EXAMINATION 2

Chemistry 3B
Professor K. Peter C. Vollhardt
April 20, 1993

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:

101 Amy Feng	_____	312 Scott Seidel	_____
111 Sonny Lee	_____	313 Sat Ida	_____
112 Scott Seidel	_____	411 Julie Duncan	_____
113 Fabienne Berree	_____	412 Mareia Frost	_____
211 Julie Duncan	_____	413 Rodney Harl	_____
212 Son Pham	_____	511 Jerry Limb	_____
301 Sat Ida	_____	512 Jared Shaw	_____
311 Eric Fallon	_____	513 Tom Woiwode	_____
000 Lecture Only	_____	703 Dave Auerbach	_____
		704 Kevin Cammack	_____

Making up an I Grade _____
(If you are, please indicate the semester in which you took previous Chem 3B or 8B_____)

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 13 numbered 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.	_____	(30)
II.	_____	(50)
III.	_____	(40)
IV.	_____	(30)
V.	_____	(50)
TOTAL	_____	(200)

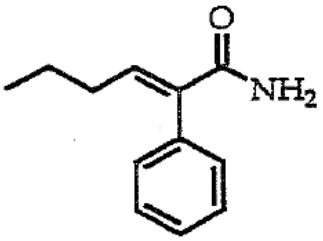
(30 Points)

Name (IUPAC) or draw, as appropriate, the following molecules, including their stereochemistry.

a.

N-Ethyl-2-propen-1-amine

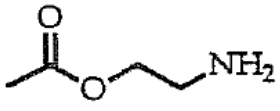
b.

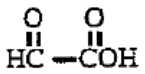


c.

(2-Bromophenyl)methanol

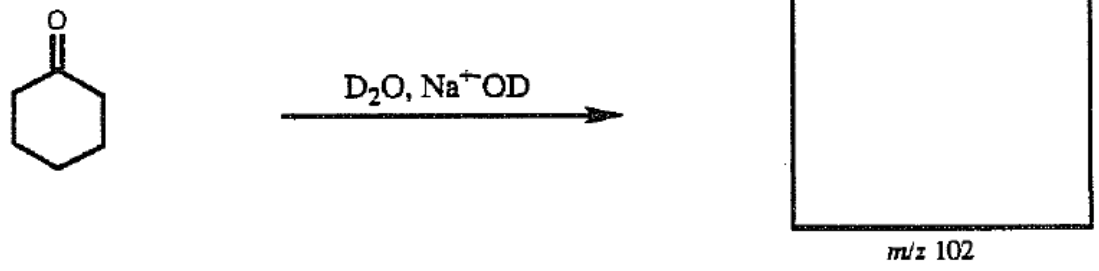
d.



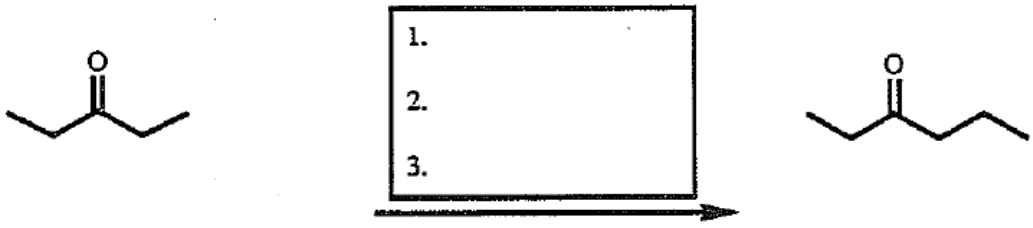
e. 

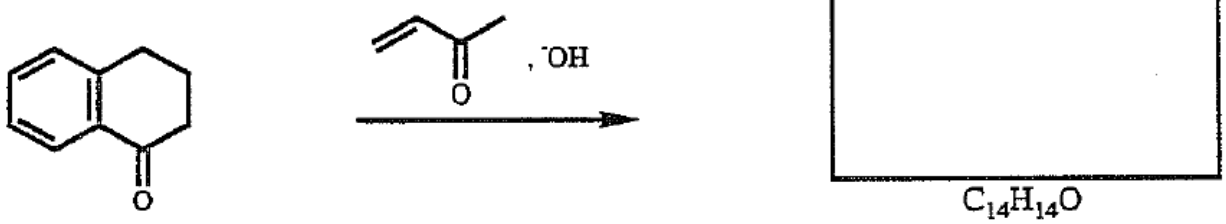
II. (50 Points)

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.

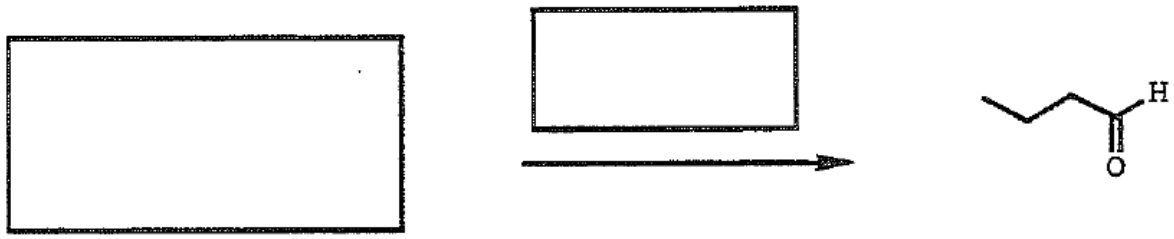
a. 

m/z 102

b. 

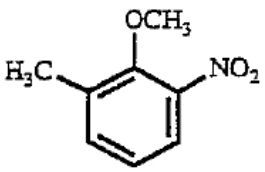
c. 

$C_{14}H_{14}O$

d. 

C_4H_7ClO

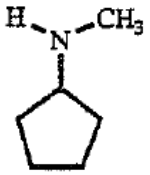
e.



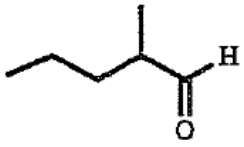
HNO_3, H_2SO_4 →

f.

→



g.



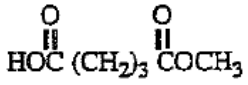
1. $NaCN$, H_2SO_4
2. H_2O, H^+, Δ →

m/z 146, IR $\tilde{\nu}$ = 3250, 1730 cm^{-1}

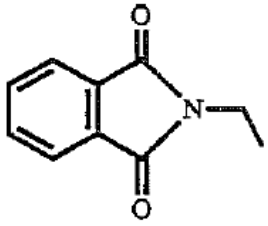
h.

$C_5H_6O_3$

CH_3OH, H^+ →

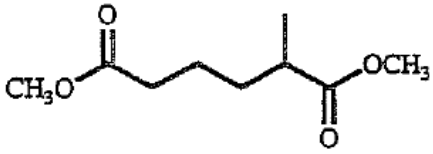


i.



$LiAlH_4$ →

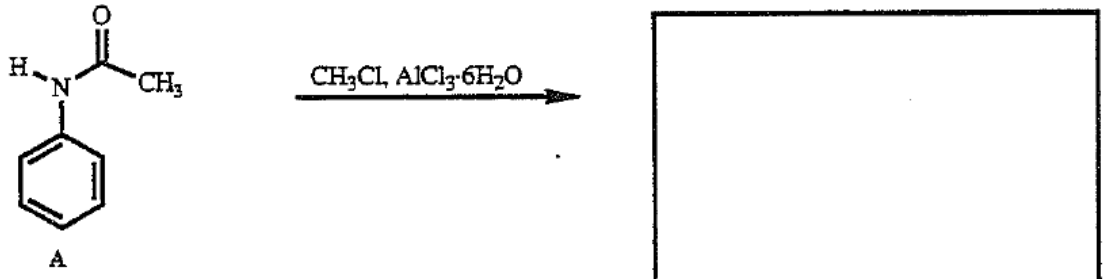
j.



$Na^{+-}OCH_3$, CH_3OH →

III. (40 Points)

A graduate student attempted the Friedel-Crafts methylation of the protected benzenamine A. By mistake, he used hydrated (instead of anhydrous) "$AlCl_3 \cdot 6H_2O$" resulting in a mixture of compounds. A minor component **B** of the latter (b.p. 214°C) gave the spectral data shown.

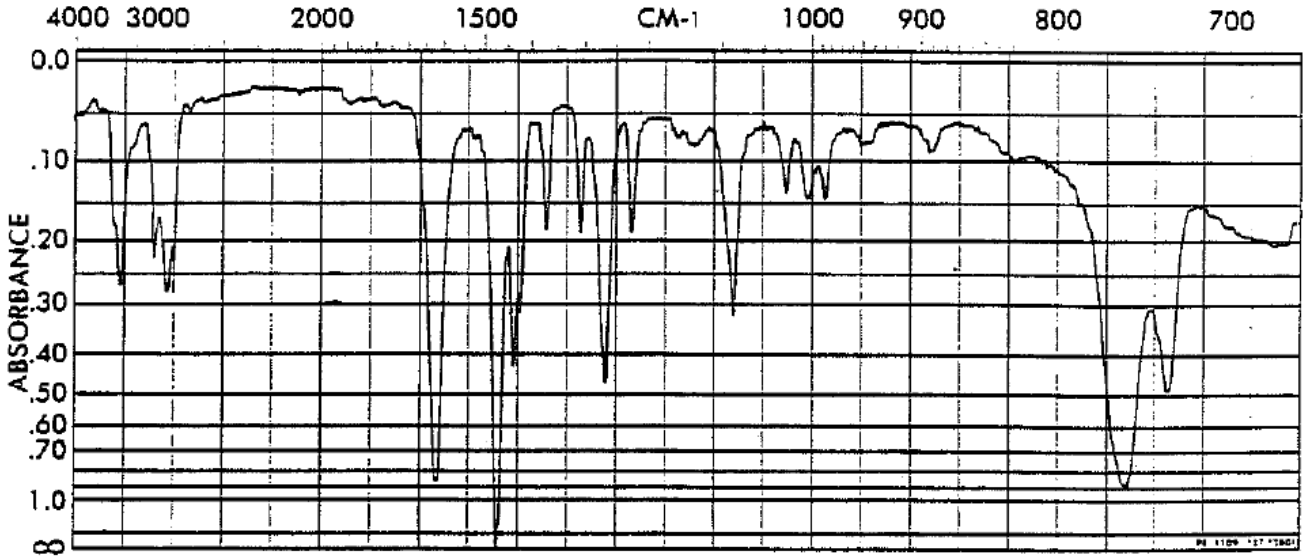


A

B

What is **B**? Interpret the spectral data as requested.

1. IR Spectrum



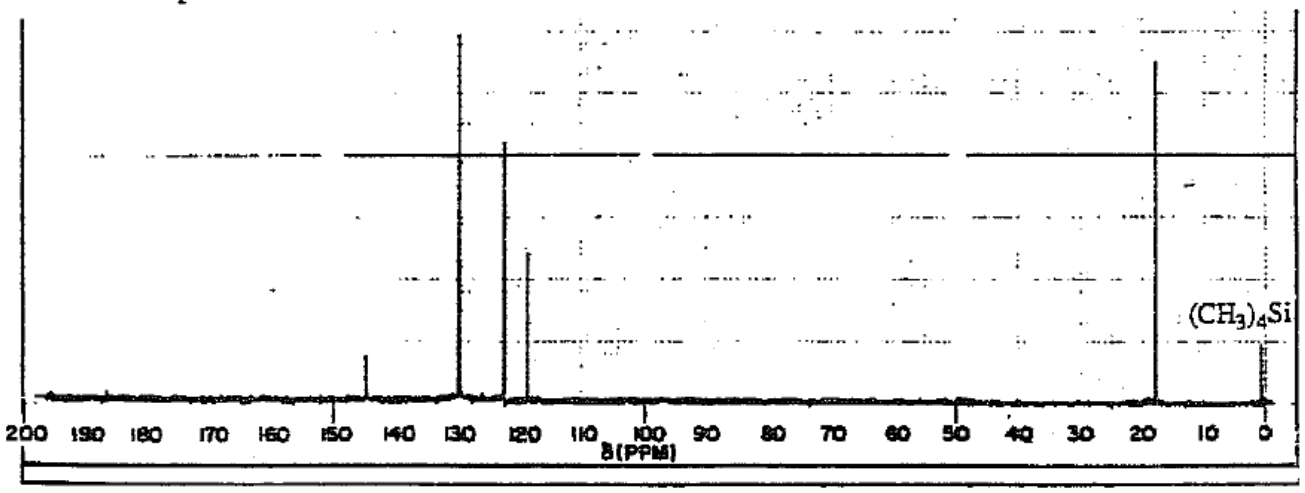
Assign the indicated three sets of absorptions above 2800 cm^{-1} to three types of stretching vibrations:

a. at 3400 cm^{-1}:

b. at 3030 cm^{-1}:

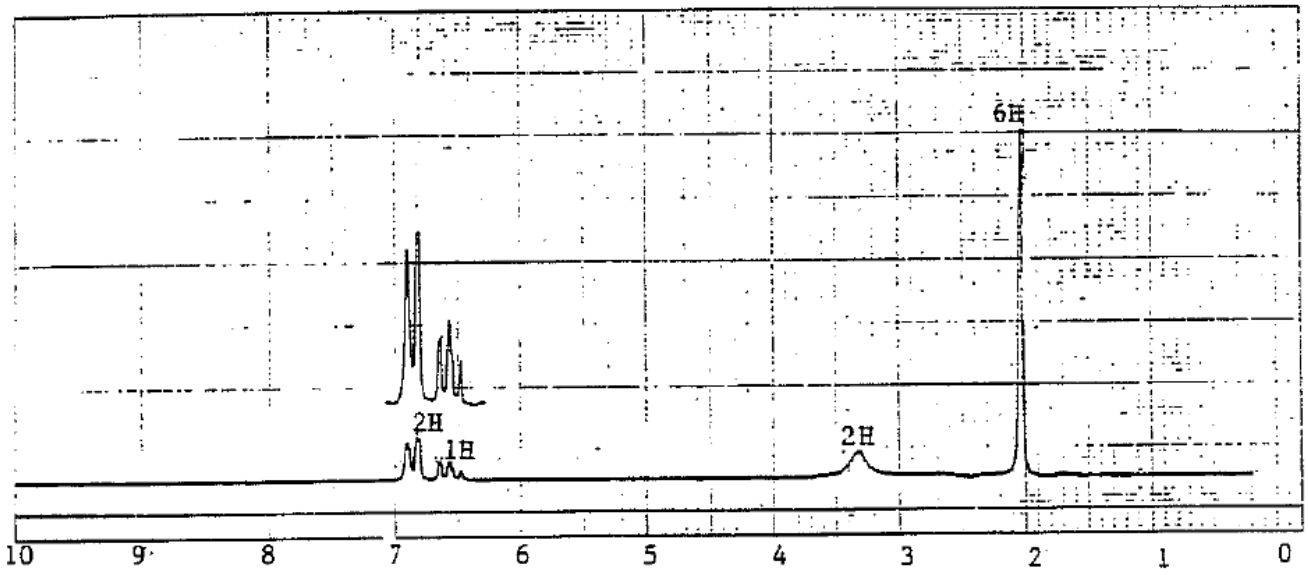
c. at 2910 cm^{-1}:

2. ^{13}C NMR Spectrum



Number of lines, chemical shift assignments.

3. ^{1}H NMR Spectrum

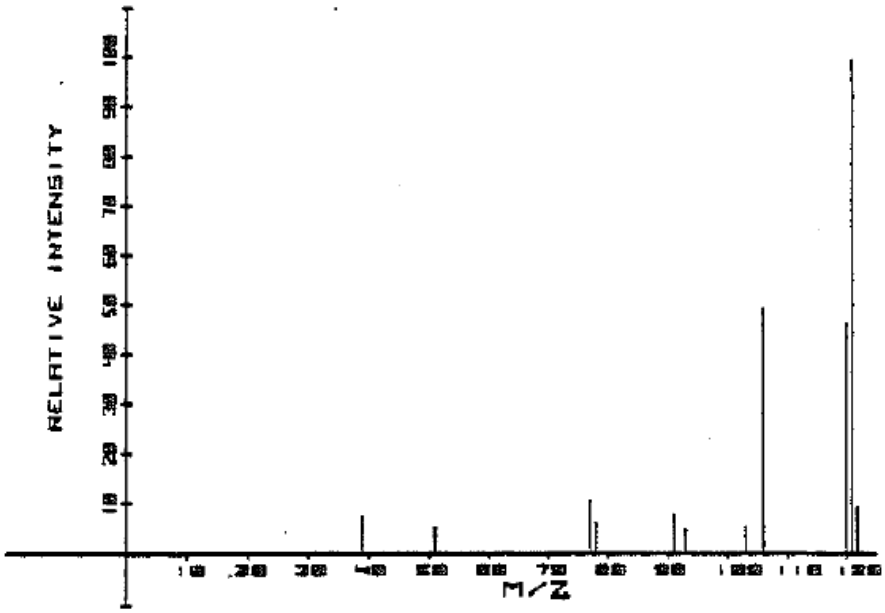


Integration, chemical shifts, multiplicities of absorptions.

4. UV Spectrum: λ_{max} 291 nm (log ε = 3.2).

   Assign the chromophore.

5. Mass Spectrum



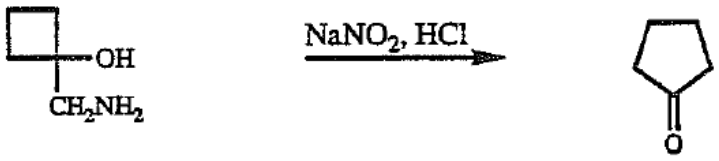
Assign the signals at *m/z* 122, 121, 120, 106, and 91.

6. Explain by a mechanism how B may have been formed from A.

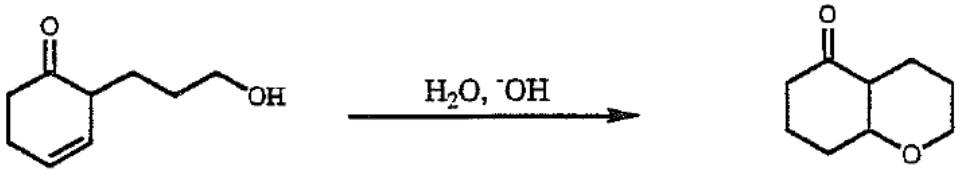
IV. (30 Points)

Write a detailed mechanism to explain of the following transformations.

a.



b.

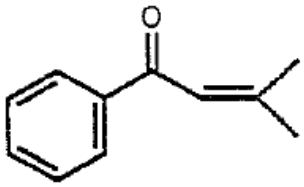


V. (50 Points)

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 to effect your conversions. Try to work backwards from the product.

a.

Hint: for a quick solution, use the Mannich reaction.

b. CH_3CH_2OH,  , $CH_3\overset{O}{\overset{\|}{C}}CH_3$ ----> 

You have to use the three given starting materials as reagents at some stage of your scheme.

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III.	_____	(40)
IV.	_____	(30)
V.	_____	(50)
TOTAL	_____	(200)

(30 Points)

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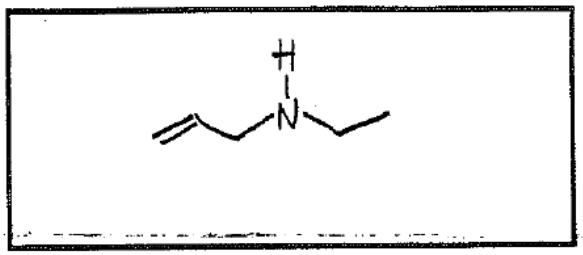
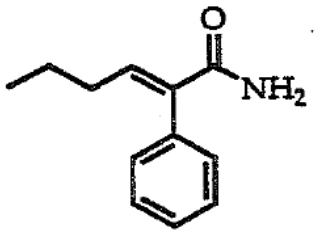
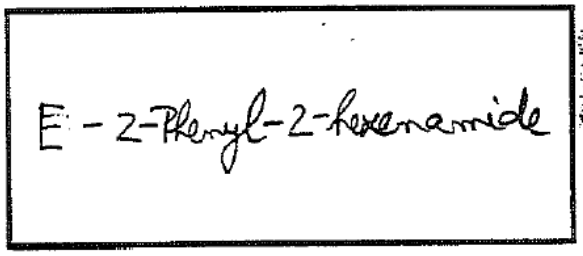


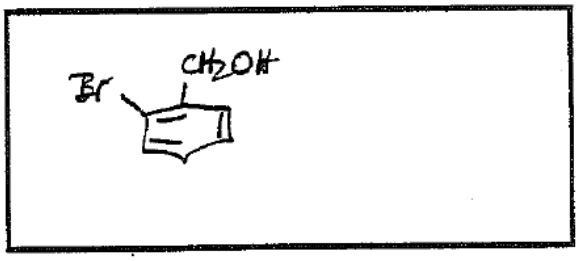
b.



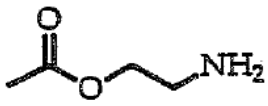


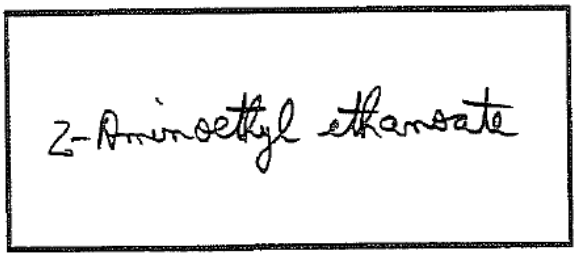
c.

(2-Bromophenyl)methanol



d.



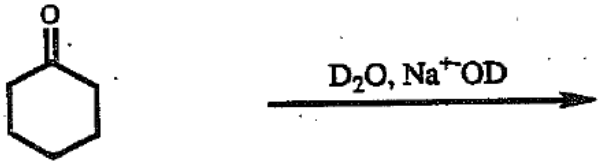


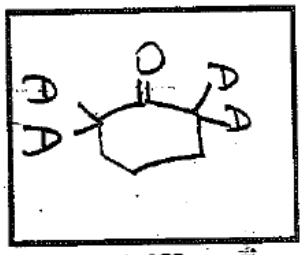
e. 

2-Oxoethanoic acid
Oxoethanoic acid O.K.

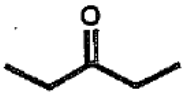
II. (50 Points)

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.

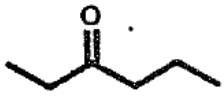
a. 

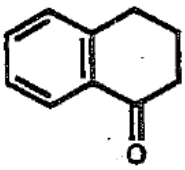


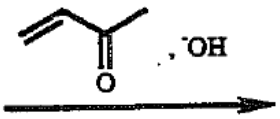
m/z 102

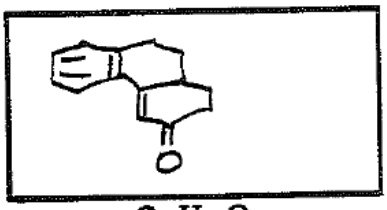
b. 

1. Cl_2, HCl
2. LDA
3. $(CH_3)_2CuLi$

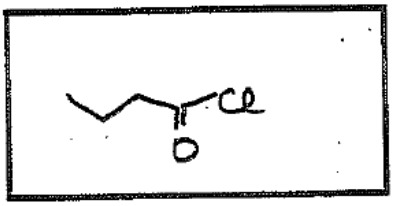


c. 



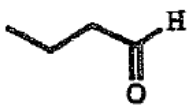


$C_{14}H_{14}O$

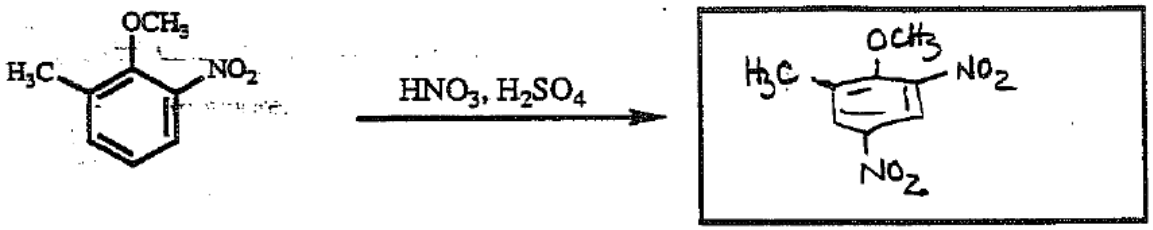
d. 

C_4H_7ClO

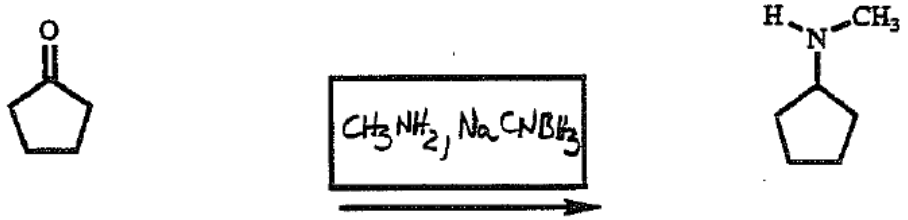
$LiAl(OR)_3H$



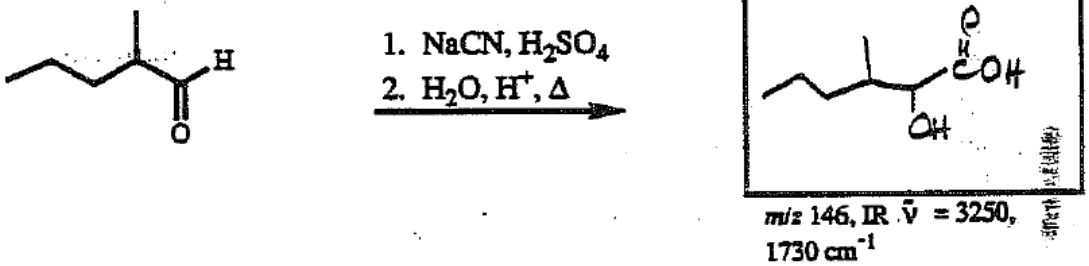
e.



f.

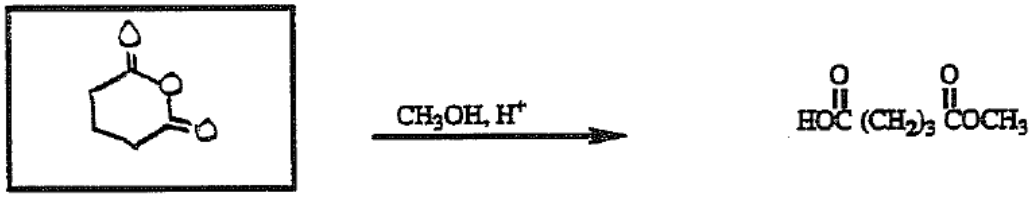


g.



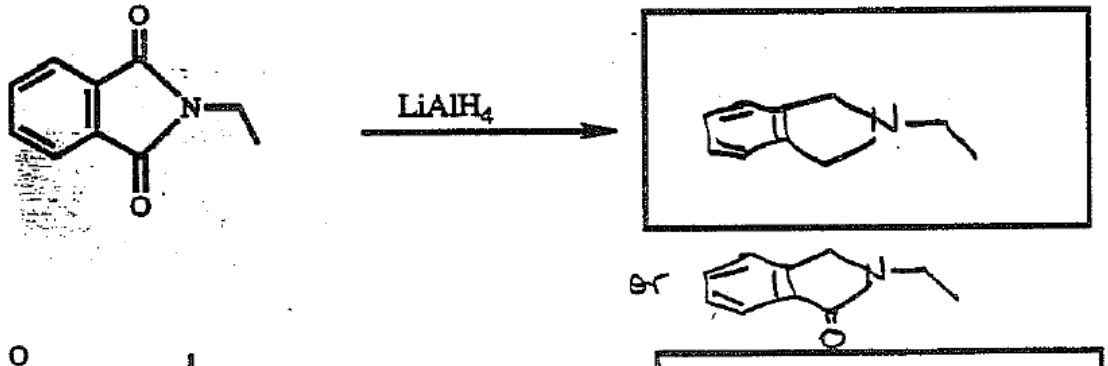
m/z 146, IR $\tilde{\nu}$ = 3250, 1730 cm^{-1}

h.

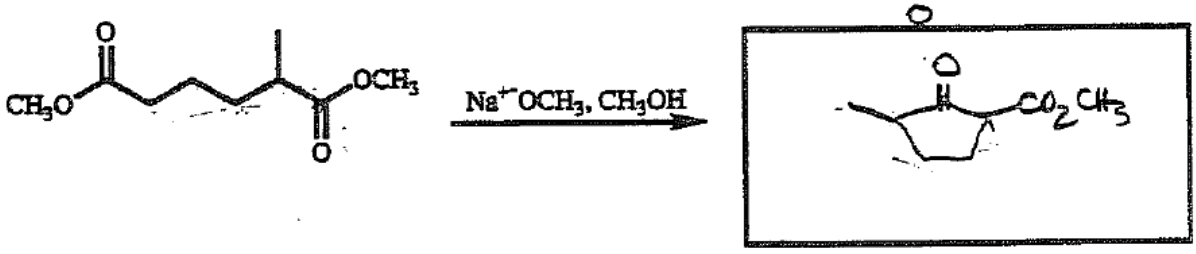


$C_5H_6O_3$

i.

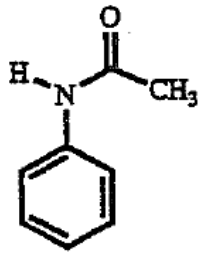


j.

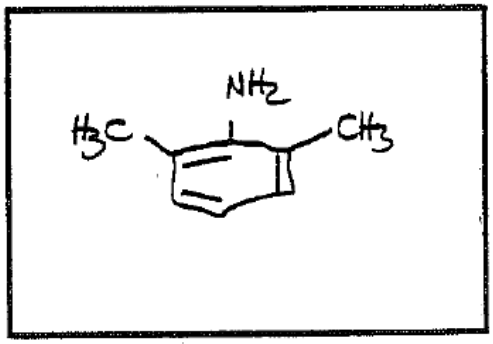


III. (40 Points)

A graduate student attempted the Friedel-Crafts methylation of the protected benzenamine A. By mistake, he used hydrated (instead of anhydrous) "$AlCl_3 \cdot 6H_2O$" resulting in a mixture of compounds. A minor component B of the latter (b.p. 214°C) gave the spectral data shown.



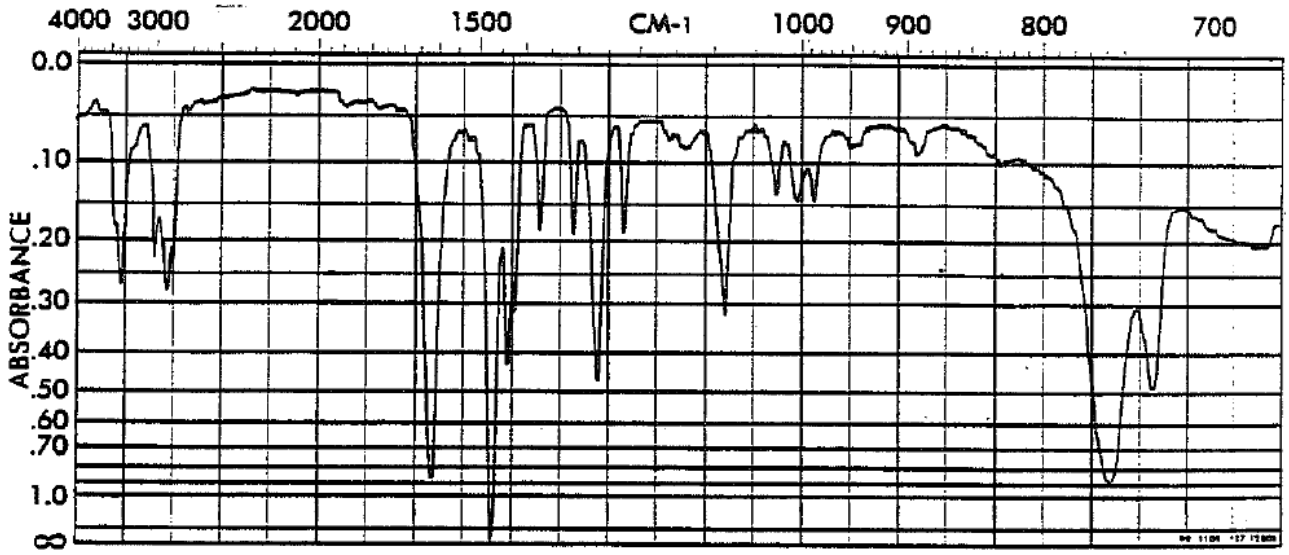
A



B

What is B? Interpret the spectral data as requested.

1. IR Spectrum



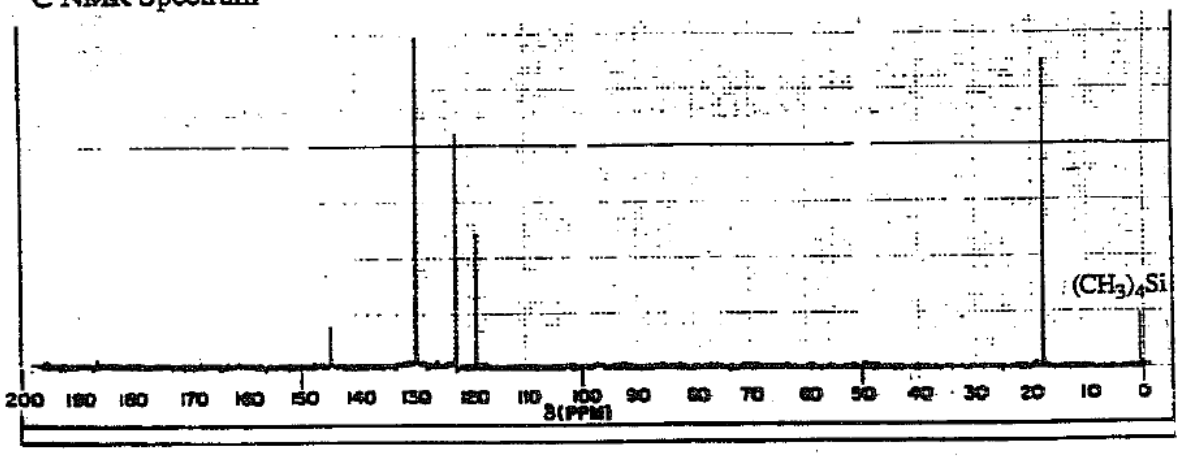
Assign the indicated three sets of absorptions above 2800 cm^{-1} to three types of stretching vibrations:

a. at 3400 cm^{-1}: $\tilde{\nu}_{N-H}$ stretch

b. at 3030 cm^{-1}: $\tilde{\nu}_{arom\ C-H}$ stretch

c. at 2910 cm^{-1}: $\tilde{\nu}_{CH_3}$ stretches

2. ^{13}C NMR Spectrum

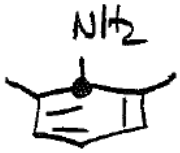


Number of lines, chemical shift assignments.

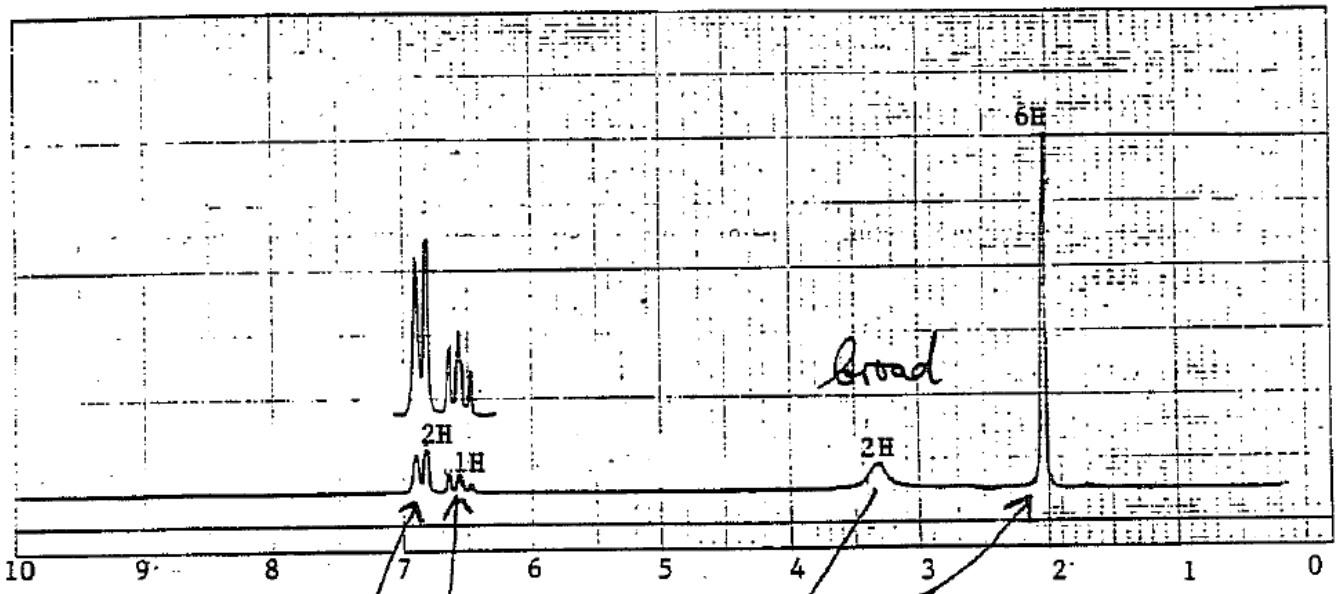
4 aromatics, 1 methyl

symmetrical 1,2,3 substitution

Peak at 145 deshielded



3. ^{1}H NMR Spectrum

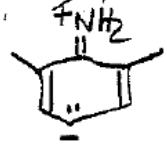


Integration, chemical shifts, multiplicities of absorptions.

doublet (one neighbor)

triplet (2 equiv. neighbors)

relatively shielded because of resonance



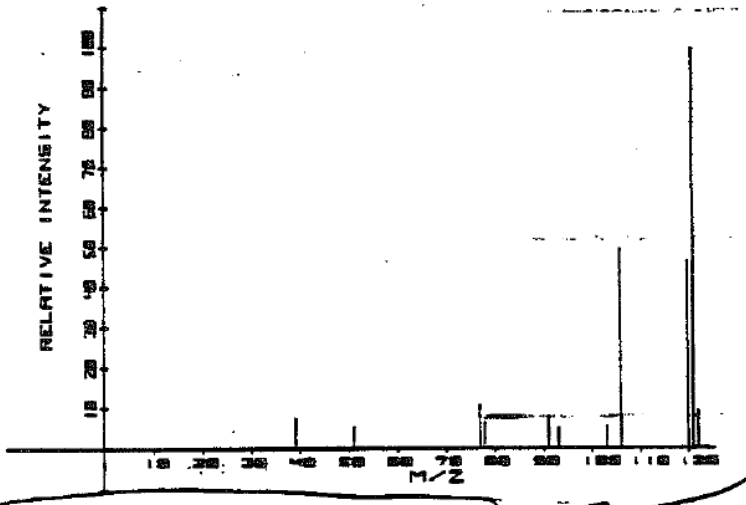
J = ortho coupling

4. UV Spectrum: λ_{max} 291 nm (log ε = 3.2).

   Assign the chromophore.

   aromatic

5. Mass Spectrum



Assign the signals at *m/z* 122, 121, 120, 106, and 91.

M+-(2CH3)

M+-1 (loss of H from C

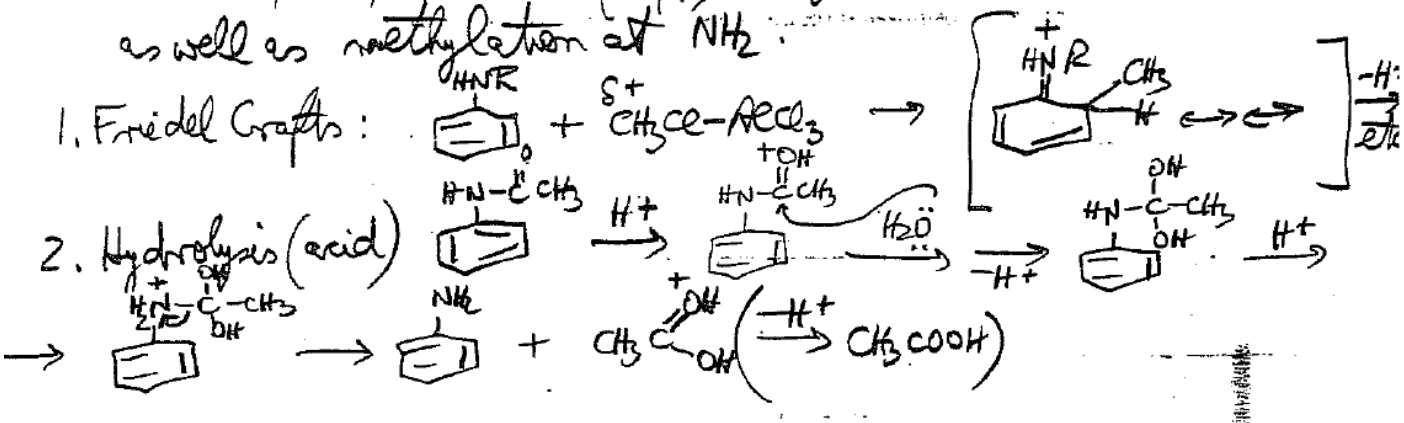
M+1 (8C, 8%)

M+ (odd, because of N)

M+-CH3

6. **Explain by a mechanism how B may have been formed from A.**

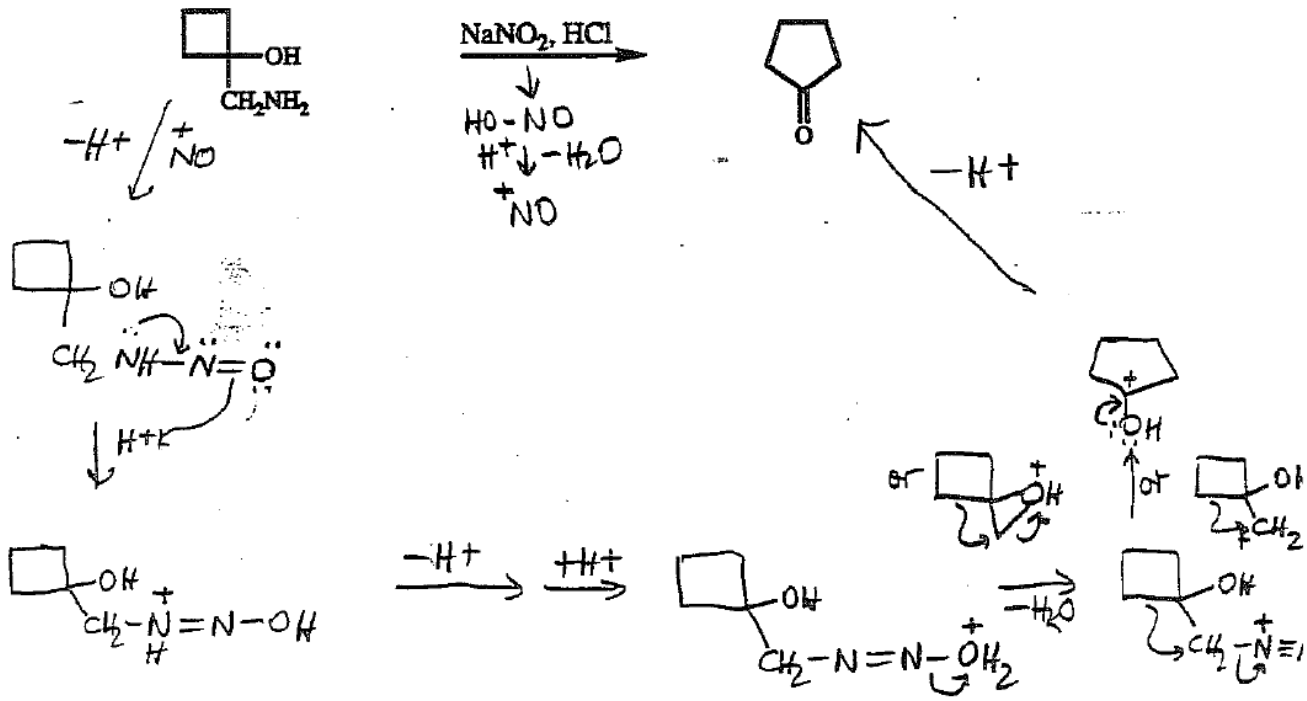
Combination of Friedel-Crafts ortho-methylation + hydrolysis. The reaction is a mess because all possible mono-, di-, and tri-(o,p) methylations can take place, as well as methylation at NH_2.



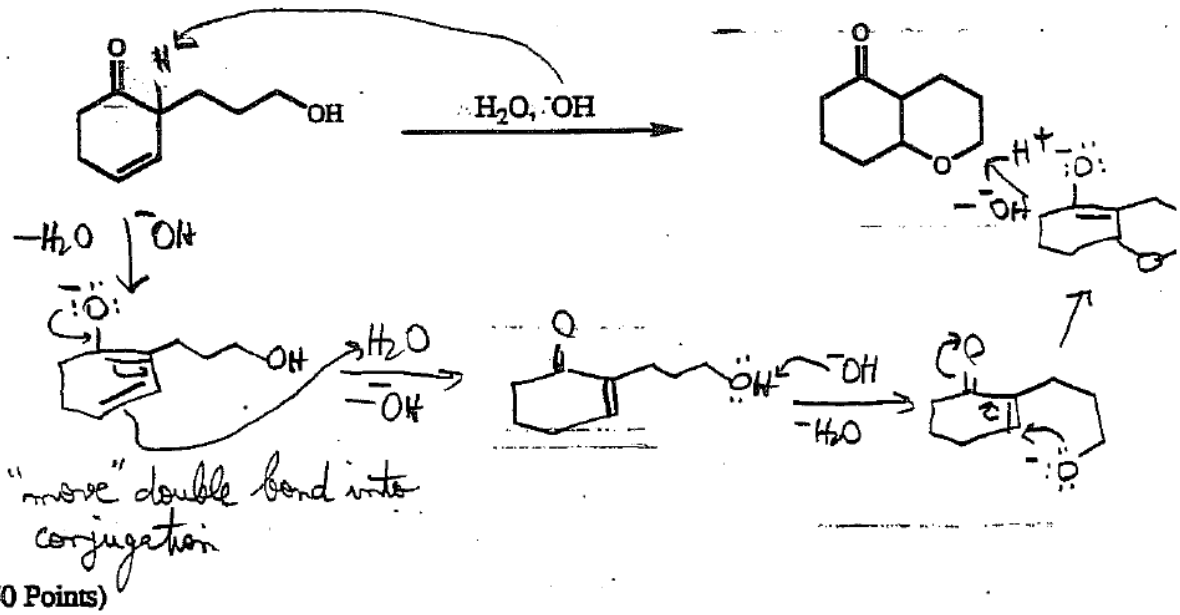
IV. **(30 Points)**

Write a detailed mechanism to explain of the following transformations.

a.



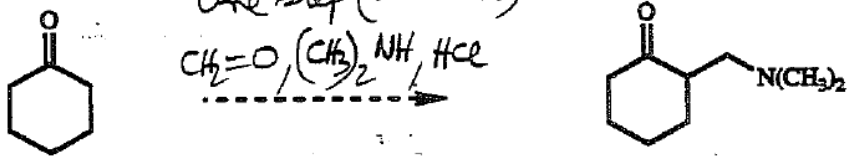
b.



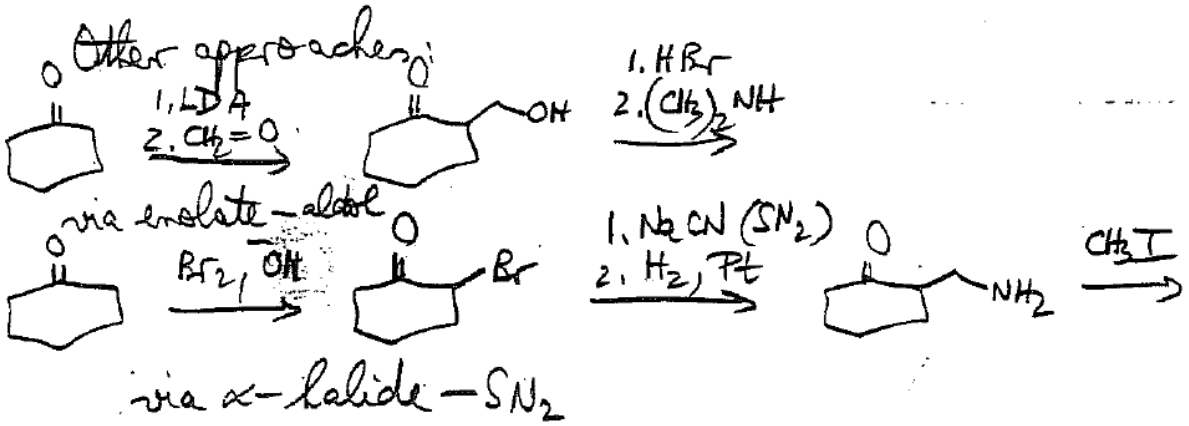
V. (50 Points)

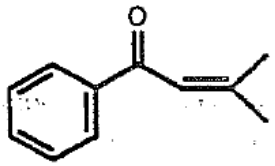
Provide a reasonable synthetic route from starting material to product. Note: several steps are required and there may be more than one solution to the problem. You may use any additional organic or organometallic reagents to effect your conversions. Try to work backwards from the product.

a.

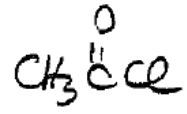


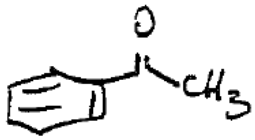
Hint: for a quick solution, use the Mannich reaction.

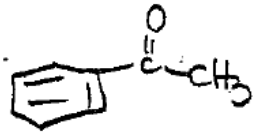


b. CH_3CH_2OH,  , CH_3CCH_3 

You have to use the three given starting materials as reagents at some stage of your scheme.

1. $CH_3CH_2OH \xrightarrow{Na_2Cr_2O_7} CH_3CO_2H \xrightarrow{SOCl_2}$ 

2.  $+ CH_3\overset{O}{\overset{\|}{C}}Cl \xrightarrow{AlCl_3}$ 

3.  $+ CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{NaOH,\ H_2O,\ \Delta}$