EXAMINATION 2

Chemistry 3B
Professor K. Peter C. Vollhardt
April 2, 1998

Name:_____
[Print first name before second! Use capital letters!]

Please check the name of your TA and corresponding section number. Complete the remaining information if applicable.

111	Jong, Kimmy	____	311	Chan, Gina	____
112	Yun, Shine Sun	____	312	Chiu, Anita	____
113	Toochinda, Tab	____	313	Lemieux, George	____
211	Cho, Joanne	____	411	Upasani, Sayli	____
212	Ong, Angeline	____	412	Ong, Angeline	____
213	Yu, Jerry	____	413	Mar-Tang, Roger	____
301	Chan, Gina	____	511	Wu, Jack	____
302	Goon, Scarlett	____	512	Cho, Joanne	____
303	Wasser, Ian	____	601	Lecture Only	____
Making up an I Grade		____			

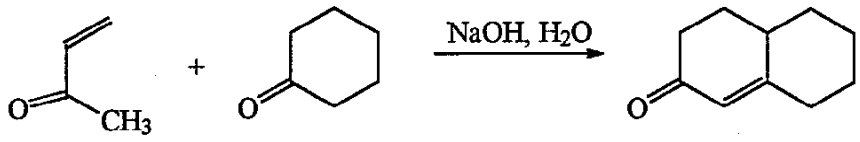
(If you are, please indicate the semester in which you took previous Chem 3B_____)

Please write the answer you wish to be graded in the spaces provided. Do scratch work on the back of the pages. This test should have 14 pages. Check to make sure that you have received a complete exam. A good piece of advice: **read carefully over the questions (at least twice); make sure that you understand exactly what is being asked; avoid sloppy structures or phrases, it is better to be pedantic in accuracy! Good Luck!**

I.	_____	**(20 Points)**
II.	_____	**(50 Points)**
III.	_____	**(50 Points)**
IV.	_____	**(40 Points)**
V.	_____	**(40 Points)**
TOTAL		**(200 Points)**

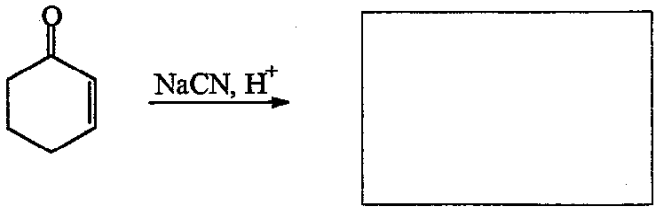
I. [20 Points]

Write the detailed mechanism of the following Robinson annelation.



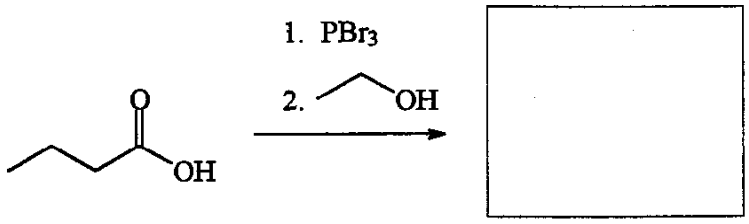
II. [50 Points] Add the missing components (starting materials, reagents, or products) of the following reactions in the boxes provided. Aqueous work-up (when required) is assumed to be part of a step. It is not part of any answer.

(a)

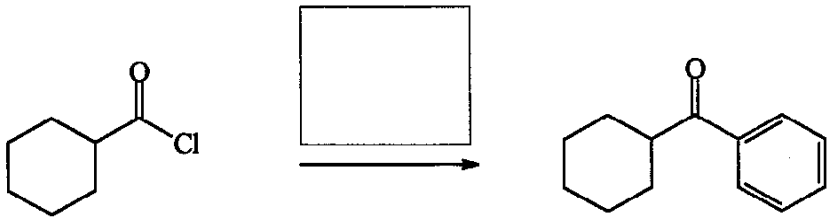


$\tilde{\nu}$ = 1720, 2250 cm^{-1}

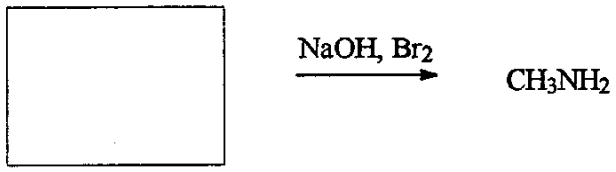
(b)



(c)

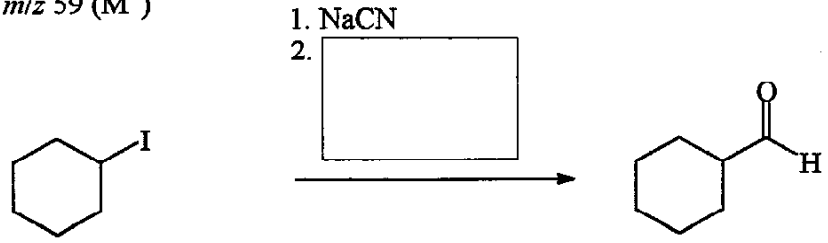


(d)



m/z 59 (M$^+$)

(e)



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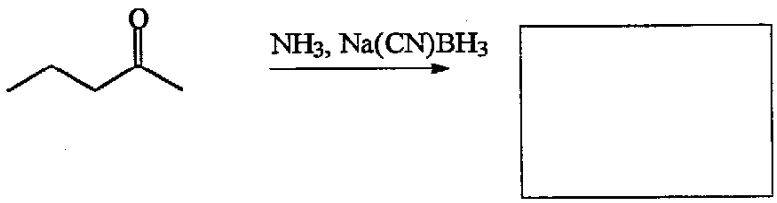
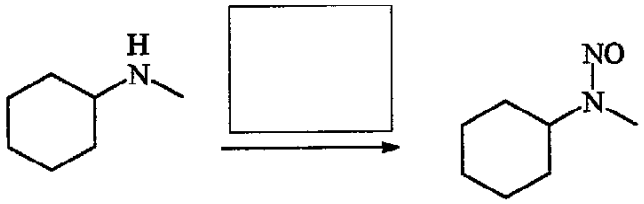
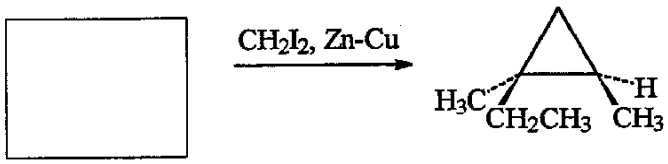
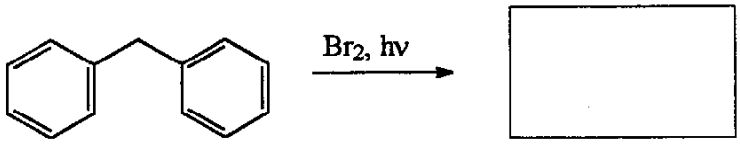
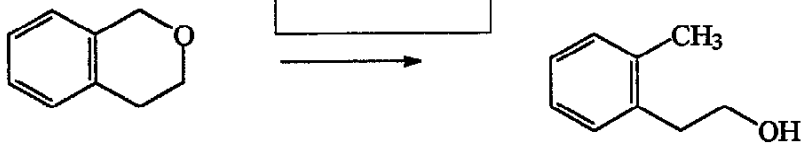
(f) 

(g) 

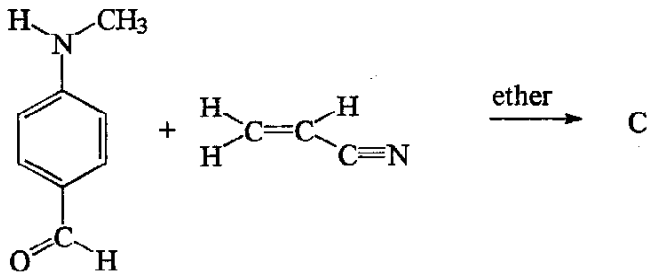
(h) 

(i) 

(j) 

III. [50 Points]

Reaction of A with B gave C in high yield.



A **B**

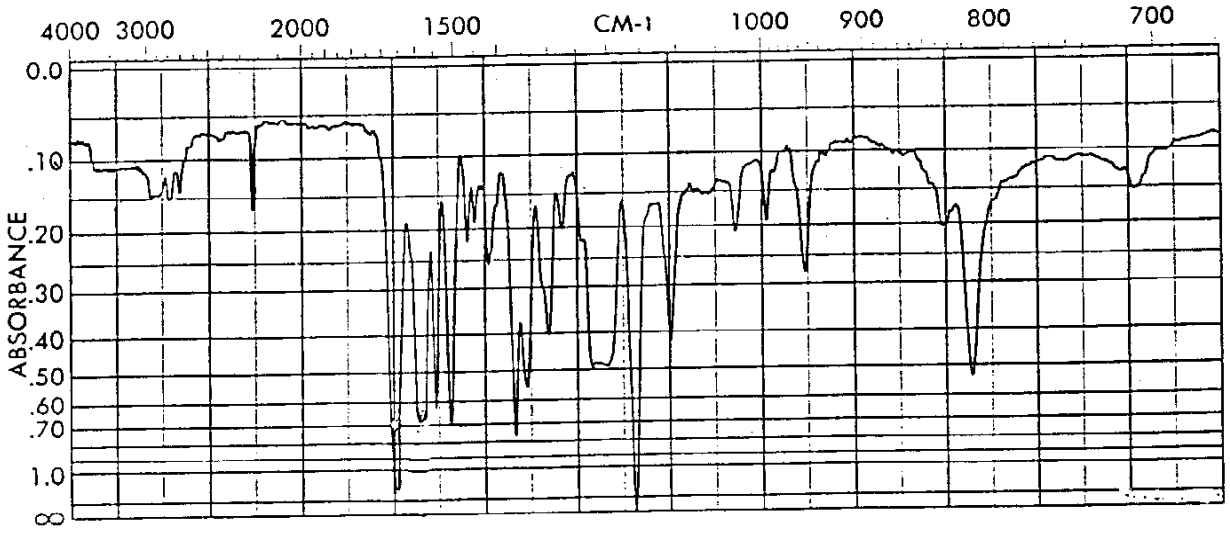
Its spectral data are depicted below.

a. What is C? (Draw in the box provided)

C

b. Interpret the spectral information as requested in the spaces provided.

1. IR spectrum of C



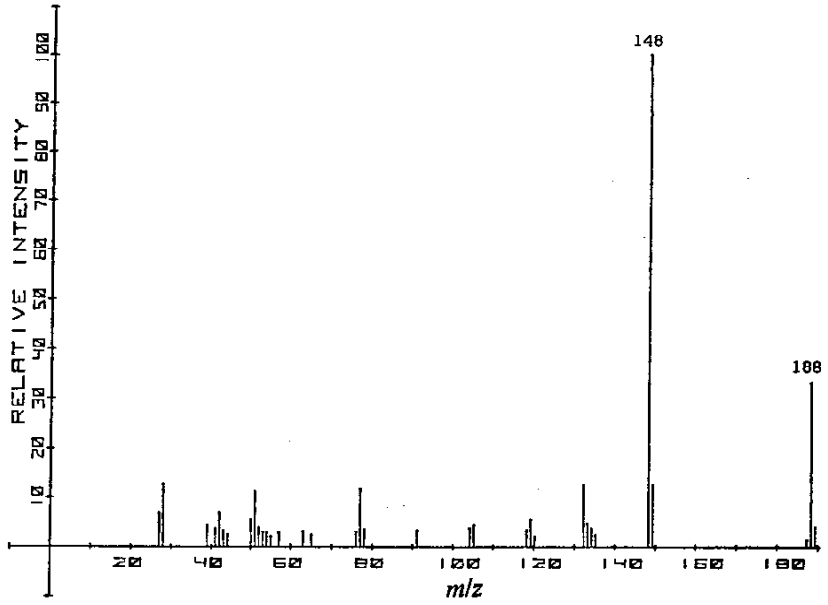
There are three characteristic peaks present in the starting materials only two of which show up in the product. Which are they? (The following refers to the product spectrum above)

peak present in A and C at _____ , due to _____

peak present in B and C at _____ , due to _____

peak present in A but absent in C _____ , due to absence of _____

2. Mass spectrum of C

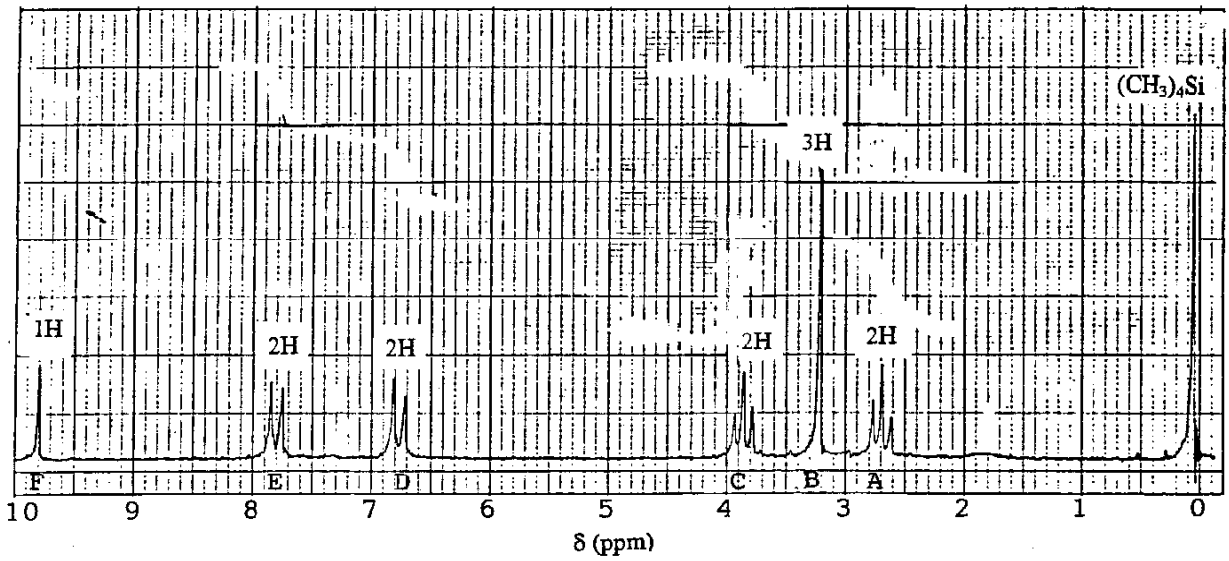


Assign the signals in the boxes provided.

m/z 188 *m/z* 148

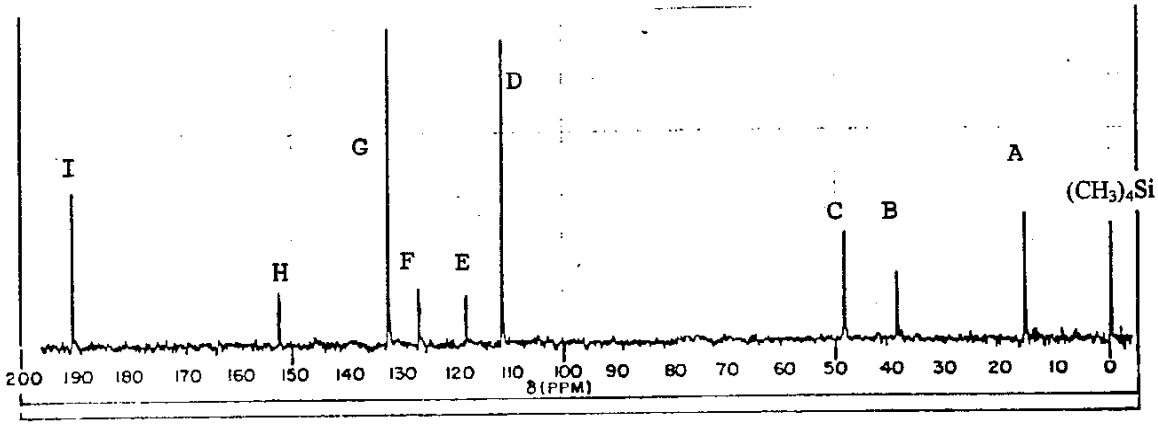
What is the process giving rise to the peak at *m/z* 148? Write an equation.

3. ^{1}H NMR spectrum of C



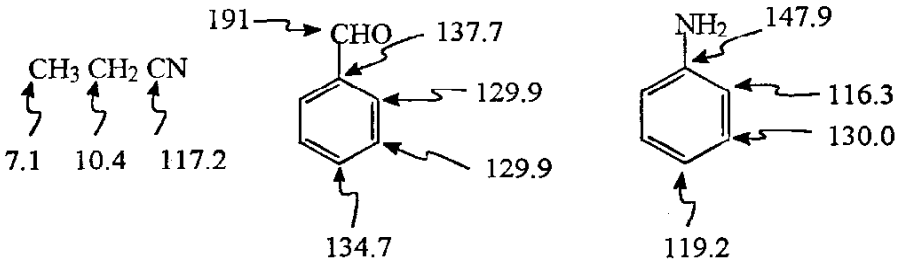
Draw your suggestion for **C** in the box below and label the hydrogens **A, B, C, D, E, F** giving rise to the correspondingly labeled signals in the spectrum.

4. ^{13}C NMR spectrum of C



Draw your suggestion for **C** in the box below and label the carbons **A, B, C, D, E, F, G, H, I** giving rise to the correspondingly labeled signals in the spectrum.

Hints: Consult the following ^{13}C NMR data (ppm) to confirm your assignments.

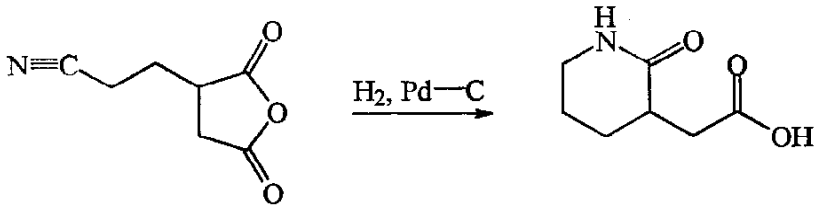


c. Write a plausible mechanism for the formation of **C**.

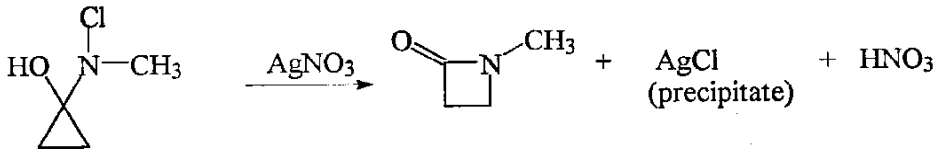
Hint: Recognize that B is an α, β– unsaturated nitrile.

IV. [40 Points] Write detailed mechanisms to explain the following observations.

(a)



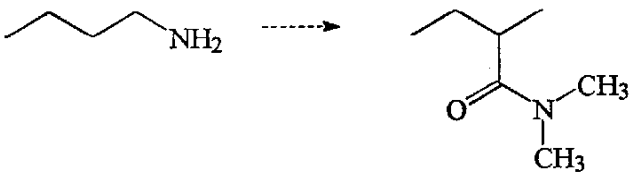
(b) The following is an example of the Stieglitz rearrangement, which provides access to β–lactams.



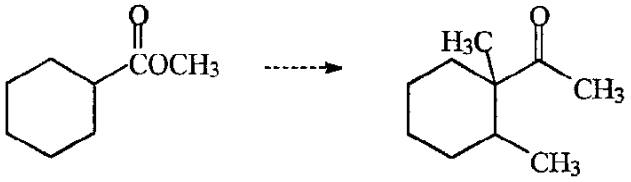
The mechanism is related to that of the Hofmann rearrangement, except that charged species are responsible.

V. [40 Points] Provide a reasonable synthetic route from starting material to product. Note: several steps are required and there may be more than one solution to the problem. You may use any additional organic or organometallic reagents, *containing four carbons or less*, to effect your conversions.

(a)



(b)



(Don't worry about stereochemistry)