Chemistry 112B: Midterm 1, Thursday March 1, 2007

Name: KEY

UCSID: _____ *GSI:* _____

Question 1 _____

Question 2 _____

Question 3 _____

Question 4 _____

Question 5 _____

Question 6 _____

Question 7 _____

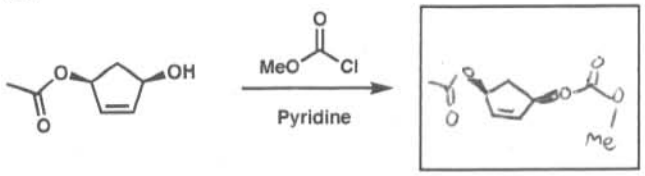
Question 8 _____

Total ———————————/175 points

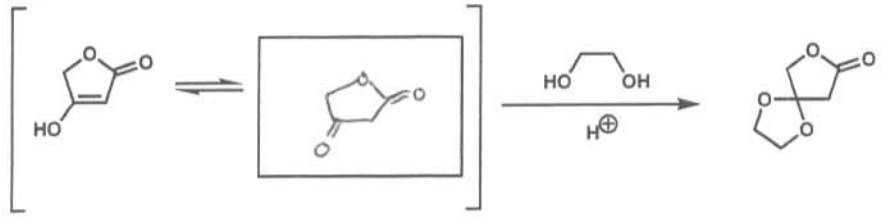
Question 1

Fill in the reagents or products. You must use the exact number of steps. (5 points each)

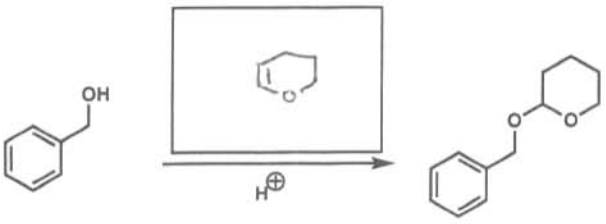
(a)



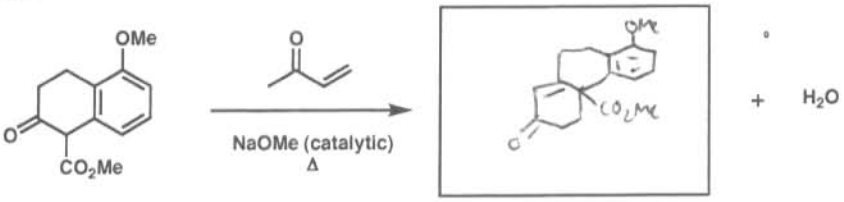
(b)



(c)

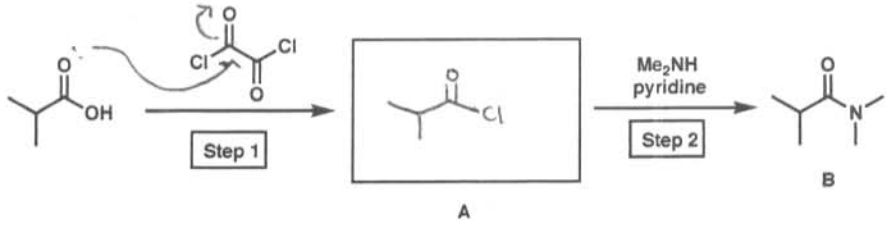


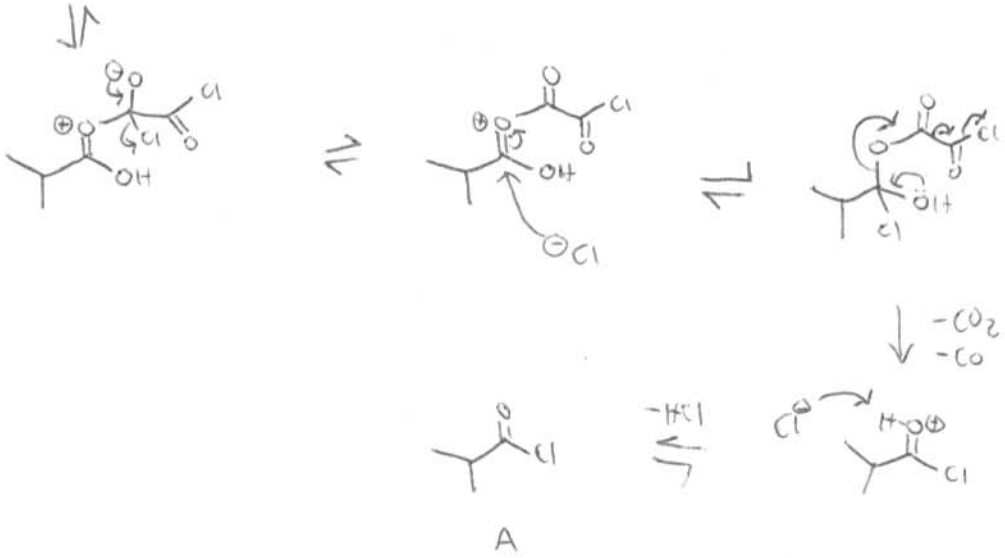
(d)

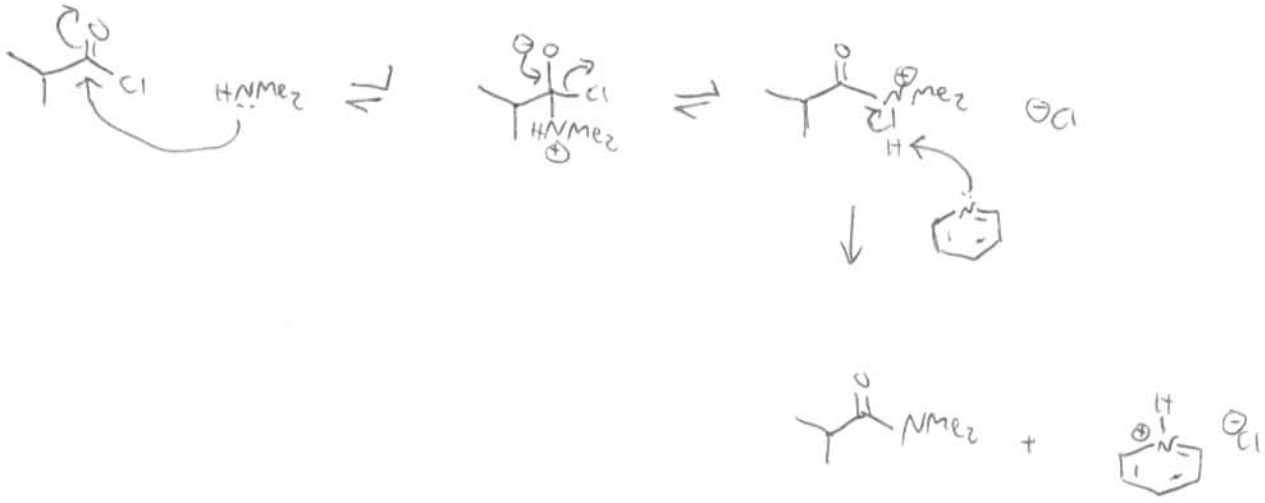


Question 2

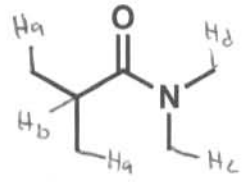
(a) Provide a mechanism for the following reactions and identify **A**. (10 points)





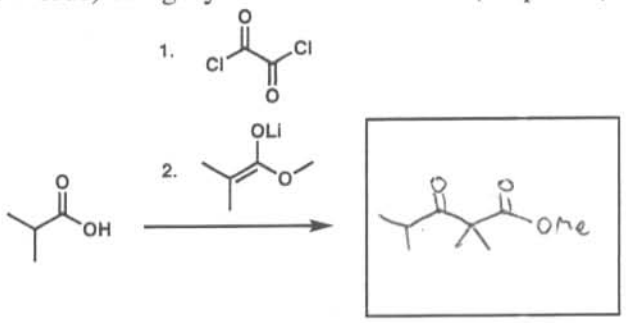


(b) How many different resonances would you expect in the *proton* NMR spectrum of **B**? Please indicate these with **a**, **b**, **c**, **d** etc. below. For example, if there are four *different* resonances, indicate these with **a**, **b**, **c**, and **d**. (10 points)

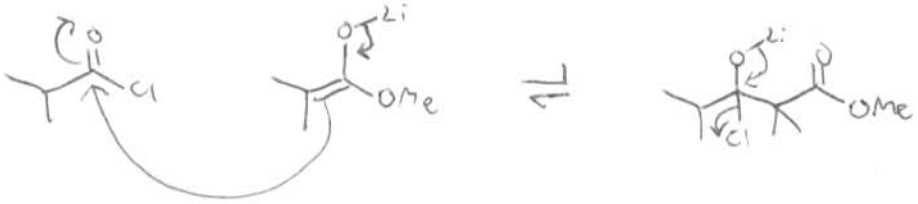


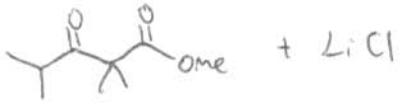
B

(c) Given your answer in part (a), predict the product of the following two-step reaction and provide a mechanism for step 2 below. What type of named reaction (two words) category does this fall into? (10 points)



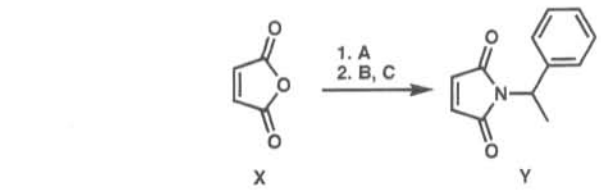
Claisen condensation

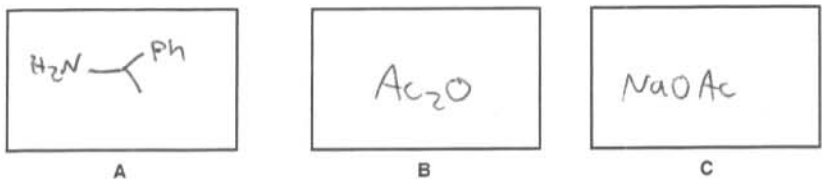


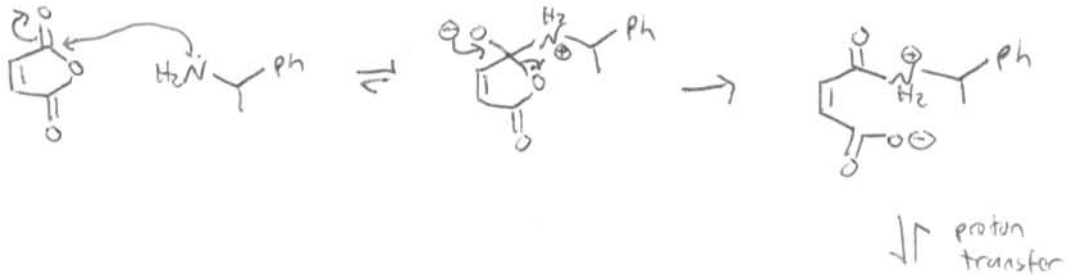


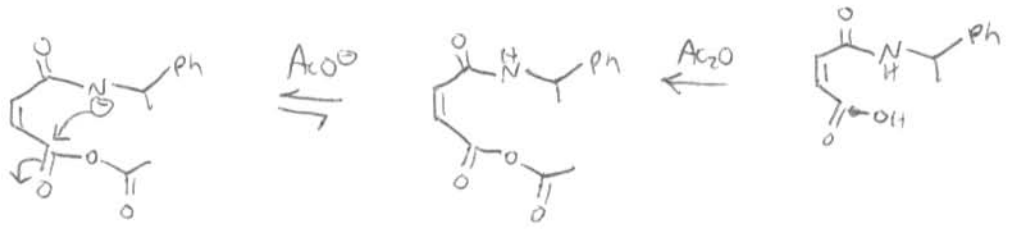
Question 3

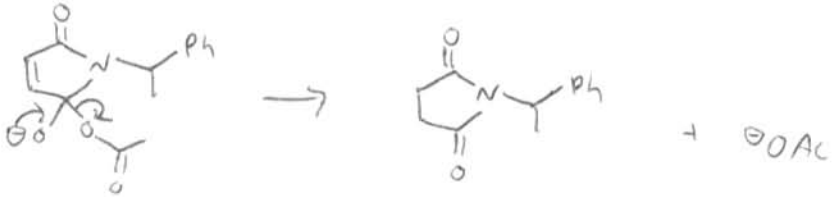
Anhydrides such as **X** provide a good starting point to access imides such as **Y**. Provide reagents **A**, **B** and **C** that will enable you to carry out this conversion. Please provide a detailed mechanism for this transformation. (15 points)





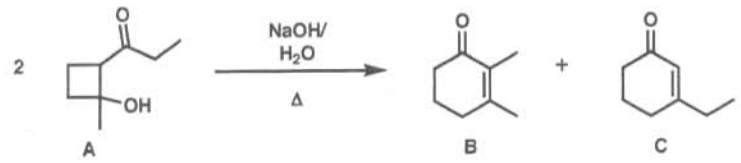


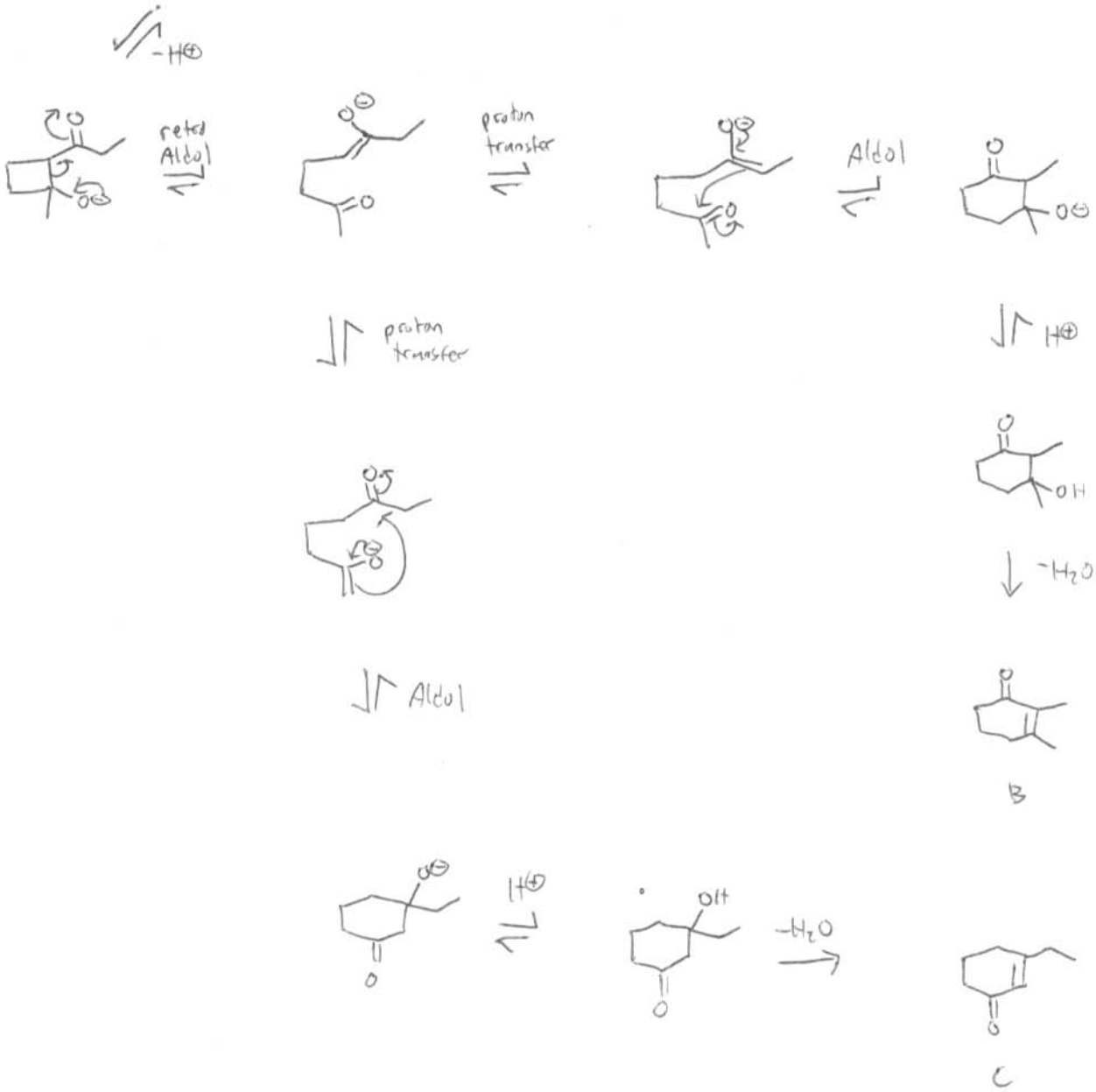




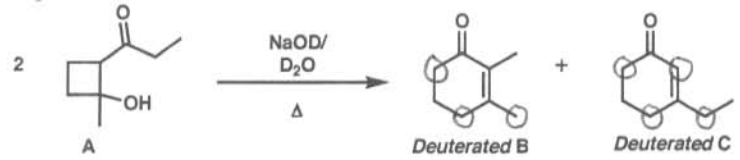
Question 4

(a) Provide a mechanism that rationalizes the formation of **B** and **C** in the following reaction. (15 points)





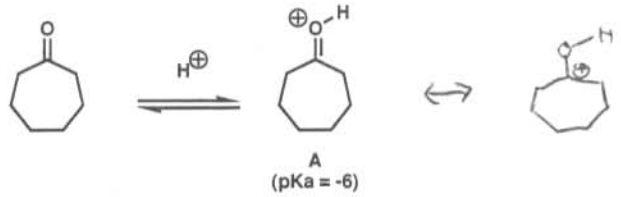
(b) On the basis of your answer in part (a), circle <u>three</u> carbon atoms in **B** or **C** below where you would expect deuterium to be incorporated in the product. Why is deuterium incorporated? (10 points)



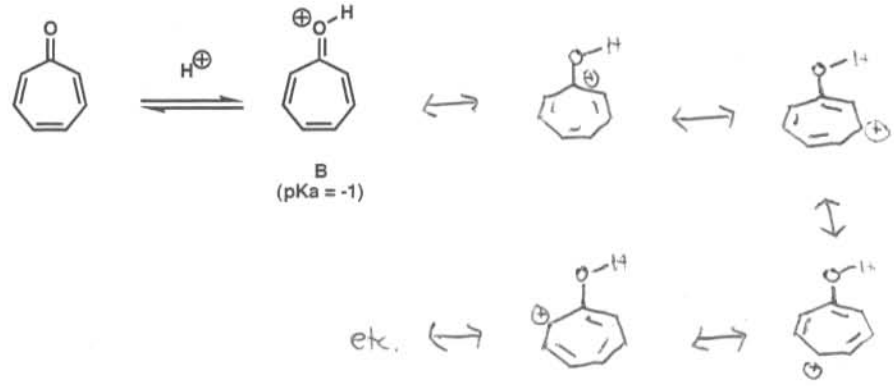
Fast, reversible proton transfers occur between H(D) ~~on~~ α to carbonyls and ⊖OD/D_2O.

Question 5

(a) Acid-catalyzed reactions involving carbonyl compounds always begin with a protonation of the carbonyl oxygen. Rationalize the differences in pka for **A** and **B**. (15 points)



A
(pKa = -6)



B
(pKa = -1)

greater resonance stabilization of the positive charge in B vs. A → more stable conjugate acid

(b) On the basis of your answer to part (a) and given your knowledge of IR spectroscopy, would you expect the carbonyl IR stretch of **X** to be at a *higher* or *lower* wavenumber than that of **Y** (1710 cm^{-1}). Explain. (15 points)

X Y

→ more resonance contributors for X (see (a))

→ lower bond order for C=O bond in X

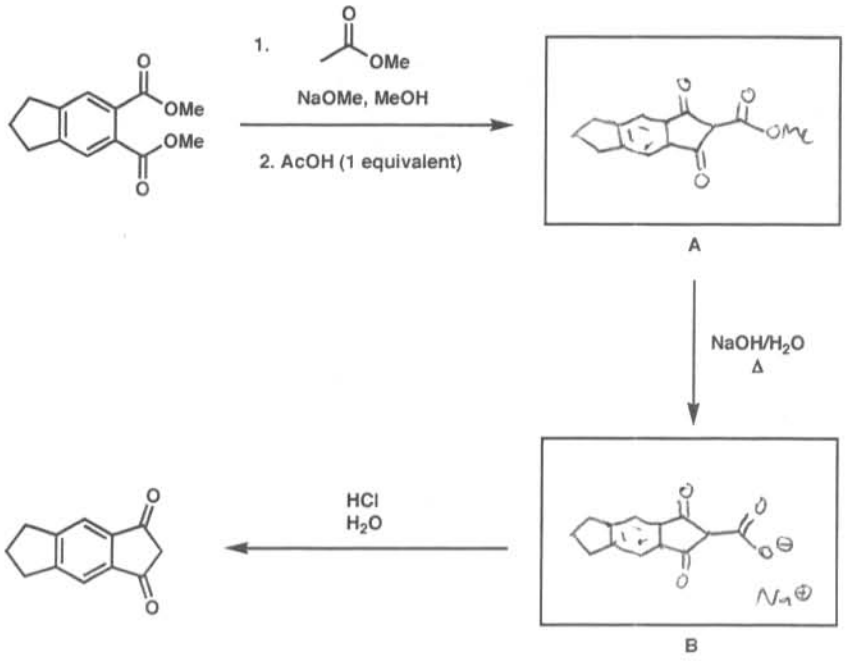
→ lower wavenumber for C=O stretch

Question 6

(a) The Claisen condensation is an important reaction for the formation of carbon-carbon bonds using carboxylic acid derivatives. What is the intramolecular version of this reaction called? (4 points)

Dieckmann condensation

(b) For the reaction sequence below, identify **A** and **B**. (10 points)

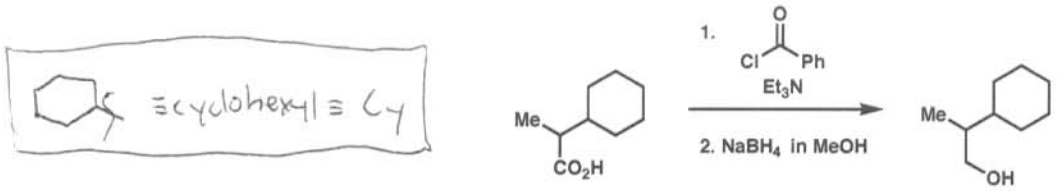


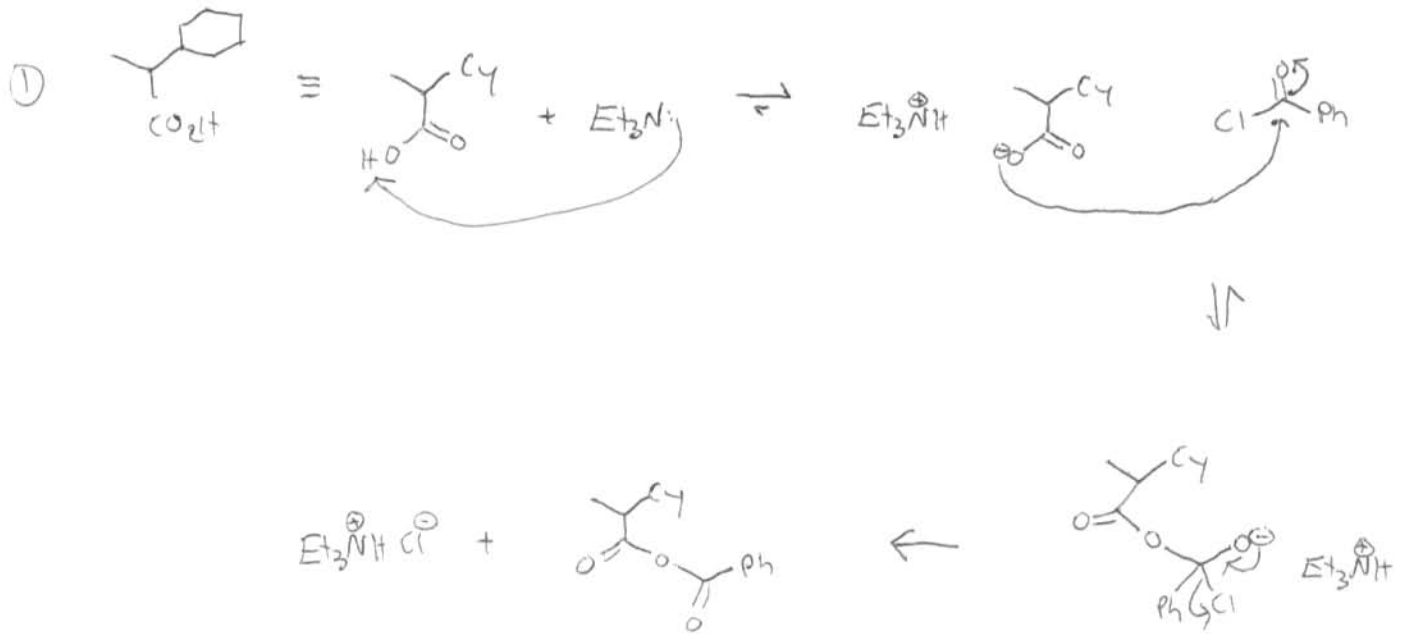
(b) The conversion of **A** to **B** has a name often associated with this type of process. What is this name? (**Hint**: it is a named reaction that I wish was named after me). (1 point)

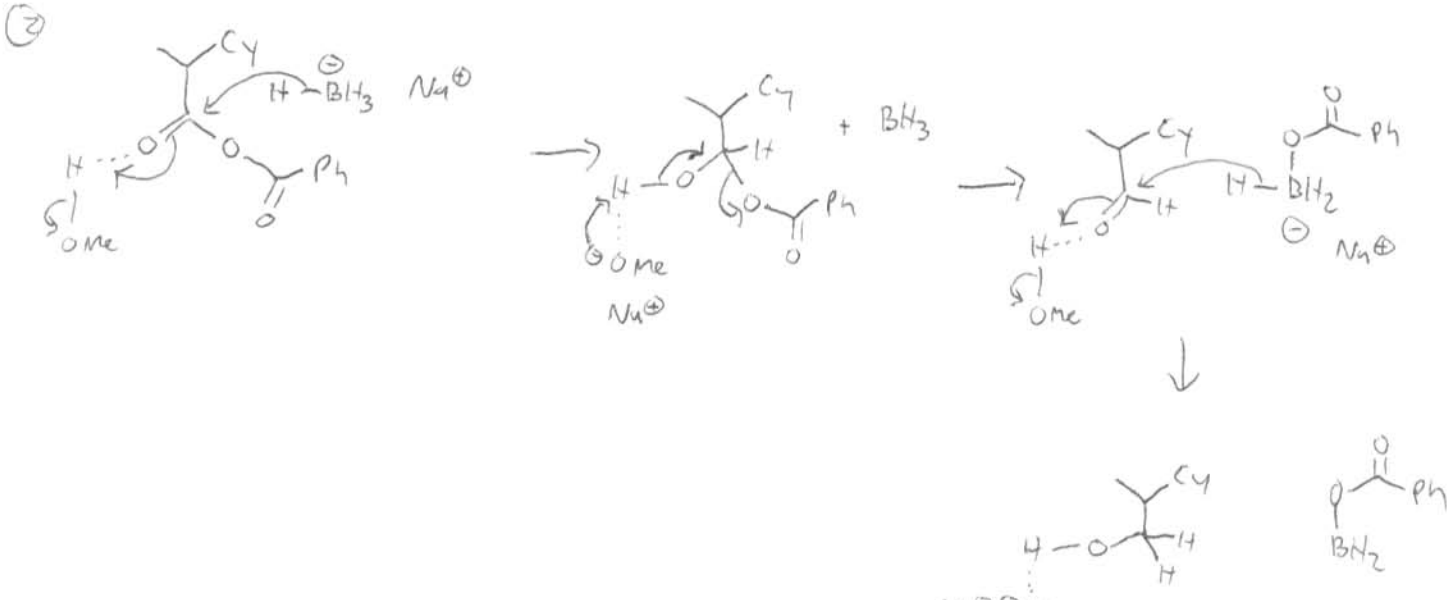
Saponification

Question 7

Sodium borohydride is known to reduce aldehydes. But, it cannot reduce acids or esters. It can however, reduce 'activated esters'. With this in mind, provide a mechanism for the transformation of **A** to **B** below. (15 points)







Question 8

Provide a synthesis for **A** using benzyl amine (**B**), methyl acrylate (**C**) and any of the reactions we have learned so far. (25 points)