NAME ________________________

ID # ________________________

ORGANIC CHEMISTRY I (2301)

1:30 pm – 3:30 pm, December 17, 2013

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 Thursday, December 19th (9:30-11 am) in Coffman Union Starbucks.
- Alternately, you will be able to pick up your exam in private from Chemistry department staff in 115 Smith beginning Friday, December 20th.

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

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 ________________________

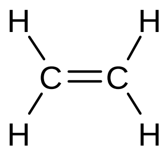
Scoring:

1. _________ / 12
2. _________ / 17
3. _________ / 3
4. _________ / 34
5. _________ / 12
6. _________ / 16
7. _________ / 15
8. _________ / 34
9. _________ / 18
10. ________ / 37

Total Score: _________ / 200

1. (12 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.

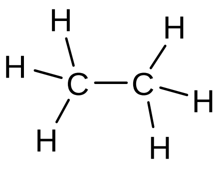
<u>Acid</u> <u>Conjugate Base</u>



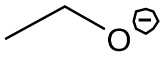
is

MORE ACIDIC **LESS ACIDIC**

than



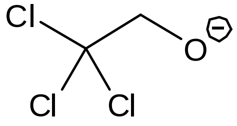
<u>Base</u> <u>Conjugate Acid</u>



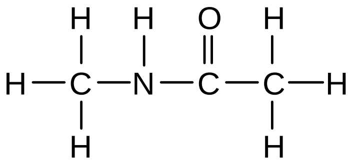
is

MORE BASIC **LESS BASIC**

than

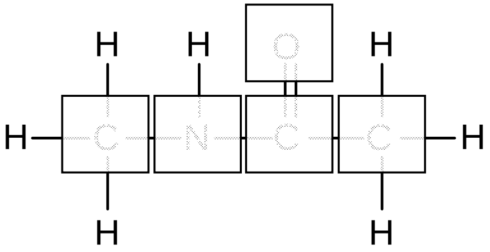


2. (17 pts) For methyl acetamide (drawn at right), in the boxes provided:



- 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

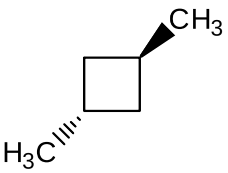
↔

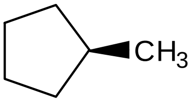
resonance structure

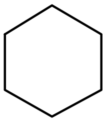
MOST *or* **LEAST** *significant?*

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

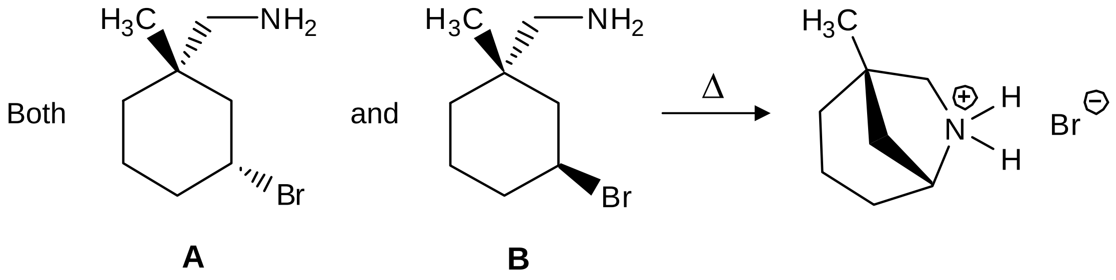
3. (3 pts) Each of the C_6H_{12} cycloalkanes on the right combusts in O_2 exothermically (with $\Delta H_{comb} << 0$) to CO_2 and H_2O. **Which one combusts the most exothermically?** (Circle one molecule.)







4. (34 pts) Each of the starting materials below, when heated, is transformed into the same product. However, the two starting materials react via different mechanisms. In this problem, you will explain why.



(a) Each of the starting cyclohexanes (which I've labeled **A** and **B**) has two equilibrating chair conformers. In the boxes below, draw the two chair conformers for each starting material. Feel free to omit the ring hydrogens, but draw all non-hydrogen substituents.

2 chair conformers for molecule **A**	*2 chair conformers for molecule* **B**
⇅	⇅

(b) Of the four conformers you drew on the previous page, only <u>one</u> will react to make product via **S_N2**. In the box on the right, re-draw that conformer. Then, "push electrons" (using curved arrows) to show how the product would be generated from this conformer. (You don't need to re-draw the product, just push electrons.)

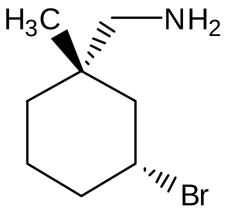
Mechanism for S_N2-reactive conformer

Is this molecule **A** *or* **B** ?
(Circle one.)

(c) Your answer to part (b) explains how one of the starting materials is converted to product. How is product generated from the <u>other</u> starting material? *Please be brief; you can probably answer this question in less than 5 words. You do not need to draw a mechanism to answer this question.*

Explain how:

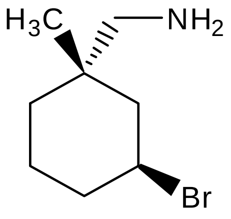
(d) Are the two starting materials chiral? For each starting material, **circle** whether you think the molecule is chiral or achiral. Then, **label each chiral center** with its appropriate Cahn-Ingold-Prelog designation [(*R*) or (*S*)]. Make it clear which atom in the drawing you are labeling.



CHIRAL

or

ACHIRAL ?



CHIRAL

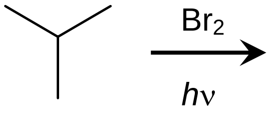
or

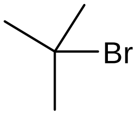
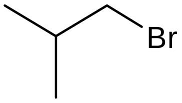
ACHIRAL ?

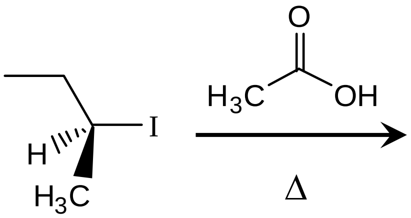
(e) What is the stereochemical relationship between the two starting materials? (Circle one answer.) Are they

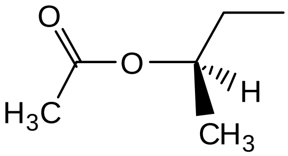
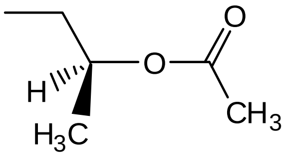
ENANTIOMERS *or* **DIASTEREOMERS** *or* **NEITHER** ?

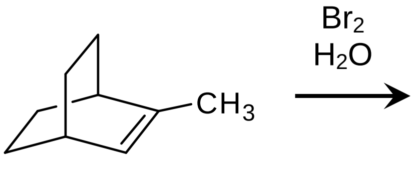
5. (12 pts) Each of the reactions below is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced equally, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**

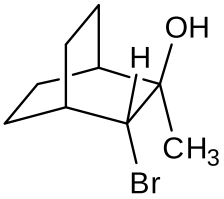
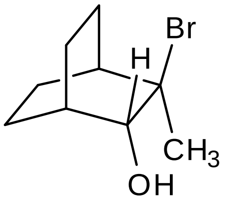


	
BOTH (equally)	NEITHER



	
BOTH (equally)	NEITHER

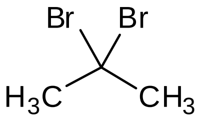


	
BOTH (equally)	NEITHER

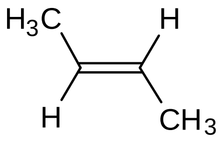
6. (16 pts) Each of the reactions *on the next page* is drawn with two possible reaction conditions. If only one of the two reaction conditions would generate the given molecule as the major product, circle those conditions. If both sets of conditions would accomplish the reaction, circle "BOTH". If neither set of reaction conditions would succeed, circle "NEITHER". **Circle one answer only.**

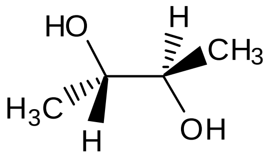
HBr *(excess)*	Br_2 *(excess)*
BOTH would work	NEITHER would work

$H_3C{-}C{\equiv}C{-}H \longrightarrow$

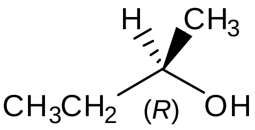


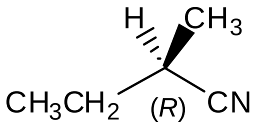
$KMnO_4$ H_2O, ^-OH (*cold, dilute*)	*m*CPBA H_2O
BOTH would work	NEITHER would work



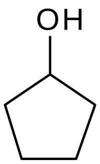


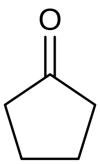
1. TsCl pyridine 2. NaCN	1. PBr_3 2. NaCN
BOTH would work	NEITHER would work



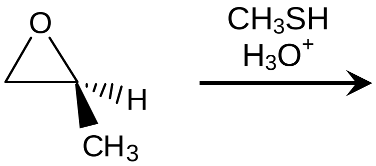


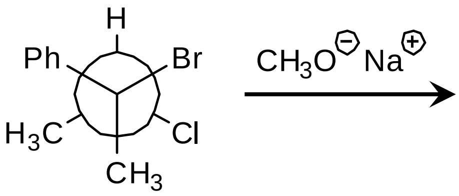
$Na_2Cr_2O_7$ H_2SO_4	1. $(COCl)_2$, DMSO -60 °C 2. Et_3N *(Swern oxidation)*
BOTH would work	NEITHER would work

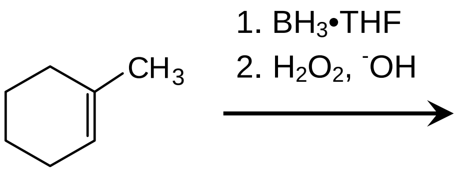




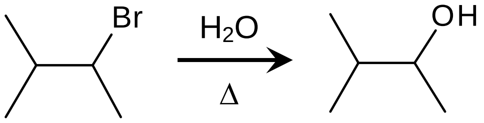
7. (15 pts) For each of the reactions on the following pages, fill in the empty box corresponding to the major product. Wherever appropriate, illustrate stereochemistry in your drawings (using wedge and dashed bonds). If multiple enantiomers or diastereomers are produced, indicate this in the answer box (e.g., by writing "+ enantiomer", etc.)





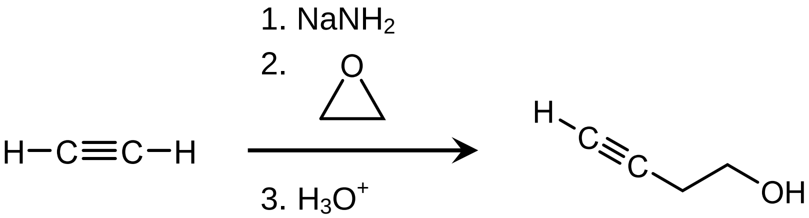


8. (34 pts) Draw a mechanism (using "electron pushing") for each reaction or series of reactions shown below. Draw each mechanistic step explicitly; don't cheat by combining multiple processes in a single step. Use only the molecules shown in the problem; don't invoke generic species. (E.g., don't use "H-A" as a generic acid.)



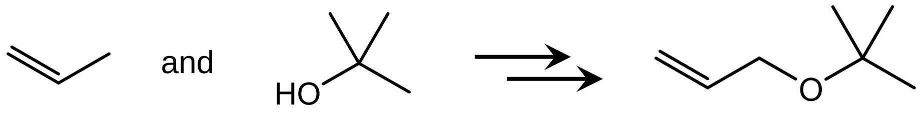
Mechanism:

One of the intermediates you drew in this mechanism could be stabilized by a 1,2-hydride shift. What alcohol product would be generated if this shift occurred?

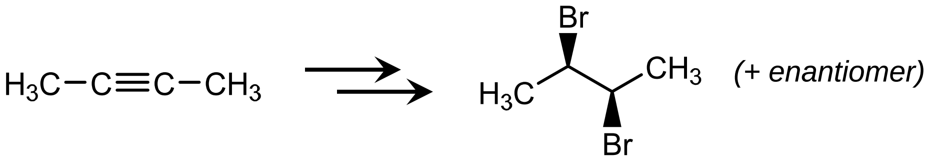


Mechanism:

9. (18 pts) For each set of starting materials and products shown on the next page, **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 each problem; draw only your best (one) synthetic route. Feel free to draw an incomplete route—we will give you partial credit where we can.

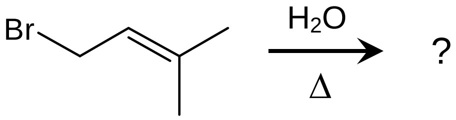


Multistep synthesis:

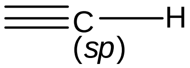


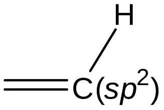
Multistep synthesis:

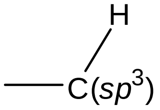
10. (37 pts) The bromoalkene starting material on the right reacts with water and heat to give a number of S_N1 substitution and E1 elimination products. One product was isolated and characterized by NMR and IR spectroscopy and mass spectrometry; the spectra of this product are shown on the following pages. High-resolution mass spectrometry determined an exact mass of 86.0732 amu for the highest-mass (parent, $\mathbf{M^+}$) peak in the MS spectrum, which corresponds to a molecular formula of $\mathbf{C_5H_{10}O}$.

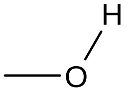


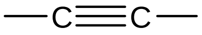
(a) Four of the peaks in the IR spectrum below are labeled with their *x*-axis (wavenumber) value. What type of bond in the product does each peak correspond to? Match each peak to its bond vibration by writing its wavenumber value in the appropriate box. *There are seven boxes, so please leave three of them empty.*

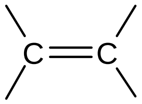


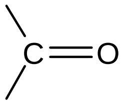




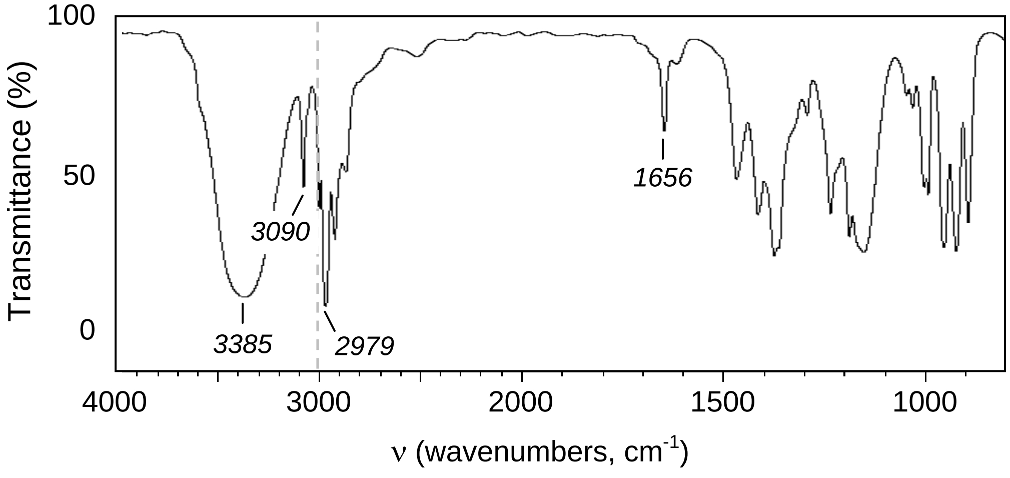








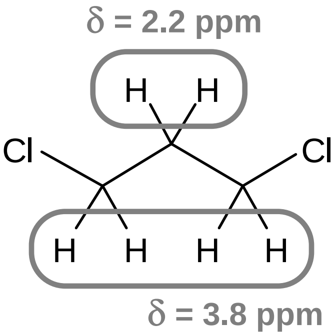
IR Spectrum:



(b) **What is the structure of the product**? In the box at right, draw the molecule's structure, <u>including all hydrogens</u>. Then, considering the ^{1}H NMR spectrum below, circle each set of equivalent H's, and label each circle with its unique ^{1}H NMR chemical shift to within 0.1 ppm. (You do <u>not</u> need to label coupling constants *J*.)

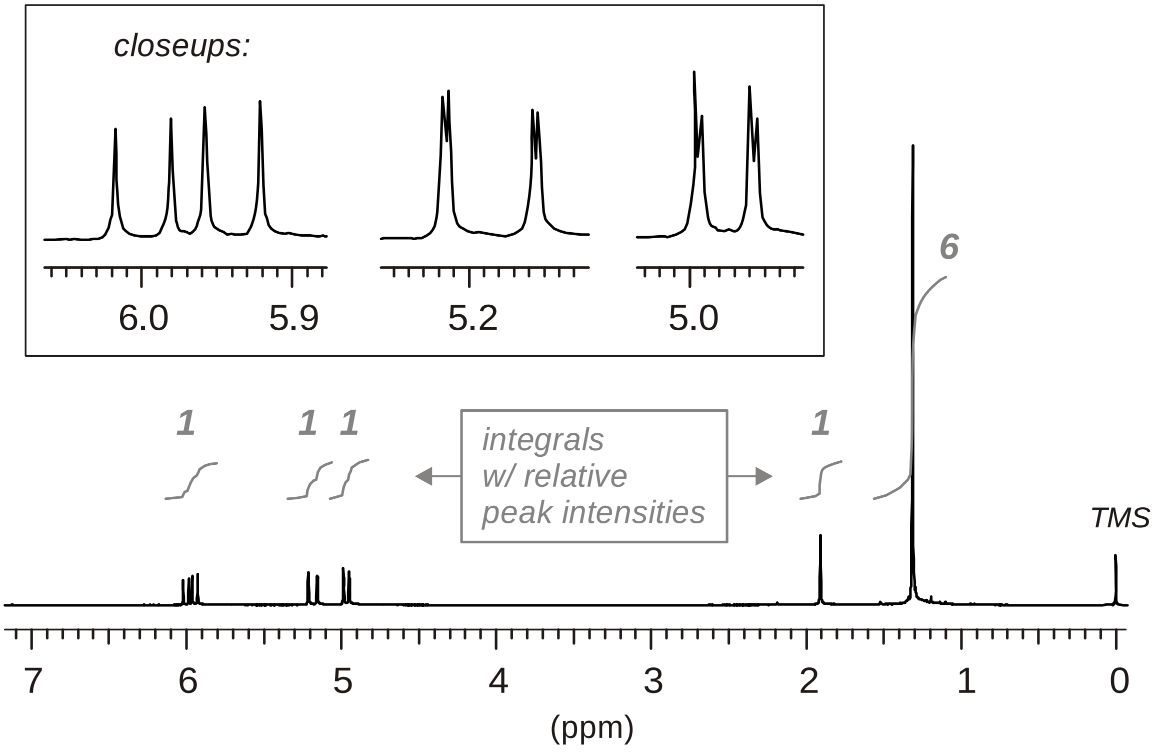
the product
($C_5H_{10}O$)

Format for answer to (b):



(c) By what mechanism was this product generated, **S_N1** *or* **E1** ? (Circle one.)

^{1}H NMR Spectrum:



^{1}H NMR, 300 MHz

(d) In the electron-ionization (EI) mass spectrum, the parent mass peak at *m*/*z* = 86 corresponds to a radical cation (**M**$^{\bullet+}$) that is generated by removing one electron from the original, neutral molecule **M**. In the box on the right, draw **M**$^{\bullet+}$; re-draw the structure you drew in part (b), but specifically indicate which electron is removed by drawing the molecule with one less electron.

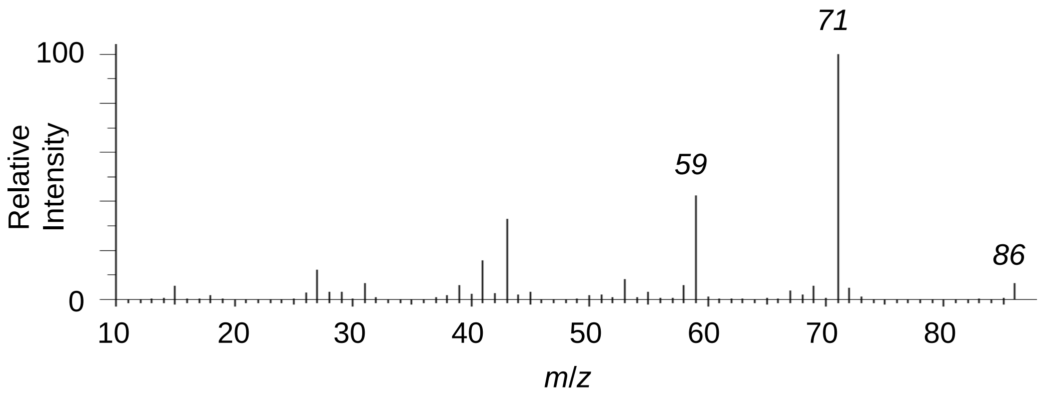
M$^{\bullet+}$
($C_5H_{10}O^+$)

(e) What are the structures of the two predominant daughter (fragment) cations in the mass spectrum that have *m*/*z* = 71 and 59? *You do not need to do electron pushing to answer this question—just draw the cations.*

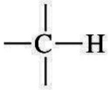
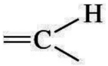
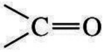
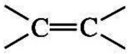
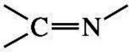
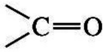
fragment cation with m/z = 71

fragment cation with m/z = 59

Mass Spectrum:



Summary of IR Stretching Frequencies

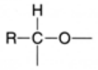
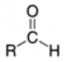
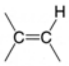
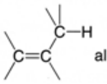
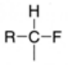
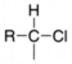
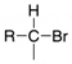
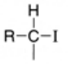
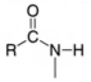
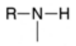
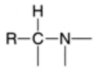
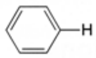
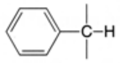
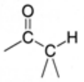
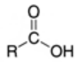
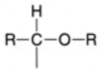
Frequency (cm^{-1})	Functional Group		Comments
3300	alcohol	O—H	always broad
	amine, amide	N—H	may be broad, sharp, or broad with spikes
	alkyne	≡C—H	always sharp, usually strong
3000	alkane		just below 3000 cm^{-1}
	alkene		just above 3000 cm^{-1}
	acid	O—H	very broad
2200	alkyne	—C≡C—	just below 2200 cm^{-1}
	nitrile	—C≡N	just above 2200 cm^{-1}
1710 (very strong)	carbonyl		ketones, aldehydes, acids esters higher, about 1735 cm^{-1} conjugation lowers frequency amides lower, about 1650 cm^{-1}
1660	alkene		conjugation lowers frequency aromatic C═C about 1600 cm^{-1}
	imine		stronger than C═C
	amide		stronger than C═C (see above)

Ethers, esters, and alcohols also show C—O stretching between 1000 and 1200 cm^{-1}.

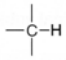
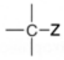
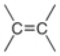
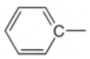
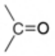
Isotopic Composition of Some Common Elements

Element	M$^+$		M+1		M+2	
hydrogen	^{1}H	100.0%				
carbon	^{12}C	98.9%	^{13}C	1.1%		
nitrogen	^{14}N	99.6%	^{15}N	0.4%		
oxygen	^{16}O	99.8%			^{18}O	0.2%
sulfur	^{32}S	95.0%	^{33}S	0.8%	^{34}S	4.2%
chlorine	^{35}Cl	75.5%			^{37}Cl	24.5%
bromine	^{79}Br	50.5%			^{81}Br	49.5%
iodine	^{127}I	100.0%				

^{1}H NMR Absorptions

Compound type	Chemical shift (ppm)
Alcohol	
R–O–H	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
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

Final Exam Chart of Reaction Conditions

Reactions to consider from Ch. 6-7 (Exam 2): Acid-Base, S_N2, S_N1, E2, E1

HBr

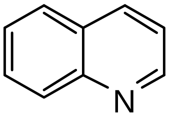
Br_2

Br_2
H_2O *or* ROH

$Pt/H_2(g)$

$NaNH_2$

Pd, $BaSO_4$
$H_2(g)$



(quinoline)
(Lindlar's catalyst)

$Na_2Cr_2O_7$
H_2SO_4

1. BH_3•THF
2. H_2O_2, OH^-

1. O_3
2. $(CH_3)_2S$

Na
NH_3

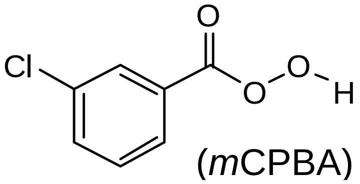
$HgSO_4$
H_2SO_4
H_2O

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

(Swern oxidation)

H_2SO_4
H_2O

*m*CPBA
H_2O



(*m*CPBA)

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

$SOCl_2$
pyridine

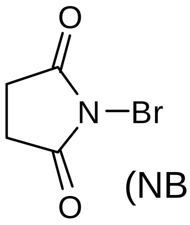
TsCl
pyridine

1. O_3
2. H_2O

$KMnO_4$
H_2O, pH 7

PBr_3

Cl_2 *or* Br_2,
hν



(NBS)
hν *or* AIBN

1. $KMnO_4$
   KOH, Δ
2. H_3O^+

Periodic Table of the Elements

Chemistry Reference Sheet

California Standards Test

Key

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

	1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 **H** Hydrogen 1.01																	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											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)

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