NAME _____

ID # _____

ORGANIC CHEMISTRY I (2301)

9:30 – 11:30 am, August 4, 2011

Final Exam

Form A

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 Friday, August 5th (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 Friday, August 5th at noon. Exams that are not picked up within two weeks will be disposed of.

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).

Right now, write your name at the top of this page, and fill in the bubbles on the multiple-choice answer sheet for your name and your 7-digit student ID number. When the exam begins, also write your name at the top of page 5.

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

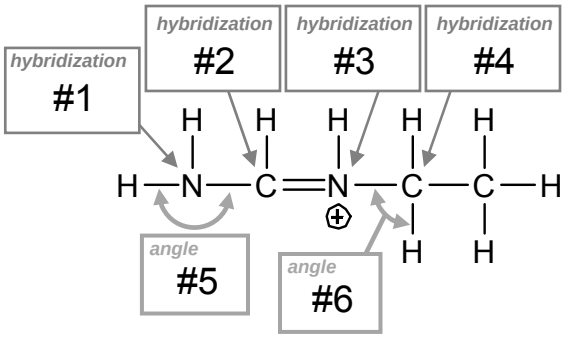
Please write your answers in the bubble sheet for the multiple choice portion of the exam, and in the boxes/spaces provided for the written portion. If your answer is not in the appropriate space in the written portion (say, for example, it's on the back of the page), draw us an arrow and/or note telling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

Multiple-Choice Problems

Please answer these problems on the bubble sheet.

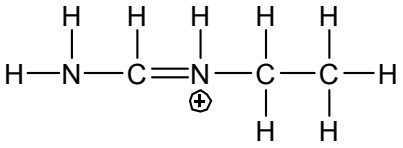
(2 pts each) For ethylformamidinium cation, drawn at right:

- For each atom marked "hybridization", indicate whether the atom is hybridized(a) *sp*, (b) sp^2, (c) sp^3, or (d) none of these.
- For each bond angle marked "angle", indicate whether the angle is closest to (a) 109.5°, (b) 120°, or (c) 180°.

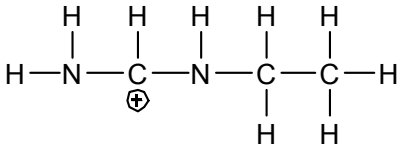


7. (3 pts) Of the resonance structures on the right, which contributes **least** to the overall electronics in ethylformamidinium cation?

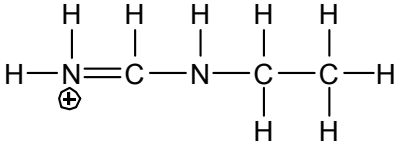
a.



b.

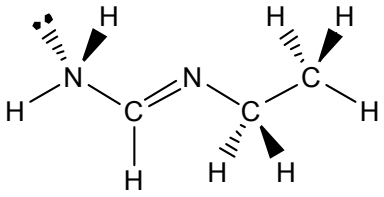


c.

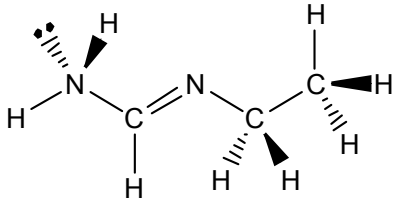


8. (3 pts) Which of the structures below represents the most stable 3-dimensional conformation of ethylformamidinium cation?

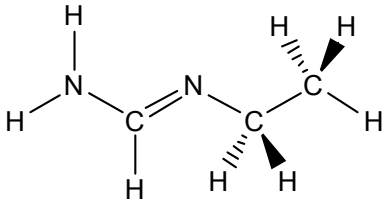
a.



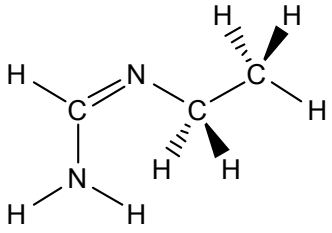
b.



c.



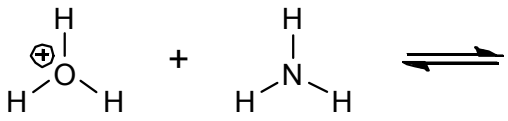
d.



(2 pts each) Does the proton-transfer equilibrium for each acid-base pair shown below favor products, or starting materials? (Is the acid strong enough to protonate the base?)

Does the equilibrium favor:

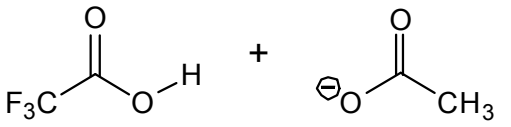
9.



conjugate acid-base products

a. products, or
b. starting materials?

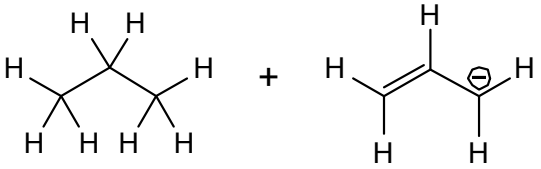
10.



conjugate acid-base products

a. products, or
b. starting materials?

11.

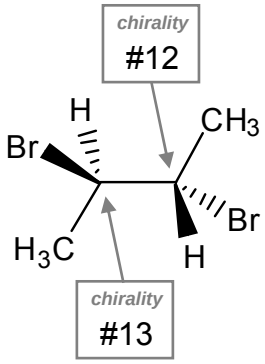


conjugate acid-base products

a. products, or
b. starting materials?

(2 pts each) For each of the molecules drawn on the right:

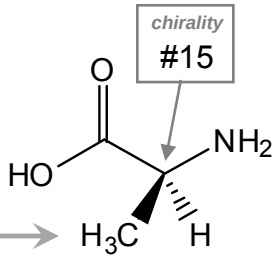
- For each atom marked "chirality", indicate whether the atom would be labeled as (a) an (*R*)-chiral center, (b) an (*S*)-chiral center, or (c) not a chiral center, according to the Cahn-Ingold-Prelog classification system.
- Indicate whether the molecule would be chiral or achiral.



14. Is this molecule
a. chiral, or
b. achiral?

17. (2 pts) Are the methyl-group hydrogens in the structure on the right

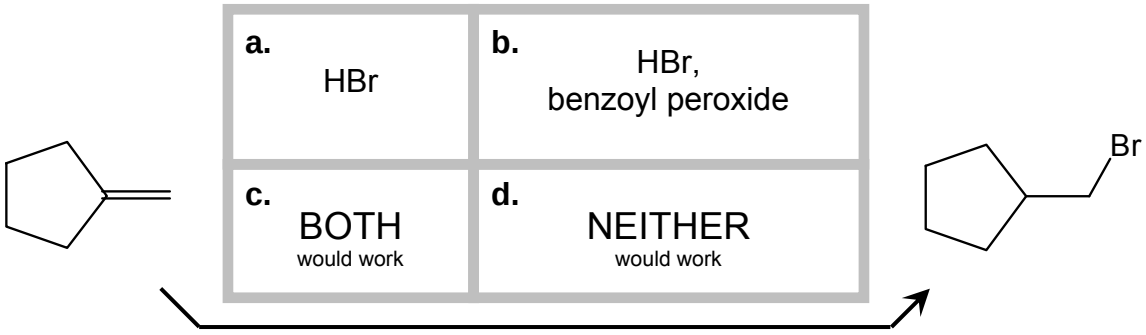
a. enantiotopic,
b. diastereotopic, or
c. neither of the above?



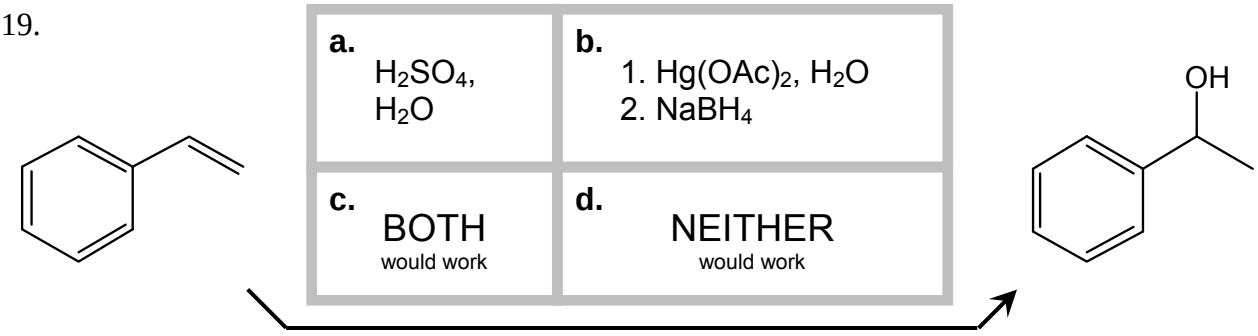
16. Is this molecule
a. chiral, or
b. achiral?

(4 pts each) 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, answer with the corresponding letter. If both sets of conditions would accomplish the reaction, answer (c) "BOTH". If neither set of reaction conditions would succeed, answer (d) "NEITHER".

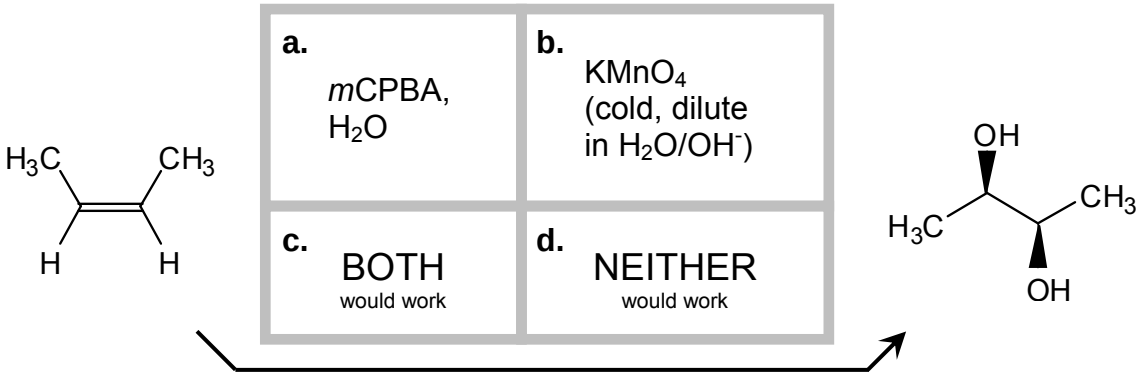
18.



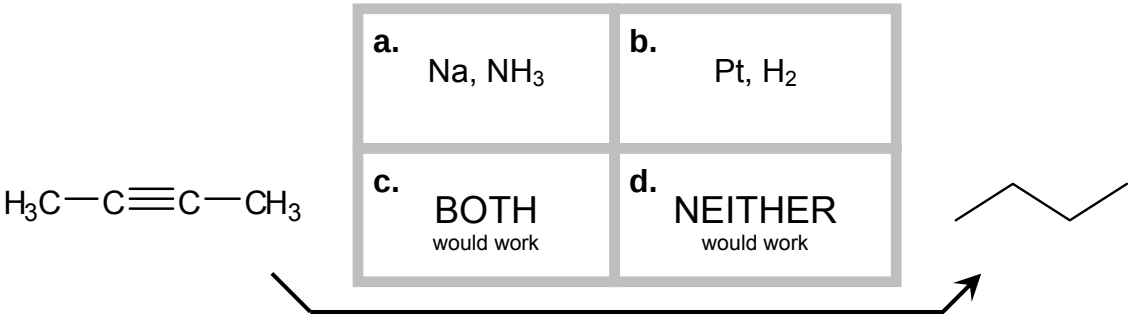
19.



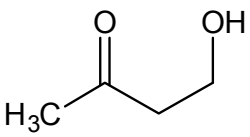
20.



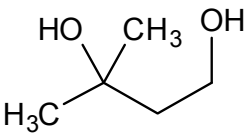
21.



22.

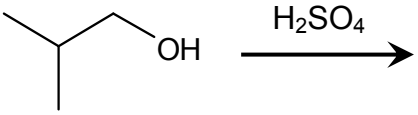


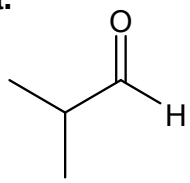
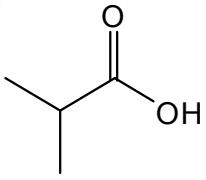
a. 1. CH_3Li *(1 equiv)* 2. H_3O^+	**b.** 1. CH_3MgBr *(1 equiv)* 2. H_3O^+
c. BOTH would work	**d.** NEITHER would work



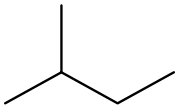
(4 pts each) Each of the reactions below is drawn with two possible products, marked (a) and (b). If one of the two products predominates, answer with the letter corresponding to the correct product. If the two products are produced equally, answer (c) BOTH. If neither product would result from the reaction, answer (d) NEITHER.

23.

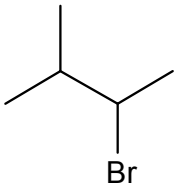
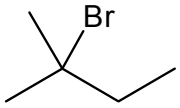


a. 	**b.** 	**c.** BOTH (equally)
		d. NEITHER

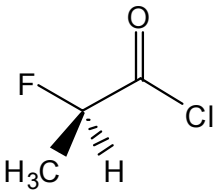
24.



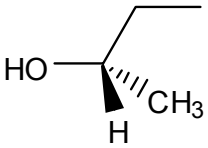
Br_2, $h\nu$

a. 	**b.** 	**c.** BOTH (equally)
		d. NEITHER

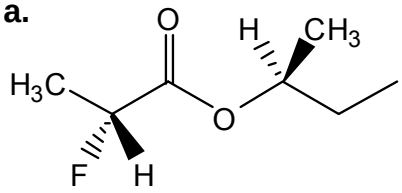
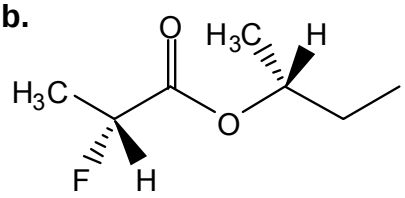
25.



+



pyridine

a. 	**b.** 	**c.** BOTH (equally)
		d. NEITHER

Multiple-choice problems 26-31 are found later in the exam, on pages 6-7.

NAME _____

Scoring: 32. _____ / 29 35. _____ / 14

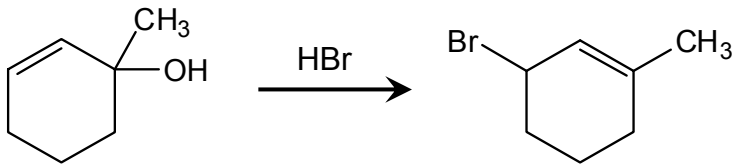
33. _____ / 25 36. _____ / 26

34. _____ / 32

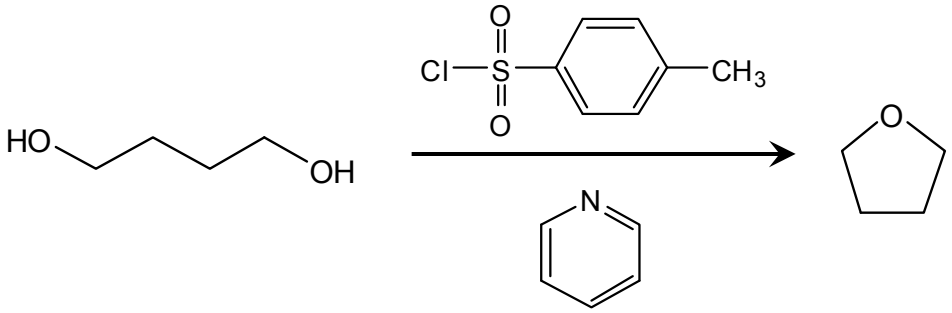
Total Score: _____ / 126

32. (29 pts) For the reactions shown below, draw a mechanism that explains how the product is generated from the starting material. In your answer, make sure that you:

- Draw each step of the mechanism separately;
- Use "electron pushing" to show where the electrons in each step go;
- Use only the molecules that you are given; do not invoke reactants or solvents that aren't in the problem.

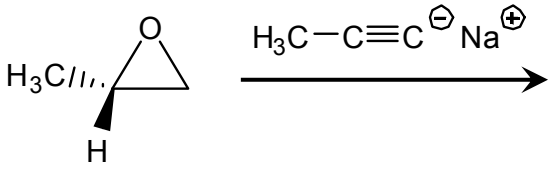


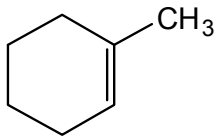
Mechanism:



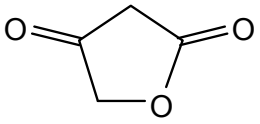
Mechanism:

33. (25 pts) Draw the missing reactant or product in the empty boxes. For products, give the predominant, most favored product. Illustrate stereochemistry in your answer where appropriate. For reactions that yield multiple enantiomers, draw only one enantiomer in the box, and include the note "+ enantiomer".

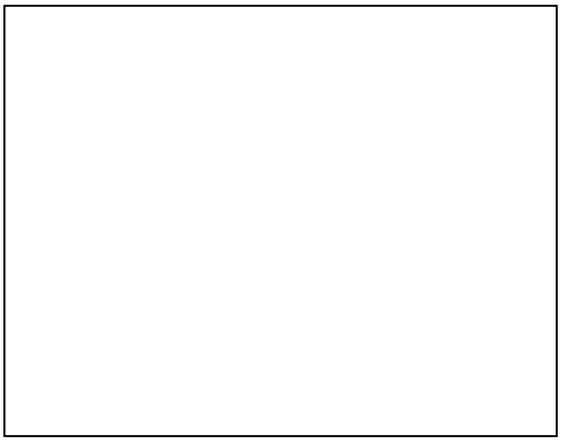


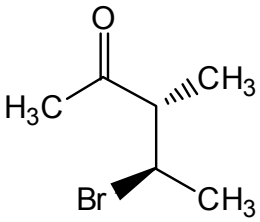


Br_2
H_2O

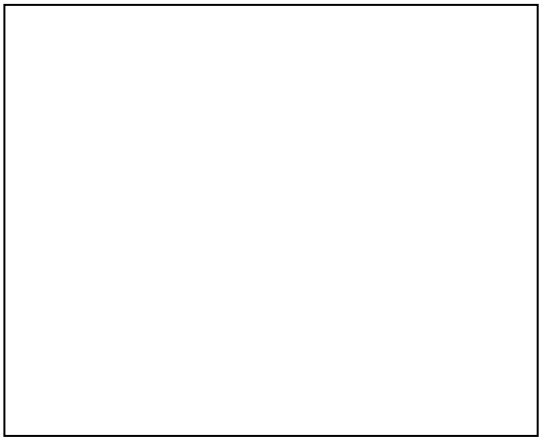


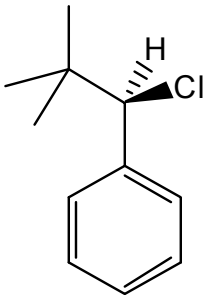
$NaBH_4$
CH_3OH

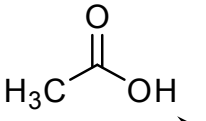




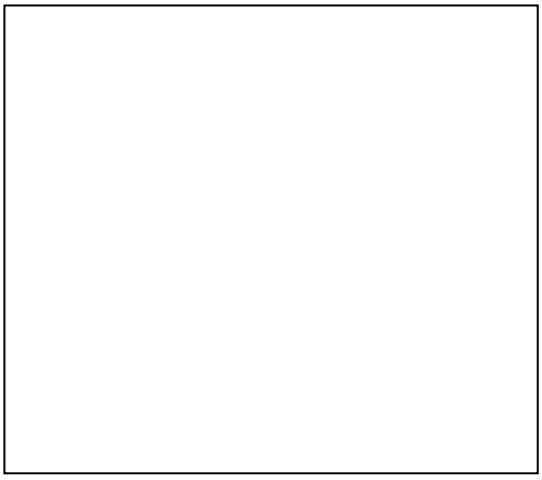
$CH_3O^{\ominus}Na^{\oplus}$



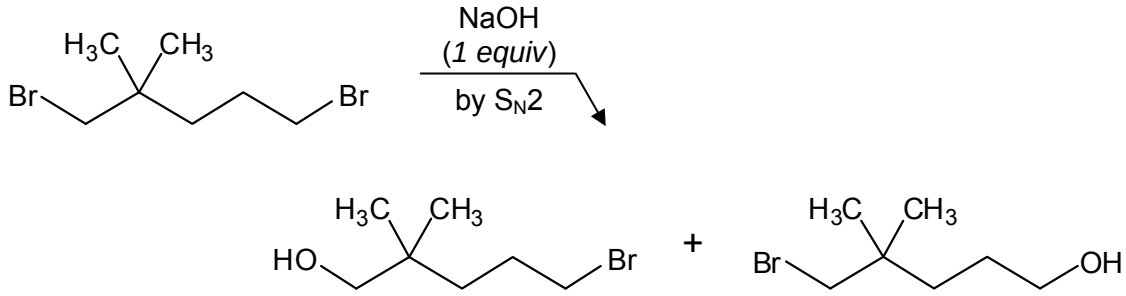




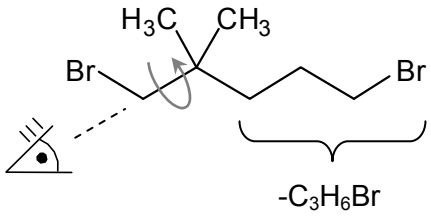
Δ

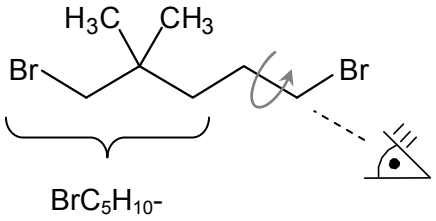


34. (32 pts) 1,5-dibromo-2,2-dimethylpentane can react with one equivalent of OH^- by S_N2 substitution at either end on the molecule, to give products in which one of the bromines has been substituted by an alcohol group. In this problem, you will describe which of these two substitution products is favored over the other, and why.



(a) The single bonds in the starting material are free to rotate, and S_N2 substitution of Br could occur in many different starting material conformations. In the boxes below, **draw Newman projections that illustrate two different staggered conformations** at the indicated bonds.



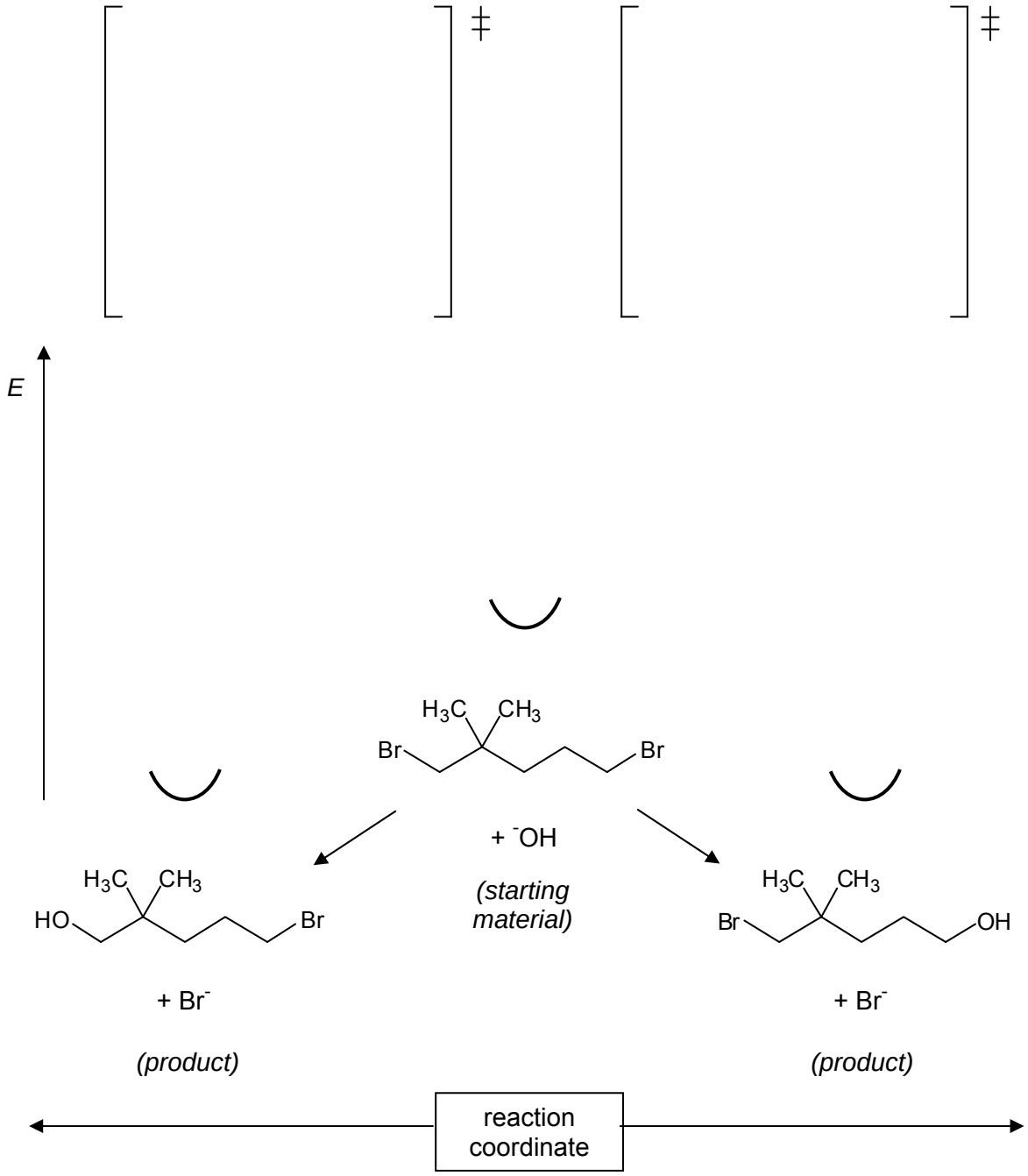


(b) Of the four Newman projections you drew above, which would react the fastest with OH^- in an S_N2 reaction? **Circle one Newman projection.**

(Problem 3 continues on the next page.)

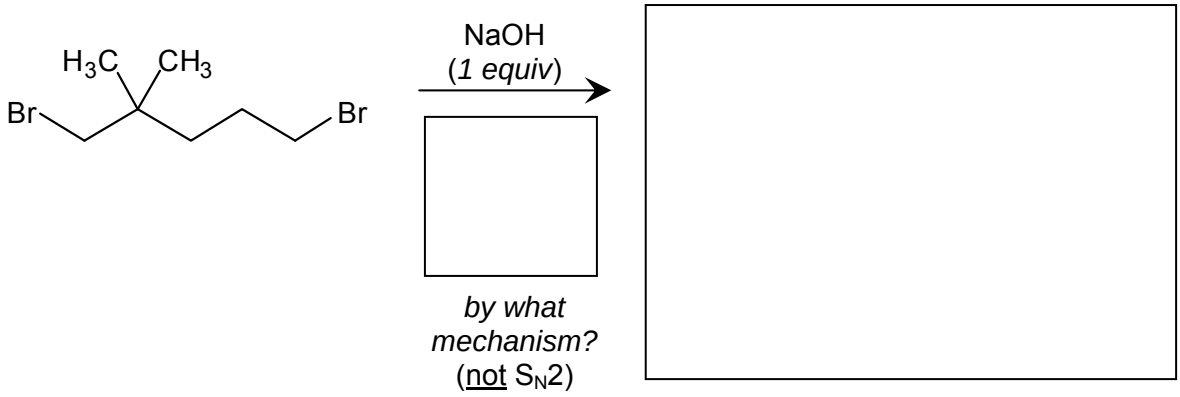
(c) On the diagram below:

- **Draw potential energy curves** for formation of each of the two S_N2 products. (I have already drawn the energies of the starting materials and products; you just need to connect them with curves.)
- **Draw activation energies (E_a)** for each of the two pathways.
- **Draw the structure** of the rate-determining transition state for each reaction. Feel free to draw these structures as Newman projections, just as you did in part (b).
- **Circle the preferred S_N2 product.**

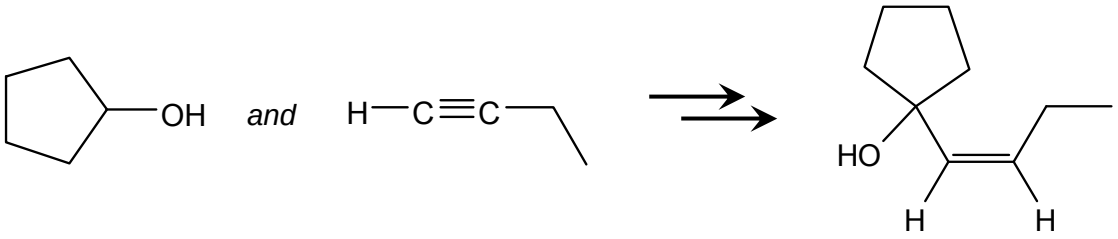


(Problem 3 continues on the next page.)

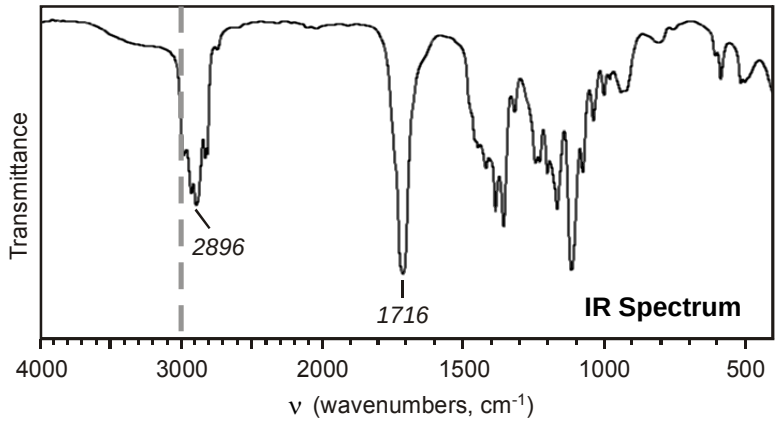
(d) In fact, both of these S_N2 products are *minor* products of the reaction between one equivalent of OH^- and the starting material, because OH^- is a stronger base than it is a nucleophile. What molecule would be the preferred product of this reaction, and by what mechanism would it be produced?

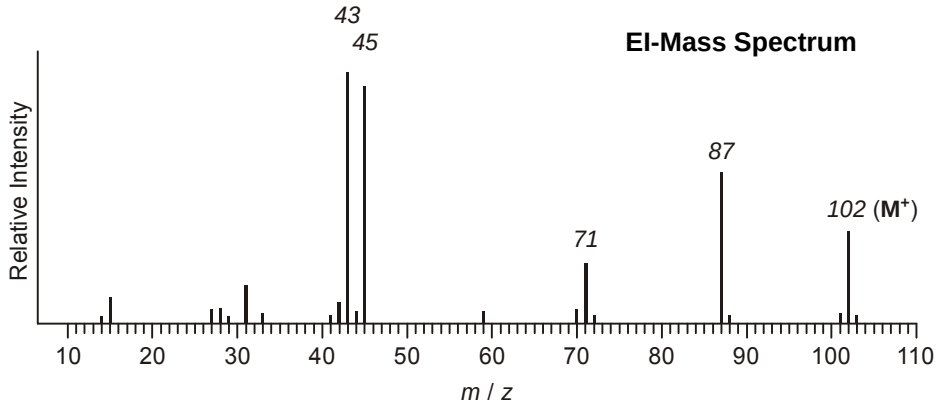


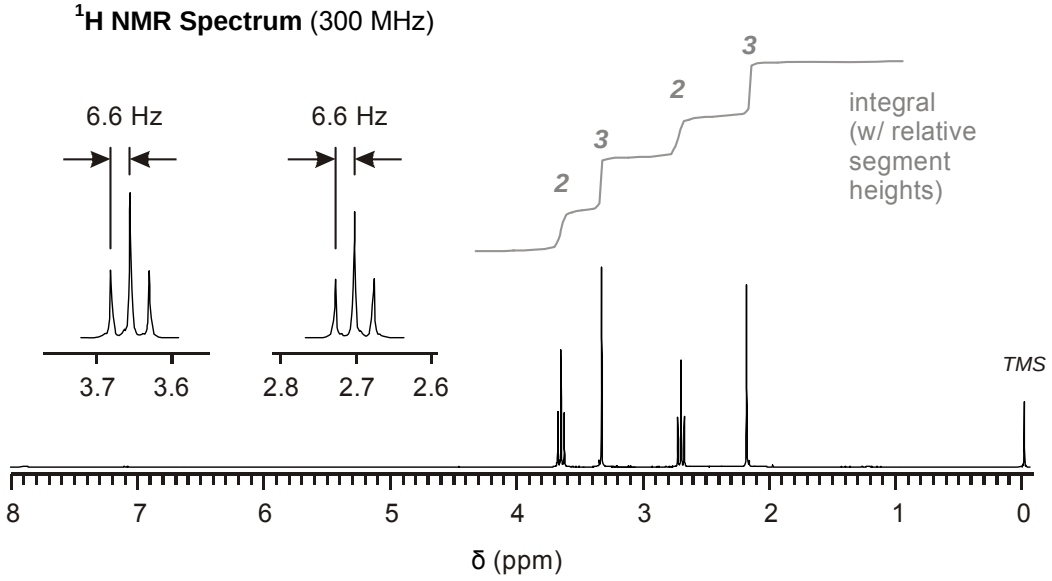
35. (14 pts) **Propose a multistep synthesis** of the product shown below from the given starting materials, along with any reagents we have covered in class. You might discover multiple answers to this problem; draw only your best (one) synthetic route. Feel free to draw an incomplete route—we will give you partial credit where we can.



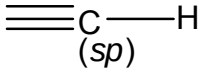
The spectra on this page correspond to a pure molecule, isolated from a chemical reaction. High-resolution mass spectrometry determined an exact mass of 102.0681 amu for the highest-mass (parent, M^+) peak in the MS spectrum, which corresponds to a molecular formula of **$C_5H_{10}O_2$**.

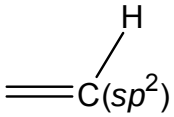


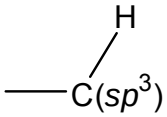


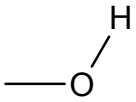


(1 pt each) Based on the features in the IR spectrum, which of the following functional groups would you expect the unknown molecule to have? Would the molecule contain a

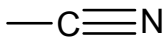
26.  ?
a. Yes
b. No

27.  ?
a. Yes
b. No

28.  ?
a. Yes
b. No

29.  ?
a. Yes
b. No

30.  ?
a. Yes
b. No

31.  ?
a. Yes
b. No

36. (26 pts)

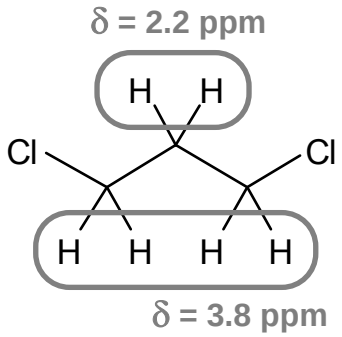
(a) The mass spectrum shows a parent mass peak at *m*/*z* = 102, and two fairly high-mass fragment ions at *m*/*z* = 87 and *m*/*z* = 71. For these fragment ions to be observed, the parent molecule must have ejected neutral (invisible) fragments with mass (102 - 87) = 15 and (102 - 71) = 31 atomic mass units (amu). What do you think are the structures of these neutral fragments?

neutral fragment with mass **15**:	*neutral fragment with mass* **31**:

(b) The mass spectrum shows a small peak at *m*/*z* = 103, *above* the mass of the parent $\mathbf{M}^+$ peak (102). Assuming that the material is pure (i.e., that there are no higher-mass contaminants in the sample), how is it possible that the mass of some molecules would be higher than expected? *Please be brief. You could probably answer this in 10 words or less.*

(c) **What is the structure of the molecule**? In the box below, draw your molecule's structure again, including all hydrogens. Then circle each set of equivalent H's, and label each with its unique ^{1}H NMR chemical shift.

Format for answer to (c):

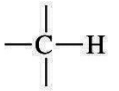
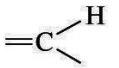
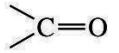
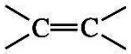
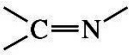
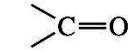


your molecule
($C_5H_{10}O_2$)

(d) Given your answer above, what is the structure of the daughter (fragment) cation in the mass spectrum that has *m*/*z* = 87? *You do not need to do electron pushing to answer this question—just draw the cation.*

fragment cation with m/z = 87

Summary of IR Stretching Frequencies

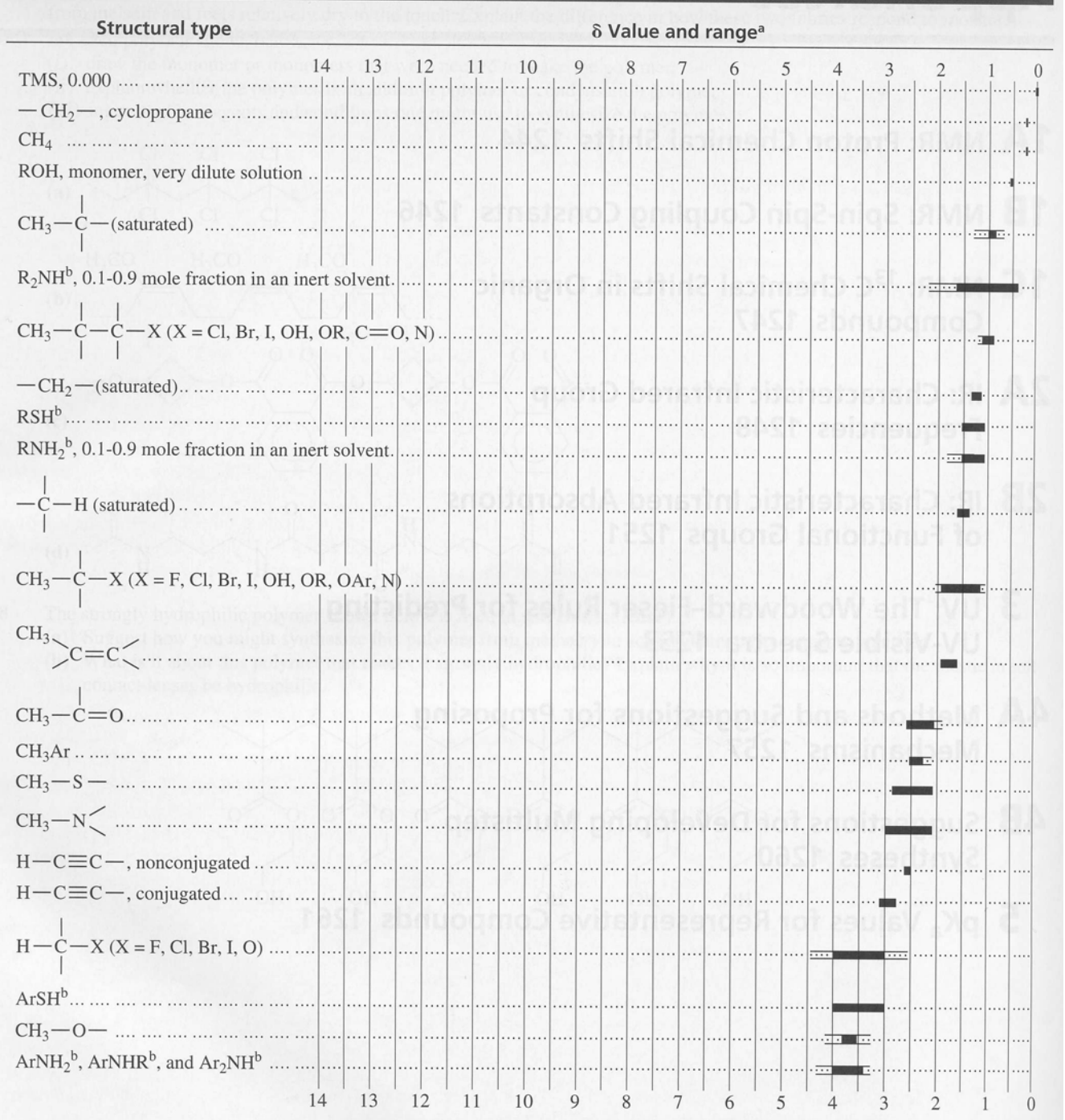
Frequency (cm^{-1})	Functional Group		Comments
3300	alcohol	O—H	always broad
	amine, amide	N—H	may be broad, sharp, or broad with spikes
	alkyne	≡C—H	always sharp, usually strong
3000	alkane		just below 3000 cm^{-1}
	alkene		just above 3000 cm^{-1}
	acid	O—H	very broad
2200	alkyne	—C≡C—	just below 2200 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%				

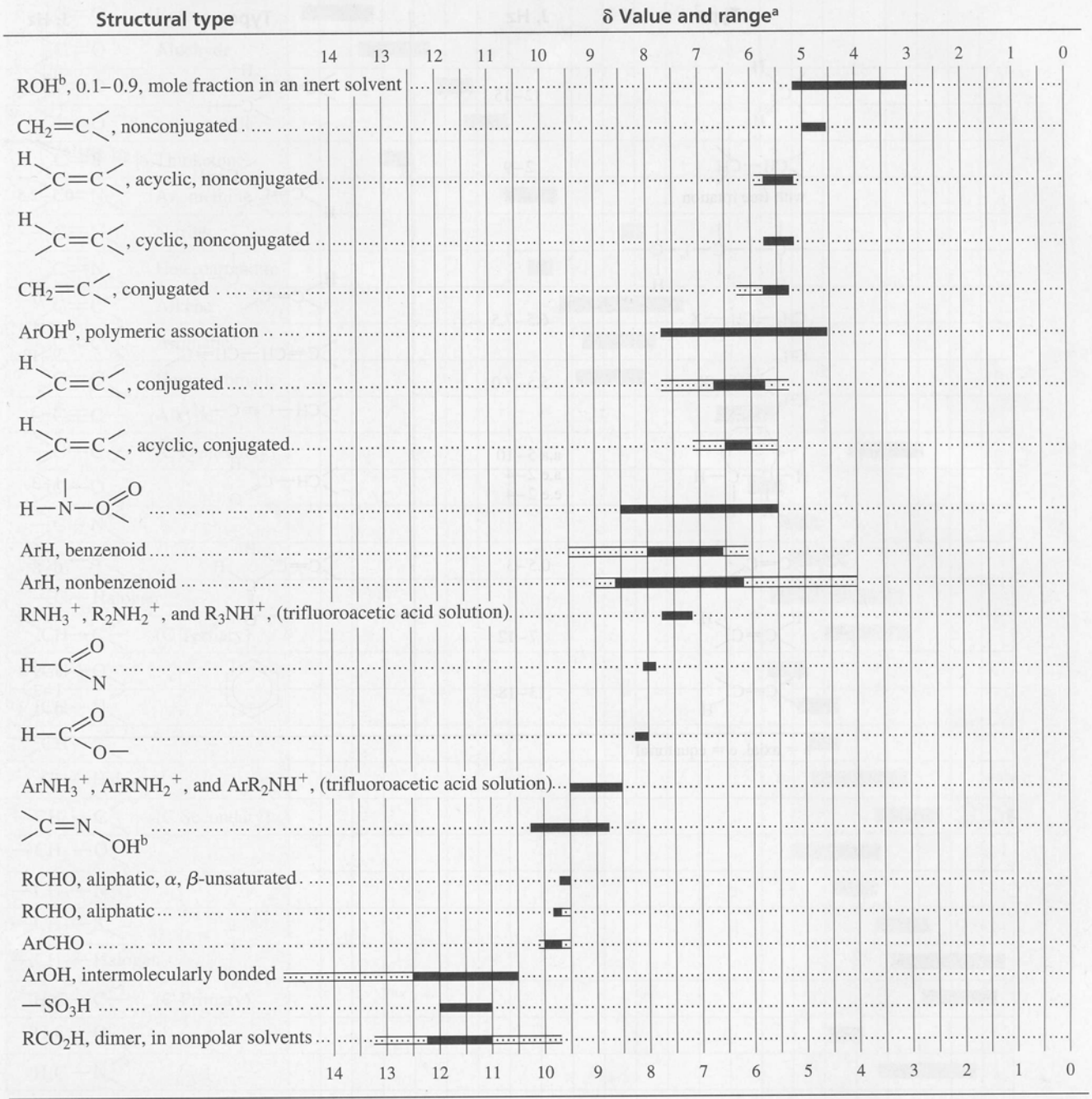
APPENDIX 1A NMR: Proton Chemical Shifts



[a] Normally, absorptions for the functional groups indicated will be found within the range shown in black. Occasionally, a functional group will absorb outside this range. Approximate limits are indicated by extended outlines.

[b] Absorption positions of these groups are concentration-dependent and are shifted to lower δ values in more dilute solutions.

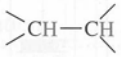
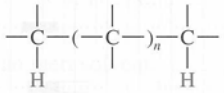
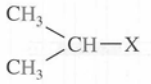
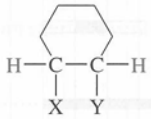
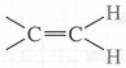
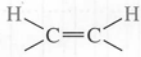
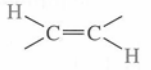
APPENDIX 1A NMR: Proton Chemical Shifts

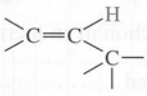
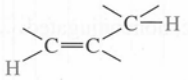
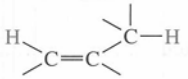
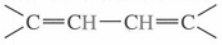
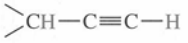
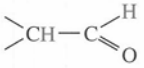
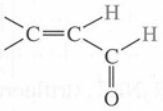
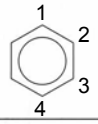


[a] Normally, absorptions for the functional groups indicated will be found within the range shown in black. Occasionally, a functional group will absorb outside this range. Approximate limits are indicated by extended outlines.

[b] Absorption positions of these groups are concentration-dependent and are shifted to lower δ values in more dilute solutions.

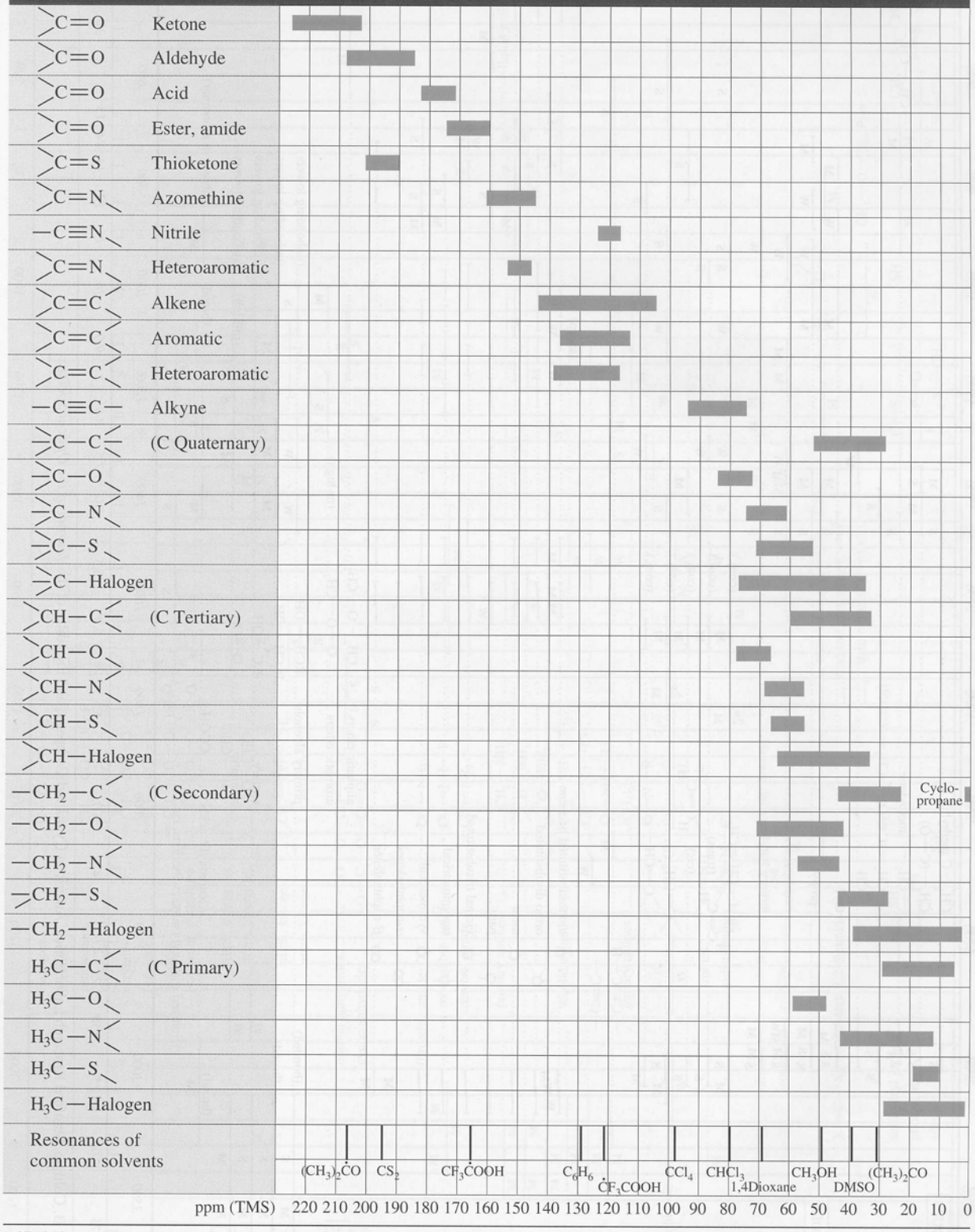
APPENDIX 1B NMR: Spin-Spin Coupling Constants

Type	J, Hz
	12–15
	2–9
with free rotation	~7
	~0
$CH_3—CH_2—X$	6.5–7.5
	5.5–7.0
	a,a 5–10 a,e 2–4 e,e 2–4
	0.5–3
	7–12
	13–18

Type	J, Hz
	4–10
	0.5–2.5
	~0
	9–13
	2–3
	1–3
	6–8
	H1-H2 6–9 H1-H3 1–3 H1-H4 0–1

a = axial, e = equatorial

APPENDIX 1C NMR: ^{13}C Chemical Shifts in Organic Compounds*:



*Relative to internal tetramethylsilane.

Final Exam Chart of Reaction Conditions

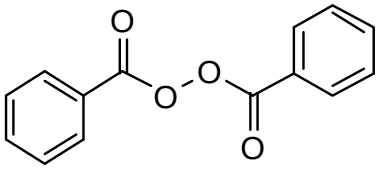
Reactions to consider from Ch. 6-7 (Exam 2): Acid-Base, S_N2, S_N1, E2, E1

Cl_2 *or* Br_2, *h*ν

HBr

Br_2

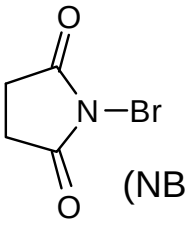
HBr



(benzoyl peroxide)

H_2SO_4
H_2O

1. $Hg(OAc)_2$
   H_2O *or* ROH
2. $NaBH_4$

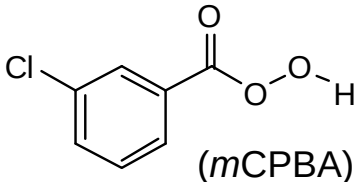


(NBS)

*h*ν *or* AIBN

Br_2
H_2O *or* ROH

1. BH_3•THF
2. H_2O_2, OH^-



(*m*CPBA)

*m*CPBA
H_2O

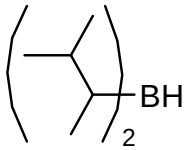
$Pt/H_2(g)$

$NaNH_2$

1. O_3
2. $(CH_3)_2S$

Na
NH_3

1.



("Sia_2BH")

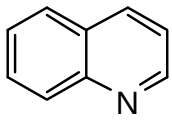
2. H_2O_2, NaOH

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

$KMnO_4$
H_2O, pH 7

1. O_3
2. H_2O

Pd, $BaSO_4$
$H_2(g)$



(quinoline)

$HgSO_4$
H_2SO_4

1. $LiAlH_4$
2. H_2O

1. $KMnO_4$
   KOH, Δ
2. H_3O^+

Mg
Et_2O

Li
hexane

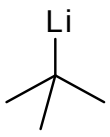
PBr_3

1. $NaBH_4$
2. H_2O

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

$Na_2Cr_2O_7$
H_2SO_4

TsCl
pyridine



(*t*BuLi)

1. Ag_2O
   NH_3
2. H_3O^+

$SOCl_2$
pyridine

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.