

Chemistry 232-001 (Prof. Grossman's Section)

Final Examination

April 30, 2007

Name (please PRINT LEGIBLY) _____
(last) (first)

<u>Problem</u>	<u>Score</u>
1(a-h).	_____ /32
2(a-b).	_____ /32
3(a-b).	_____ /40
4(a-f).	_____ /24
5(a-e).	_____ /22
Total.	_____ /150

Please observe the following.

1) Write LARGE and LEGIBLY. This will help me assign partial credit.

2) READ THE INSTRUCTIONS to each question CAREFULLY before answering. Many, many points are not awarded on each exam because of the failure of students to read the instructions.

TABLE OF ATOMIC WEIGHT MULTIPLES.

C ₂	24	O ₁	16
C ₃	36	O ₂	32
C ₄	48	O ₃	48
C ₅	60	O ₄	64
C ₆	72	O ₅	80
C ₇	84	O ₆	96
C ₈	96		
C ₉	108	N ₁	14
C ₁₀	120	N ₂	28
C ₁₁	132	N ₃	42
C ₁₂	144	N ₄	56
C ₁₃	156	N ₅	70
³⁵ Cl ₁	35	⁷⁹ Br ₁	79
³⁵ Cl ₂	70	⁷⁹ Br ₂	158

TABLE OF IR STRETCHES IN INTERPRETABLE REGION.

<u>Functional Group</u>	<u>Absorbance</u>
X-H region	2800–3500 cm ⁻¹
O-H alcohol	about 3500 cm ⁻¹ , strong and broad
N-H	about 3300 cm ⁻¹ , strong
C-H	2850–3300 cm ⁻¹ , strong to moderate
C≡C-H	3300 cm ⁻¹
C=C-H	3000–3100 cm ⁻¹
C(sp ³)-H	2850–3000 cm ⁻¹
O=C-H	2750 cm ⁻¹
O-H carboxylic acid	2800–3500 cm ⁻¹ , strong and <i>very</i> broad
C(sp) region	2200–2300 cm ⁻¹
C≡N	about 2250 cm ⁻¹ , moderate
C≡C	about 2200 cm ⁻¹
R-C≡C-H	moderate
R-C≡C-R	no absorption seen
C(sp ²) region	1500–1800 cm ⁻¹
C=O	1670–1780 cm ⁻¹ , <i>very</i> strong
acyclic and 6-membered cyclic ketones	1715 cm ⁻¹
3- to 5-membered cyclic ketones	1740–1780 cm ⁻¹
aldehydes RCHO	1735 cm ⁻¹
esters RCO ₂ R'	1740 cm ⁻¹
amides RCONR' ₂	1670 cm ⁻¹
any C=O adjacent to C=C or phenyl	subtract 20–25 cm ⁻¹ , sometimes more
C=C	1500–1650 cm ⁻¹
	(very sharp absorption; can vary from strong absorption to none.)

TABLE OF TYPICAL ^1H NMR RESONANCES.

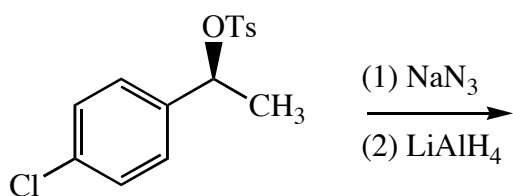
Type of C atom	Chemical Shift (δ)
saturated alkyl	0.5–1.5
$\text{C}=\text{C}-\text{C}-\text{H}$, $\text{O}=\text{C}-\text{C}-\text{H}$, $\text{C}\equiv\text{C}-\text{H}$	1.5–2.5
$\text{X}-\text{C}-\text{H}$ (X= O, N, Hal)	2.5–4.5
$\text{C}=\text{C}-\text{H}$	4.5–6.5
aryl H	6.5–8.5
$\text{O}=\text{C}-\text{H}$	7.8–10.5
CO_2H	11–14
O–H, N–H	varies

TABLE OF TYPICAL ^{13}C NMR RESONANCES.

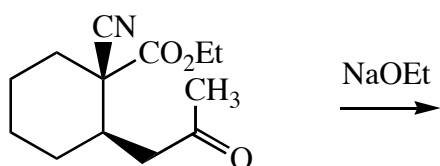
Type of C atom	Chemical Shift (δ)
alkyl C	0–50
$\text{C}(\text{sp}^3)-\text{N}$, O, Cl, Br	40–80
$\text{C}\equiv\text{C}$	60–95
$\text{C}\equiv\text{N}$	110–120
$\text{C}=\text{C}$	100–160
$\text{C}=\text{O}$	165–210

1. (4 pts. each, 32 pts. total.) Draw the *major* product of each of the following reactions, including the stereochemistry, if appropriate. **Do not draw mechanisms!**

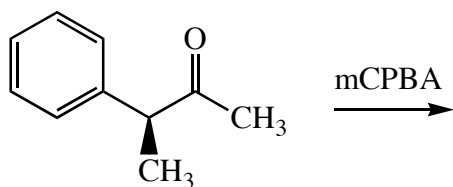
(a)



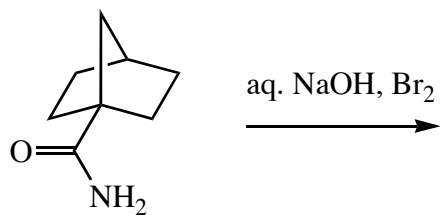
(b)



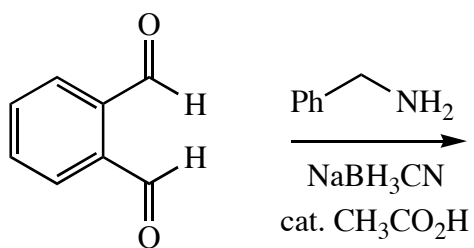
(c)



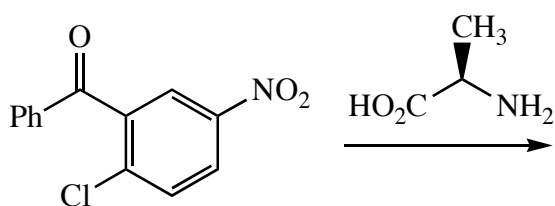
(d)



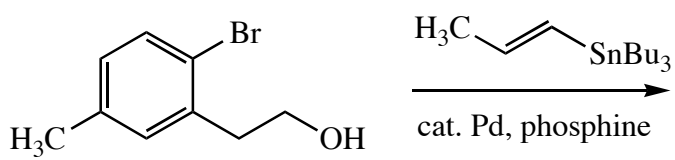
(e)



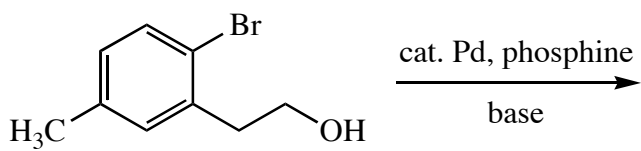
(f)



(g)

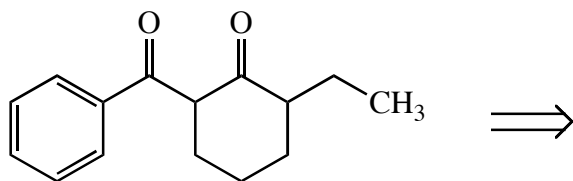


(h)



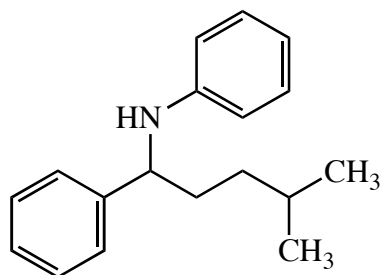
2. (16 pts. each, 32 pts. total.) Design a synthesis of each of the following compounds from the given starting materials. Each synthesis will require more than one step. Show each intermediate compound and all reagents you will need for each step. (Don't panic if you can't remember the reagents for a particular step; partial credit will be given.) There may be more than one correct answer. **Do not show mechanisms. You are strongly advised to do a retrosynthetic analysis before drawing the synthetic sequence in the forward direction.**

(a) (16 pts.)



starting materials containing no more than
six (6) contiguous carbon atoms each

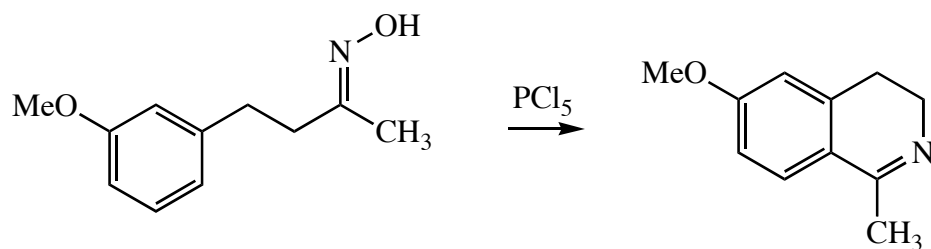
(b) (16 pts.)



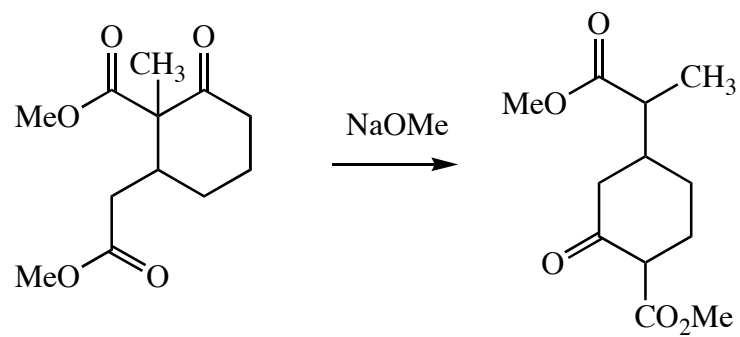
starting materials containing no more than six (6) contiguous carbon atoms each AND that do NOT contain EITHER of the C-N bonds that are present in the product

3. (20 pts. each, 40 pts. total.) Draw a reasonable mechanism for each of the following reactions. Use the conventional curved arrows to show the movement of electrons in each step. **You are strongly advised to obey Grossman's rule and to number your atoms.**

(a) (20 pts.)



(b) (20 pts.)

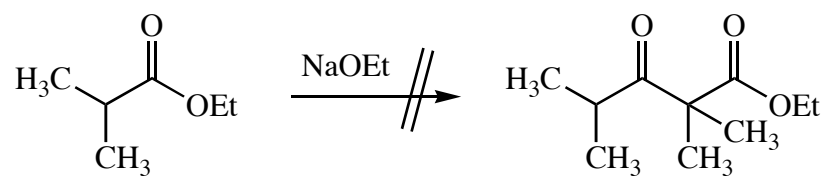


4. (4 pts. each, 24 pts. total.) Clearly explain each of the following observations in one or two grammatically correct English sentences and as many structural drawings as you need.

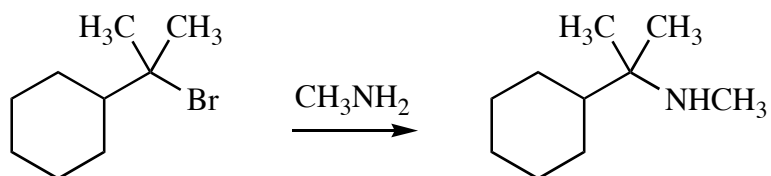
(a) The ^1H NMR spectrum of benzyl fluoride, PhCH_2F , shows a *doublet* for the CH_2 group, whereas the ^1H NMR spectra of benzyl chloride and benzyl bromide show *singlets* for their CH_2 groups.

(b) It is easy to tell whether an IR absorbance at 3300 cm^{-1} is due to an NH or a $\text{C}(\text{sp})\text{-H}$.

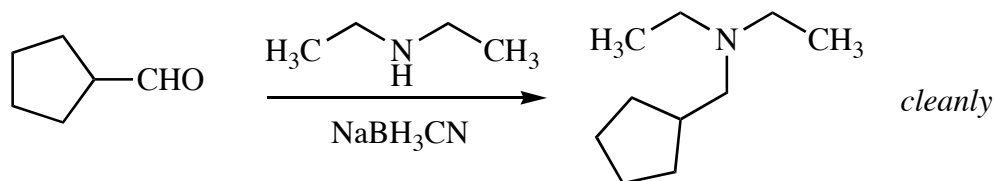
(c) Claisen condensations do not proceed well when the ester has only one acidic H atom.



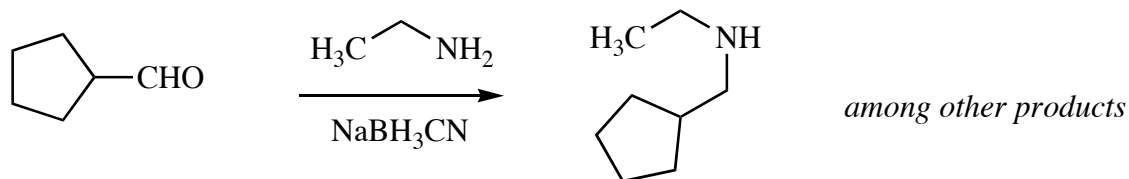
(d) The following reaction is *NOT* a good way to prepare the target compound.



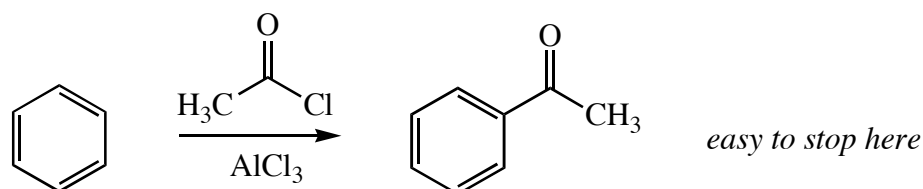
(e) The reductive amination of secondary amines with aldehydes to give tertiary amines, works very well, but the reductive amination of primary amines with aldehydes to give secondary amines does not often give the product cleanly.



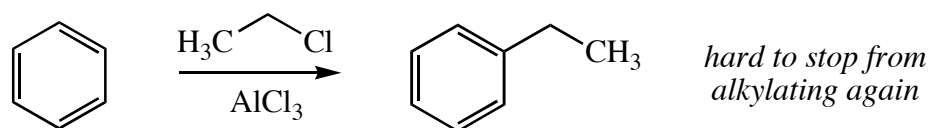
but



(f) It is easy to stop a Friedel–Crafts *acylation* after one substitution, but it is difficult to stop a Friedel–Crafts *alkylation* after one substitution.



but



5. (22 pts. total.) The last three pages of this exam show the MS, IR, and ^1H NMR spectra of an organic compound. Answer the following questions using these spectra.

(a) (4 pts.) What does the mass spectrum indicate about the number of N, Cl, and Br atoms in this compound?

(b) (4 pts.) Based on the mass and NMR spectra, propose a reasonable formula for this compound.

(c) (4 pts.) Name a functional group whose presence in this compound is indicated by the IR spectrum, and briefly describe the spectral features that lead to this conclusion. *Be specific.*

(d) (4 pts.) What group do the ^1H NMR resonances at 7–8 ppm suggest is present in this compound? *Be specific.*

(e) (6 pts.) Draw a structure consistent with all three spectra and your answers to (a–d).