Chemistry 112B: Midterm 1, Tuesday February 21, 2017

Name: KEY

UCSID: _____ *GSI:*_____

There are a total of 11 pages on this exam including this one. Time for the exam 8:10AM –9:30 AM. By writing your name on this exam, you have acknowledged that you have all 11 pages and written your answers only on the designated pages with page numbers (*answers written on the back pages will NOT be graded*).

Question 1 _____(17 pts)

Question 2 _____(10 pts)

Question 3 _____(10 pts)

Question 4 _____(12 pts)

Question 5 _____(14 pts)

Question 6 _____(12 pts)

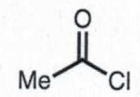
Question 7 _____(10 pts)

Question 8 _____(15 pts)

Total ——————————/100 points

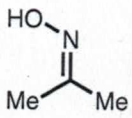
Question 1

(a) List the names of the following functional groups on the lines (1 pt each)



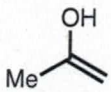
Acid chloride

+1



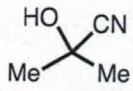
oxime

+1



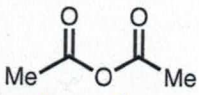
enol

+1



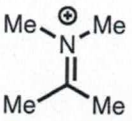
cyano-hydrin

+1



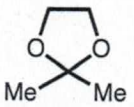
Acid anhydride

+1



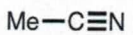
iminium ion

+1



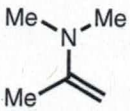
Acetal/Ketal

+1



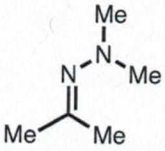
Nitrile

+1



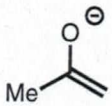
Enamine

+1



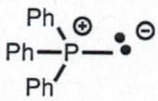
Hydrazone

+1



Enolate

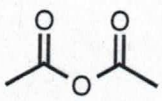
+1



ylide(e)

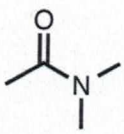
+1

(b) Rank the following functional groups from 1–5 with the most electrophilic as 1 (1pt each)



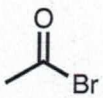
2

+1



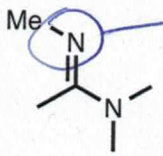
4

+1



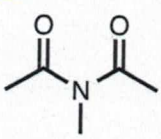
1

+1



5

+1



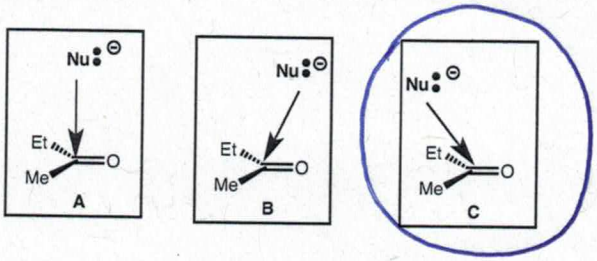
3

+1

Less e- ve compared to 0

Question 2

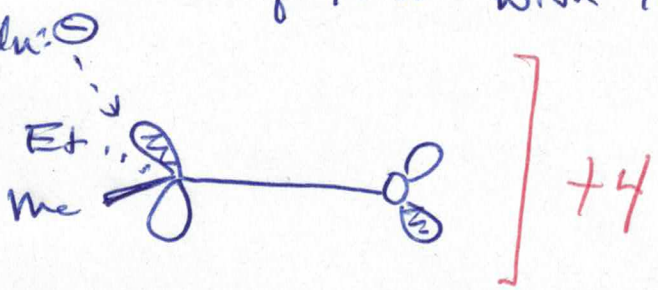
A) Circle the diagram (**A**, **B**, or **C**) that best represents the approach of a nucleophile to form a tetrahedral intermediate (2 pts)



B) Provide a rationalization for your answer in Part A in no more than 2 sentences and 2 figures. (8 pts)

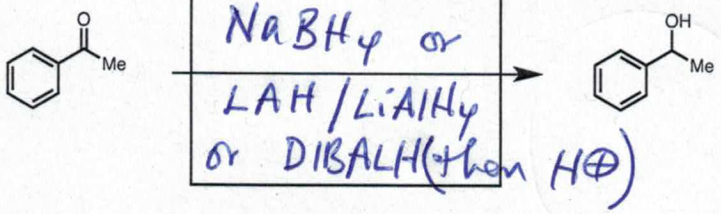
Bürgi-Dunitz angle

Interaction of Nu:⊖ with π*] +4

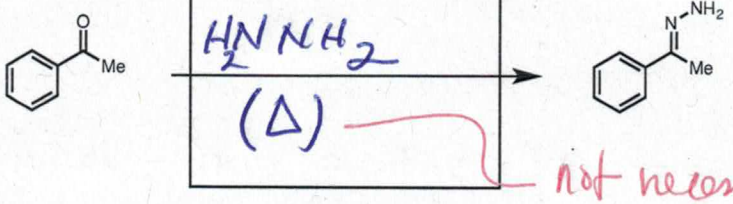


Question 3

Provide reagents (in the boxes) for the following transformations (2 pts each)

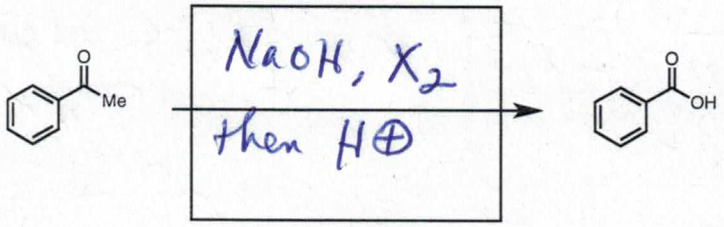
A) 

+2

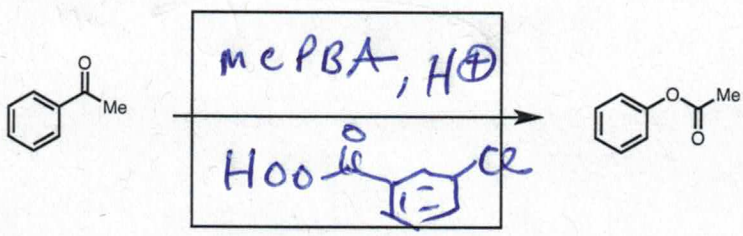
B) 

+2

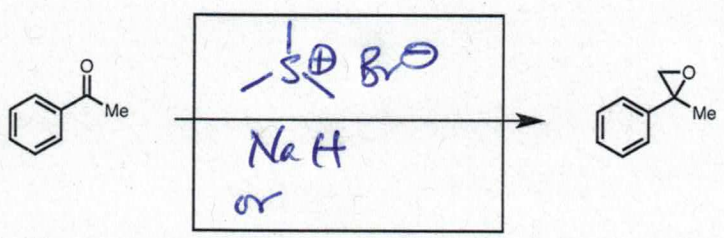
not necessary to indicate

C) 

Haloform reaction +2

D) 

Baeyer-Villiger reaction +2

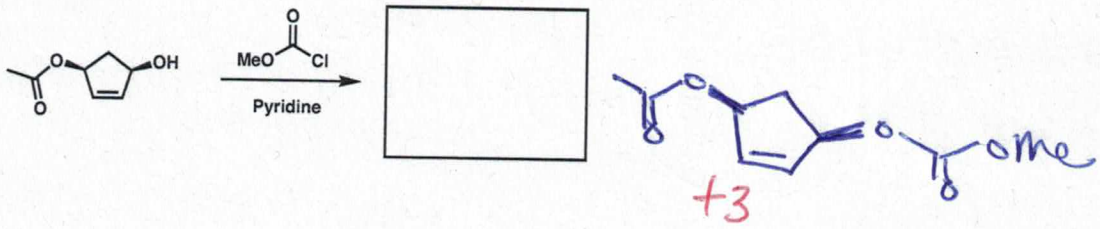
E) 

Corey-Chaykovsky reaction +2

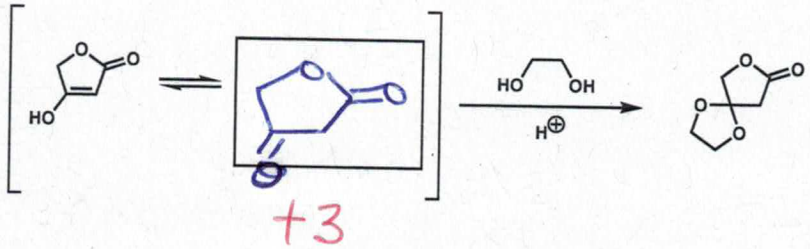
Question 4

Fill in the reagents or products in the boxes that are provided. (3 points each)

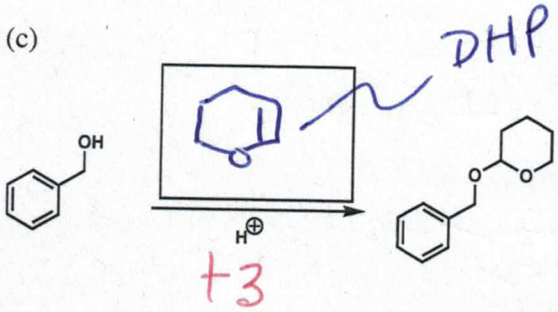
(a)



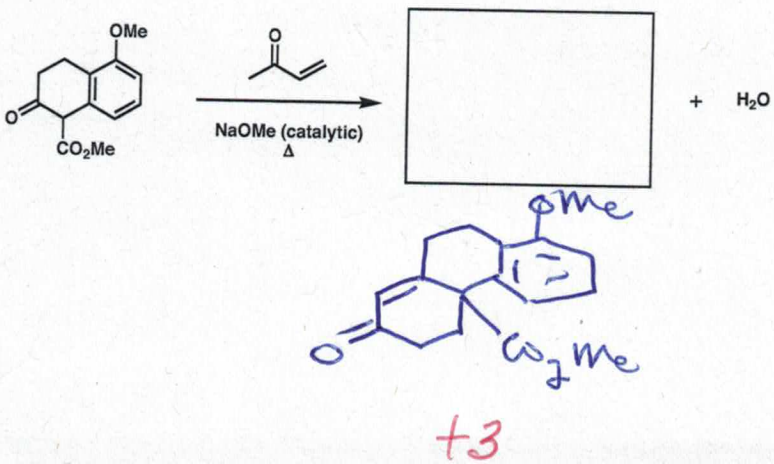
(b)



(c)



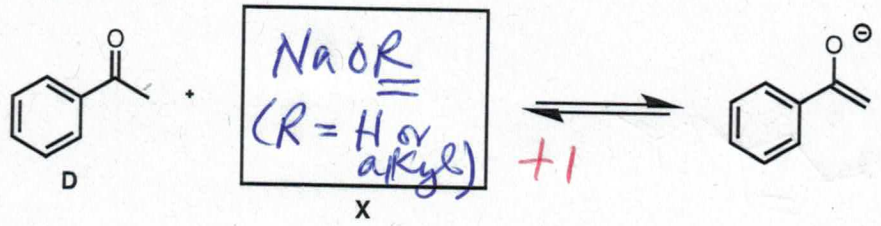
(d)

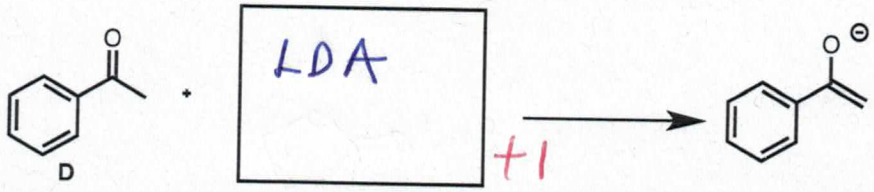


Robinson annulation

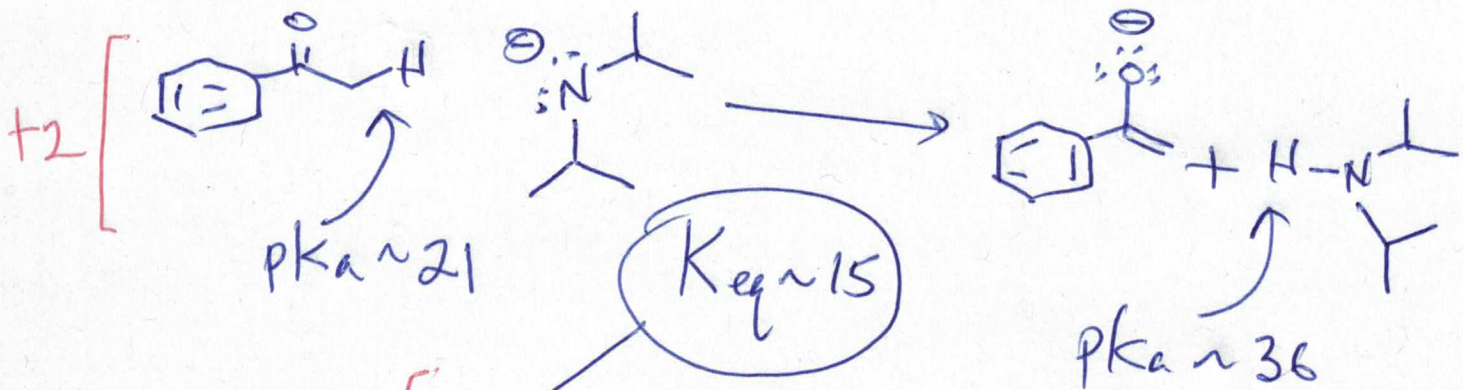
Question 5

(a) Provide a base (**X**) that will lead to the *reversible* deprotonation of **D** (indicated with equilibrium arrows) or a base (**Y**) that would lead to *irreversible* deprotonation of **D** (1 pt each).



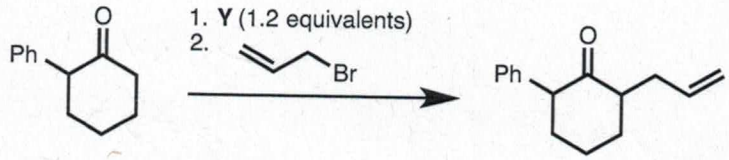


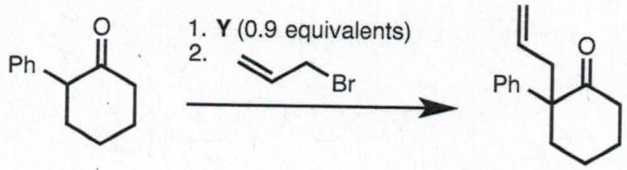
(b) Explain with one figure and in three sentences or less why deprotonation of **D** with **Y** in Part(a) leads to irreversible deprotonation (4 pts) (**Hint:** Consider the conjugate acid that is formed).



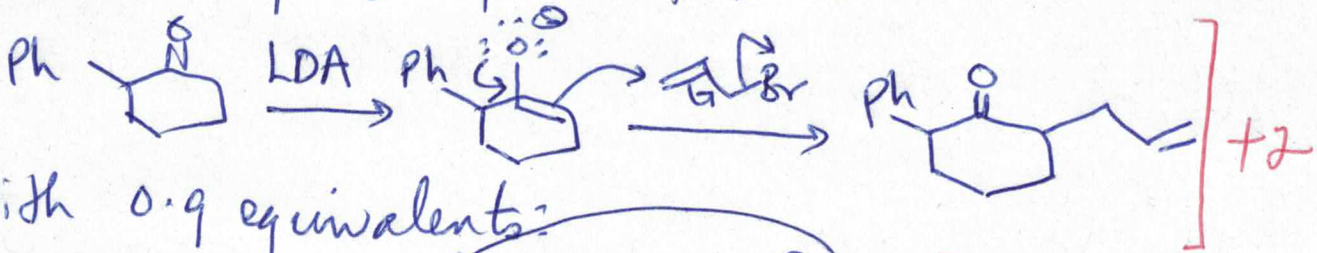
+2 this is a large and essentially irreversible equilibrium constant

(c) Provide a rationalization for the following observations using base **Y** from Part (a) (or any base that gives *kinetic*, *irreversible* deprotonation). You may use up to four figures and five sentences. (8 pts)

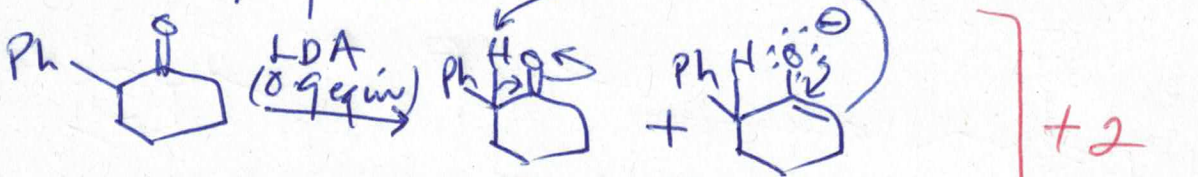




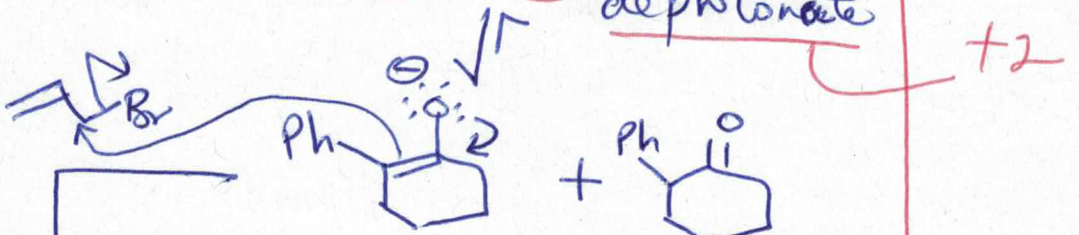
With 1.2 equiv; complete deprotonation



With 0.9 equivalents:

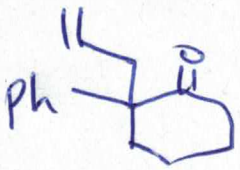


0.1 0.9 enolate can deprotonate



0.9 0.1 +2

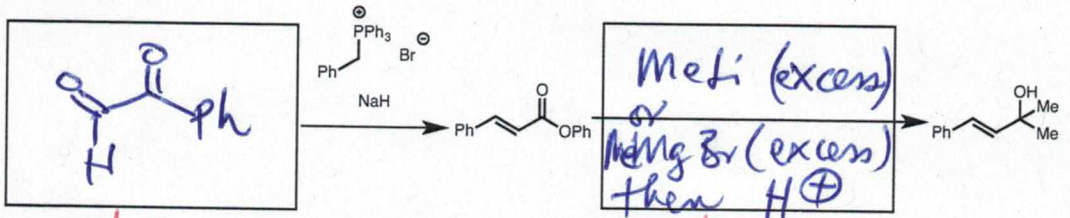
thermodynamically favored



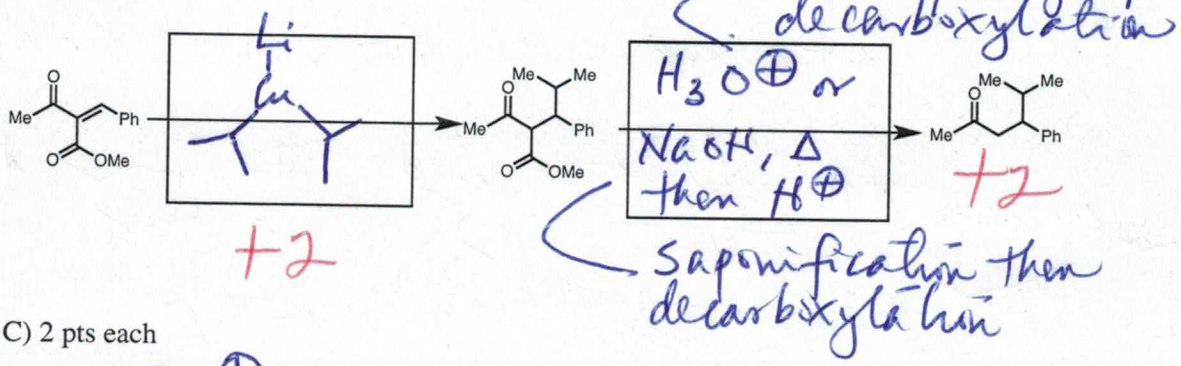
Question 6

Fill in the blank boxes below with the required compounds, reagents, or names.

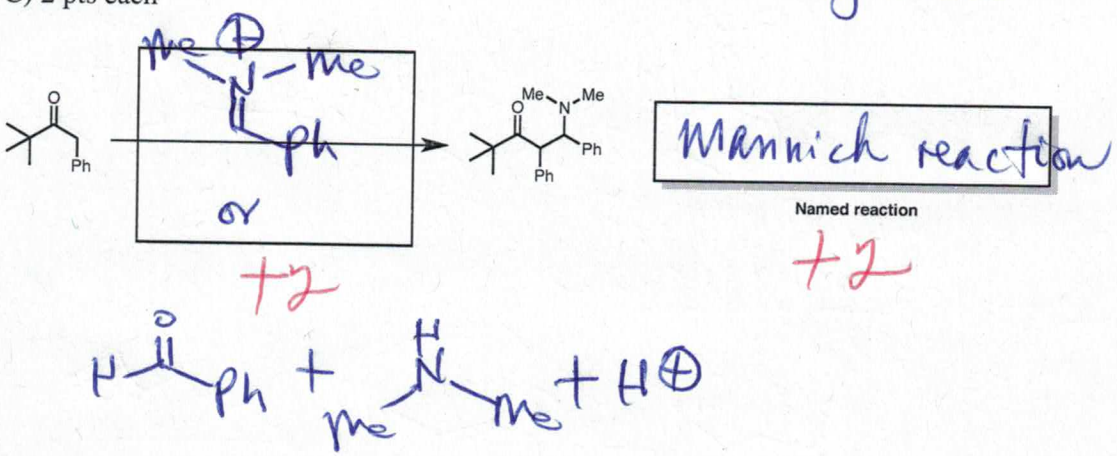
A) 2 pts each



B) 2 pts each

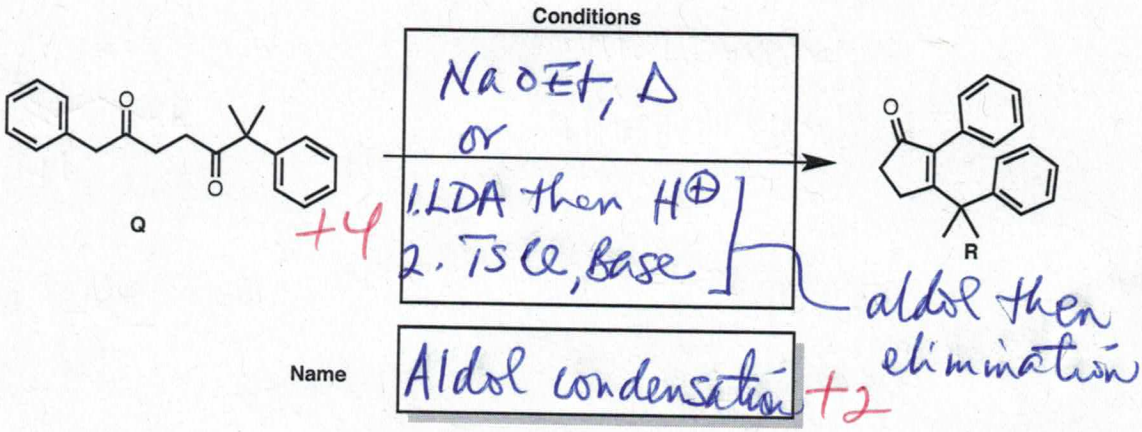


C) 2 pts each

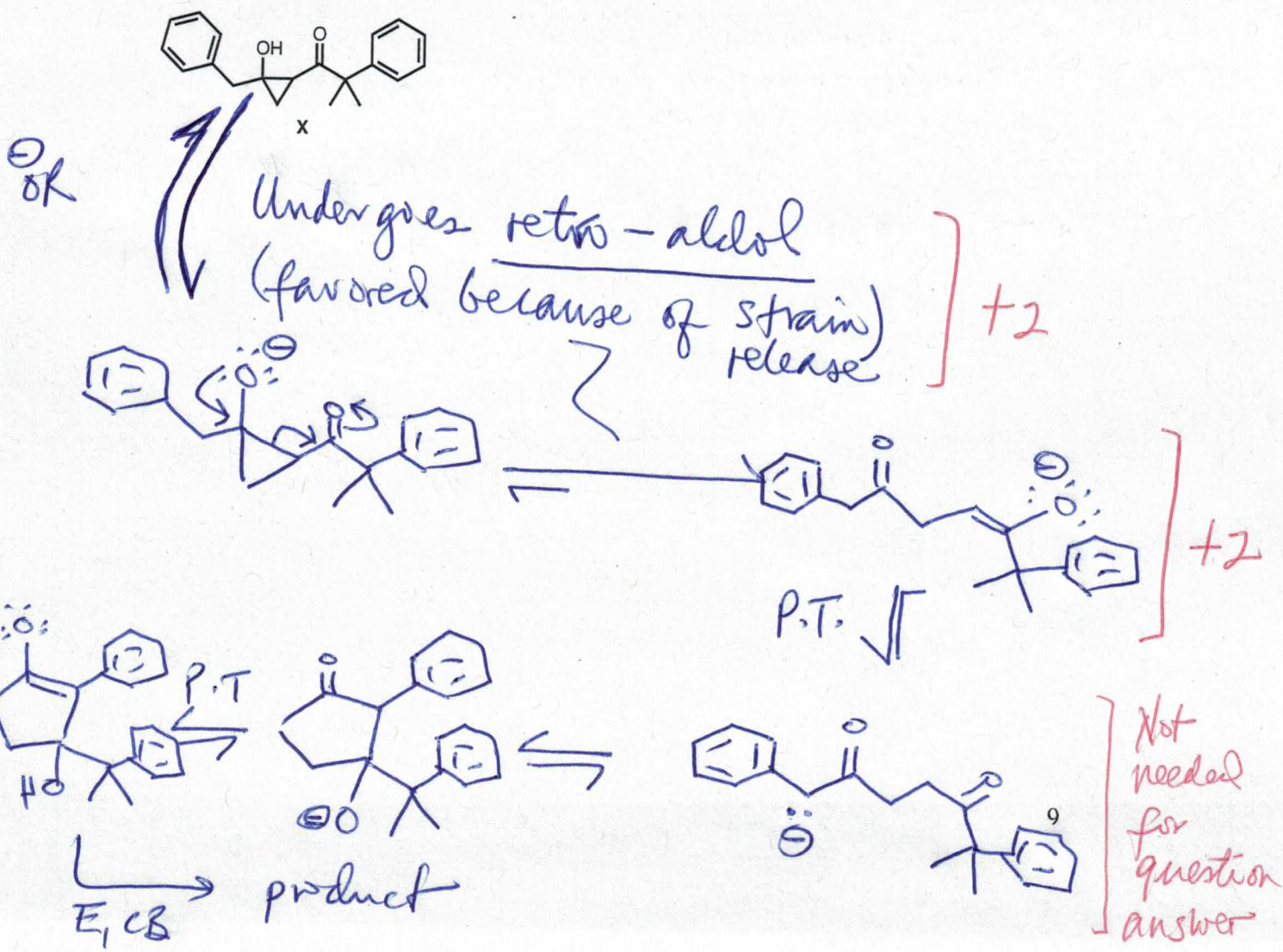


Question 7

(a) Provide conditions and the name associated with the conversion of **Q** to **R** shown below. (4 pts + 2 pts)

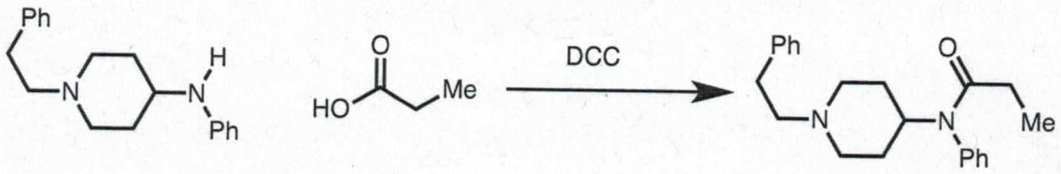


(b) Why isn't **X** (below) the final product in the reaction of **Q** under the conditions you listed above? Explain in three (or less) sentences and three (or less) structures (4 pts)



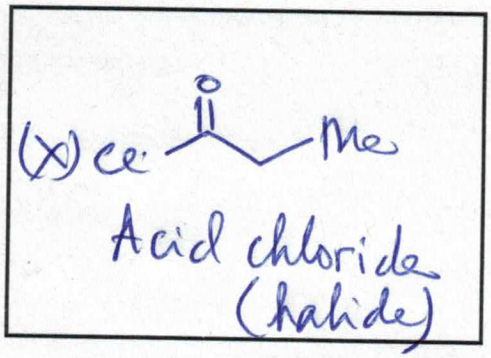
Question 8

Amide bond forming reactions are used regularly in the pharmaceutical industry to make many medicines including the pain medication fentanyl. Fentanyl may be prepared from amine **XX** and acid **YY** through a DCC coupling.

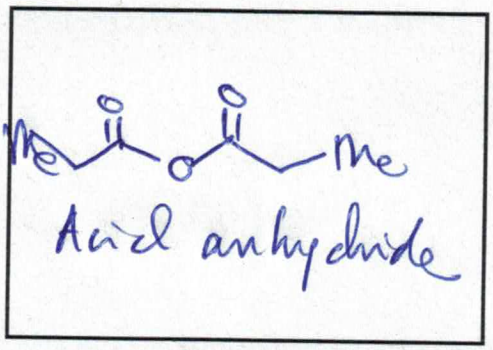


XX **YY** **Fentanyl**

A) Provide the structures of two <u>different</u> "active ester" functional groups that can be prepared from **YY** separate from the one that is generated from DCC. (3 pts each)

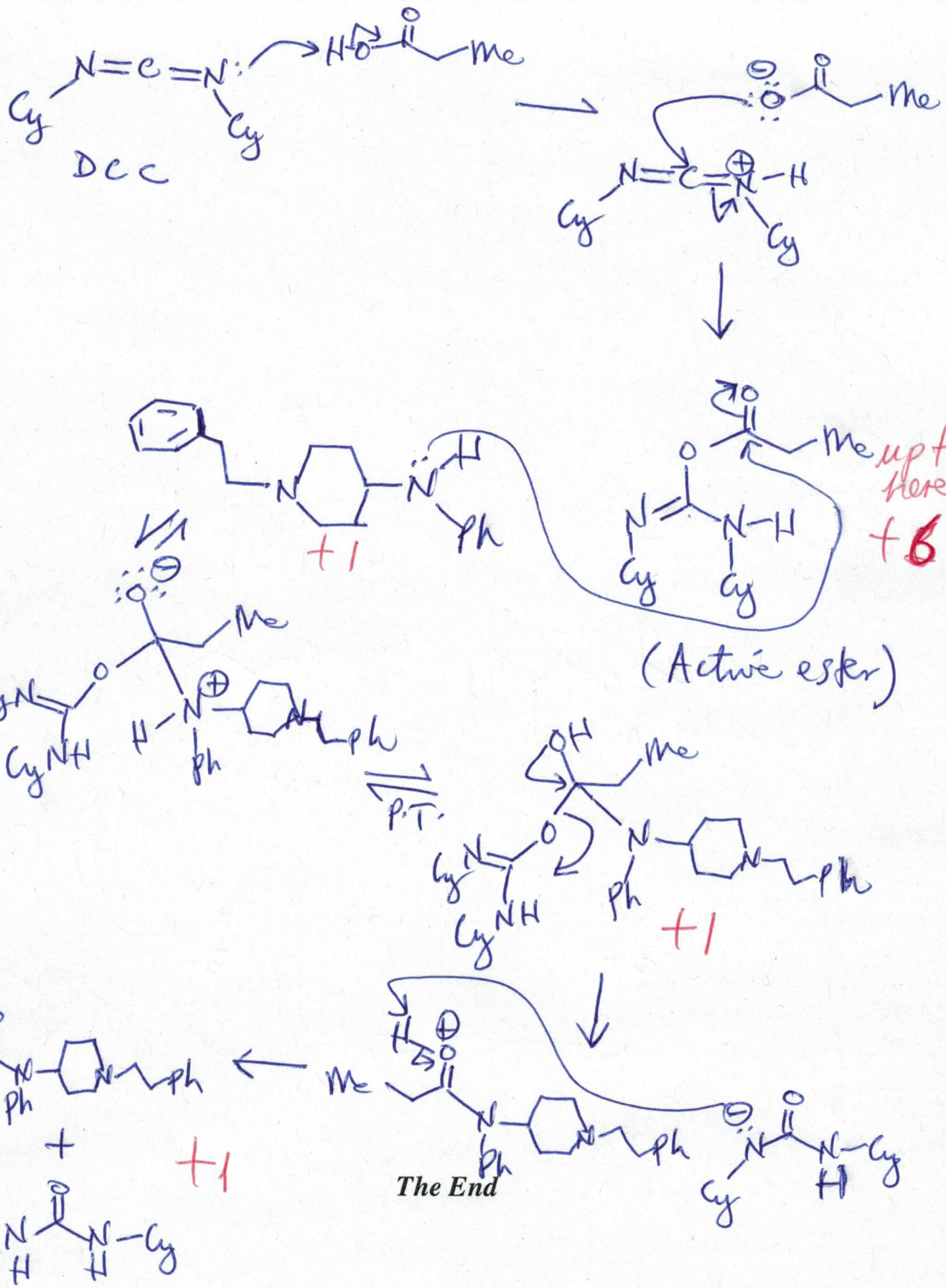


+3



+3

B) <u>One the following page</u>, provide a detailed mechanism for the formation of fentanyl from **XX** and **YY** using DCC. (9 points)


Dcc
+1
up to here
+6
(Active ester)
P.T.
+1
+1
The End