FINAL EXAMINATION

Chemistry 3B
Professor K. Peter C. Vollhardt
May 20, 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.

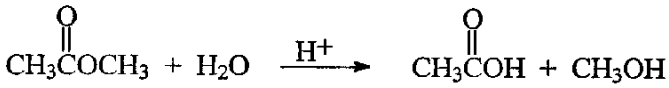
111	Jong, Kimmy	____	311	Chan, Gina	____
112	Yun, Shine Sun	____	312	Chiu, Anita	____
113	Toochinda, Tab	____	313	Lemieux, George	____
211	Cho, Joanne	____	411	Upasani, Sayli	____
212	Ong, Angeline	____	412	Ong, Angeline	____
213	Yu, Jerry	____	413	Mar-Tang, Roger	____
301	Chan, Gina	____	511	Wu, Jack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

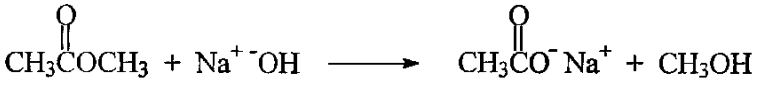
(If you are, please indicate the semester in which you took previous Chem 3B_____)

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 20 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! Grades will be posted 9 am, Monday, May 25, outside 320 Latimer Hall (Lab B). Good luck and have a good summer!**

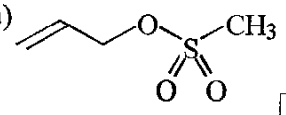
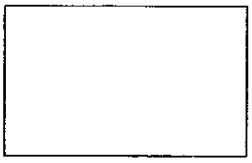
Subtotals				Totals	
IV.	(a) ____	V.	(a) ____	I. ____	(30)
	(b) ____		(b) ____	II. ____	(100)
	(c) ____		(c) ____	III. ____	(90)
				IV. ____	(60)
Total	____	Total	____	V. ____	(60)
				VI. ____	(60)
				Total ____	(400)

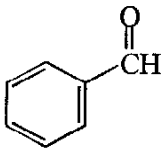
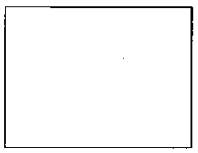
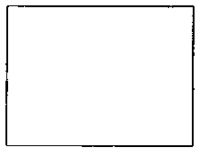
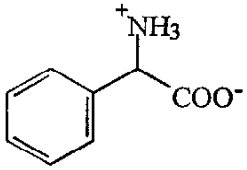
I. [30 Points] Write detailed mechanisms for the hydrolyses of methyl acetate in acid (a) and base (b).

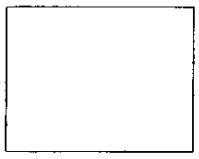
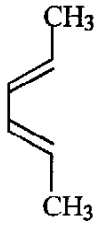
(a) 

(b) 

II. [100 Points; (a) - (j) 5 Points each, (k) - (o) 10 Points each] 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.

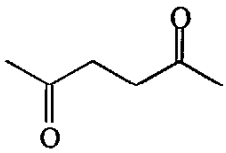
(a)  CH_3OH, $-CH_3SO_3H$ 

(b)  1.  2.  

(c)  Δ 

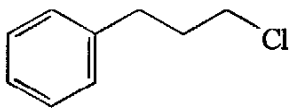
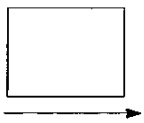
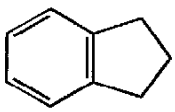
C_6H_{10}

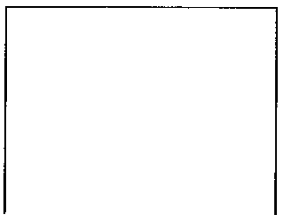
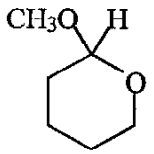
^{13}C NMR : δ 23.4, 32.9, 137.2 ppm

(d)  H^+, H_2O 

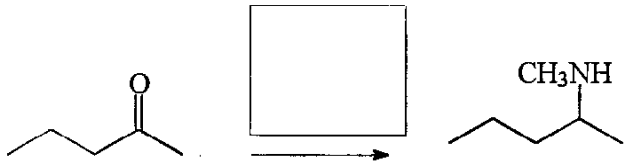
C_6H_8O

^1H NMR : δ = 6.20(s, 2H), 2.01 (s, 6H)

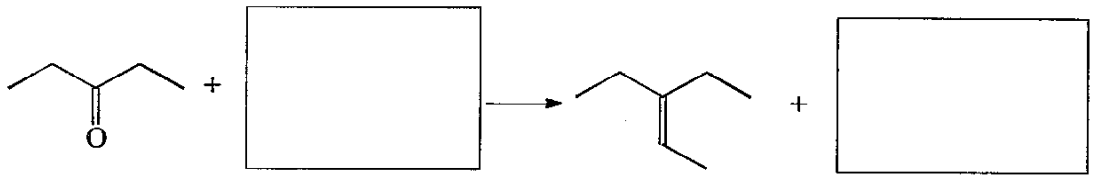
(e)   

(f)  H^+, CH_3OH 

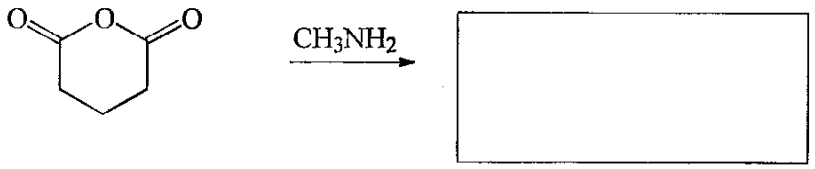
(g)


O
CH3NH

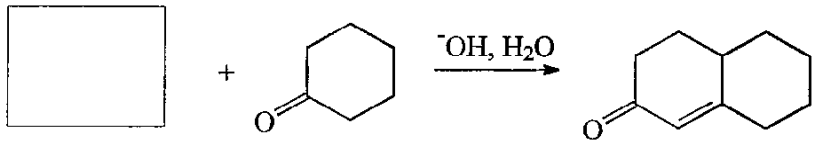
(h)


O
+
+

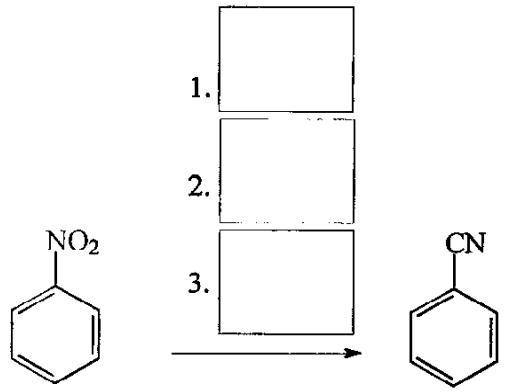
(i)


O
O
O
CH3NH2

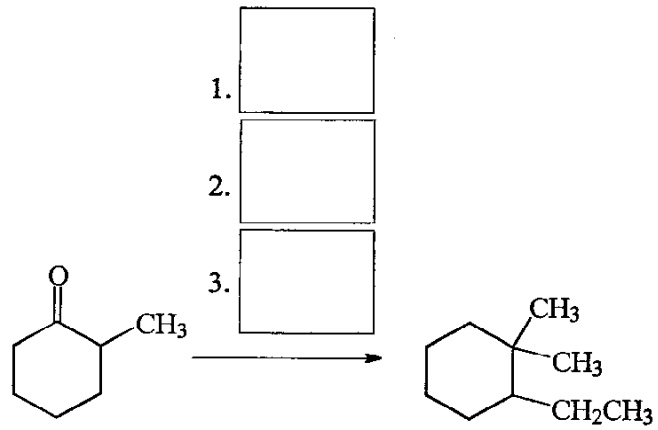
(j)


+
O
-OH, H2O
O

(k)

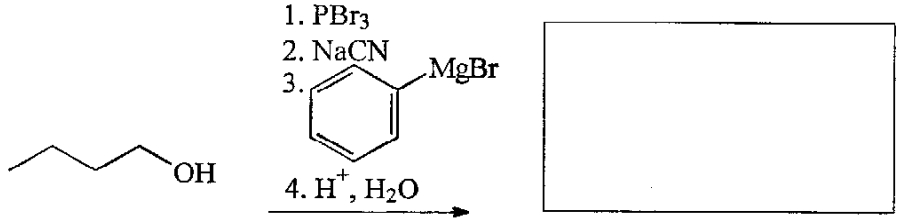

1.
2.
3.
NO2
CN

(l)

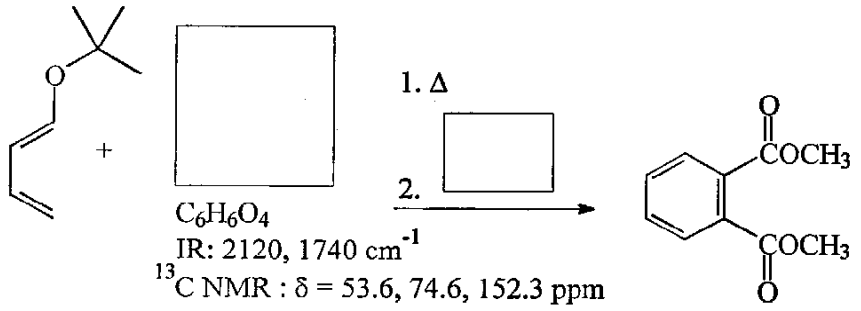

1.
2.
3.
O
CH3
CH3
CH3
CH2CH3

Chemistry 3B, Final Examination

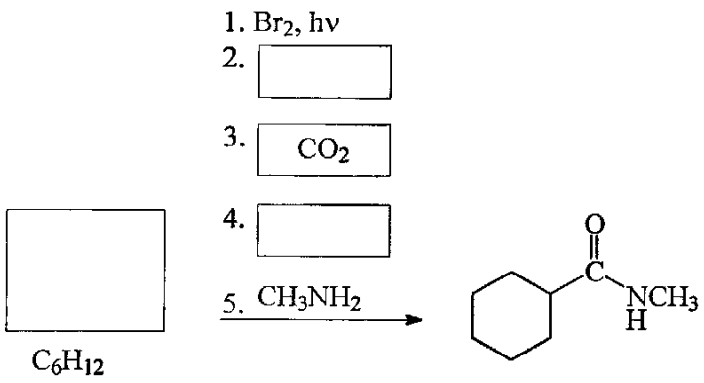
(m)



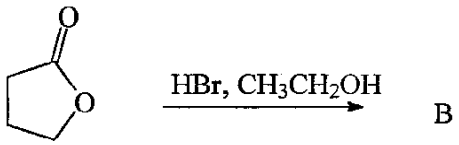
(n)



(o)



III. [90 Points] Treatment of lactone A with HBr in ethanol gave a new compound B.



A

Its spectral data are depicted below.

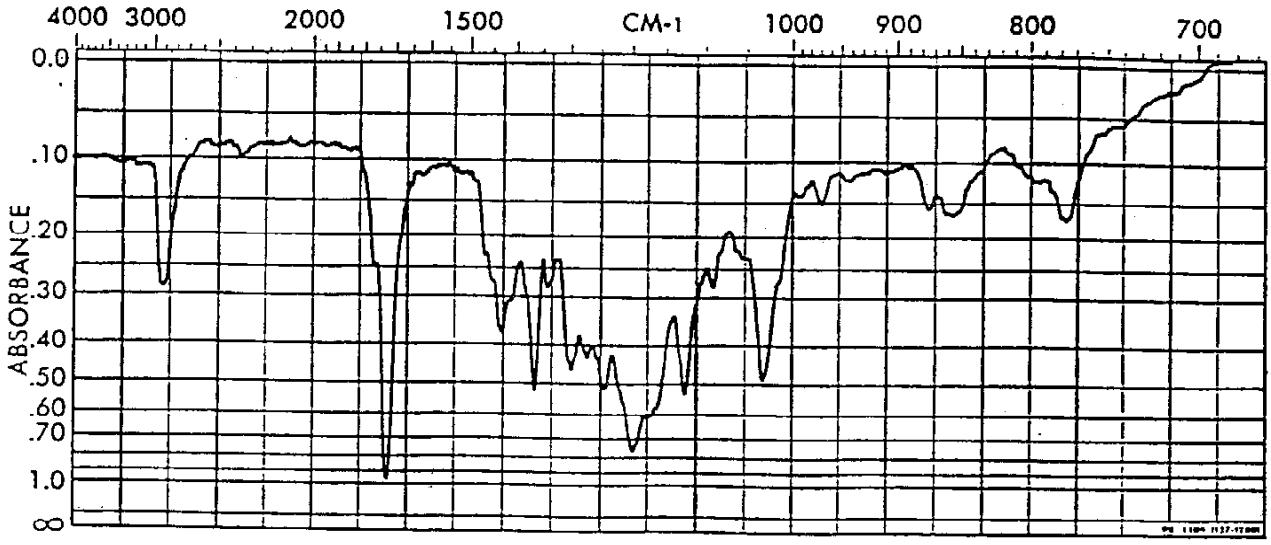
(a) What is B? (Draw in the box provided.)

C

B

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

1. IR spectrum of B

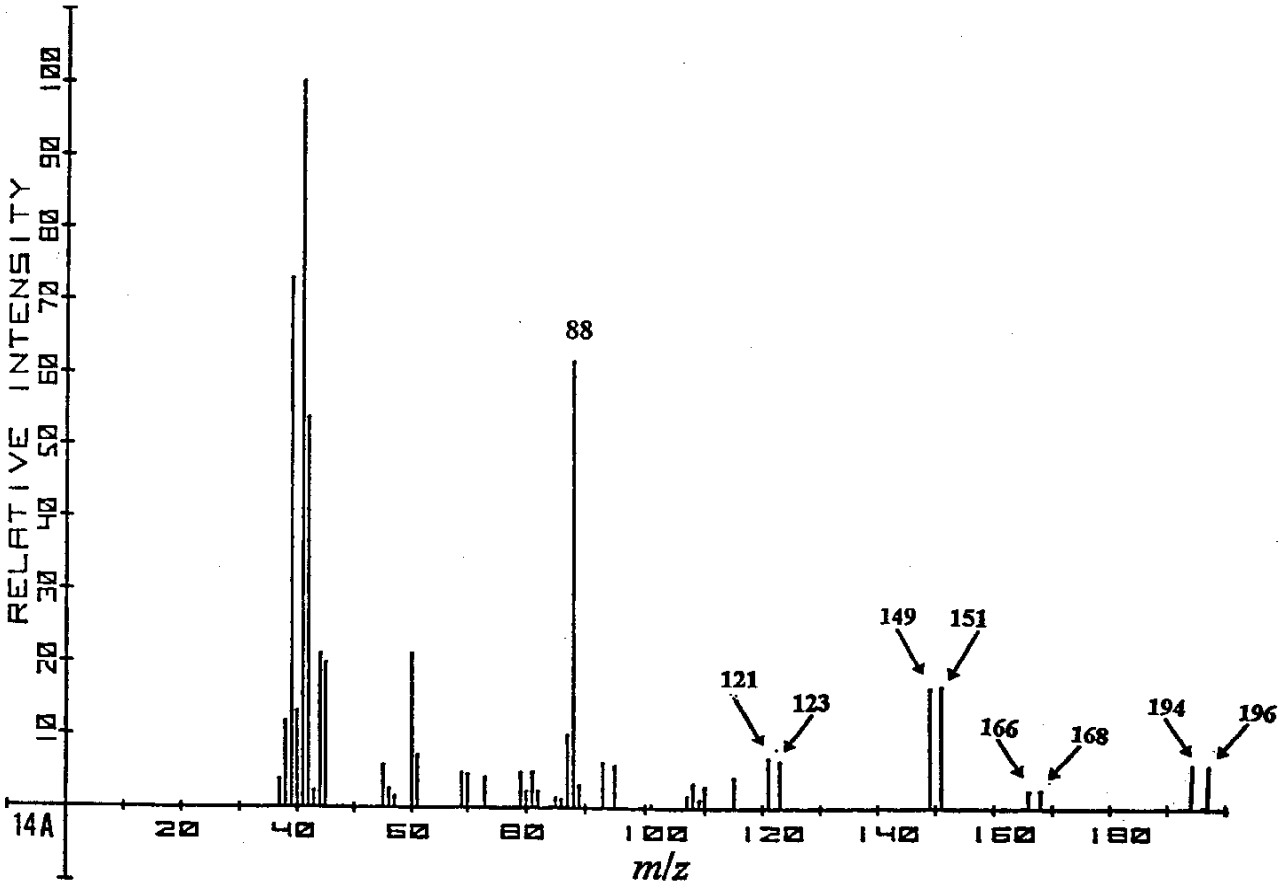


Assign the following peaks to their respective (vibrating) bonds:

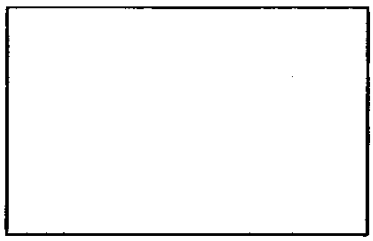
Peak at 2900 cm^{-1} due to

Peak at 1700 cm^{-1} due to

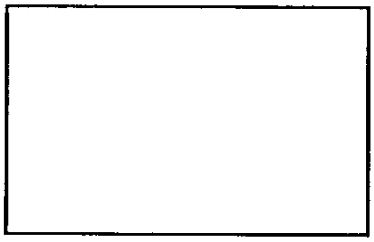
2. Mass spectrum of B



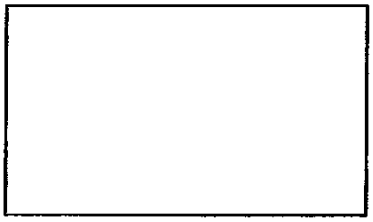
Assign the signals in the boxes provided. (**Hints**: 1. Br exists as two isotopes 79 and 81, in a 1:1 ratio. 2. Think McLafferty rearrangements and α-cleavages.)



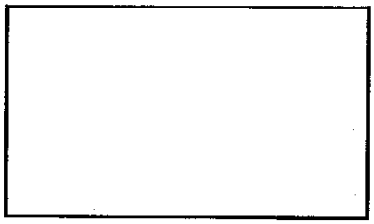
m/z 194, 196 (1:1)



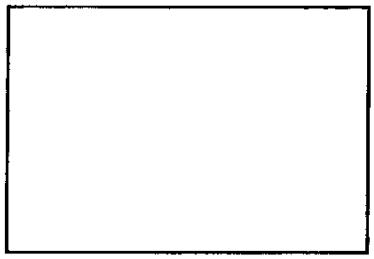
m/z 166, 168 (1:1)



m/z 149, 151 (1:1)

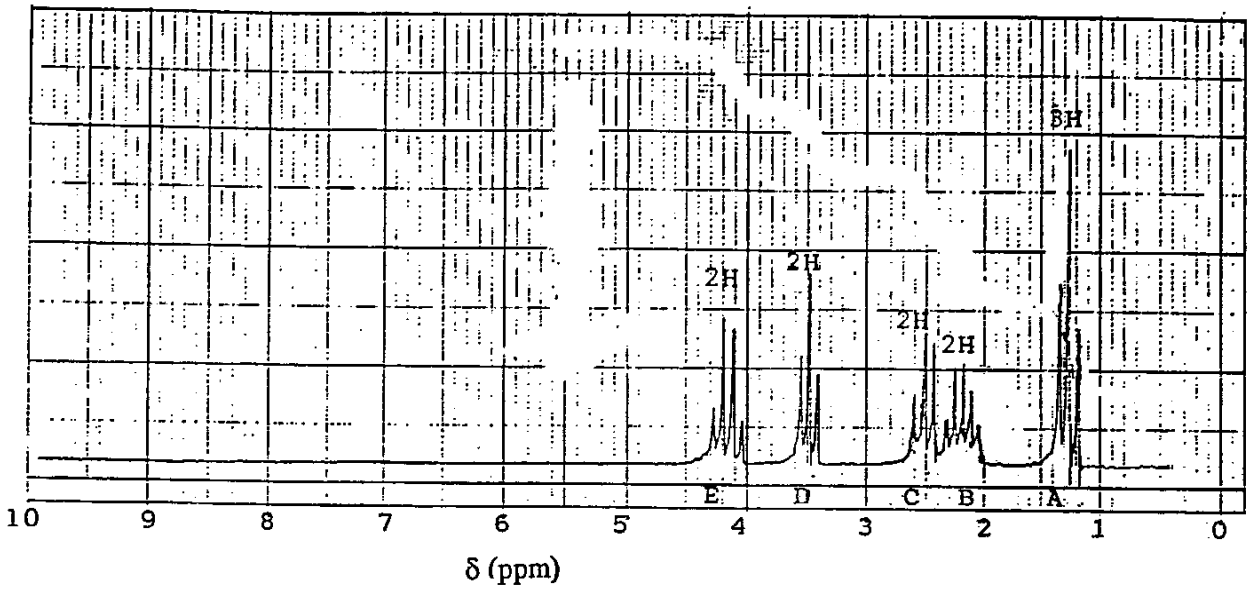


m/z 121, 123 (1:1)



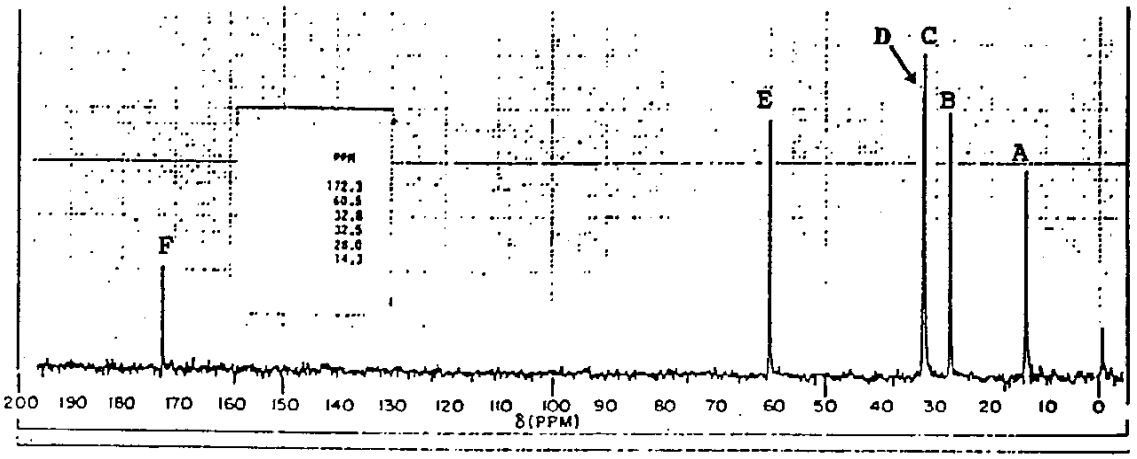
m/z 88

3. ^{1}H NMR Spectrum of B



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

4. ^{13}C NMR spectrum of B

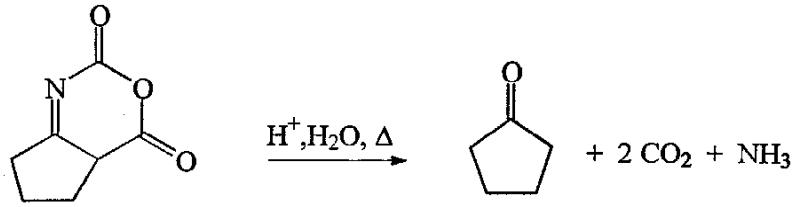


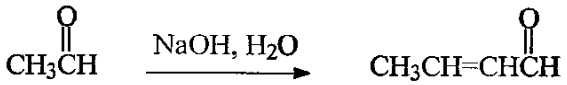
Note that there are six signals (see chemical shift table in the insert).

Draw your suggestion for B in the box below and label the carbons A, B, C, D, E, F giving rise to the correspondingly labeled (above the signals) peaks in the spectrum.

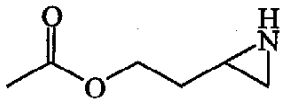
(c) Write a mechanism for the formation of B.

IV. [60 Points] Write detailed mechanisms to explain the following observations.

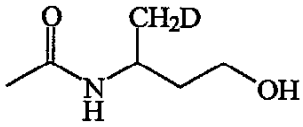
(a) 

(b) 

(c)

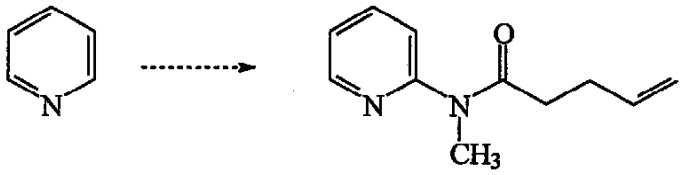


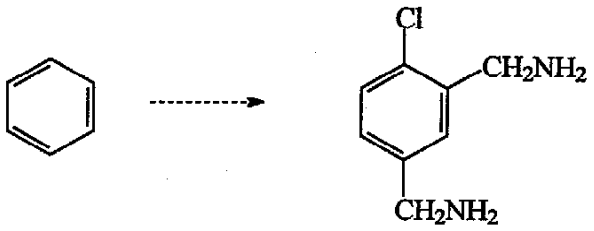
1. $LiAlD_4$
2. H^+, H_2O (work up)

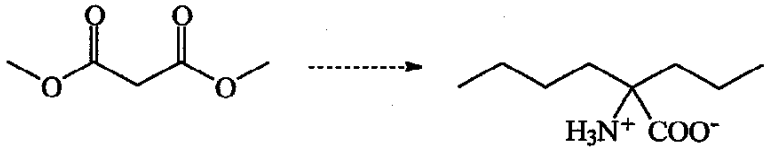


V. [60 Points] Provide a reasonable synthetic route from starting material to product. Note: several steps are required and there may be more than one solution to the problem. You may use any additional organic or organometallic reagents, *containing four carbons or less*, to effect your conversions.

(a)



(b) 

(c) 

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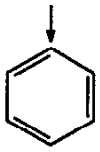
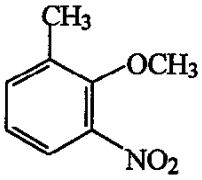
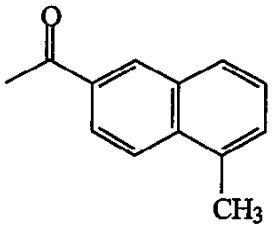
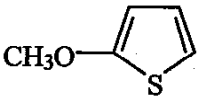
p. 20 not included (no questions)

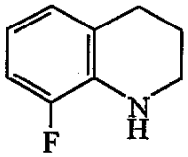
VI. [60 Points]

(a) Mark with an arrow, e.g.  , the site of preferential electrophilic attack in the following molecules.

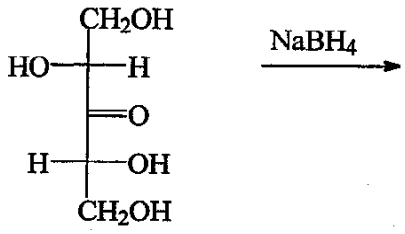








(b) The ketopentose A gives only one compound on reduction with $NaBH_4$ (draw in the box below). Explain. Is the product optically active? (circle the correct answer)



Product

optically active: yes ☐ ; no ☐

(c) Among the following compounds, circle the ones which are aromatic.