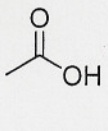
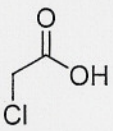
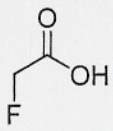
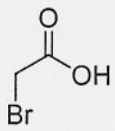
Part 1 Multiple Choice and Short Answer

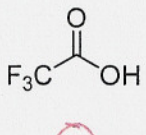
1. (2 points) Which of the following is the strongest acid?


a

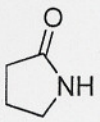

b

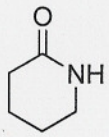

c

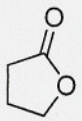

d


e

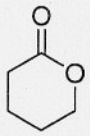
2. (2 points) Which of the following is a γ-lactam?


a

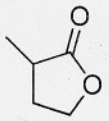

b


c


d

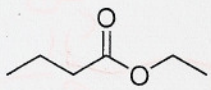

e

3. (6 points) Name the following compounds:



5-methyl-2-oxacyclopentanone

5 methyl γ-lactone – 2 points



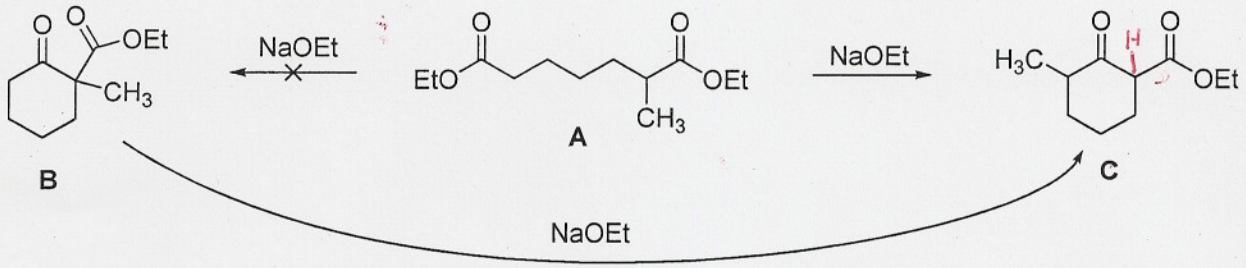
ethyl butanoate (butyrate)

4. a) (4 points) Explain why hydrolysis of an ester is reversible in acid but irreversible in base.

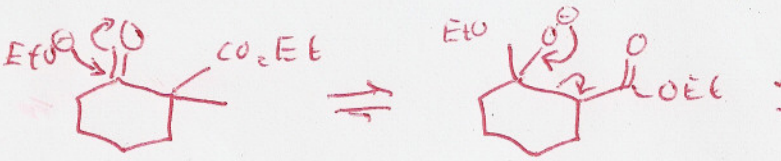
$RCO_2H + {}^-OH \longrightarrow$ irreversible

$RCO_2^{\ominus}$ ↑ not attacked easily by nucleophile

4b) (6 points + 6 bonus) The diester **A** shown below has two different carbons α- to a carbonyl, and thus two different enolates that can form, and one might therefore anticipate two different Dieckmann cyclization products **B** and **C**. However, in practice *only* **C** is formed from **A**. In fact, if you obtain **B** by other means and treat it with NaOEt it converts to **C**! Explain why only **C** is formed from **A**. For bonus points, give a mechanism that shows how **B** is converted to **C** by treatment with NaOEt.



6 points: Claisen-Dieckmann: driving force is final deprotonation, C has a H α- to both carbonyls; B doesn't. (Before deprotonation, equilibrium favours A).

6 bonus: 

⇌ enolate of A.

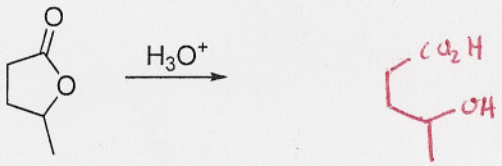
4 points: - 2 H's at α-C needed for Dieckmann's condensation to occur ~~Give~~

Note: this is v. similar to assigned homework (19.46, 19.47), as well as 19.65.

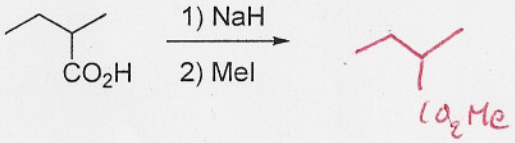
Part 2: Reactions and Synthesis

5. (36 points) Give the major organic product(s) for 9 of the following 11 reactions. **CLEARLY INDICATE THE QUESTIONS THAT YOU <u>DON'T</u> WANT GRADED! Otherwise, the first 9 questions that show work will be graded.**

a)

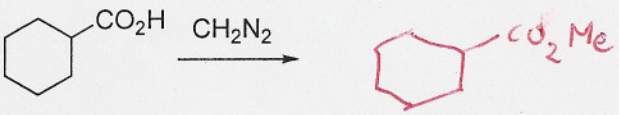


b)



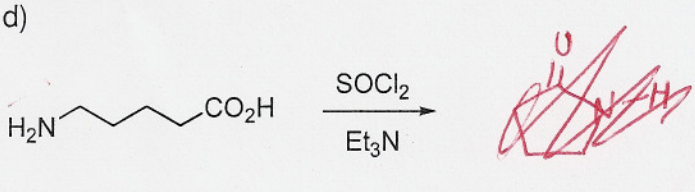
-2 if no -OMe

c)



-2 if incorrect ester

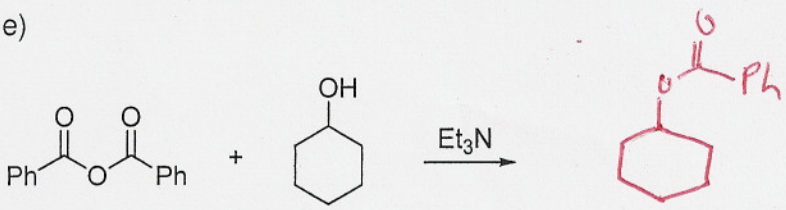
d)



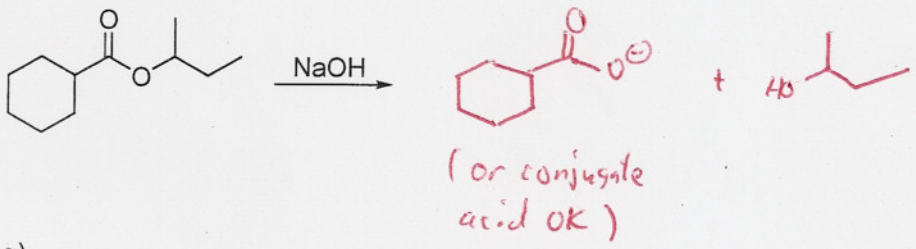
-2 if no cyclize

-1 +

e)



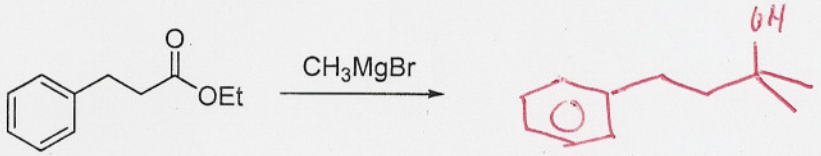
f)



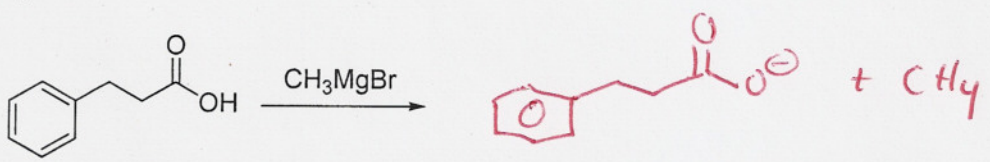
(or conjugate acid OK)

-2 if only 1 product

g)



h)

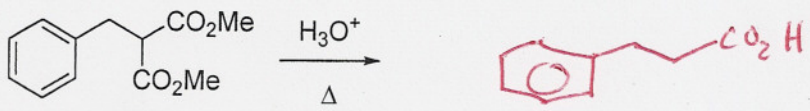


-2 if have methyl

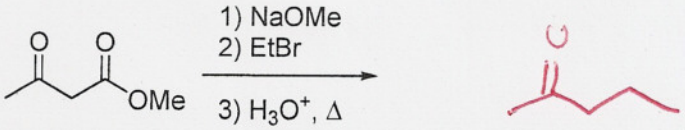
i)

-2 if only one $-CH_2OH$

j)

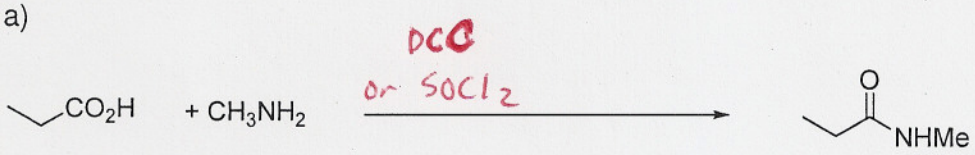


k)

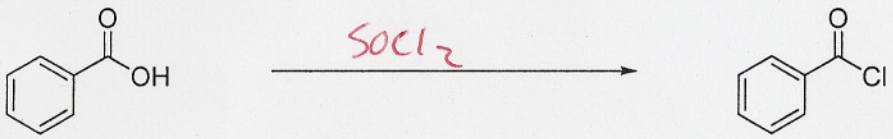


6. (24 points) Give reactants for 8 of the following 10 transformations. **CLEARLY INDICATE THE QUESTIONS THAT YOU <u>DON'T</u> WANT GRADED! Otherwise, the first 8 questions that show work will be graded.**

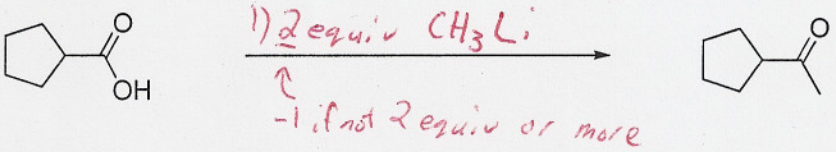
a)



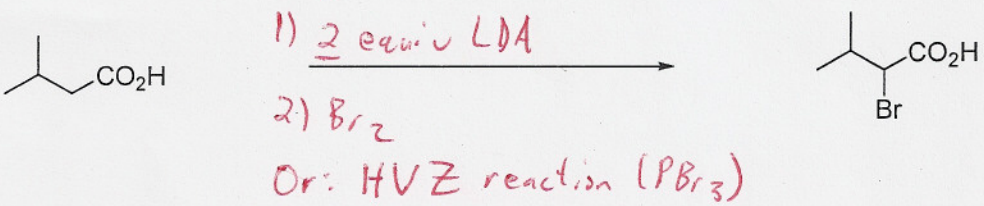
b)



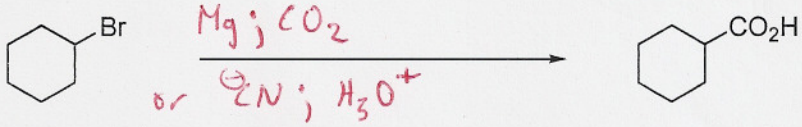
c)



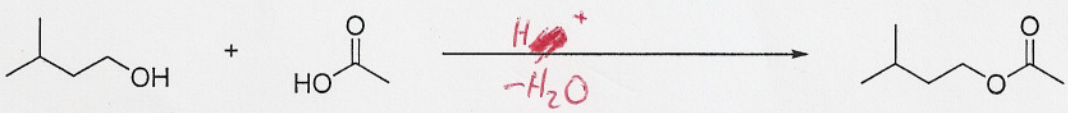
d)



e)



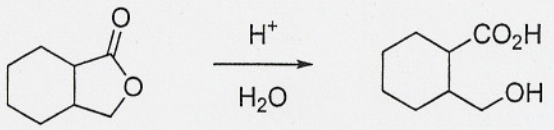
f)



half ~~fart~~ credit if DCC or $SOCl_2$

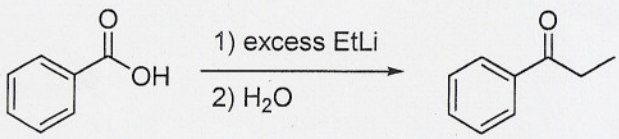
7. (10 points) Give mechanisms for ONE of the following two transformations. **CLEARLY INDICATE THE QUESTION THAT YOU WANT GRADED! Otherwise, the first question that shows work will be graded.**

a)



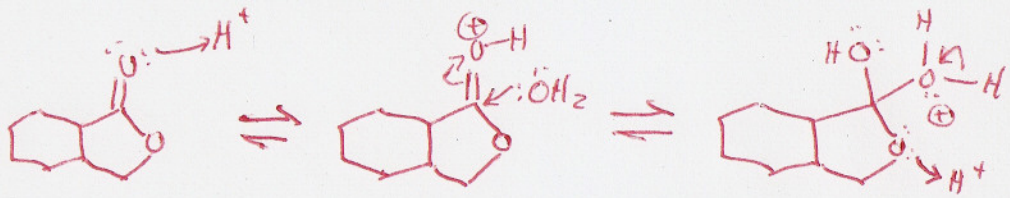
Compare to Fig. 19.32

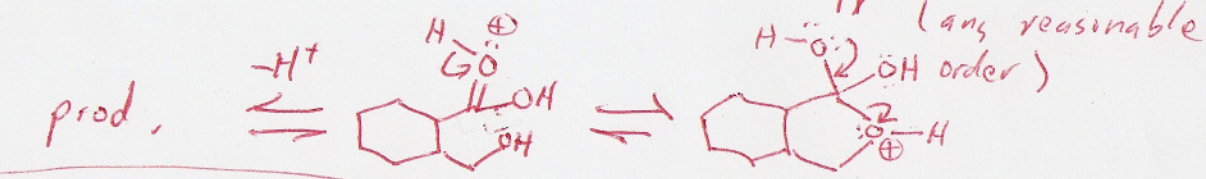
b)



See Fig. 18.49-18.50

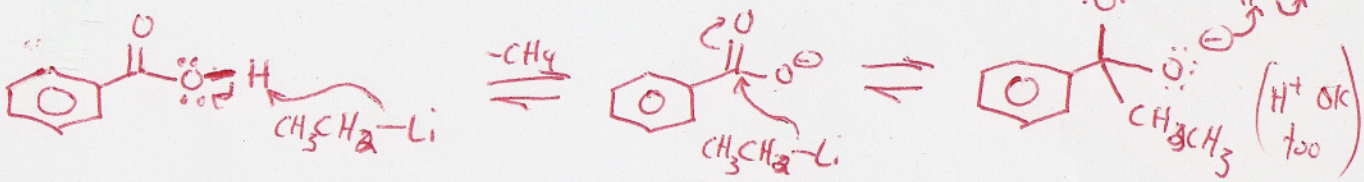
a)



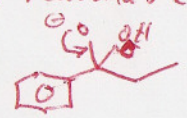


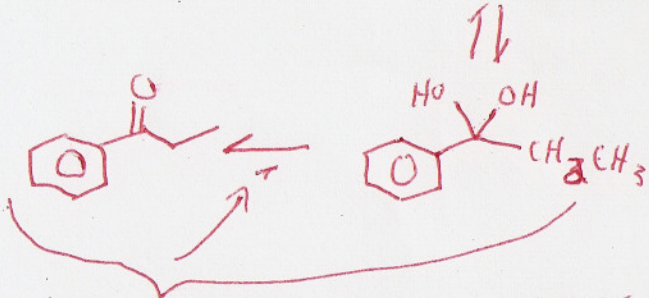
~2 pts. per step.
watch formal charges, arrows etc.

b)

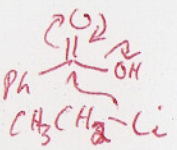


eg: also reasonable is





If just

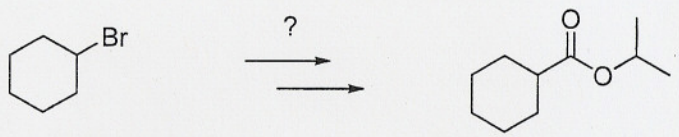


) 3 points max

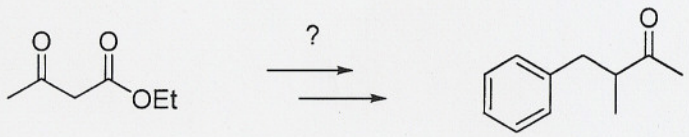
hydrate to ketone: any proper mechanism. If just the above, with no mech, 6/10

8. (10 points) Provide a synthesis for ONE of the two following compounds from the indicated starting materials. **CLEARLY INDICATE THE QUESTION THAT YOU WANT GRADED! Otherwise, the first question that shows work will be graded.**

a)



b)

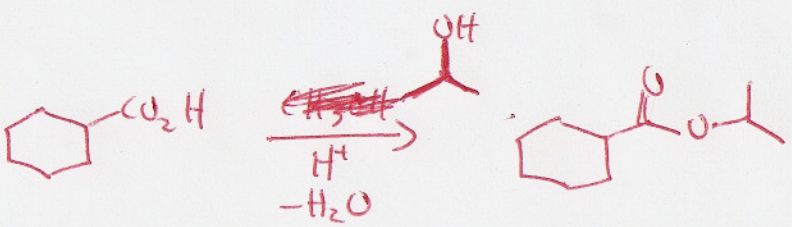


a) "$+CO_2H$" can be via $Mg; CO_2$ or $^{\ominus}CN; H_3O^{\oplus}$, etc.
esterification: any suitable method (or alkylation with $\overset{X}{\curlyvee}$)

b) double-alkylation, eg: $\xrightarrow[2)\ PhCH_2X]{1)\ NaOEt}$ $\xrightarrow[2)\ CH_3X]{1)\ NaOEt}$ or v.v., then $\xrightarrow[\Delta]{H_3O^+}$

Examples:

a) $\xrightarrow[2)\ CO_2\\ 3)\ H^+(\text{neutralize})]{1)\ Mg}$



b) $\xrightarrow[2)\ PhCH_2Br]{1)\ NaOEt}$