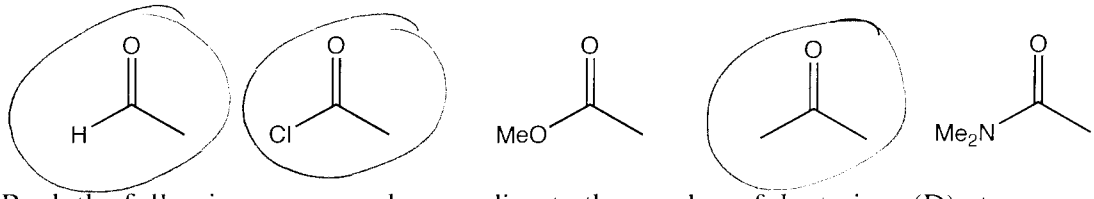
Calculators Not Needed
Be Sure Your Exam Has 12 Pages
Budget Your Time Carefully!
Be Sure to Try All Parts of Each Problem

1. (28 pts) Answer the following questions. Every wrong answer cancels a correct answer.

(a) Circle the carbonyl compound(s) that would give the corresponding aldol **self-condensation** product upon treatment with NaOH, H_2O and heat (Δ).



(b) Circle the carbonyl compound(s) that would be reduced by $NaBH_4$.



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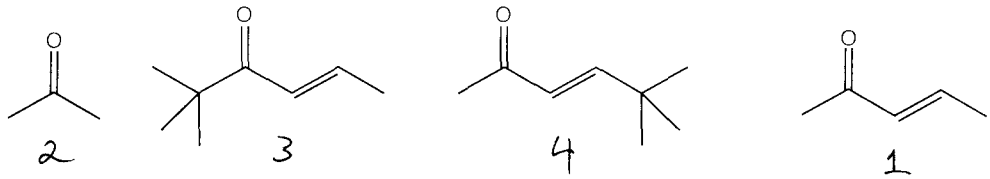
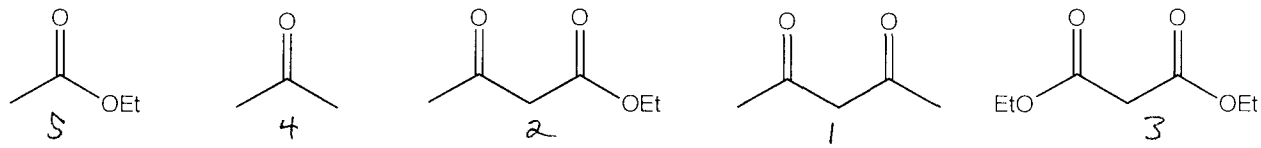
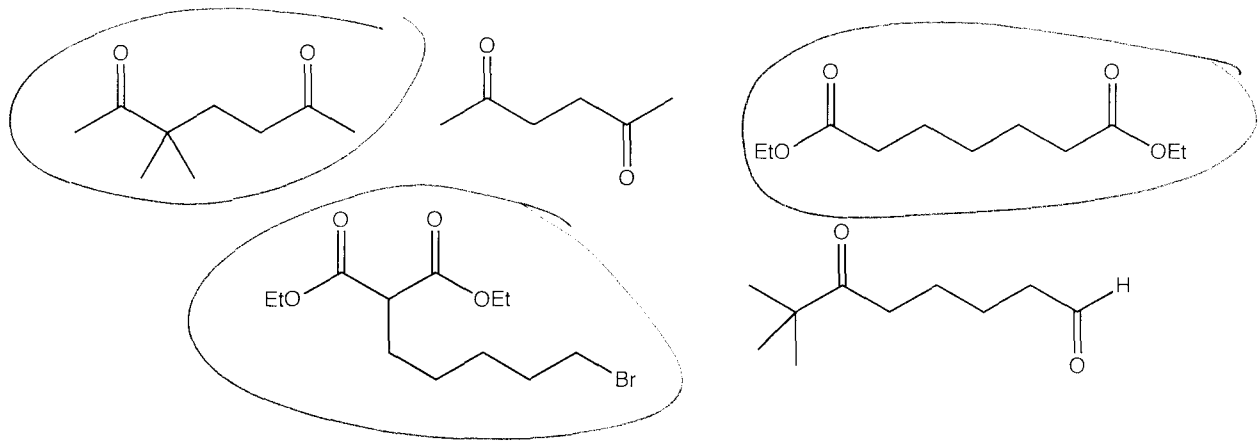
(c) Rank the following compounds according to the number of deuterium (D) atoms incorporated upon treatment with NaOD and D_2O. [1 = **most** deuterium atoms, 5 = **fewest** deuterium atoms]



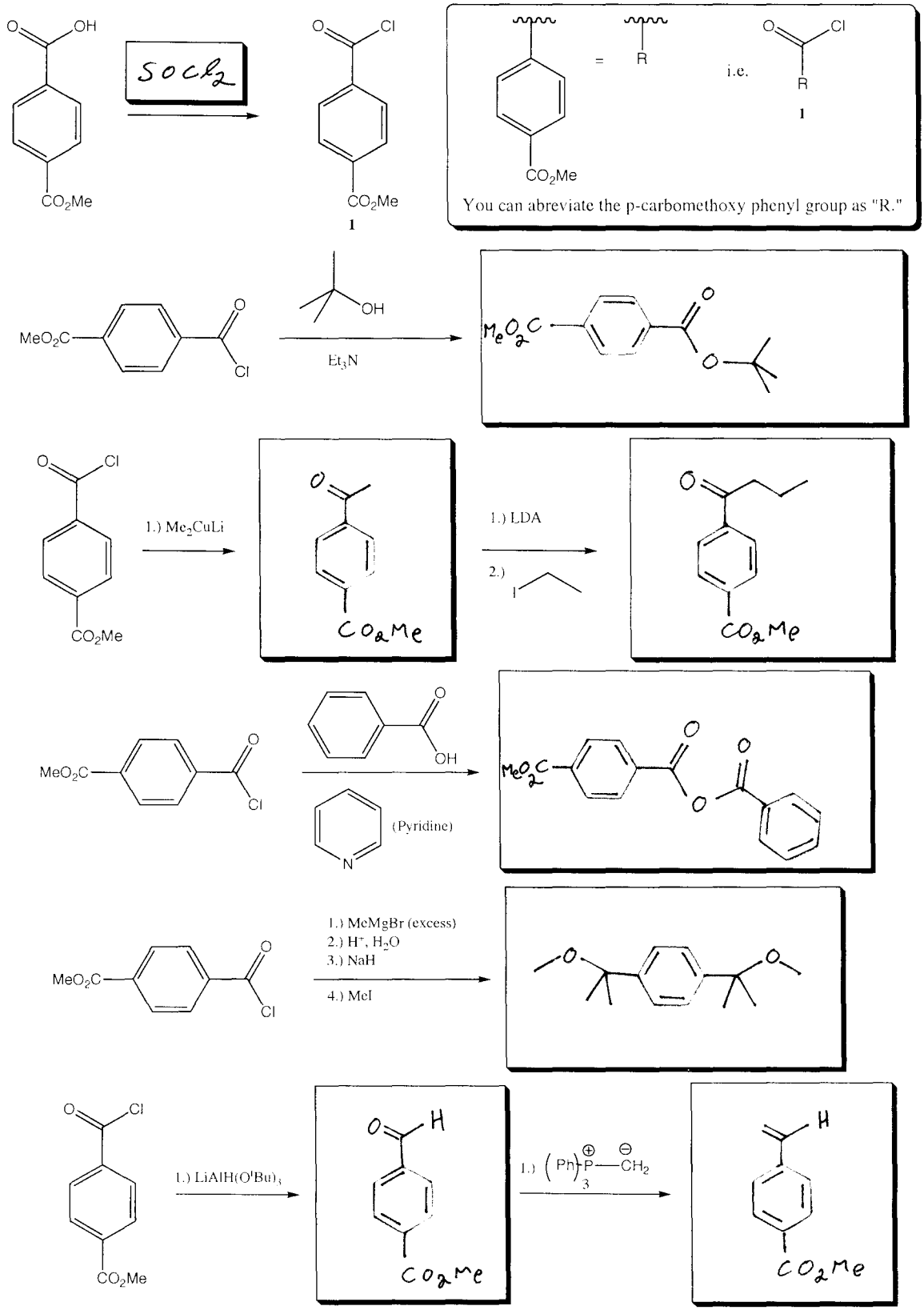
(d) Number the compounds below from most to least acidic [1 = **most** acidic, 5 = **least** acidic]. Recall that the most acidic compound has the lowest pK_a and the least acidic has the highest pK_a.



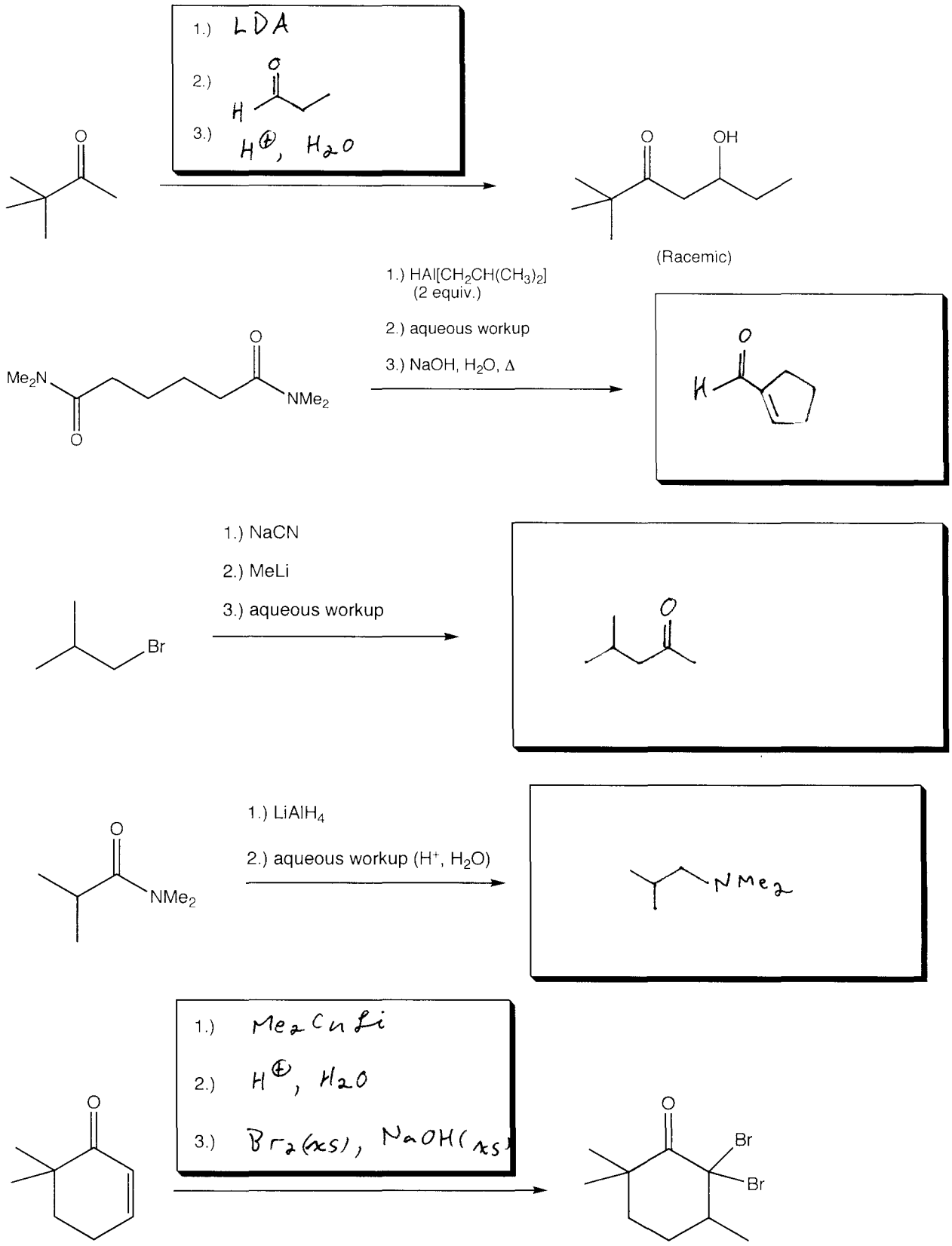
(e) Circle the compounds that would undergo a reaction to give a **6-membered ring** upon heating with NaOEt in EtOH. Remember: Proton transfer is faster than S_N2.



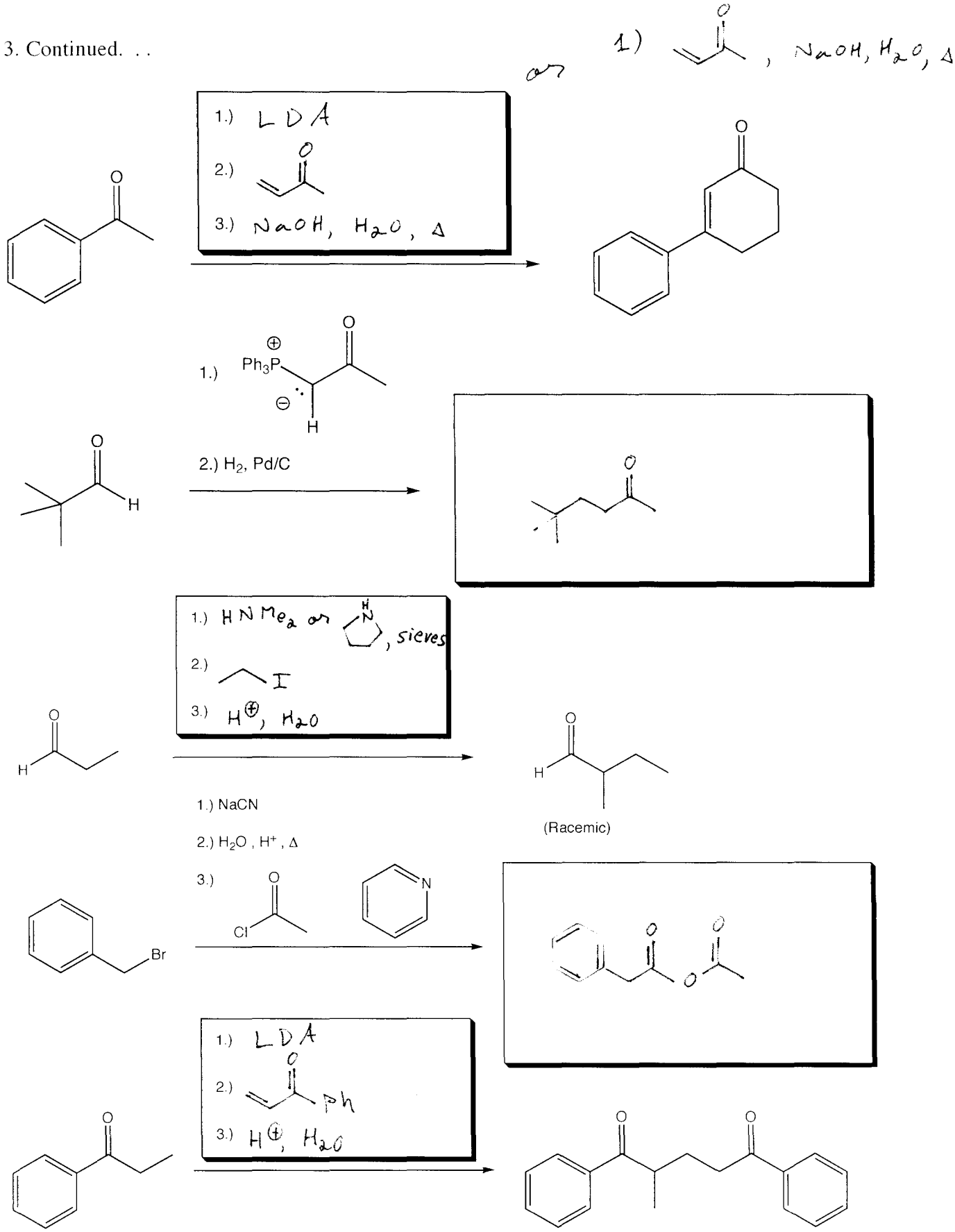
2. (32 pts) Just recently, your instructor made 4-carbomethoxybenzoyl chloride (**1**). Fill in the reagents and products for the reactions below as necessary.



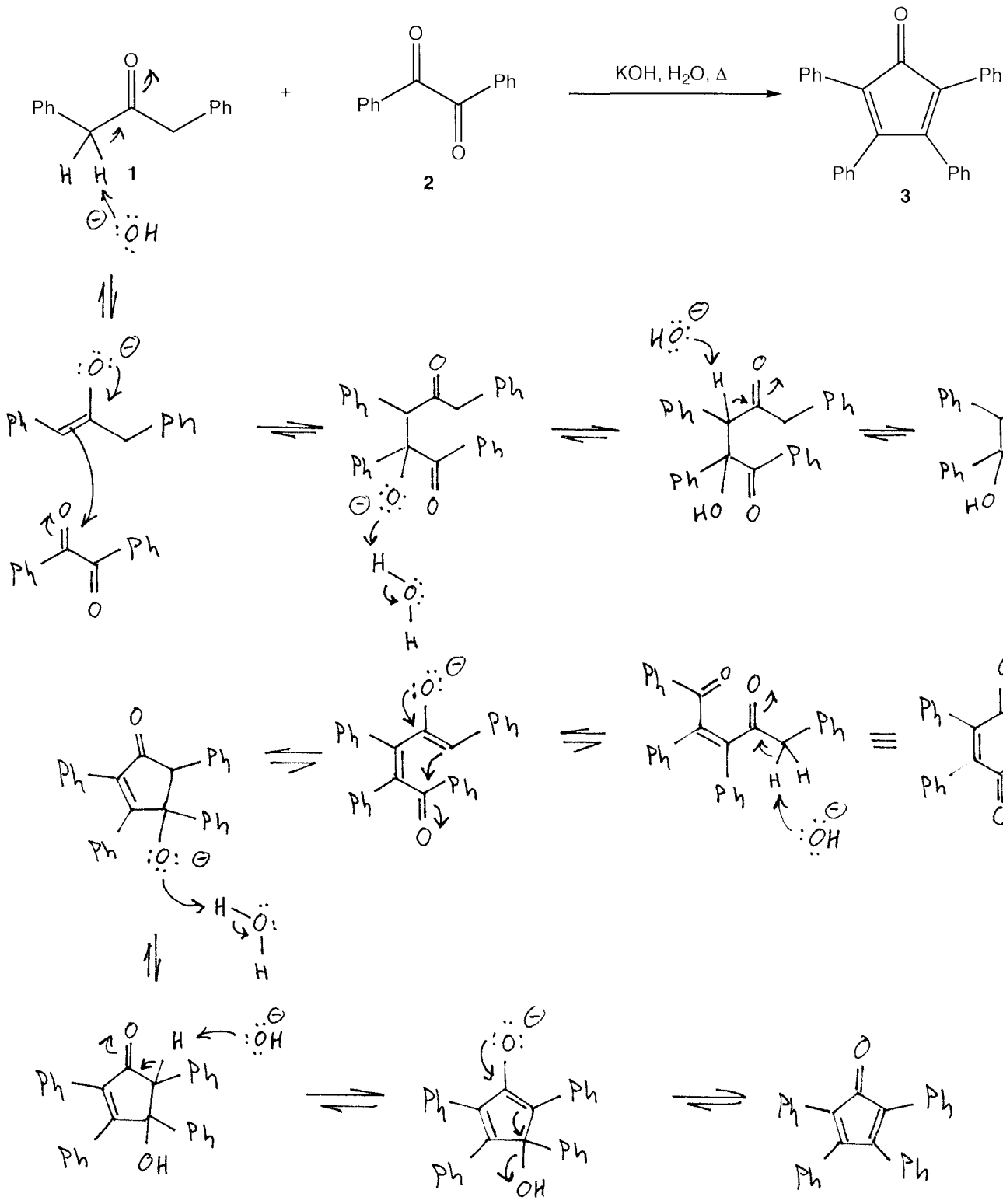
3. (40 pts) Supply the missing reagents or the major organic product(s) in the provided boxes.



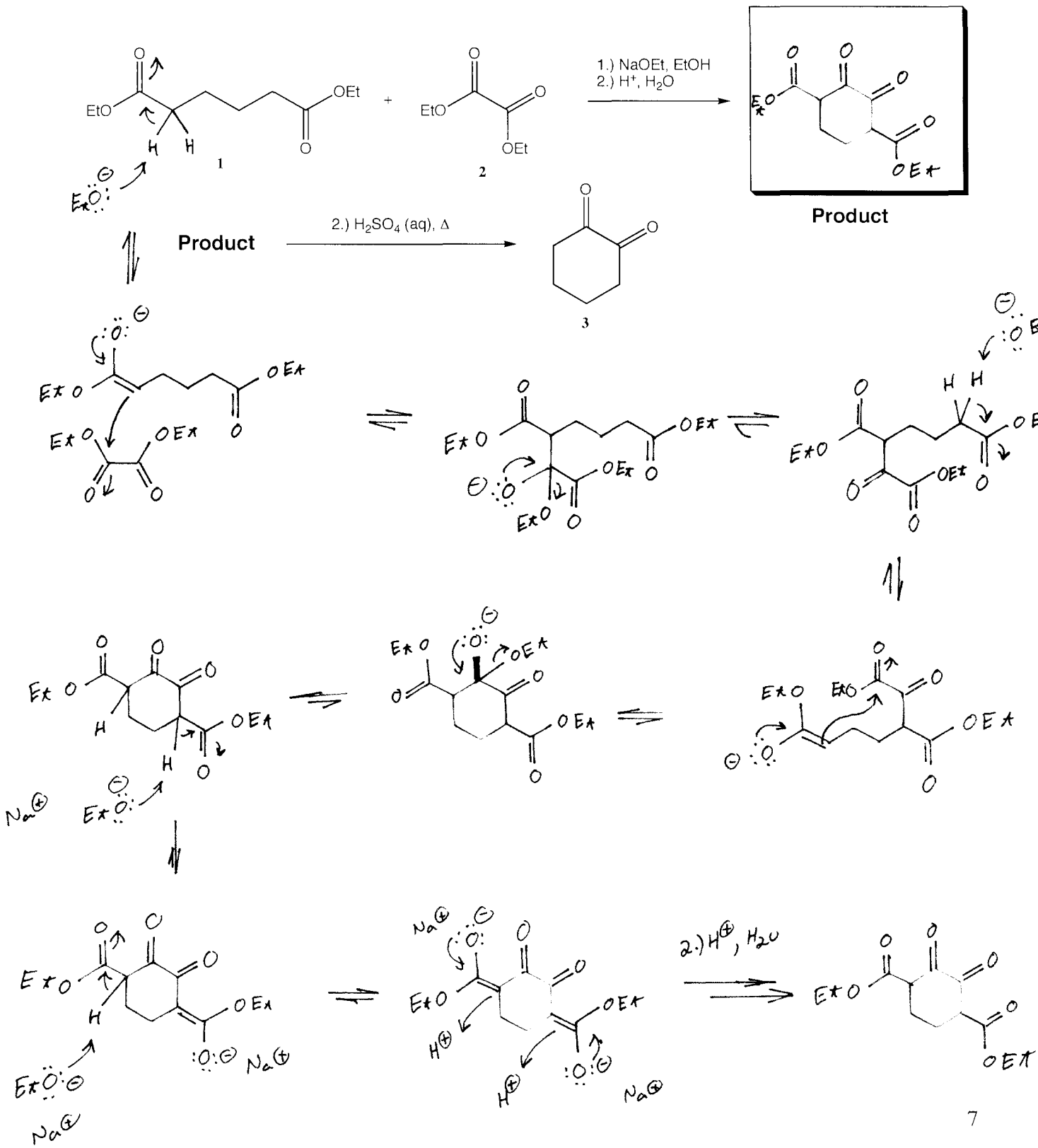
3. Continued. . .


1.) LDA
2.)
3.) NaOH, H2O, Δ
or
1)
, NaOH, H2O, Δ
1.)
2.) H2, Pd/C
1.) HNMe2 or
, sieves
2.)
3.) H⊕, H2O
1.) NaCN
2.) H2O , H+ , Δ
3.)
(Racemic)
Br
Cl
N
1.) LDA
2.)
Ph
3.) H⊕, H2O

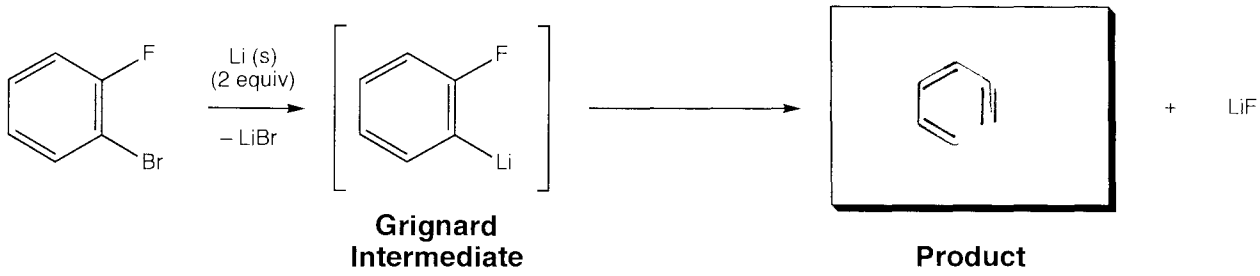
4. (25 pts) When 1,3-diphenylpropanone (**1**) and benzil (**2**) are heated with KOH and H_2O, the major recovered organic product is 2,3,4,5-tetraphenylcyclopentadien-one (**3**). Write a detailed mechanism for this reaction.



5. (25 pts) When diethyl adipate (**1**) and diethyl oxalate (**2**) are treated with NaOEt in EtOH, there is one major recovered organic **Product**. When this **Product** is heated in aqueous sulfuric acid, carbon dioxide evolves and 1,2-cyclohexanedione (**3**) and ethanol are produced. Write an ***arrow-pushing, step-wise mechanism*** for the reaction of (**1**) and (**2**) in NaOEt and EtOH, followed by aqueous work-up, and write a structure for the **Product** in the box.

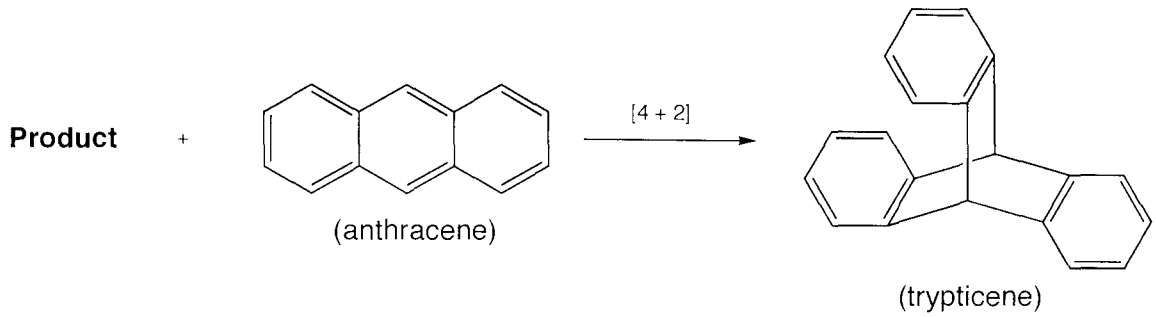


6. (15 pts) When 1-bromo-2-fluorobenzene (**1**) is treated with lithium metal, a transitory **Grignard Intermediate** is formed that decomposes into a highly reactive **Product**. In fact, when 1-bromo-2-fluorobenzene is treated with lithium in the presence of anthracene, the **Product** reacts with anthracene in a [4 + 2] cycloaddition reaction to give trypticene.



Grignard Intermediate

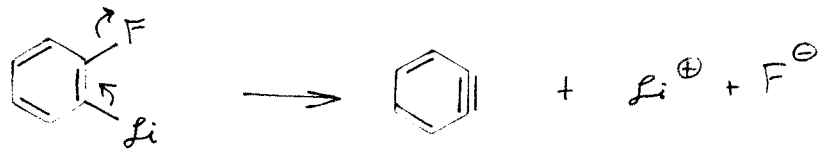
Product



(anthracene)

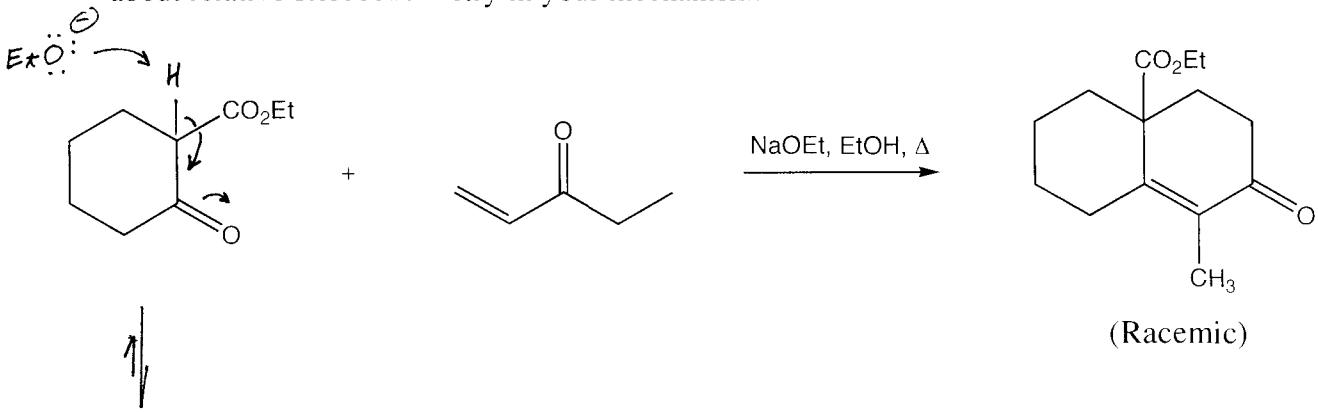
(trypticene)

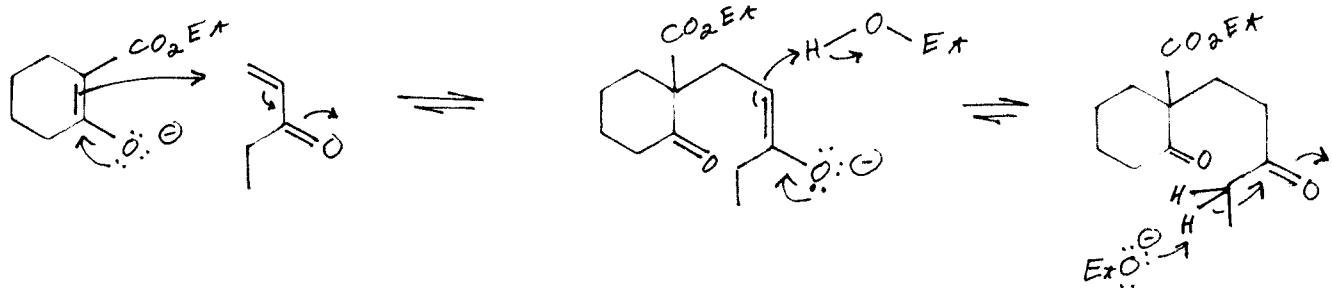
Write a rational, arrow pushing mechanism for the decomposition of the **Grignard Intermediate**, and draw the structure of the **Product** that is thus produced in the box provided above.

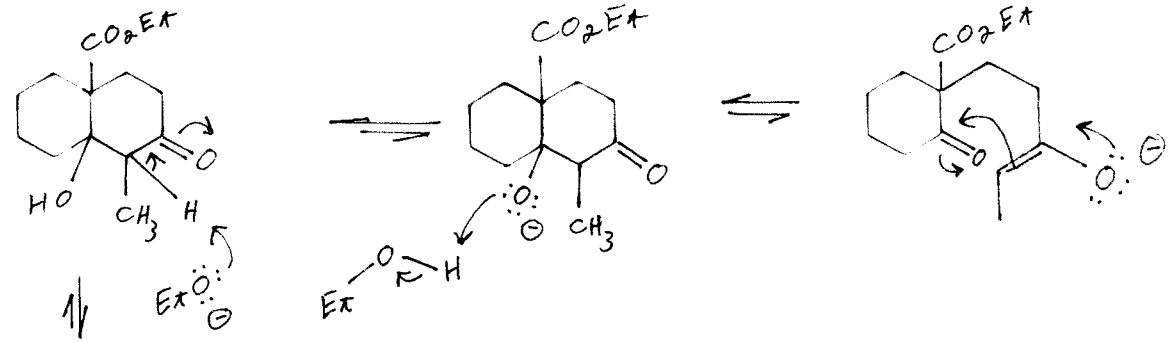


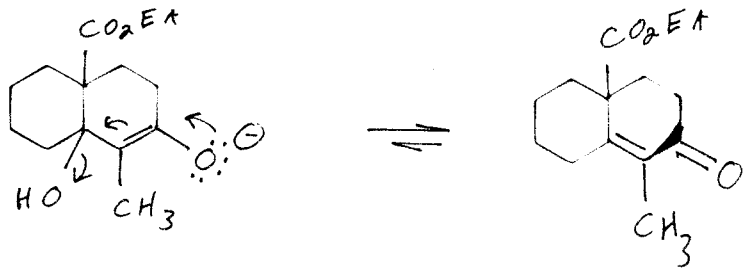
most acidic H removed first!

7. (25 pts) Show a detailed, arrow-pushing mechanism for the following reaction. Do not worry about relative stereochemistry in your mechanism.

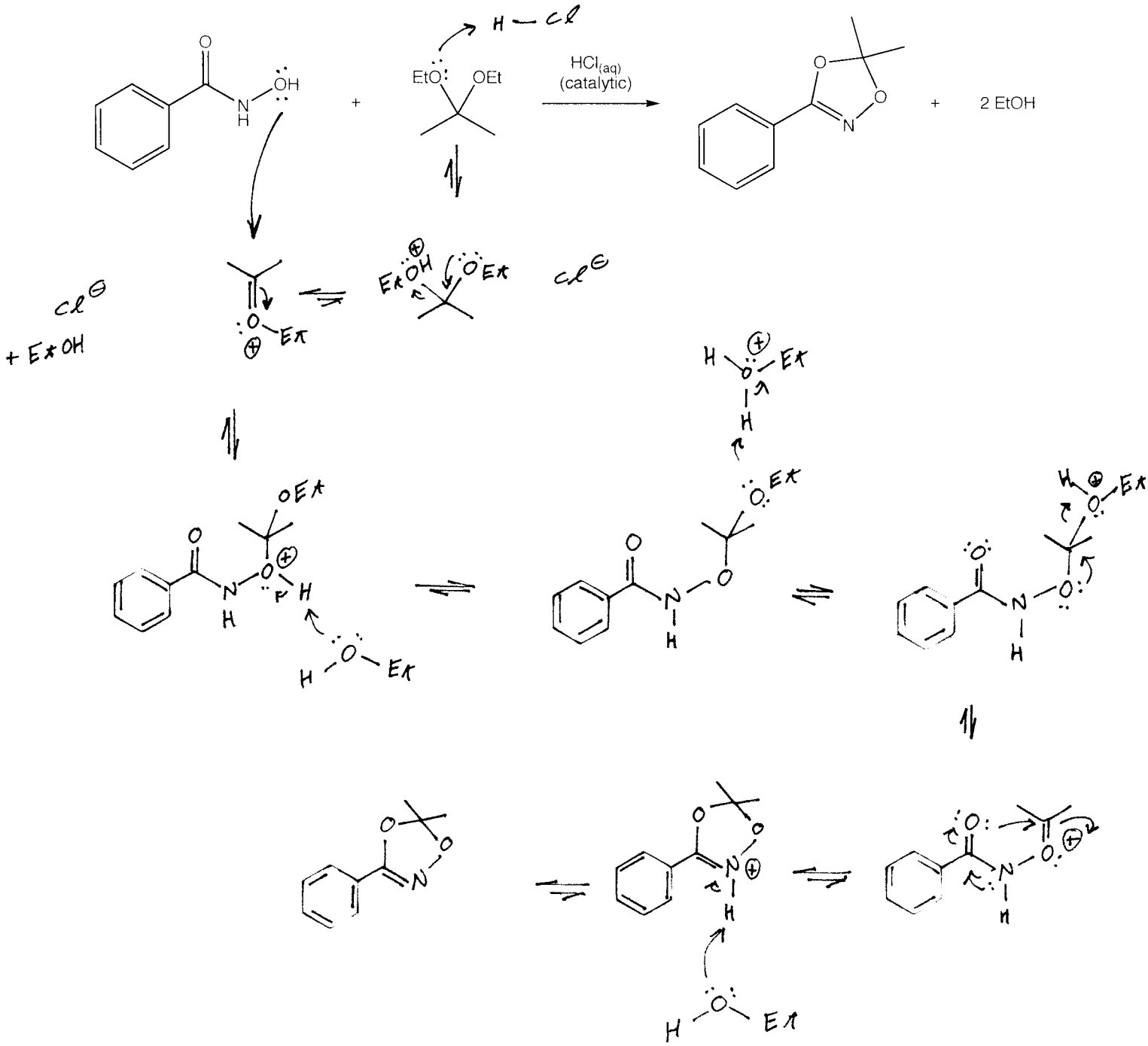




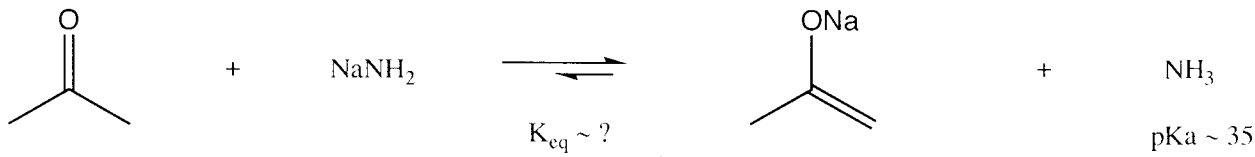




8. (25 pts) N-hydroxylamides can be useful synthetic intermediates. Write a step-wise, arrow-pushing mechanism for the following reaction.

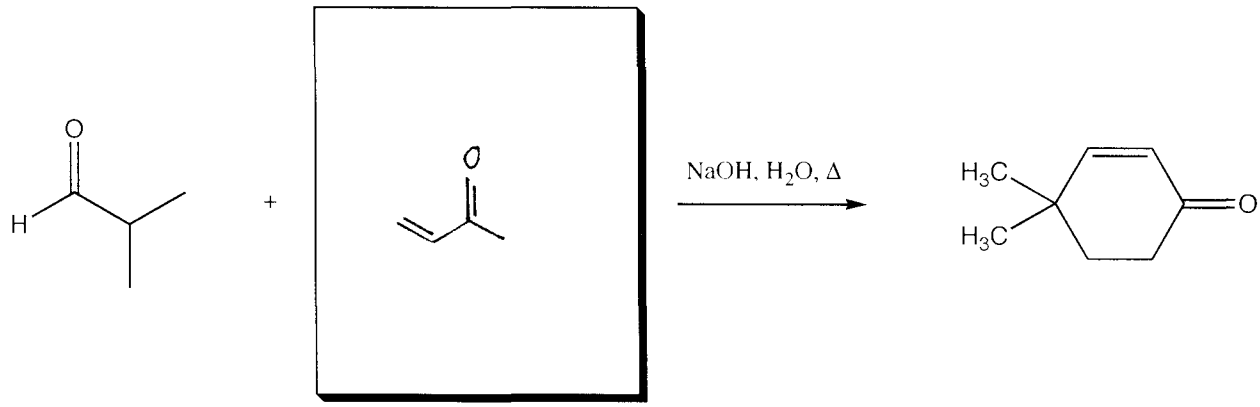


9. (a) (4 pts) Determine the equilibrium constant (K_{eq}) for the reaction of acetone with $NaNH_2$.

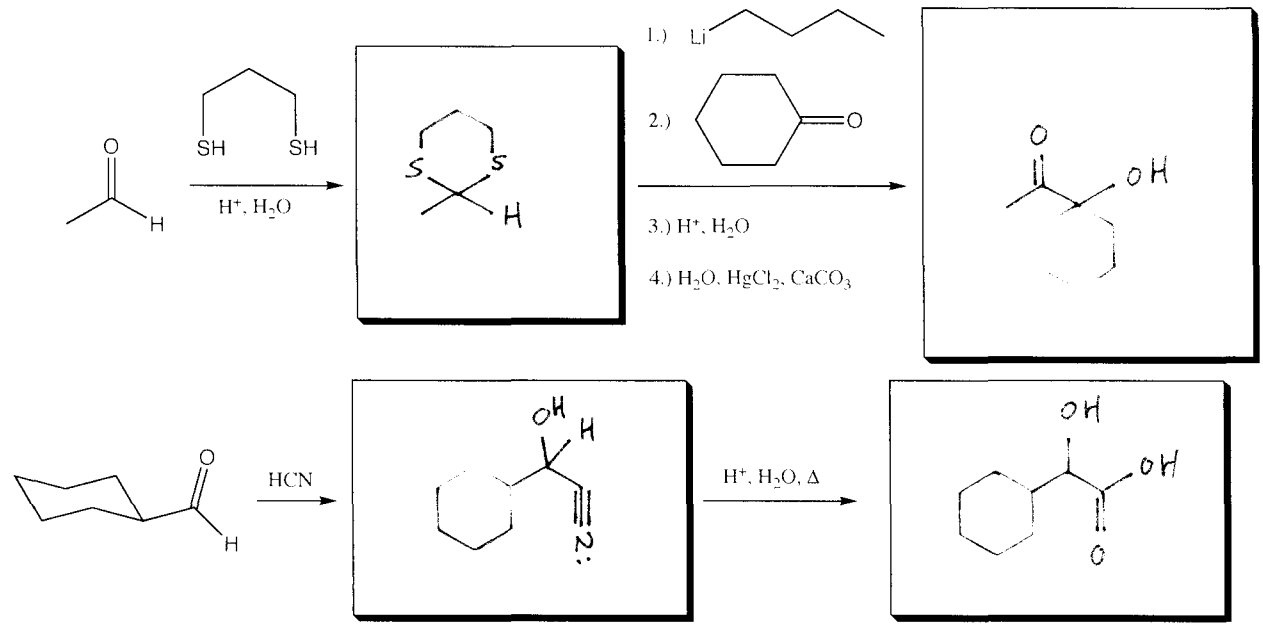


$K_{eq} = 10^{35-19} = 10^{16}$

(b) (8 pts) Provide a structure for the additional reagent necessary to synthesize 4,4-dimethyl-2-cylcohexen-1-one from isobutyraldehyde under conditions of NaOH, H_2O and heat.



(c) (8 pts) Provide the structures of the products of the reactions below in the boxes.



10. (15 pts) Provide the structures of the products of the reactions below in the boxes.