EXAMINATION 1

Chemistry 3B
Professor K. Peter C. Vollhardt
February 24, 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.

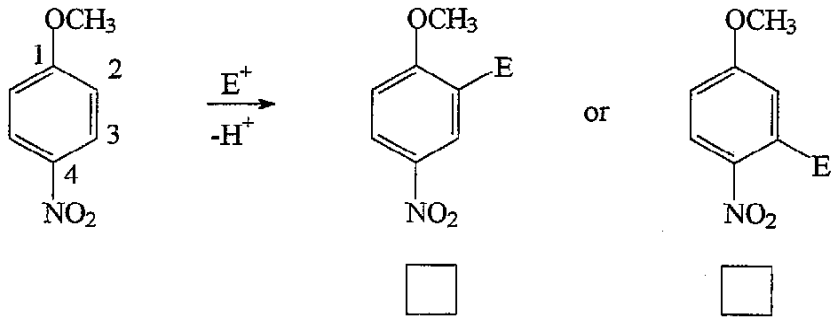
111	Jong, Kimmy	_____	311	Chan, Gina	_____
112	Yun, Shine Sun	_____	312	Chiu, Anita	_____
113	Toochinda, Tab	_____	313	Lemieux, George	_____
211	Cho, Joanne	_____	411	Upasani, Sayli	_____
212	Ong, Angeline	_____	412	Ong, Angeline	_____
213	Yu, Jerry	_____	413	Mar-Tang, Roger	_____
301	Chan, Gina	_____	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.	_____	**(30 Points)**
II.	_____	**(50 Points)**
III.	_____	**(50 Points)**
IV.	_____	**(40 Points)**
V.	_____	**(30 Points)**
TOTAL		**(200 Points)**

I. [30 Points] 1-Methoxy-4-nitrobenzene **A** undergoes preferential electrophilic attack by E^+ to give only one of the two products shown.



(a) Which one? Mark the box below your choice.

(b) Write the resonance forms of the intermediate formed on attack of E^+ at:

C-2 :

Four resonance forms

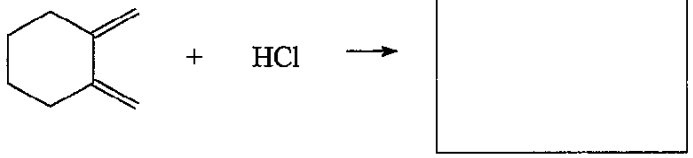
C-3:

Three resonance forms

(c) Circle (in your answer above) the most strongly contributing resonance form of the attack at C-2 and the least contributing counterpart of attack at C-3.

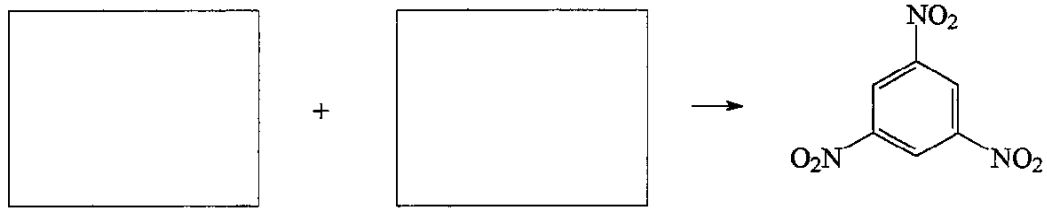
II. [50 Points] Add the missing components (starting materials, reagents, or products) of the following reactions in the boxes provided. Aqueous work-up (when required) is assumed to be part of a step. It is not part of any answer.

(a)



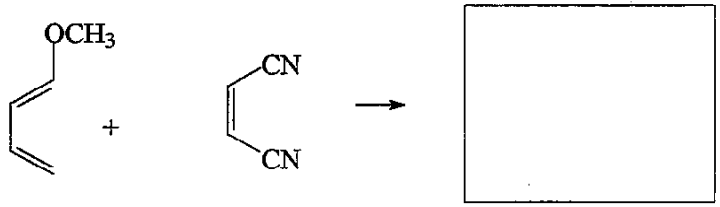
Thermodynamic product

(b)

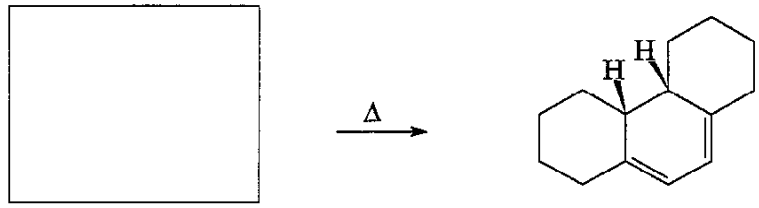


A dinitrobenzene

(c)

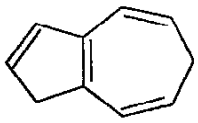


(d)



A hexatriene isomer of product

(e)

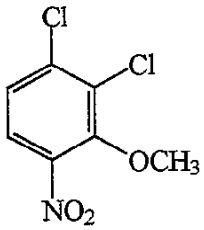


$Na^+ {}^-NH_2$

13C NMR: 10 lines

13C NMR: 6 lines

(f)

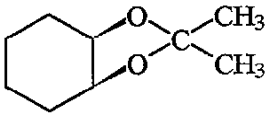


SO_3, H_2SO_4

(g)

+ CH_3CCH_3 (O)

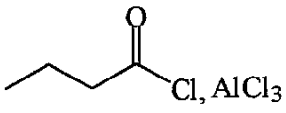
H^+



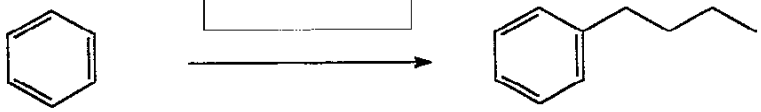
IR : $\tilde{\nu}$ = 3500 cm^{-1}

13C NMR : 3 lines

(h)

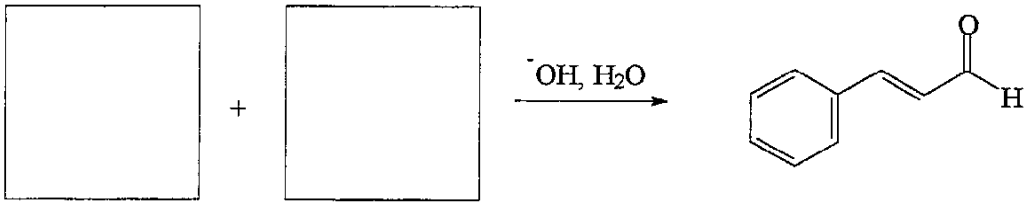
1. 

2.



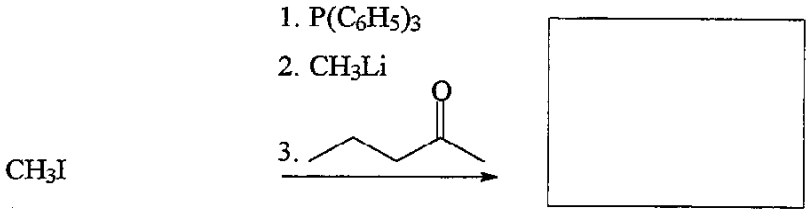
You can write the conditions for a one-step conversion in 2. (as indicated by the simple box) or a two step sequence (if you can't remember the one-step procedure).

(i)

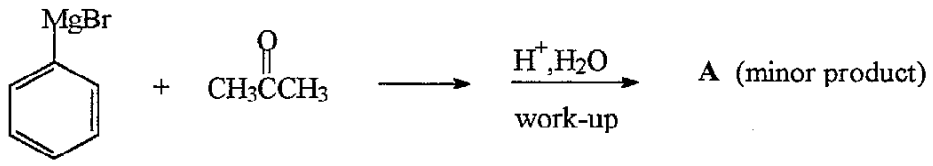


An aldehyde A second aldehyde

(j)



III. [50 Points] Treatment of acetone with phenylmagnesium bromide gave, in addition to the desired alcohol, a small amount of compound **A**, as shown:

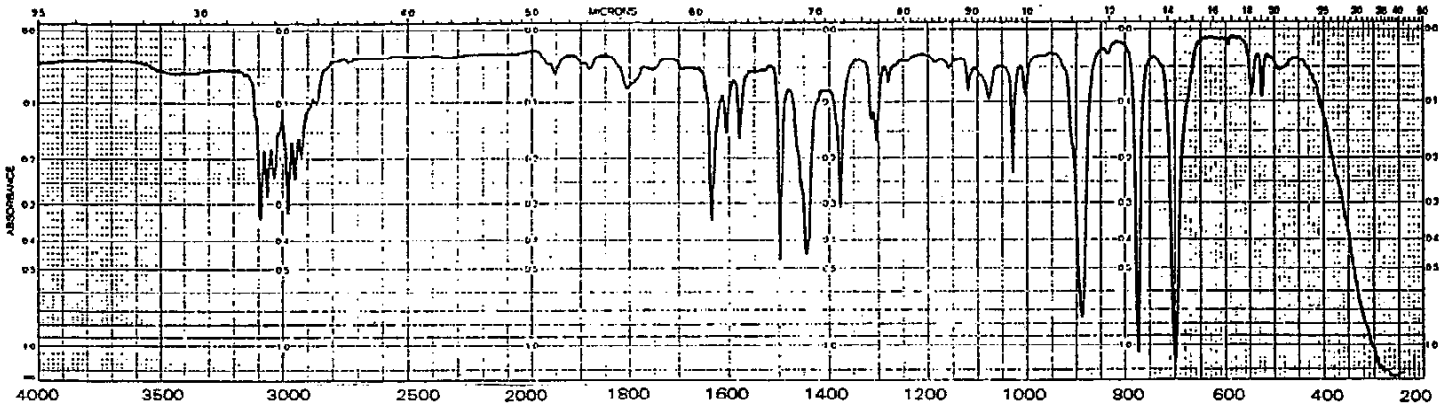


Its spectral data are depicted below.

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

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

1. IR SPECTRUM

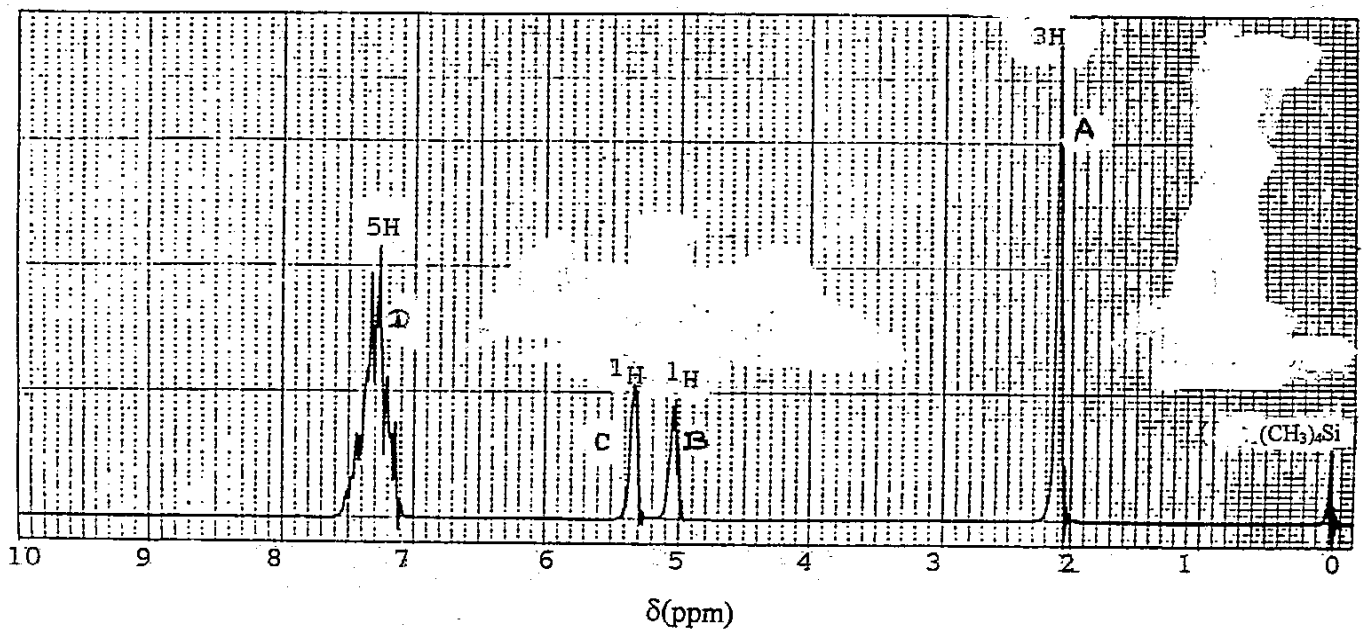


There are two characteristic areas in which peaks occur and one in which a peak is noticeably absent (considering the starting materials). Specify and assign to stretching frequencies (for example, "peak present at 900 cm^{-1}, due to Mg-C stretch"---- I made this up) the

peak present at _____ , due to _____

peak absent at _____ , due to absence of _____

2. ^{1}H NMR SPECTRUM



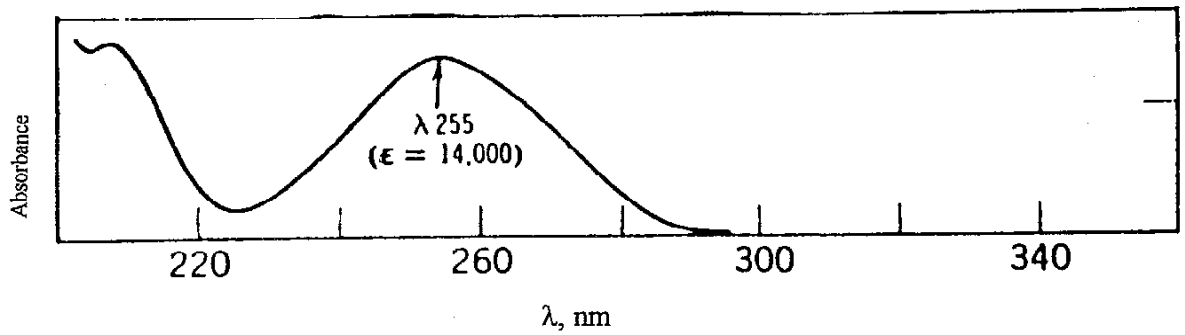
Draw your suggestion for **A** and label the hydrogens A, B, C, D giving rise to the correspondingly labeled signals in the spectrum.

3. ^{13}C NMR Spectrum

δ = 25.8, 112.4, 125.9, 127.9, 128.0, 141.6, 143.1 ppm.

How does this spectrum confirm your structural assignment of **A**?

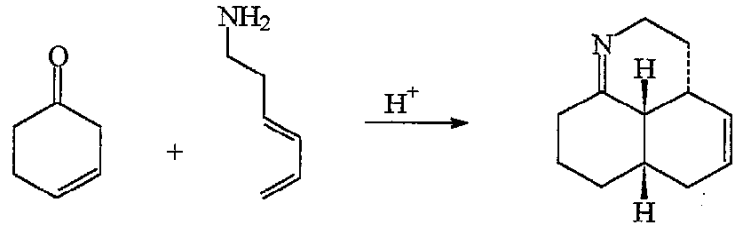
4. UV Spectrum



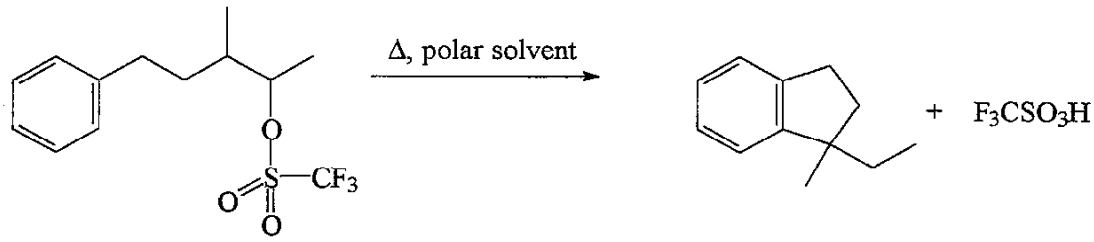
How does this spectrum confirm your structural assignment of **A**?

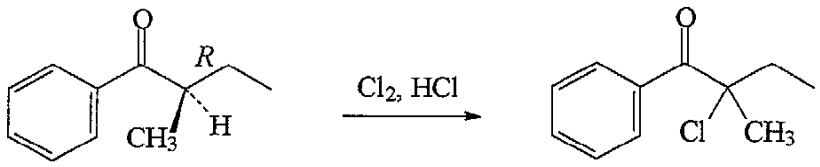
IV. [40 Points] Write detailed mechanisms to explain the following observations.

(a)



(b)

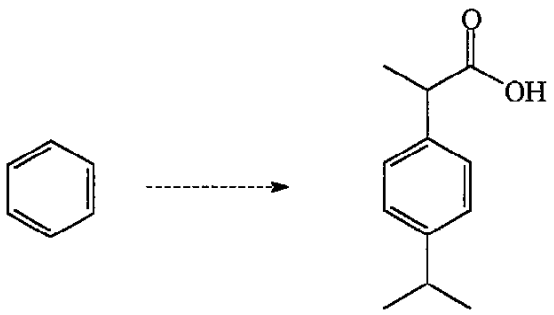


(c) 

enantiomerically pure racemate

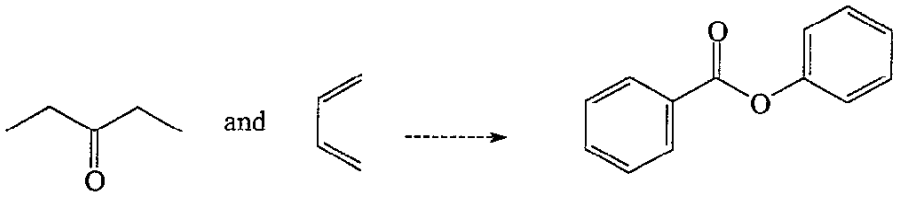
V. (30 Points) Provide a reasonable synthetic route from starting material to product. Note: several steps are required and there may be more than one solution to the problem. You may use any additional organic or organometallic reagents to effect your conversions.

(a) Ibuprofen (Advil) from benzene :

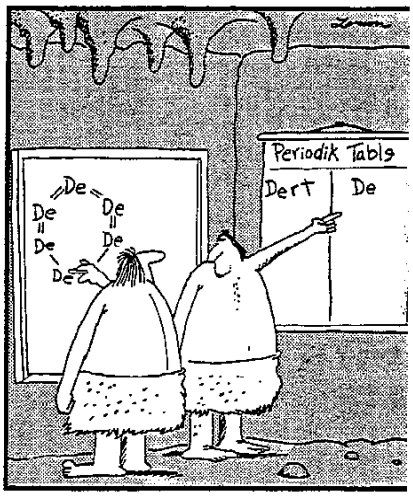


Ibuprofen

(b) Phenyl benzoate from 3-pentanone and 1,3-butadiene.



Phenyl benzoate



Early chemists describe the first dirt molecule.