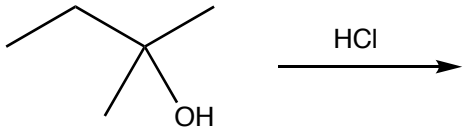
Name _____ Test 1 (~~2/24~~ 2/27)
CHEM 0201 (Organic) Spring 2023

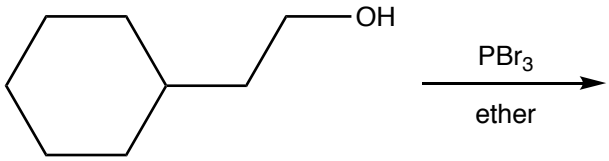
1. (12 pts) Alcohols have electrophilic carbon atoms, but unmodified alcohols are not good substrates for nucleophilic substitution reactions. Explain briefly.

(8 pts. each) Determine whether the following occur predominantly by an S_N1 or an S_N2 mechanism and predict the major organic product(s). There is no need to indicate the stereochemistry of the product(s). Ether and tetrahydrofuran are aprotic solvents.

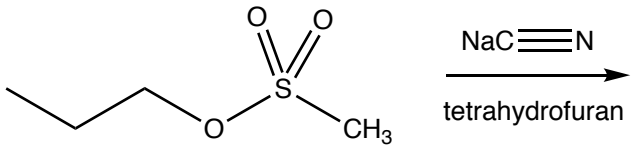
2.



3.

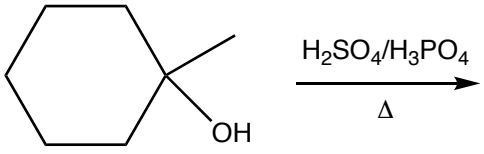


4.



(8 pts.) Predict the most likely organic product for the following elimination reaction.

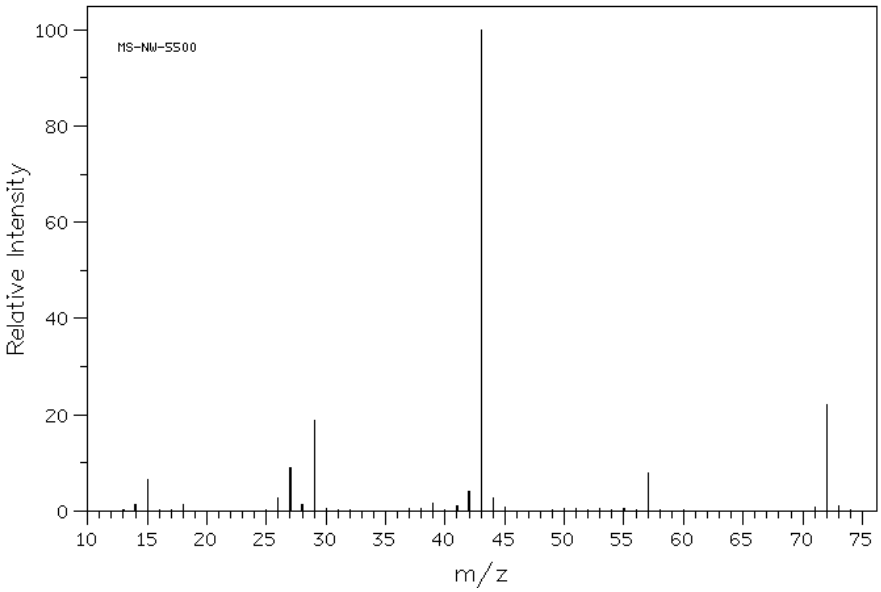
5.



1. _____
2. _____
3. _____
4. _____
5. _____
6. _____
7. _____
8. _____
9. _____
10. _____
11. _____
12. _____
13. _____

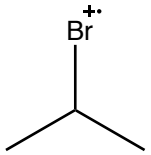
6. a. (4 pts.) Label the molecular ion and the base peak in the following mass spectrum.

   b. (8 pts.) Determine the formula of the molecular ion (there is one O atom in the molecule.)



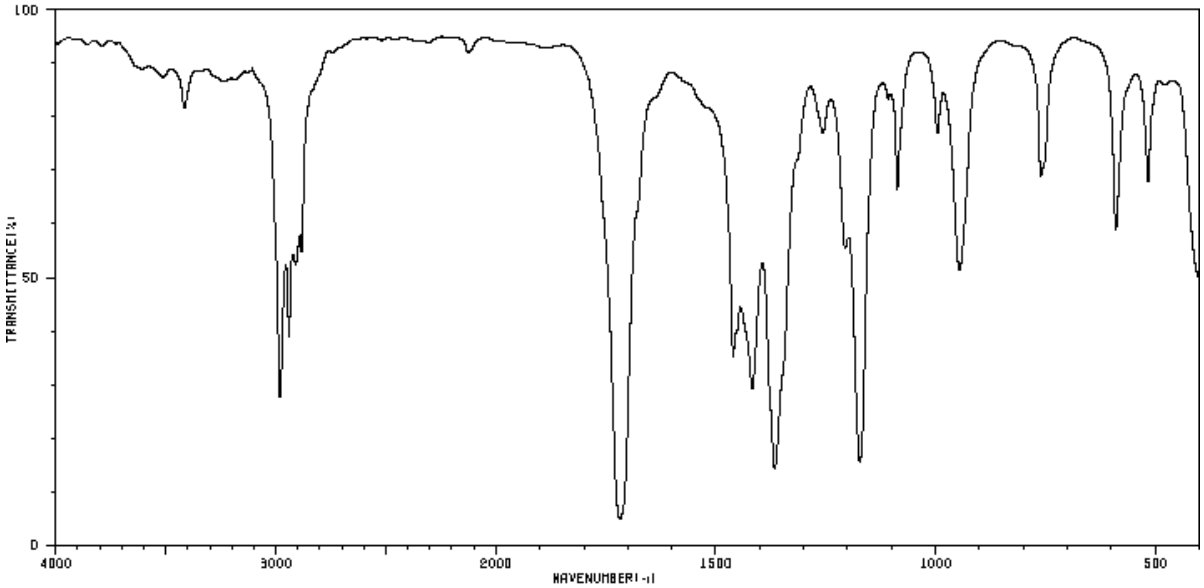
7. (12 pts.) In the mass spectrum of 2-bromopropane there is no peak that corresponds to the average molar mass for 2-bromopropane. Briefly explain why there is no peak that corresponds to the average molar mass and determine the mass to charge ratio of the peak or peaks that are expected for the molecular ion.

8. (12 pts.) The structure of 2-bromopropane is drawn below. (**a.**) Draw the structure of the molecular fragment that would be observed in the mass spectrum due to homolytic cleavage (also called α-cleavage), and (**b.**) determine the mass to charge ratio of the fragment.



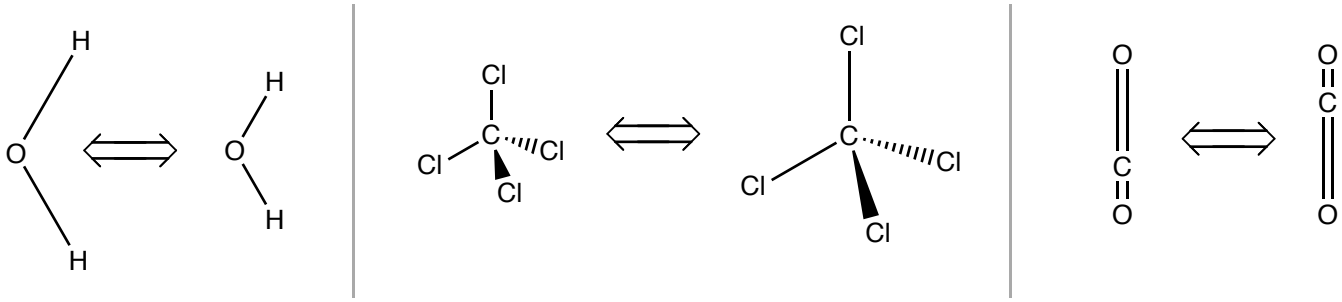
9. (8 pts.) For a vibration to be IR active, what must the vibration do to the molecule?

10. (12 pts.) The IR spectrum of a molecule with the formula C_4H_8O appears below. Identify two vibrations and the functional groups causing them. For example, if there is an OH peak label it with a star and an OH. When identifying the functional groups be as specific as possible.

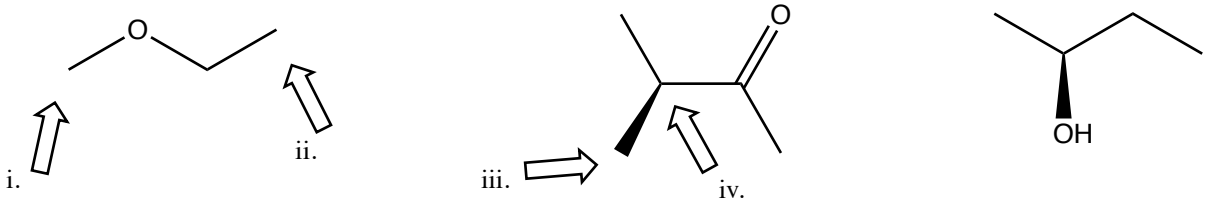


3611	84	1718	4	1173	14
3416	79	1461	34	1087	64
2981	26	1454	38	996	74
2964	44	1417	27	946	49
2940	37	1366	13	761	66
2909	50	1257	74	590	57
2883	62	1206	53	617	66

11. (12 pts.) Which of the following vibrational modes would be IR active (give rise to a peak in the IR spectrum)?



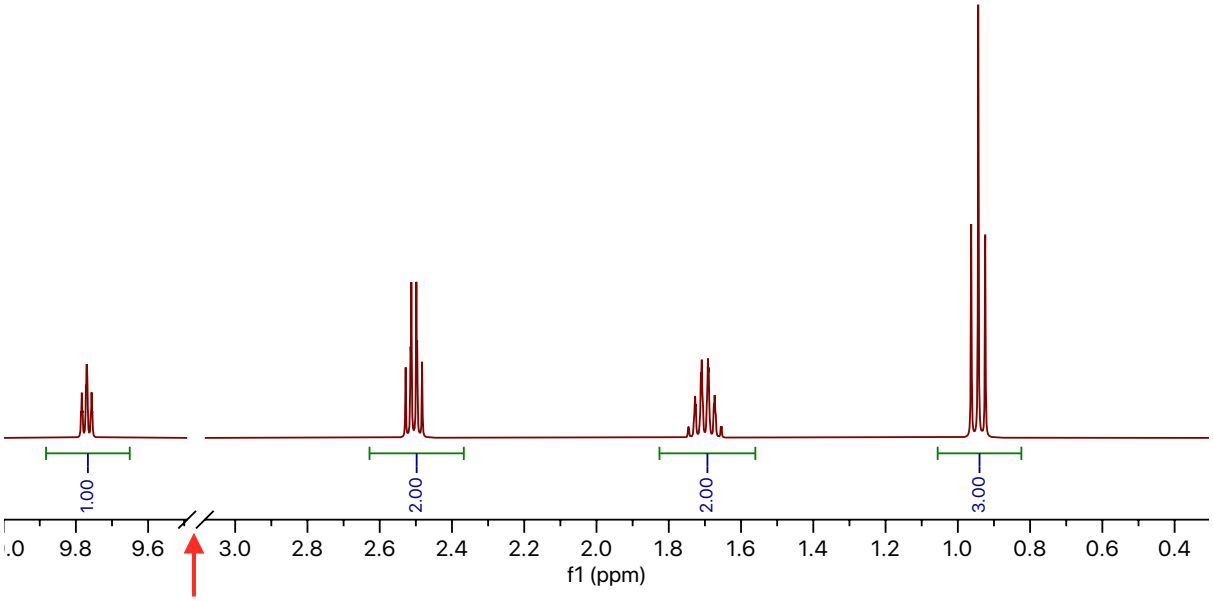
12 a. (12 pts.) Determine the number of peaks expected in the ^1H NMR spectra of the following molecules.



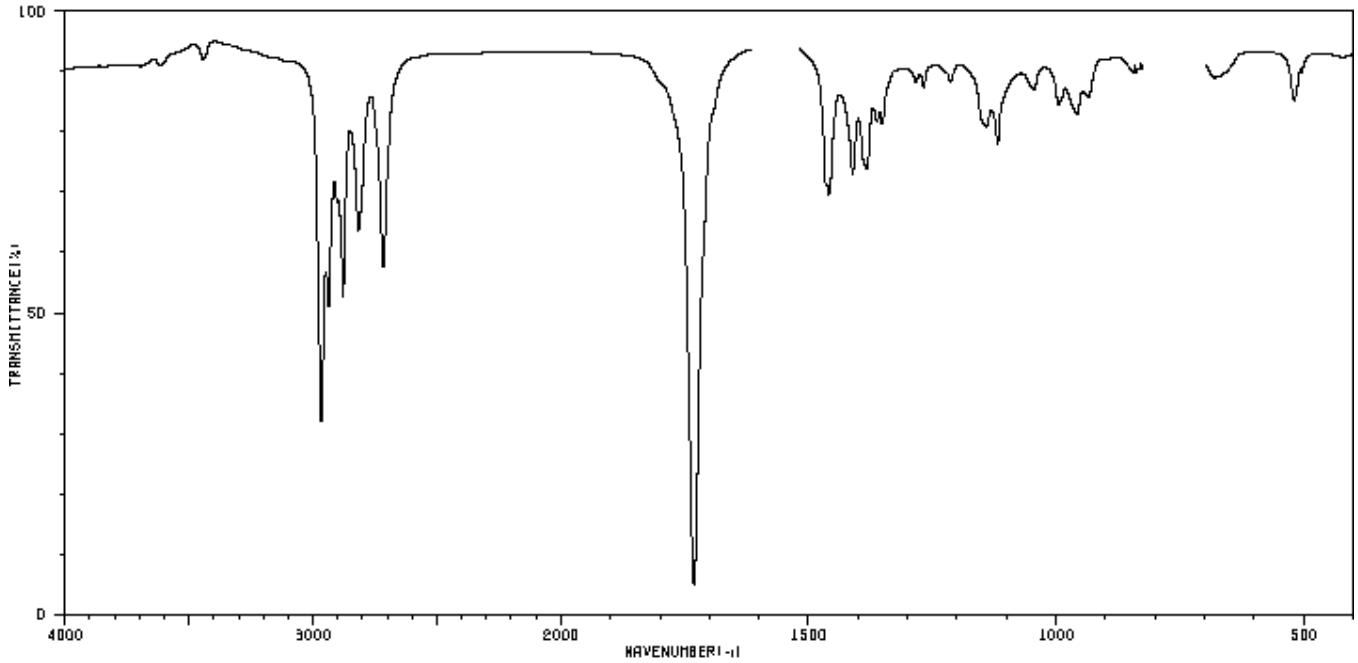
b. (12 pts.) Determine the multiplicity of the peaks for the indicated H atoms.

i. _____ ii. _____ iii. _____ iv. _____

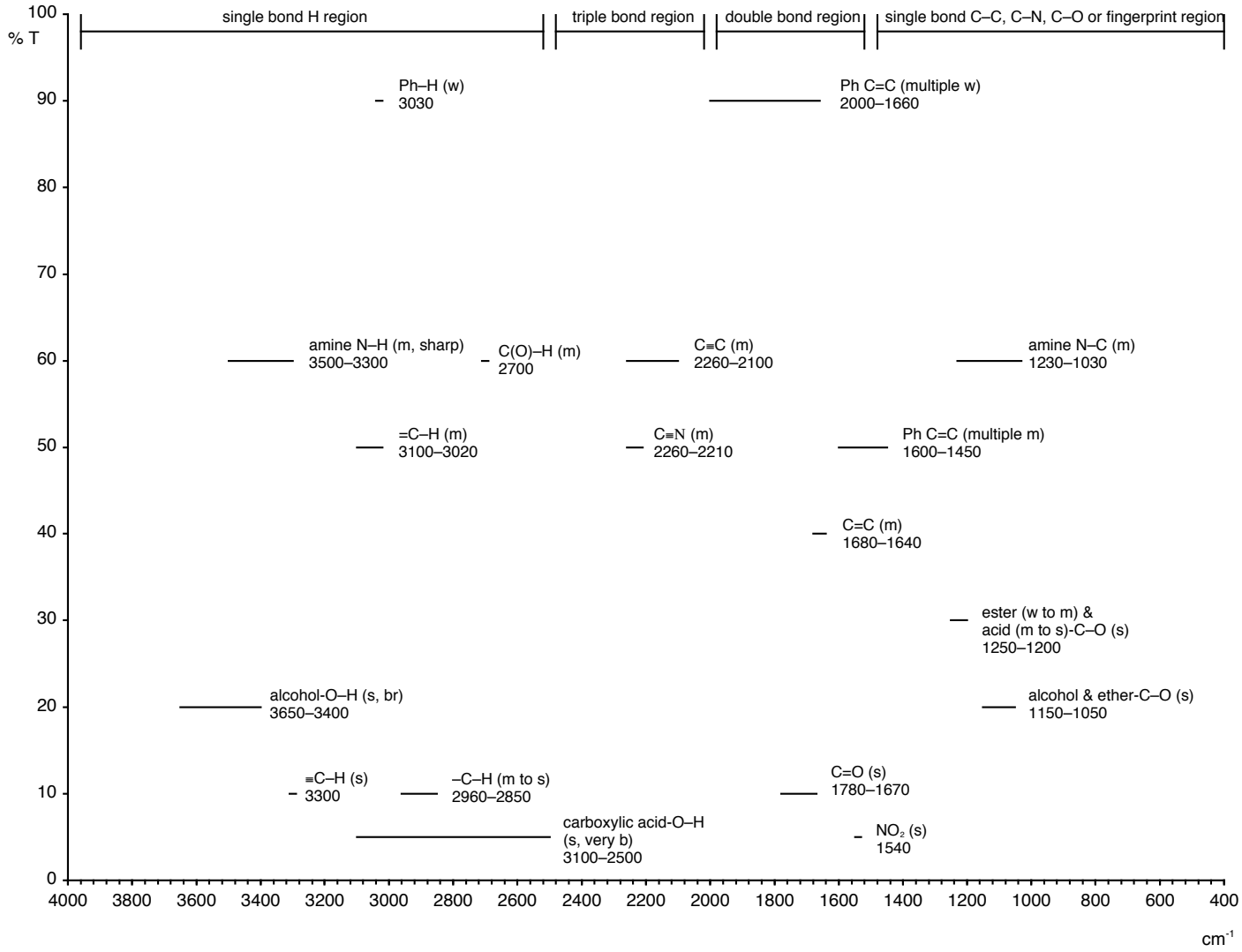
13. IR and ^{1}H NMR spectra are provided for an unknown molecule with the formula C_4H_8O. (**a. 10 pts.**) Determine the structure of the unknown, (**b. 4 pts.**) identify the peaks for two functional groups in the IR spectrum, and (**c. 4 pts.**) unambiguously assign the peaks in the ^{1}H NMR spectrum. That is, label each peak in the ^{1}H NMR spectrum alphabetically starting with an "a" at the left end of the spectrum and label the protons on your structure with the corresponding letter.



Note the break in the axis here to better fit the spectrum onto the page.



2966	31	1469	66	1268	84	994	81	613	84		
2937	49	1411	70	1222	86	958	79				
2876	50	1388	72	1214	84	934	81				
2817	62	1382	70	1141	77	843	86				
2716	55	1362	79	1118	74	677	86				
1731	4	1351	79	1056	84	672	86				
1464	68	1284	84	1045	84	620	81				

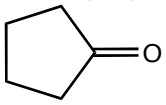


Additional information for analyzing C=O stretches:

amide: $R(C{=}O)NH_2 < 1700$

acid: 1710 usually broad for a C=O

unstrained ketone: RC(=O)R 1715, resonance stabilized ketone R=CHC(=O)R 1690

strained ketone:  1750

aldehyde: RC(=O)H 1730, resonance stabilized aldehyde R=CHC(=O)H 1705

ester: RC(=O)OR 1735, resonance stabilized ester R=CHC(=O)OR 1715.

Additional information for analyzing C–H stretches:

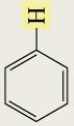
If sp^3 C–H stretch at < 3000 cm^{-1} then look around 1400, sp^3 C–H bend is at 1430 and if peak at 1380 also present then sp^3 C–H is CH_3.

If sp^2 C–H stretch at > 3000 cm^{-1}, and not benzene gives rise to bending vibrations from 1000–600.

1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.1797
11 Na 22.989	12 Mg 24.305											13 Al 26.981	14 Si 28.086	15 P 30.974	16 S 32.065	17 Cl 35.453	18 Ar 39.948
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br 79.904	36 Kr
37 Cs	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Rb	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112		114		116		118

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Table 14.1 Approximate Values of Chemical Shifts for ^{1}H NMR[a]

Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0		6.5–8
$-CH_3$	0.9		9.0–10
$-CH_2-$	1.3		2.5–4
	1.4		2.5–4
	1.7		3–4
	2.1		4–4.5
	2.3	RNH_2	Variable, 1.5–4
	2.4	ROH	Variable, 2–5
$R-O-CH_3$	3.3	ArOH	Variable, 4–7
	4.7		Variable, 10–12
	5.3		Variable, 5–8

[a]The values are approximate because they are affected by neighboring substituents.