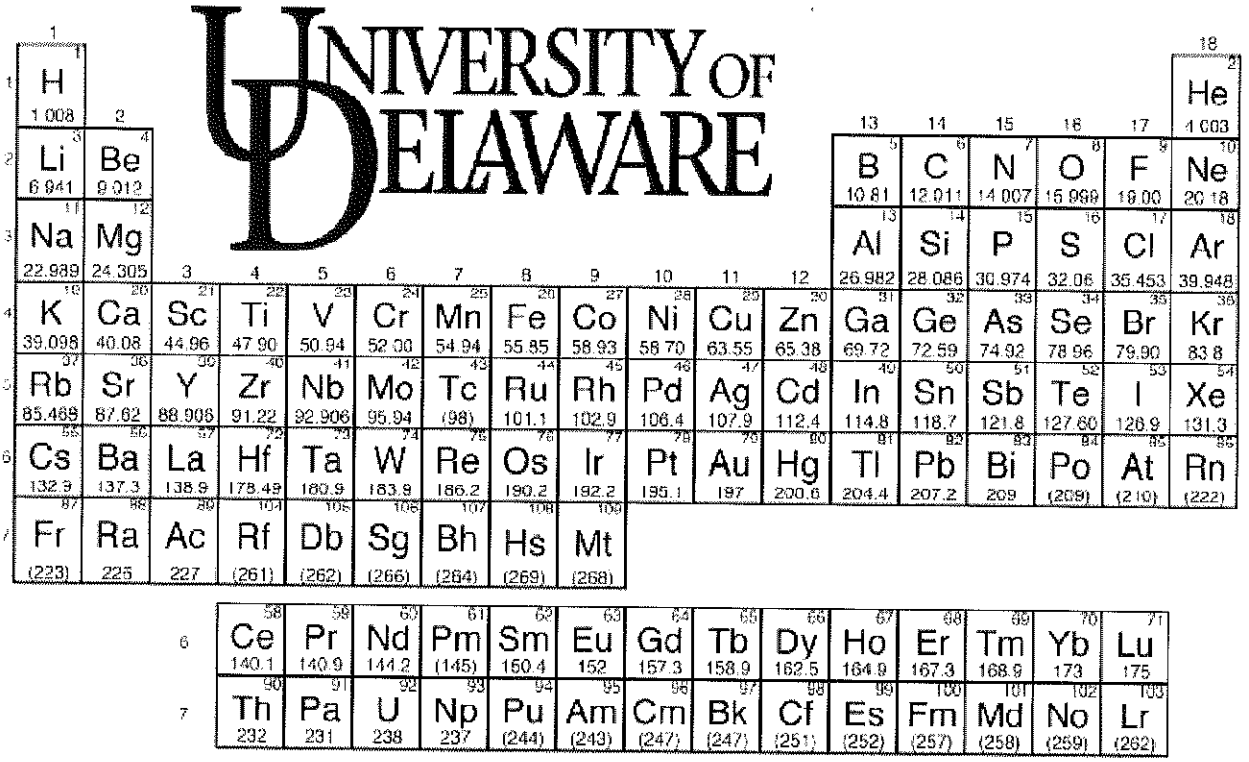
Name: Key

(Print your name clearly!)

Sametz: CHEM 322 Spring 2012

Organic Chemistry Exam 3

All answers should be written CLEARLY in the space provided. (If it's not clear, it's wrong).



You may raise your hand to ask a question if you are unsure what a question is asking of you.

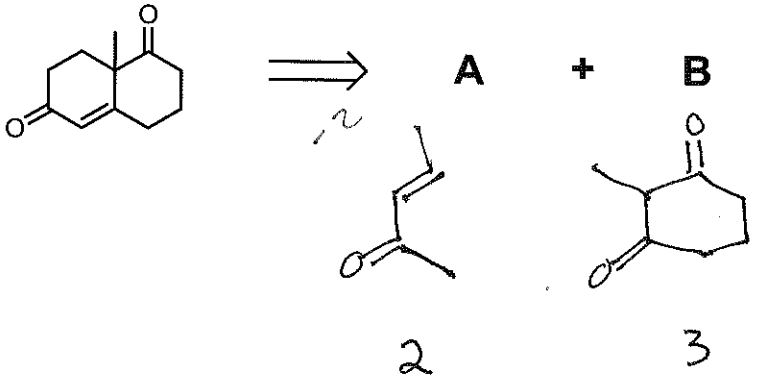
other bases okay if react w/ EtI

a. (2) 1) LDA or NaH →
(1) 2) EtI (or similar)

b. P_2O_5

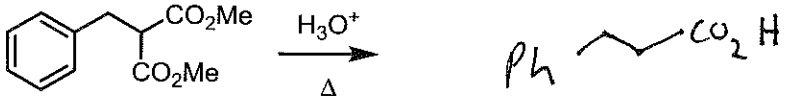
c. (or other base)
NaOMe / NaH / LDA
1pt for aldehyde/ketone

1. (5 points) The Wieland-Miescher ketone (shown below) has been used as a starting material in the synthesis of many natural products. It is synthesized from two precursors by a Robinson annulation. Give the structures for the two organic starting materials required for this annulation.

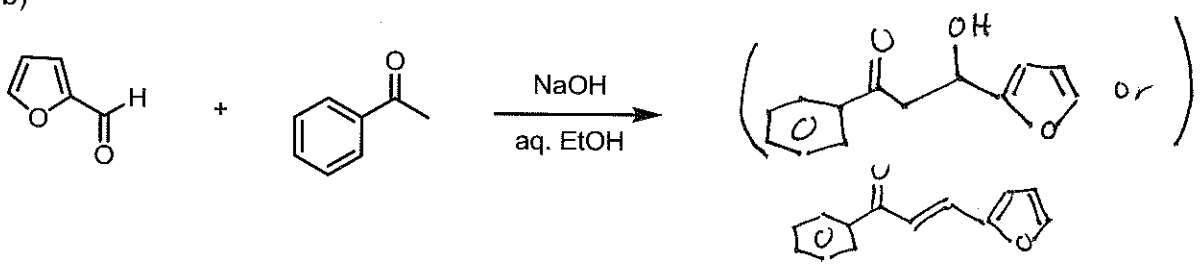


2. (52 points) Give the major organic product(s) for the following reactions 4ea

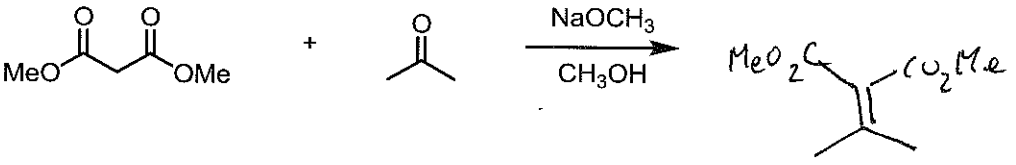
a)



b)

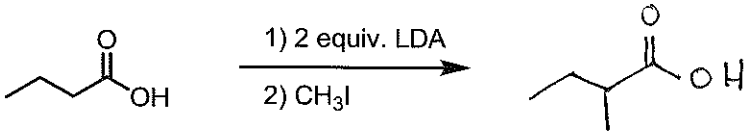


c)

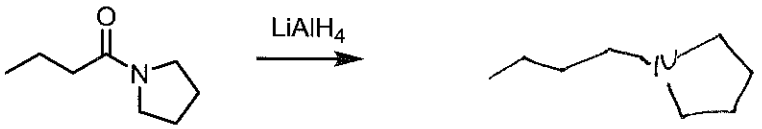


aldol (no $-H_2O$) 2/4

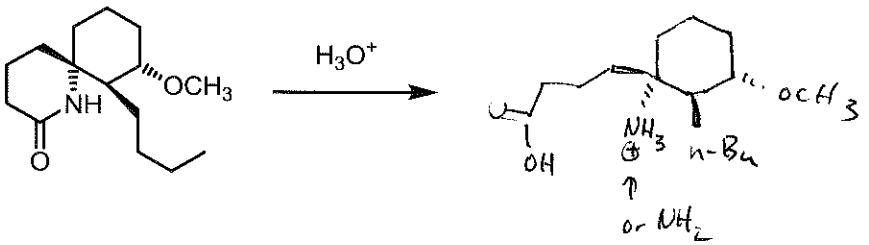
d)



e)

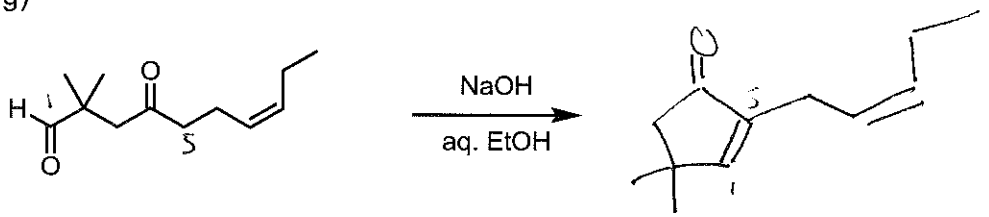


f)

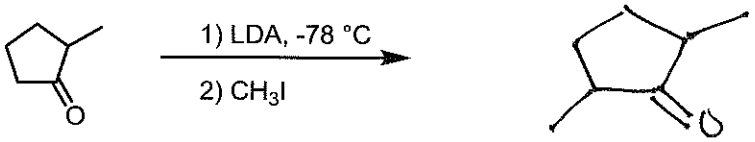


Stereo wrong (-1)

g)

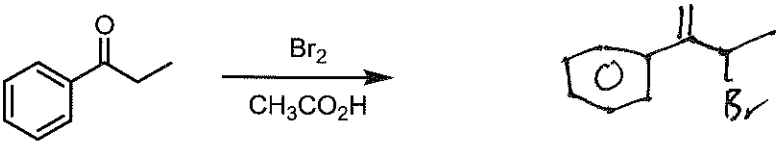


h)



(1/4 2,2-dimethyl)

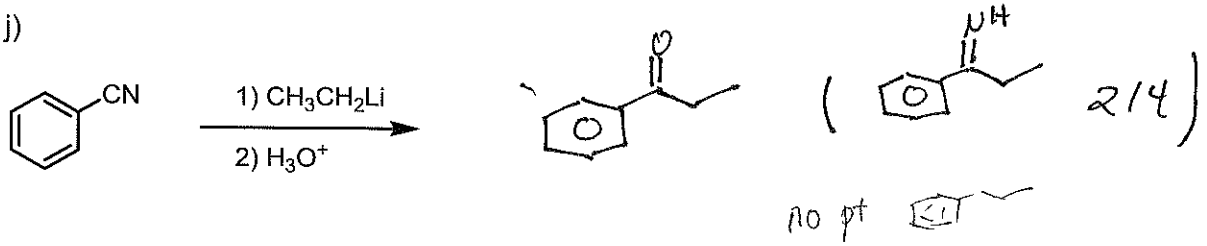
i)



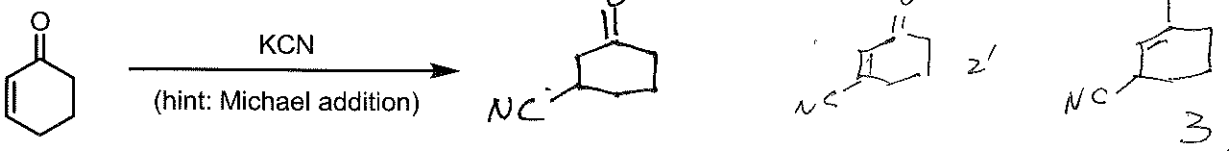
(2 Br 2/4)

4 ea.

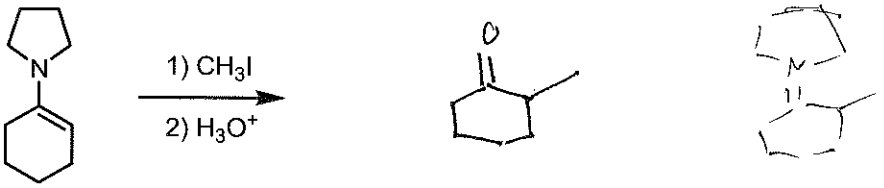
j)


CN
1) CH_3CH_2Li
2) H_3O^+
O
NH
O
2/4
no pt

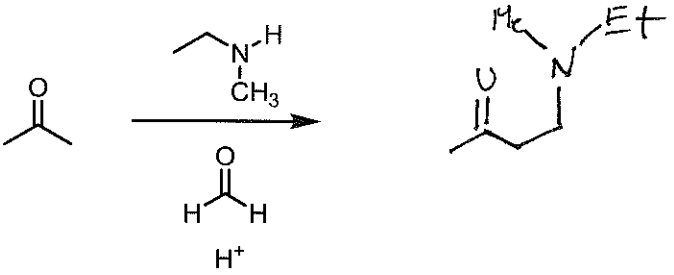
k)


O
KCN
(hint: Michael addition)
O
NC
O
NC
2
OH
NC
3

l)

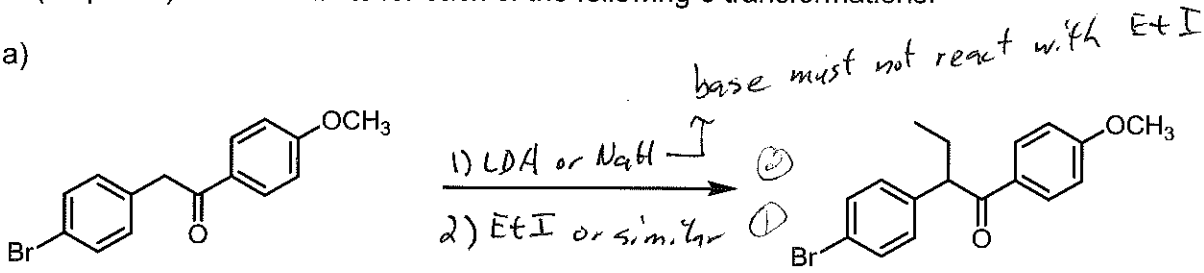

N
1) CH_3I
2) H_3O^+
O
N

m)

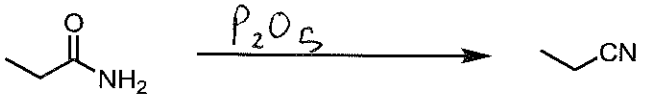

O
N
H
CH_3
O
H
H
H^+
Me
Et
N
O

3. (18 points) Give reactants for each of the following 6 transformations.

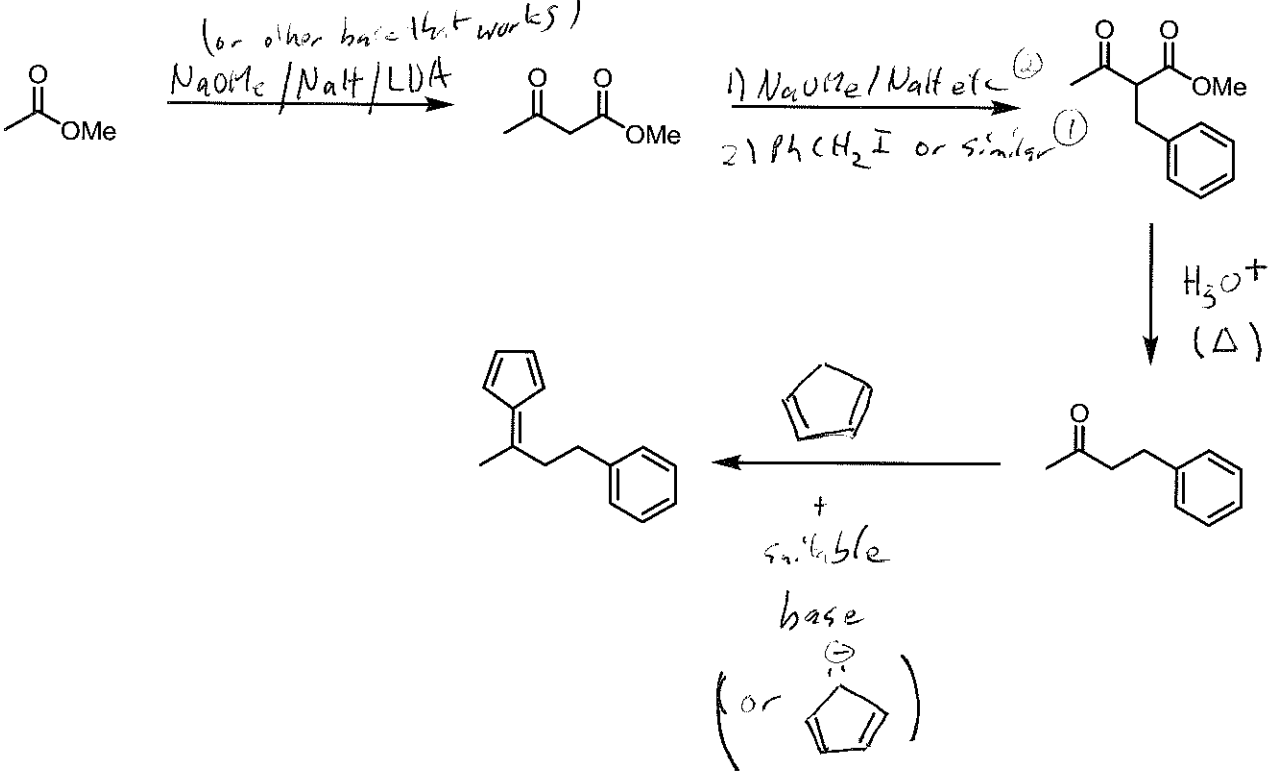
a)



b)

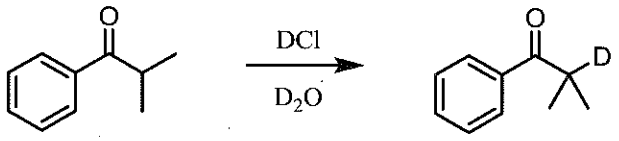


c)-f)

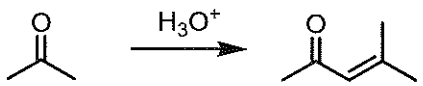


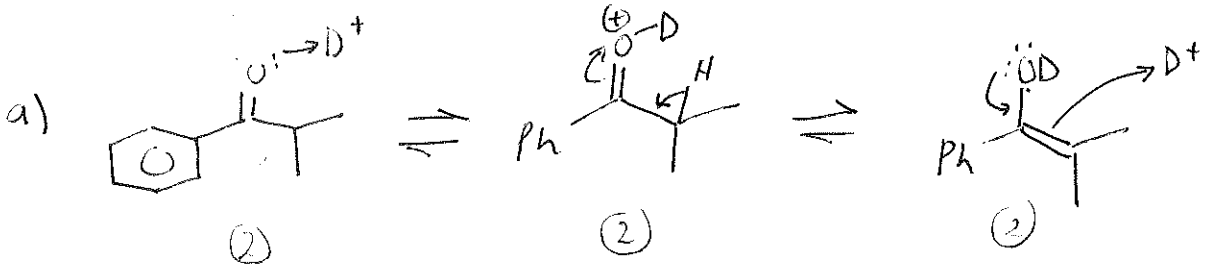
4. (8 points) Give a complete reaction mechanism for **one** of the following two reactions. If you show work on both, **CLEARLY** indicate which of the two you wish to be graded; if it's not clear to the grader, they will choose one to grade.

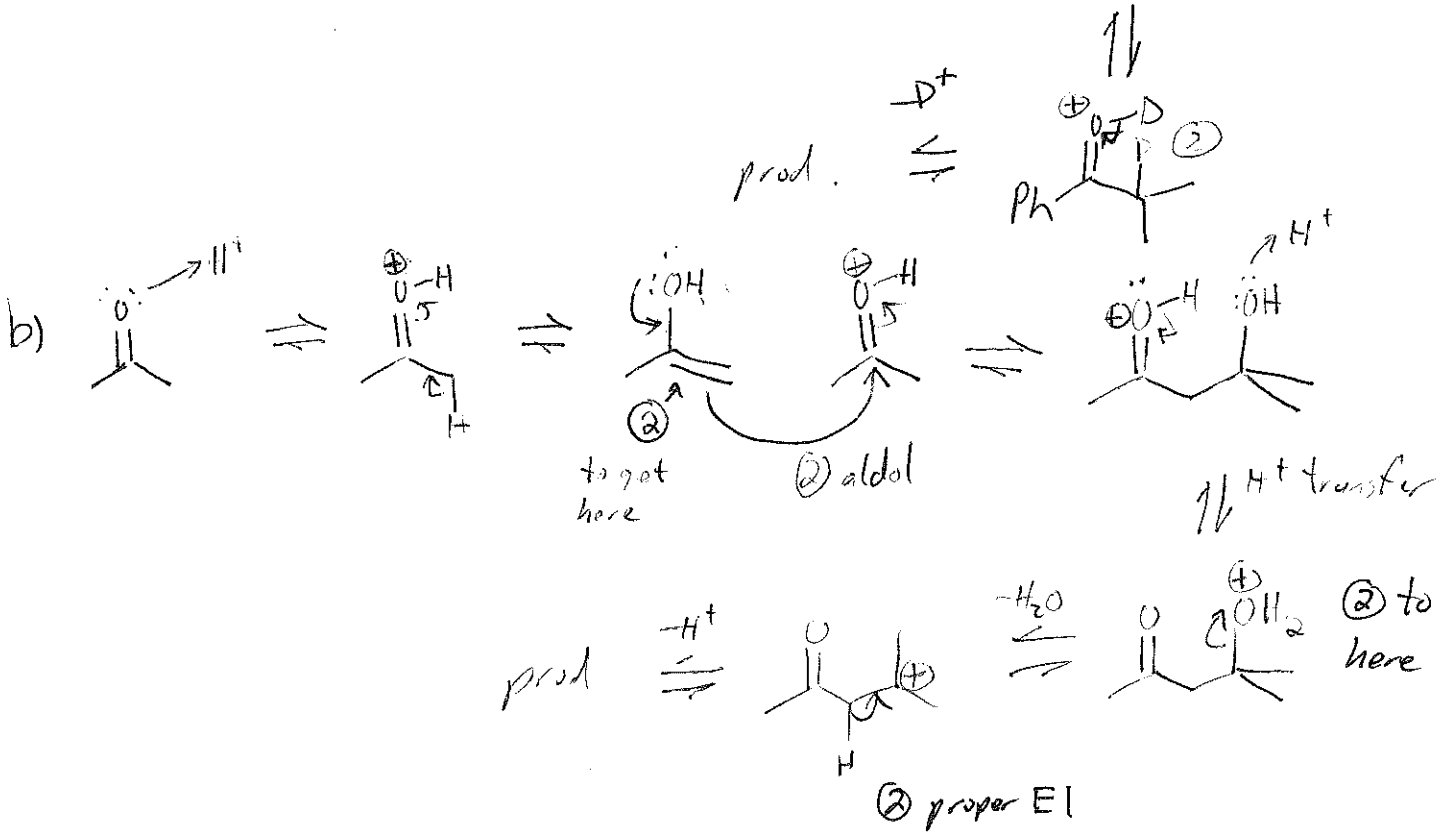
a)



b)

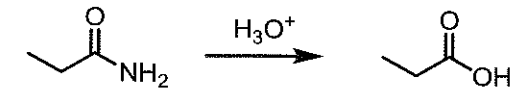


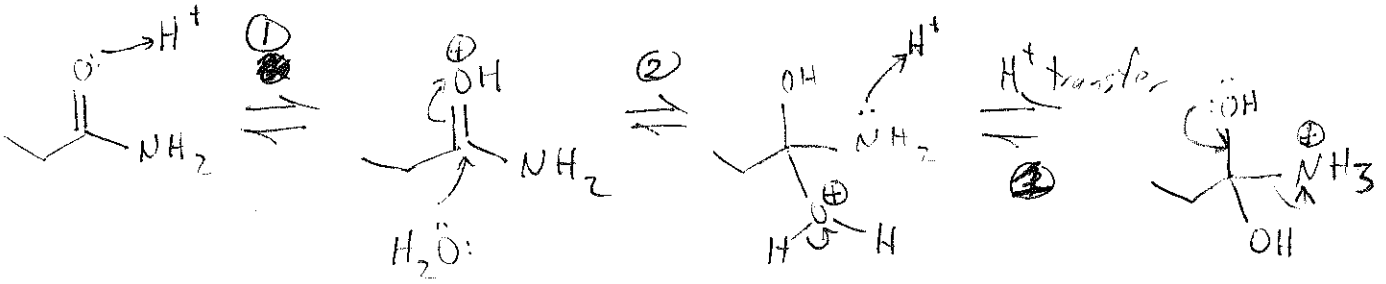


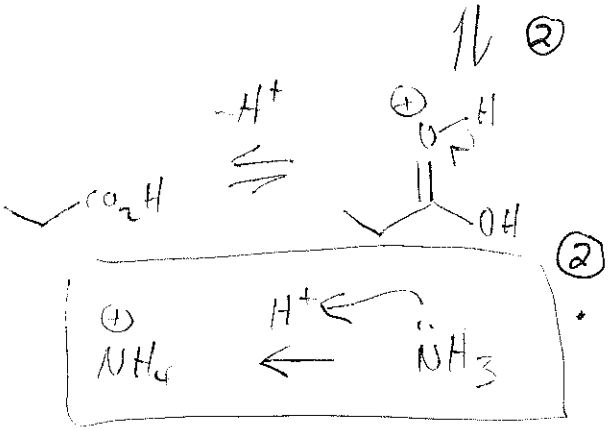


base-promoted rxs: 2ß max.

5. (10 points) Amides are irreversibly hydrolyzed in acid. Show a complete reaction mechanism for the hydrolysis of propanamide in aqueous acid. Explain, using your mechanism, why the process is essentially irreversible.

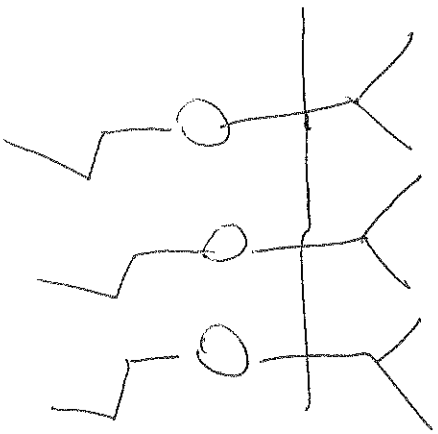




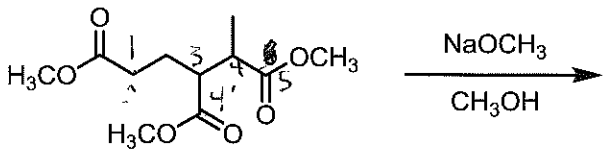


(2) protonation to non-nucleophilic NH_4^+ drives rxn by L.C.P.

X: ⟶ $H_3\overset{+}{O}$



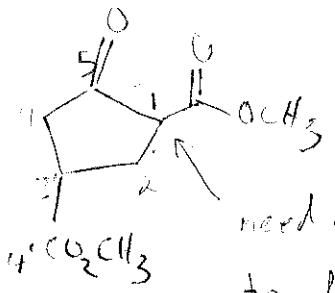
6. (12 points) The following compound has several ester groups and several α-hydrogens. However, Dieckmann cyclization using sodium methoxide yields a single major product. Give its structure, and explain why only this Dieckmann product is formed.



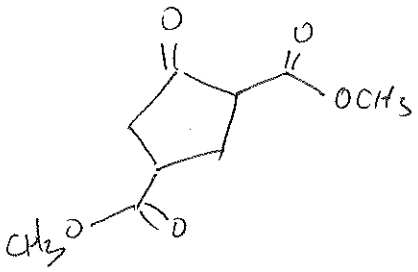
- need 2 α-H ∴ enolate at C-1 (2.) 3

- 4-membered ring strained; 5 better 3

∴ 6



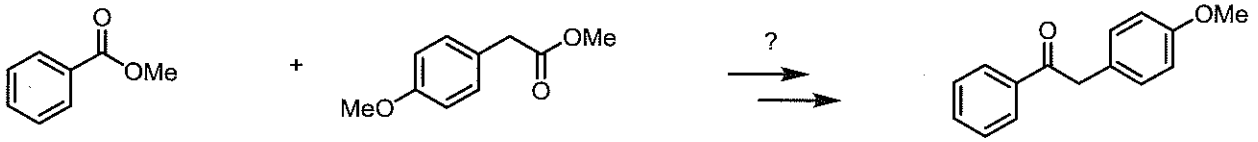
need 2nd H here to deprotonate and drive rxn forwards



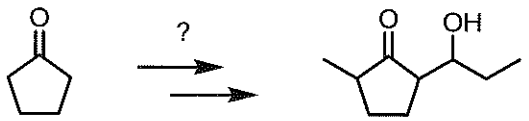
12

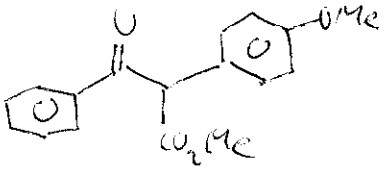
7. (8 points) Provide an efficient synthesis for **one** of the following two products on the right from the indicated starting material(s) on the left. If you show work on both, **CLEARLY** indicate which of the two you wish to be graded; if it's not clear to the grader, they will choose one to grade.

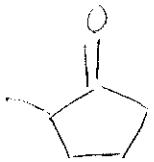
a)

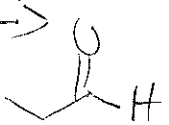


b)



a) (4) $NaOMe$ or NaH etc. →  (4) H_3O^+ (Δ) → prod.

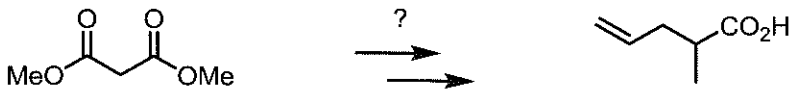
b) (4) 1) LDA/NaH/other suitable base →  2) CH_3I or similar

(4) 1) LDA, -78°C → 2)  prod.

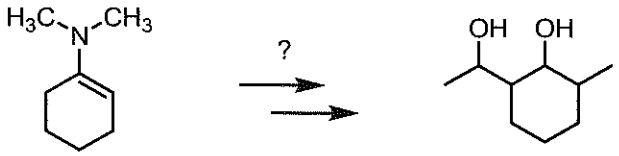
(reverse order: problematic but consider for part credit)

9. (12 points) Provide a synthesis for **one** of the following two products on the right from the indicated starting material(s) on the left. If you show work on both, **CLEARLY** indicate which of the two you wish to be graded; if it's not clear to the grader, they will choose one to grade.

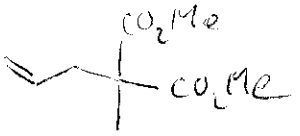
a)



b)

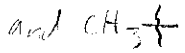


a) 1) NaH or NaOMe
2) R-X
3) NaH or NaOMe
4) R'-X



H_3O^+, (Δ) → prod

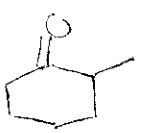
(4)

R, R' =  and CH_3

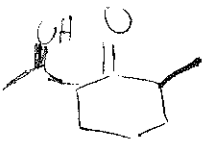
either order OK

(4)

b) 1) MeI, 2) H_3O^+



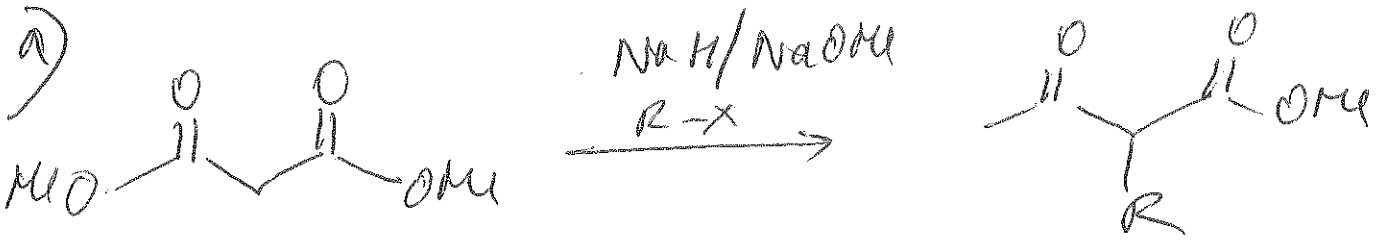
1) LDA, -78°C, 2) 



$NaBH_4$ or LAlH → prod.

(4) (4) (4)

a)



b)