NAME _____

ID # _____

ORGANIC CHEMISTRY I (2301)

9:30 – 10:45 am, August 2, 2012

Final Exam

There will be two ways that you can pick up your graded Final Exam:

- You can pick up your graded exam from Andy at office hours that he will hold on Monday, August 6th (9:30-10:30 am) at Coffman Union Starbucks.
- Alternately, you will be able to pick up your graded exam from Chemistry department staff in 115 Smith beginning Monday, August 6th at noon. Exams that are not picked up within two weeks will be disposed of.

A periodic table, a chart of reaction conditions, and a table of typical NMR chemical shifts are attached to the back of this exam as aids. Otherwise, you are not permitted to use any other materials (including notes, books, or electronic devices of any kind).

Right now, write your name and student ID number at the top of this page. When the exam begins, please write your name at the top of the next page.

You may use pen or pencil. However, re-grades will be considered only for exams completed in pen.

Please write your answers in the boxes/spaces provided. If your answer is not in the appropriate space (say, for example, it's on the back of the page), draw us an arrow and/or note telling us where to look.

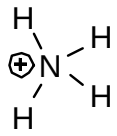
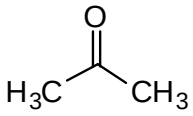
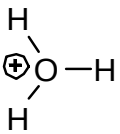
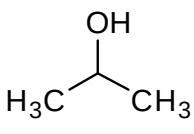
NAME _____

Scoring:

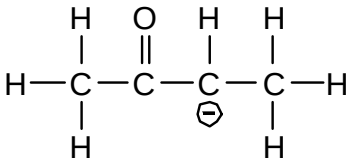
1. _____ / 14	6. _____ / 25
2. _____ / 15	7. _____ / 16
3. _____ / 12	8. _____ / 16
4. _____ / 15	9. _____ / 29
5. _____ / 8	

Total Score: _____ / 150

1. (14 pts) For each of the pairs of acids (or bases) below,
   - Draw the conjugate base (or acid).
   - Circle whether you think the first acid (or base) is more or less acidic (or basic) than the second.

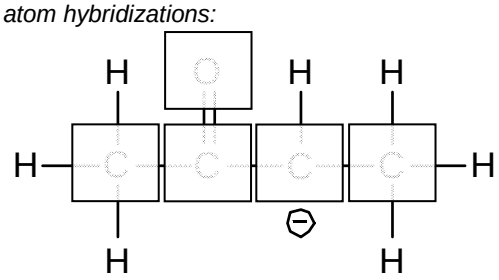
Acid	Conjugate Base	Base	Conjugate Acid
			
is		is	
MORE ACIDIC **LESS ACIDIC**		**MORE BASIC** **LESS BASIC**	
than		than	
			

2. (15 pts) For the anion drawn at right, in the boxes provided:



- Draw all significant resonance structures. In each structure, draw all atoms, bonds, lone pairs of electrons, and formal charges. Then, circle which resonance structure you think is the most significant, and which is the least. **Circle only one MOST and one LEAST.**
- Draw a Lewis wedge/dashed-bond structure that illustrates the most stable three-dimensional conformation of the molecule. Draw all atoms, bonds, and charges, but omit lone pairs.
- In the boxes provided, write the hybridization state on any atom heavier than hydrogen.

atom hybridizations:



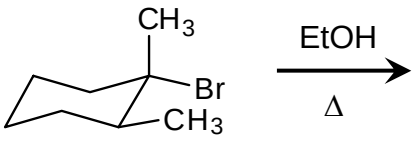
MOST *or* **LEAST** *significant?*

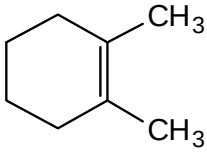
3-dimensional representation

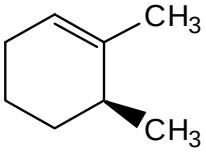
resonance structure

MOST *or* **LEAST** *significant?*

3. (12 pts) Each of the reactions below and on the next page is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced equally, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**

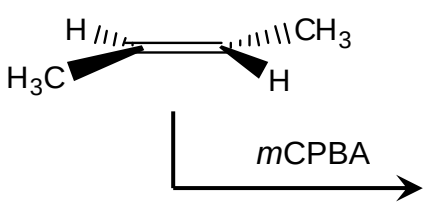


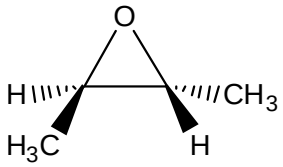
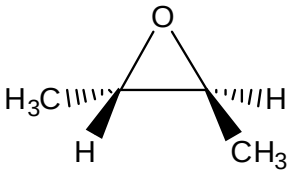


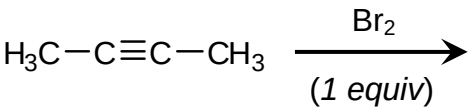


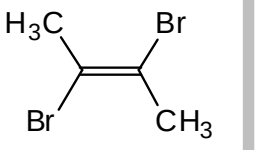
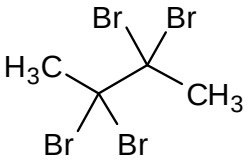
BOTH
(equally)

NEITHER

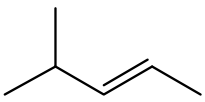


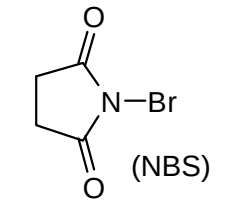
	
BOTH (equally)	NEITHER

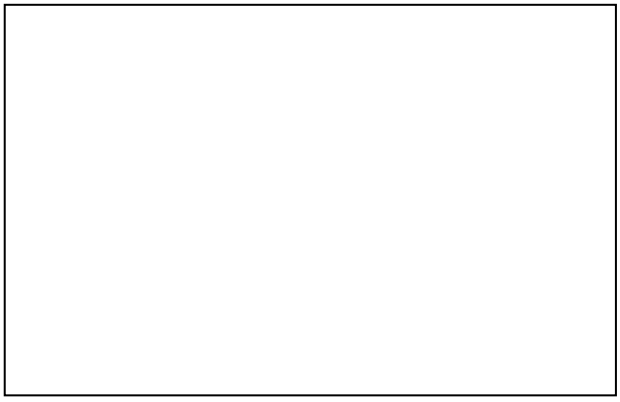


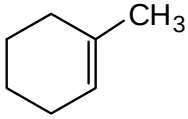
	
BOTH (equally)	NEITHER

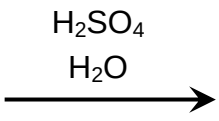
4. (15 pts) For each of the reactions below, fill in the empty box corresponding to the major product. Wherever appropriate, illustrate stereochemistry in your drawings (using wedge and dashed bonds). If multiple enantiomers or diastereomers are produced, indicate this in the answer box (e.g., by writing "+ enantiomer", etc.)

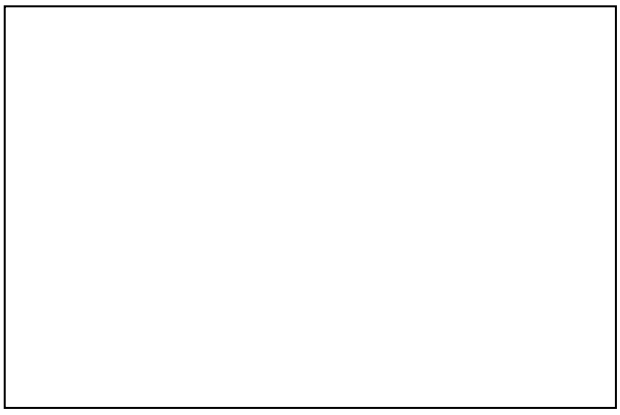


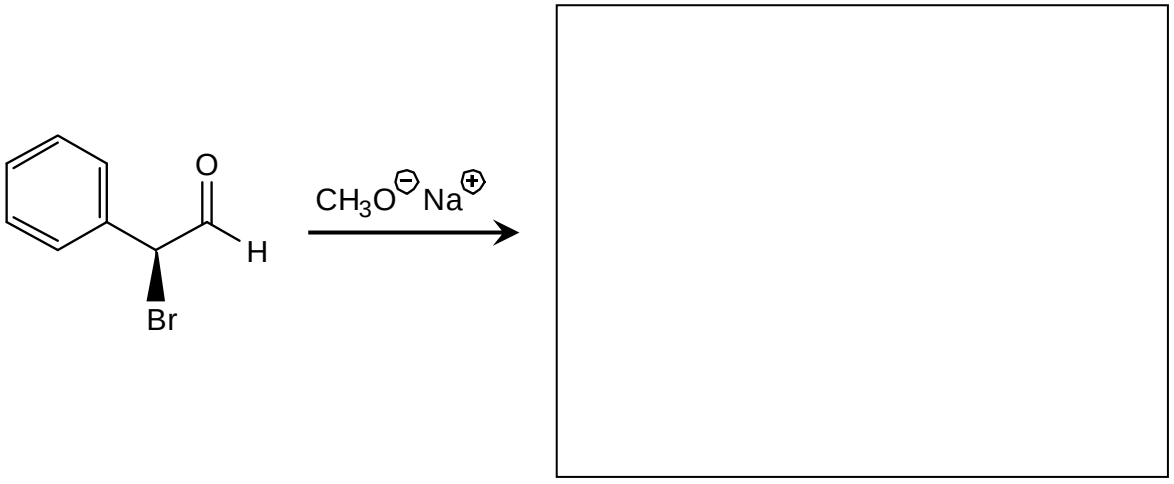




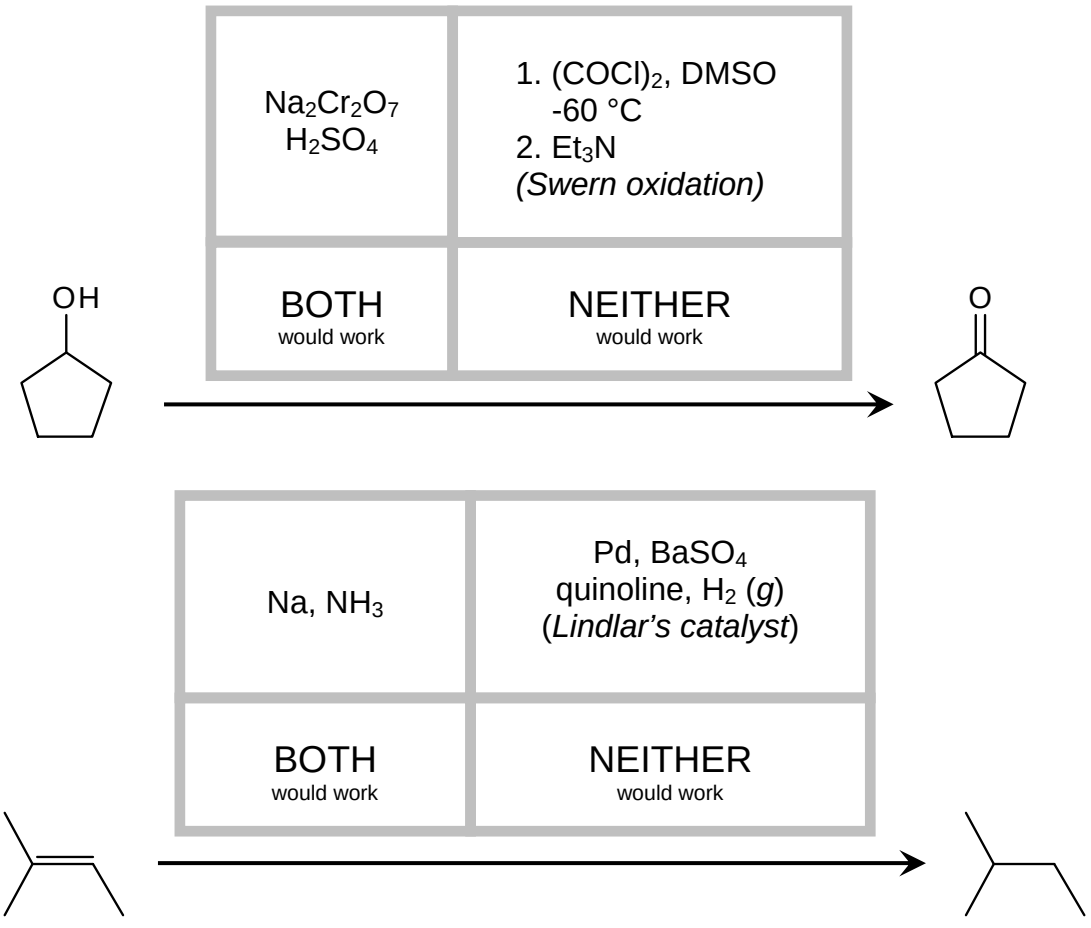




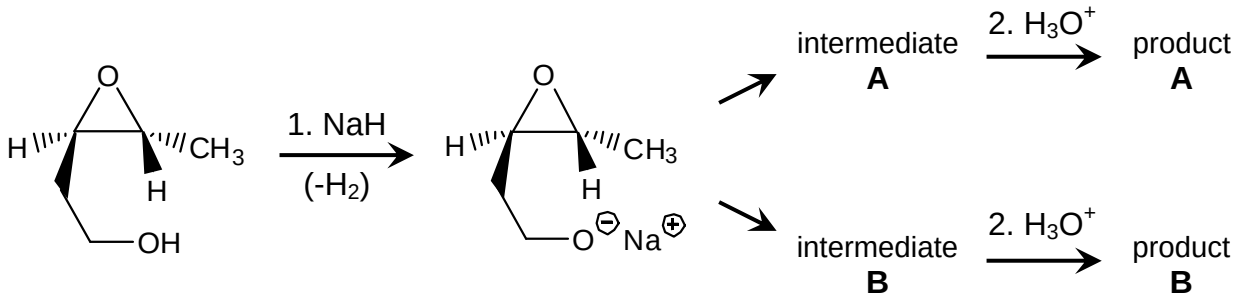




5. (8 pts) Each of the reactions below is drawn with two possible reaction conditions. If only one of the two reaction conditions would generate the given molecule as the major product, circle those conditions. If both sets of conditions would accomplish the reaction, circle "BOTH". If neither set of reaction conditions would succeed, circle "NEITHER". **Circle one answer only.**



6. (25 pts) When the epoxide-alcohol starting material below is deprotonated with NaH, the resulting alkoxide reacts with itself to open the epoxide. That reaction, followed by acidic workup, can produce two different products; the difference between the products is dictated by which epoxide carbon is attacked by the alkoxide.



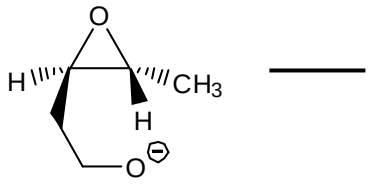
In this problem, we will name the products **A** and **B**, which are formed by protonation of intermediates **A** and **B**.

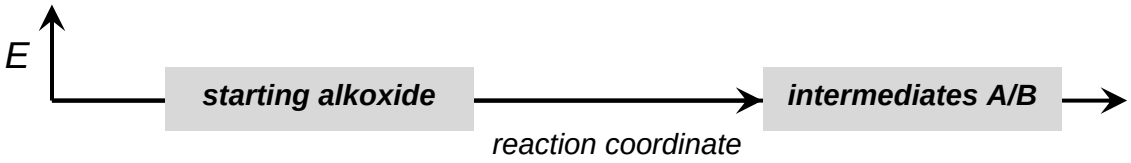
(a) Using "electron pushing", draw a mechanism that illustrates the formation of intermediates **A** and **B** from the alkoxide. I've drawn the starting material for you—just add curved arrows to my structure. Then, draw the structures of intermediate **A** and intermediate **B**. Wherever appropriate, illustrate stereochemistry.

intermediate **A**	*intermediate* **B**

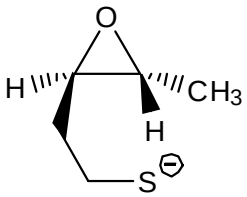
(b) Is intermediate **A** **MORE STABLE** than **LESS STABLE** than the **SAME ENERGY** as intermediate **B**? (*Circle one.*)

(c) On the potential energy diagram below, draw two curves that represent the two reactions you drew in part (a). The starting material (alkoxide) energy has already been drawn for you—you need to connect this starting point to energies of the reaction transition states, intermediate **A**, and intermediate **B**.



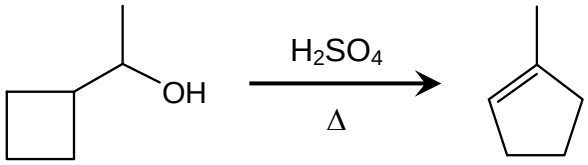


(d) How would the rate of the two reactions be affected if the starting material were a thiol instead of an alcohol? Assume that the thiolate on the right has the same energy as the alkoxide above, and that the sulfur-containing intermediates $\mathbf{A_S}$ and $\mathbf{B_S}$ are also the same energy as intermediates **A** and **B**. Would the thiolate react



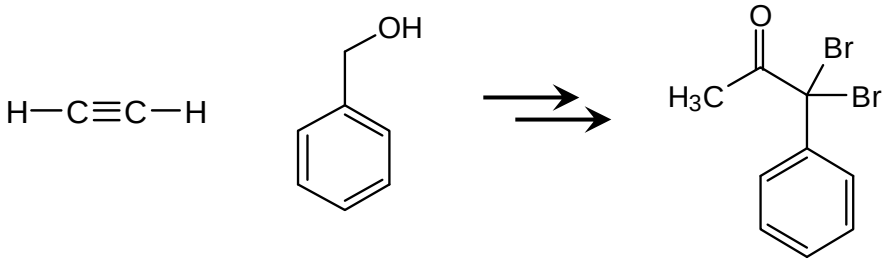
FASTER than | **SLOWER** than | **SAME RATE** as the | the alkoxide? (*Circle one.*)

7. (16 pts) Draw a mechanism (using “electron pushing”) for each of the reactions shown on the next page. Draw each mechanistic step explicitly; don’t cheat by combining multiple processes in a single step. Use only the molecules shown in the problem; don’t invoke generic species. (E.g., don’t use “H-A” as a generic acid.)



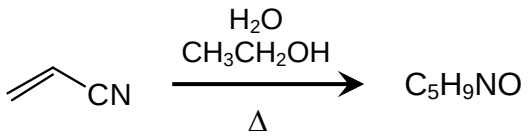
Mechanism:

8. (16 pts) For each set of starting materials and products shown below, **propose a multistep synthesis**. In addition to the molecules shown, you can use any reagents and reactions we've learned about in class. You might discover multiple answers to this problem; draw only your best (one) synthetic route. Feel free to draw an incomplete route—we will give you partial credit where we can.

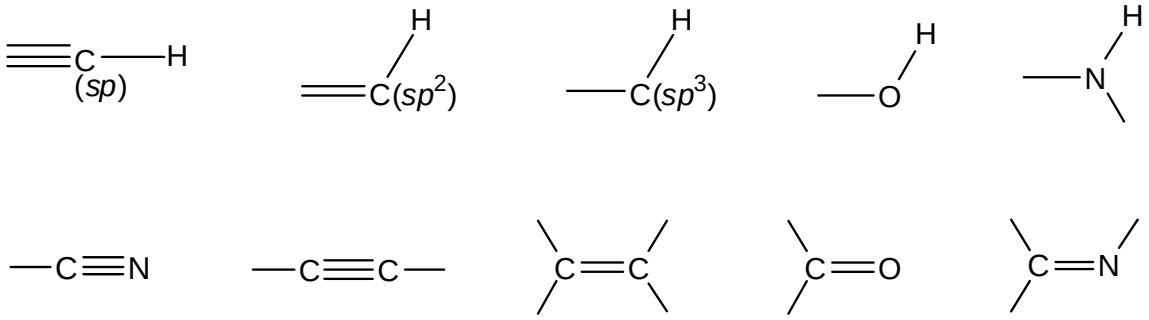


Multistep synthesis:

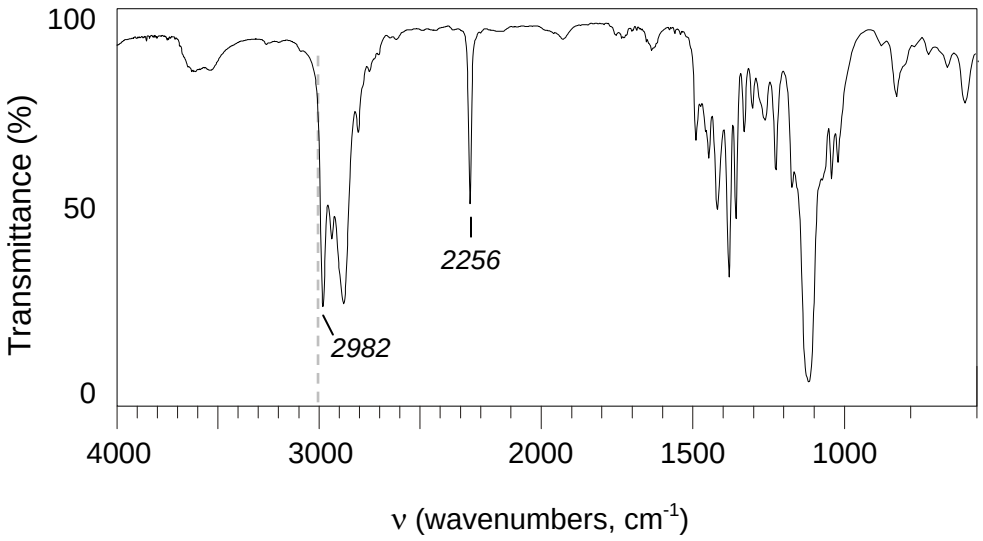
9. (29 pts) Acrylonitrile, the starting material on the right, can be polymerized into polyacrylonitrile (a component of plastic consumer goods) by heating it in solvent, but heating acrylonitrile in a mixture of ethanol and water generates a small molecule product instead. This product was isolated and characterized by NMR and IR spectroscopy and mass spectrometry; the spectra of this product are shown on the next two pages. High-resolution mass spectrometry determined an exact mass of 99.06840 amu for the highest-mass (parent, $\mathbf{M}^+$) peak in the MS spectrum, which corresponds to a molecular formula of $\mathbf{C_5H_9NO}$.



(a) Based on the features in the IR spectrum below, what functional groups would you expect the unknown molecule to have? **Circle all answers that apply.**



IR Spectrum:

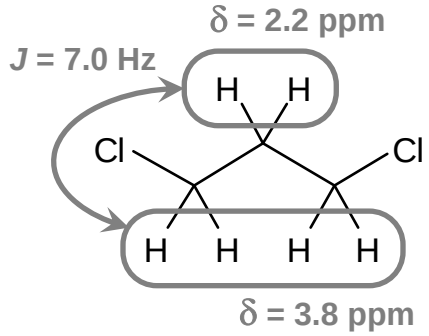


(b) **What is the structure of the product**? In the box on the next page, draw the molecule's structure, including all hydrogens. Then, considering the ^{1}H NMR spectrum,

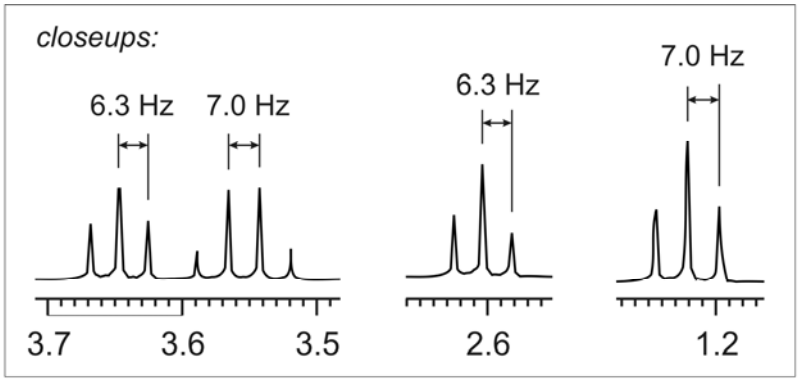
- Circle each group of equivalent H's;
- Assign a ^{1}H chemical shift (δ) to each circled group, within 0.05 ppm;
- Connect any pair of coupled, inequivalent groups of H's with a double-headed arrow, and then label that arrow with the corresponding coupling constant (*J*).

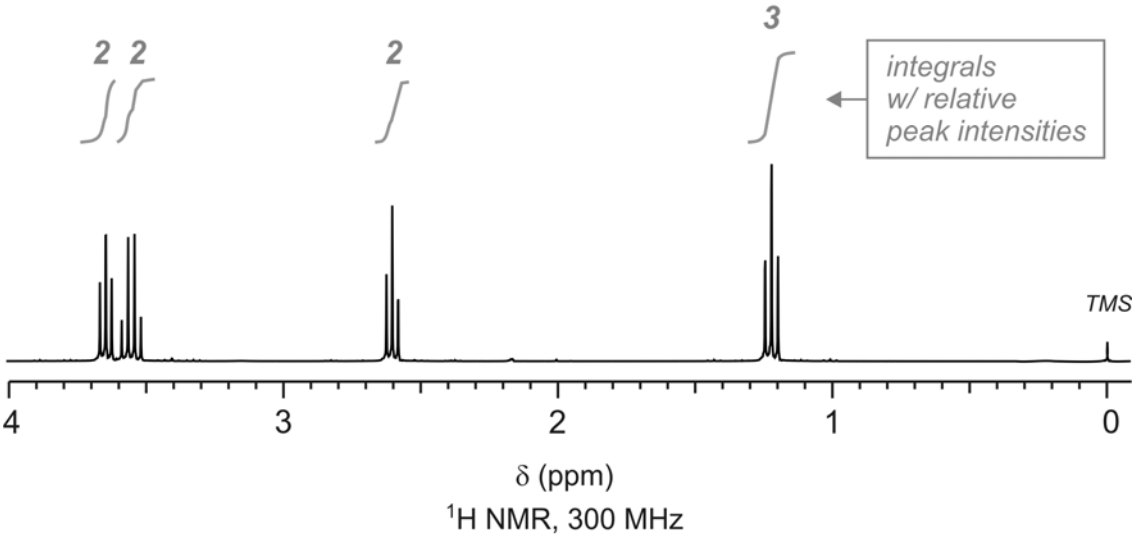
the product
(C_5H_9NO)

Format for answer to (c):

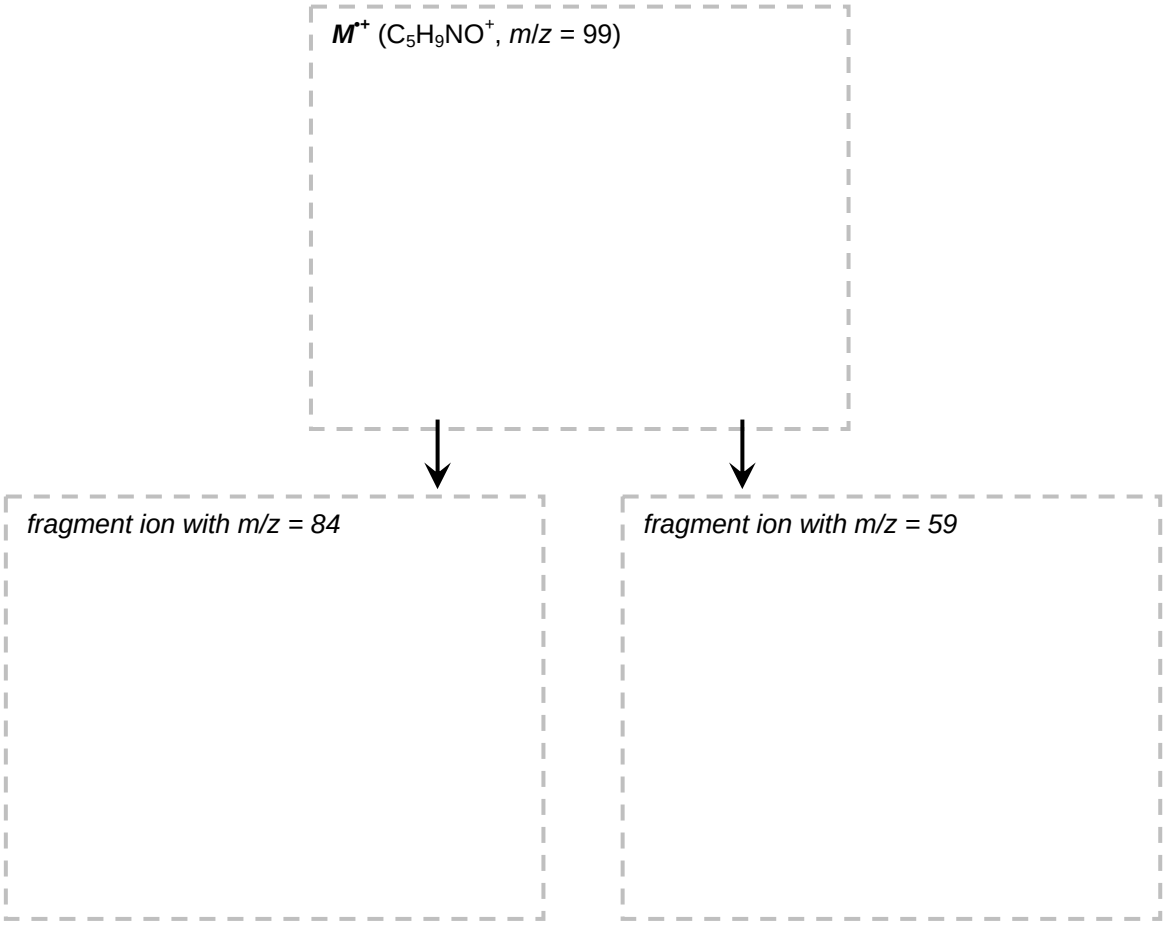


^{1}H NMR Spectrum:

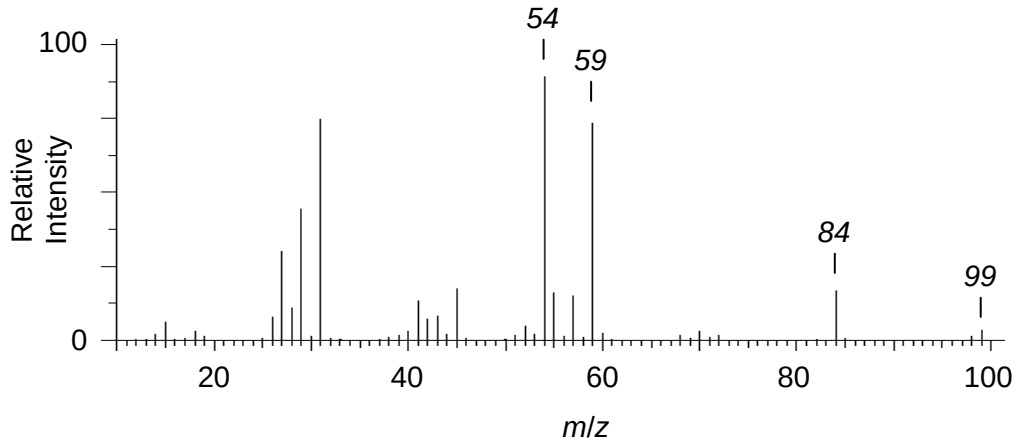




(c) In an electron-ionization (EI) mass spectrometry experiment, parent ions often fragment into daughter ions that give information about the parent's molecular structure. In the EI mass spectrum below, the parent mass peak at *m*/*z* = 99 corresponds to a radical cation ($\mathbf{M}^{\bullet+}$) that fragments into ions with mass 84 and 59. In the boxes below, draw the structures of these ions. *You do not need to do electron pushing to answer this question—just draw the cations.* On all ion structures, make sure to specifically illustrate where the formal charge lies.



Mass Spectrum:

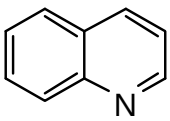


Final Exam Chart of Reaction Conditions

$Pt/H_2(g)$

$NaNH_2$

$Pd, BaSO_4$
$H_2(g)$



(quinoline)

$Na_2Cr_2O_7$
H_2SO_4

1. BH_3•THF
2. H_2O_2, OH^-

1. O_3
2. $(CH_3)_2S$

Na
NH_3

$HgSO_4$
H_2SO_4

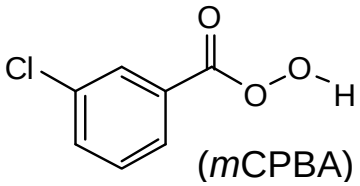
1. $(COCl)_2$
   DMSO
   -60 °C
2. Et_3N

(Swern oxidation)

H_2SO_4
H_2O

$SOCl_2$
pyridine

*m*CPBA
H_2O



(*m*CPBA)

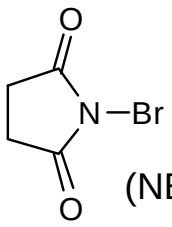
$KMnO_4$
(cold, dilute)
H_2O, OH^-

1. O_3
2. H_2O

$KMnO_4$
H_2O, pH 7

TsCl
pyridine

Cl_2 *or* Br_2,
$h\nu$



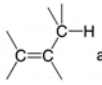
(NBS)

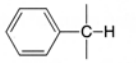
$h\nu$ *or* AIBN

1. $KMnO_4$
   KOH, Δ
2. H_3O^+

PBr_3

^{1}H NMR Absorptions

Compound type	Chemical shift (ppm)
Alcohol	
	1–5
	3.4–4.0
Aldehyde	
	9–10
Alkane	0.9–2.0
RCH_3	~0.9
R_2CH_2	~1.3
R_3CH	~1.7
Alkene	
 sp^2 C–H	4.5–6.0
 allylic sp^3 C–H	1.5–2.5
Alkyl halide	
	4.0–4.5
	3.0–4.0
	2.7–4.0
	2.2–4.0
Alkyne	
—C≡C–H	~2.5

Compound type	Chemical shift (ppm)
Amide	
	7.5–8.5
Amine	
	0.5–5.0
	2.3–3.0
Aromatic compound	
 sp^2 C–H	6.5–8
 benzylic sp^3 C–H	1.5–2.5
Carbonyl compound	
 sp^3 C–H on the α carbon	2.0–2.5
Carboxylic acid	
	10–12
Ether 	3.4–4.0

^{13}C NMR Absorptions

Carbon type	Structure	Chemical shift (ppm)
Alkyl, sp^3 hybridized C		5–45
Alkyl, sp^3 hybridized C bonded to N, O, or X	 Z = N, O, X	30–80
Alkynyl, *sp* hybridized C	—C≡C—	65–100
Alkenyl, sp^2 hybridized C		100–140
Aryl, sp^2 hybridized C		120–150
Carbonyl C		160–210

IR Absorption Frequencies

Bond	Functional group	Wavenumber (cm^{-1})	Comment
O – H			
	• ROH	3600–3200	broad, strong
	• RCOOH	3500–2500	very broad, strong
N – H			
	• RNH_2	3500–3300	two peaks
	• R_2NH	3500–3300	one peak
	• $RCONH_2$, RCONHR	3400–3200	one or two peaks; N – H bending also observed at 1640 cm^{-1}
C – H			
	• C_{sp} – H	3300	sharp, often strong
	• C_{sp^2} – H	3150–3000	medium
	• C_{sp^3} – H	3000–2850	strong
	• C_{sp^2} – H of RCHO	2830–2700	one or two peaks
C ≡ C		2250	medium
C ≡ N		2250	medium
C = O			strong
	• RCOCl	1800	
	• $(RCO)_2O$	1800, 1760	two peaks
	• RCOOR	1745–1735	increasing $\tilde{\nu}$ with decreasing ring size
	• RCHO	1730	
	• R_2CO	1715	increasing $\tilde{\nu}$ with decreasing ring size
	• R_2CO, conjugated	1680	
	• RCOOH	1710	
	• $RCONH_2$, RCONHR, $RCONR_2$	1680–1630	increasing $\tilde{\nu}$ with decreasing ring size
C = C			
	• Alkene	1650	medium
	• Arene	1600, 1500	medium
C = N		1650	medium

Periodic Table of the Elements

Chemistry Reference Sheet

California Standards Test

	1 1A												13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 **H** Hydrogen 1.01	2 2A																2 **He** Helium 4.00
2	3 **Li** Lithium 6.94	4 **Be** Beryllium 9.01											5 **B** Boron 10.81	6 **C** Carbon 12.01	7 **N** Nitrogen 14.01	8 **O** Oxygen 16.00	9 **F** Fluorine 19.00	10 **Ne** Neon 20.18
3	11 **Na** Sodium 22.99	12 **Mg** Magnesium 24.31	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 **Al** Aluminum 26.98	14 **Si** Silicon 28.09	15 **P** Phosphorus 30.97	16 **S** Sulfur 32.07	17 **Cl** Chlorine 35.45	18 **Ar** Argon 39.95
4	19 **K** Potassium 39.10	20 **Ca** Calcium 40.08	21 **Sc** Scandium 44.96	22 **Ti** Titanium 47.87	23 **V** Vanadium 50.94	24 **Cr** Chromium 52.00	25 **Mn** Manganese 54.94	26 **Fe** Iron 55.85	27 **Co** Cobalt 58.93	28 **Ni** Nickel 58.69	29 **Cu** Copper 63.55	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.72	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92	34 **Se** Selenium 78.96	35 **Br** Bromine 79.90	36 **Kr** Krypton 83.80
5	37 **Rb** Rubidium 85.47	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.91	40 **Zr** Zirconium 91.22	41 **Nb** Niobium 92.91	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.91	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.87	48 **Cd** Cadmium 112.41	49 **In** Indium 114.82	50 **Sn** Tin 118.71	51 **Sb** Antimony 121.76	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90	54 **Xe** Xenon 131.29
6	55 **Cs** Cesium 132.91	56 **Ba** Barium 137.33	57 **La** Lanthanum 138.91	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.95	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.21	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.22	78 **Pt** Platinum 195.08	79 **Au** Gold 196.97	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.38	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
7	87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (266)	107 **Bh** Bohrium (264)	108 **Hs** Hassium (269)	109 **Mt** Meitnerium (268)									

58 **Ce** Cerium 140.12	59 **Pr** Praseodymium 140.91	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.96	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.93	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.97
90 **Th** Thorium 232.04	91 **Pa** Protactinium 231.04	92 **U** Uranium 238.03	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

Key

11 — Atomic number
Na — Element symbol
Sodium — Element name
22.99 — Average atomic mass*

* If this number is in parentheses, then it refers to the atomic mass of the most stable isotope.