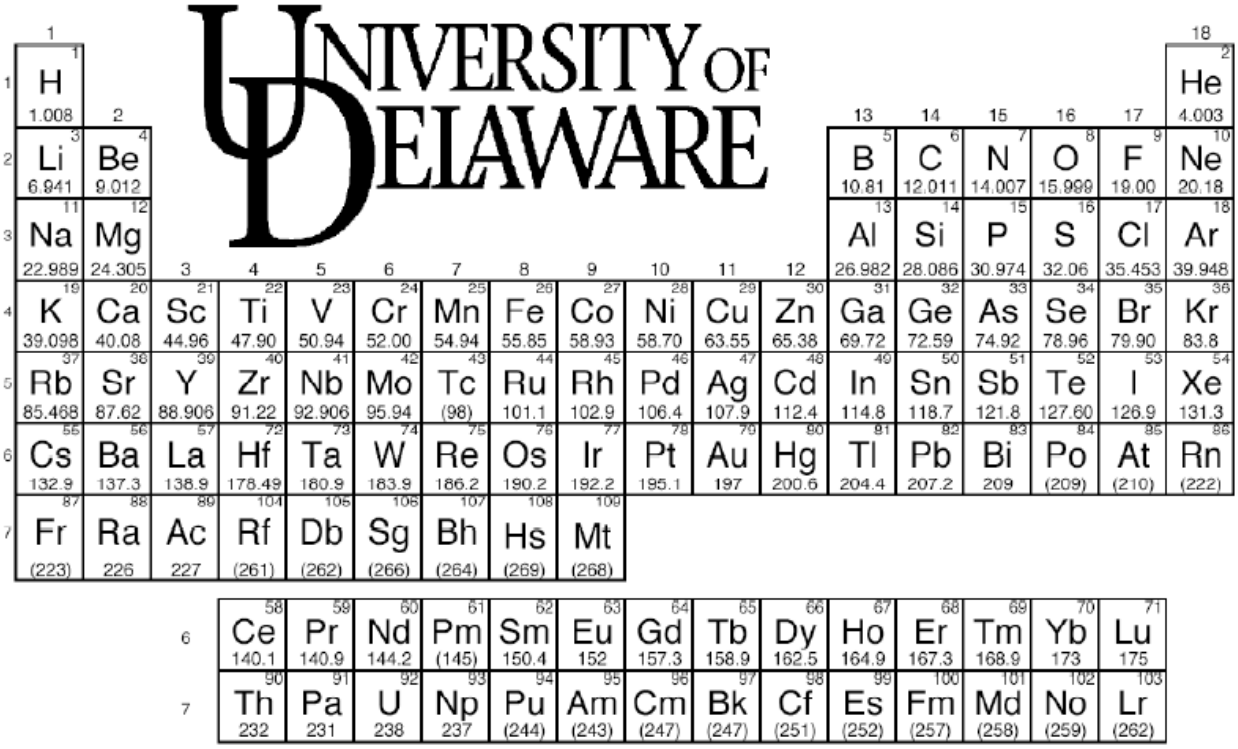
Name:_____

(Print your name clearly!)

Sametz: CHEM 322 2010

Organic Chemistry Final

All answers should be written CLEARLY in the space provided. (If it's not clear, it's wrong).



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 19.00	10 Ne 20.18
11 Na 22.989	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.70	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.8
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.60	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.49	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226	89 Ac 227	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (269)	109 Mt (268)									

6	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173	71 Lu 175
7	90 Th 232	91 Pa 231	92 U 238	93 Np 237	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

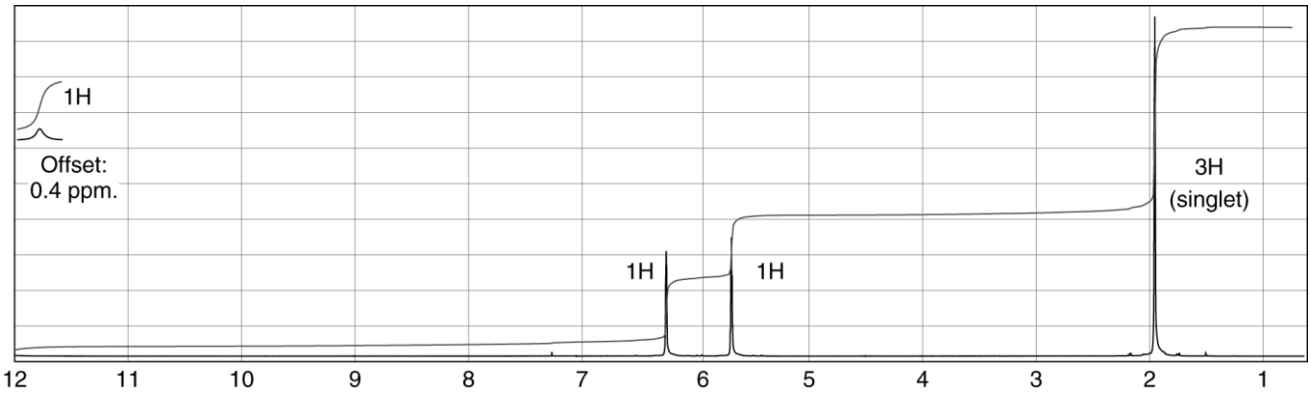
You may raise your hand to ask a question if you are unsure what a question is asking of you.

Part I: Multiple Choice (18 points)

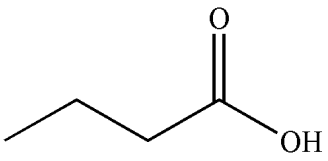
1. Chemical shift is:

a. the area under a given signal
b. the total number of neighbors that a given hydrogen has
c. the location of a signal along the x-axis, reported in ppm
d. the number of peaks into which a signal is split
e. the distance between the individual "lines" in a signal, reported in Hz

2. Which of the following compounds corresponds to the ^{1}H NMR spectrum shown here?



a.



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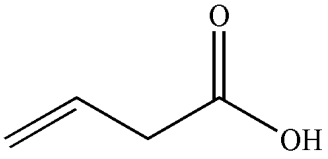
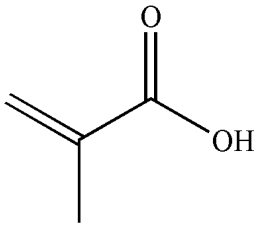
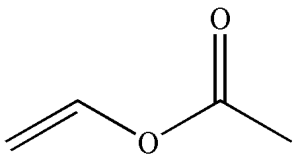


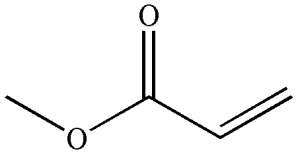
c.



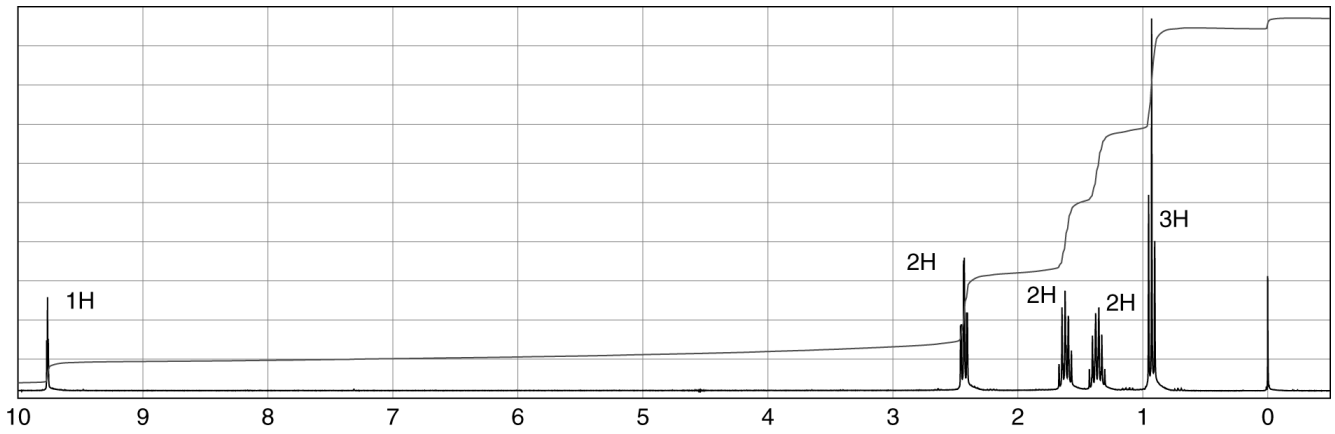
d.



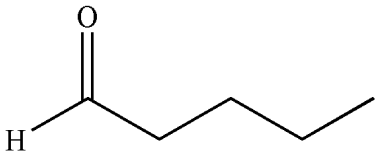
e.



3. To which structure does this ^{1}H NMR spectrum correspond?



a.



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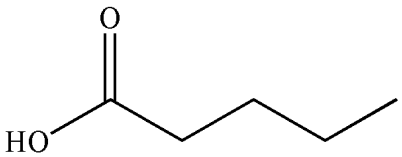

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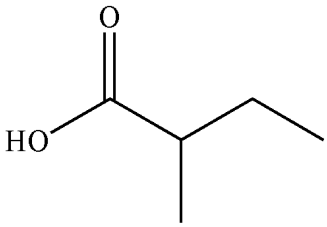

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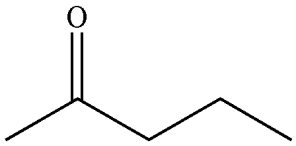
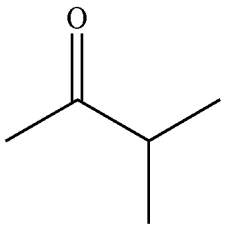
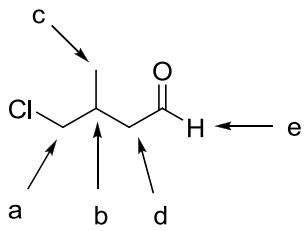


e.



For the following compound:



4. How many signals do you expect to see in the proton NMR?

a) 3

b) 4

c) 5

d) 6

e) 9

5. Which of the protons on the indicated carbons should appear the furthest **downfield** in the proton NMR?

a) a

b) b

c) c

d) d

e) e

6. What should be the splitting pattern of the **protons at position "a"**?

a) singlet

b) doublet

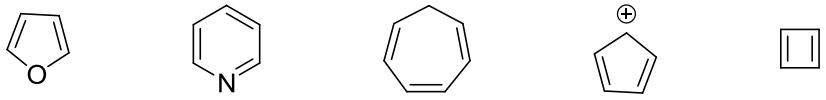
c) triplet

d) quartet

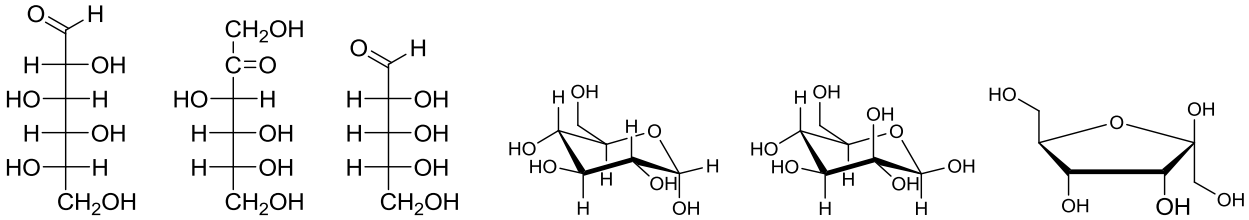
e) pentet

Part II: Short Answer (18 points)

7. (5 points) For each of the following chemical species, indicate whether they are aromatic, antiaromatic, or neither:



Questions 8-12 (7 points) refer to structures a-f below:



8. Which **one** of the six structures is an L-sugar? _____

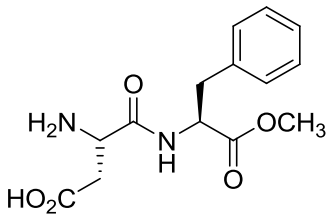
9. Which **two** of the six structures are ketoses? _____

10. Which structure(s) is/are in their furanose form? _____

11. Which structure(s) is/are in their pyranose form? _____

12. Which **one** of the six structures is shown as a β-anomer? ____

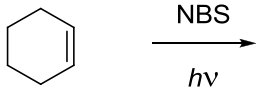
13. (6 points) The structure of aspartame (NutraSweet™) is shown below. Show the products that would result if it were completely hydrolyzed in aqueous acid. HINT: no content from the food chemistry lectures is required to answer this question



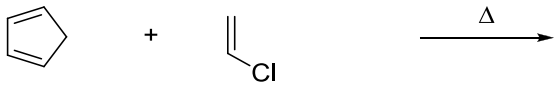
Part III: Reactions and Synthesis (84 points)

14. (48 points) Give the major organic product(s) for **12** of the following **15** reactions: **YOU CAN SKIP 3 problems by checking the "SKIP" box.**

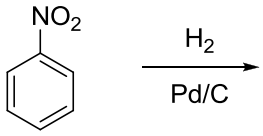
a. ❑SKIP this one



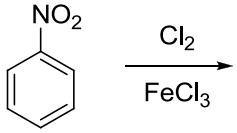
b. ❑SKIP this one



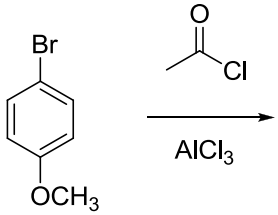
c. ❑SKIP this one



d. ❑SKIP this one

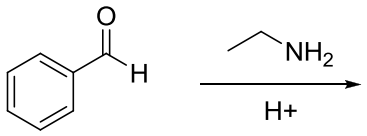


e. ❑SKIP this one

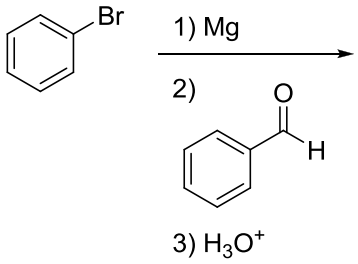


f. ❑SKIP this one

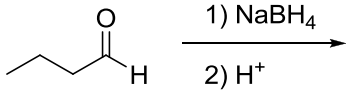
g. ❑SKIP this one



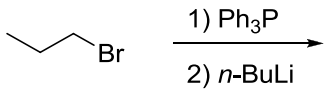
h. ❑SKIP this one



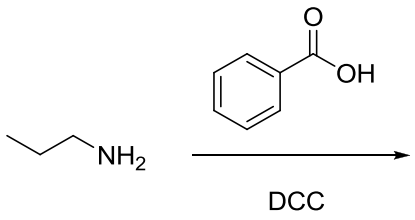
i. ❑SKIP this one



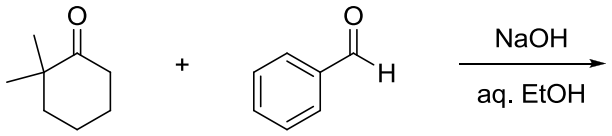
j. ❑SKIP this one



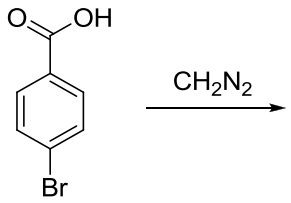
k. ❑SKIP this one



l. ❑SKIP this one



m. ❑SKIP this one



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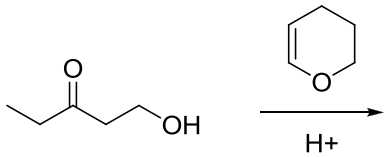
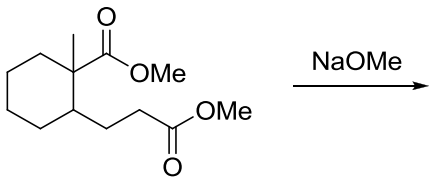
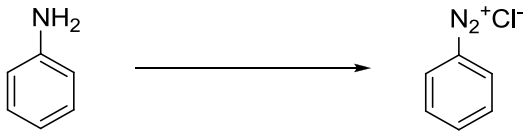


o. ❑SKIP this one

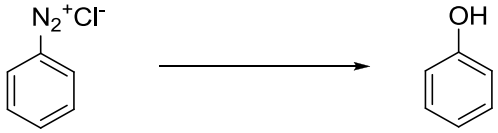


15. (36 points) Provide reagents to effect the following transformations. **DO 12 OUT OF 15 PARTS. (YOU CAN SKIP 3 parts of Problem 15 by checking the "Skip" box).**

a. ❑SKIP this one



b. ❑SKIP this one



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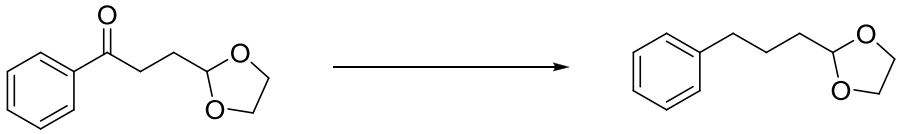
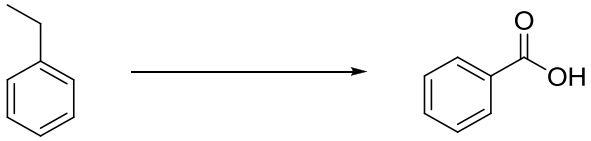
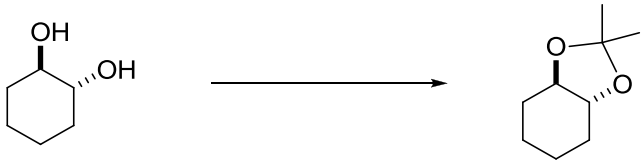


d. ❑SKIP this one



e. ❑SKIP this one



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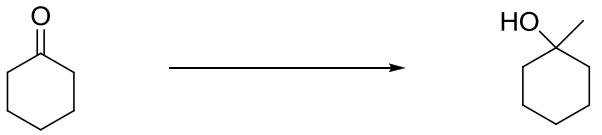

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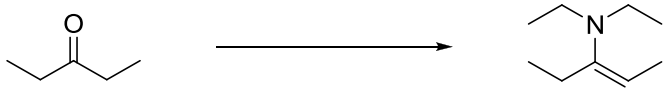

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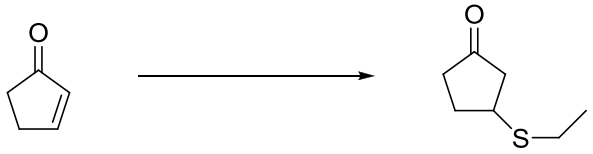
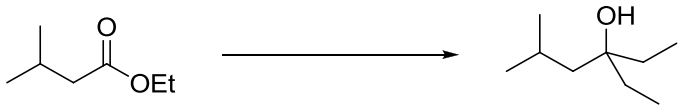


i. ❑SKIP this one



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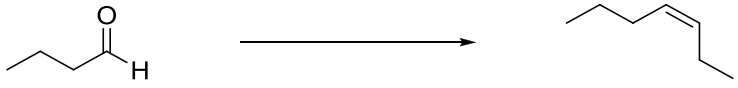
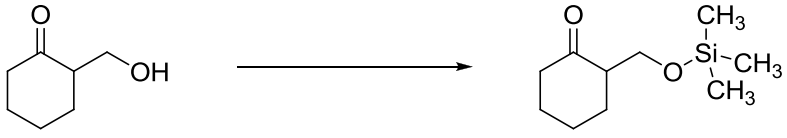
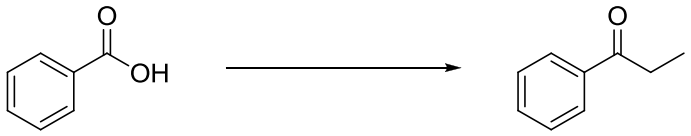


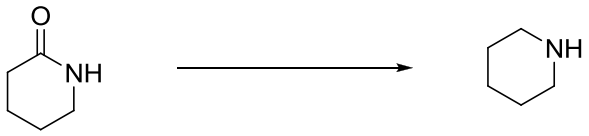
k. ❑SKIP this one



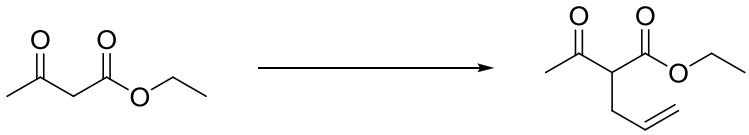
l. ❑SKIP this one



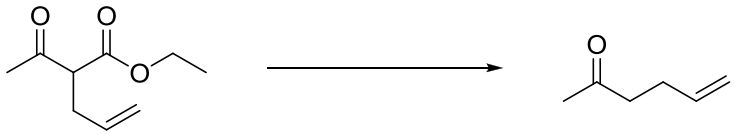
m. ❑SKIP this one



n. ❑SKIP this one

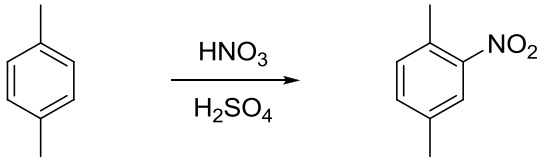


o. ❑SKIP this one

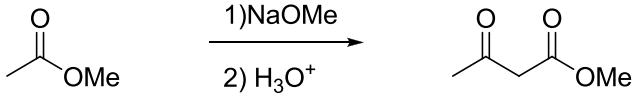


16. (10 points) Give a detailed mechanism for **1** of the following **4** reactions. **If you work on more than one, clearly indicate which one you wish to be graded for credit**; otherwise, your first answer will be the one graded.

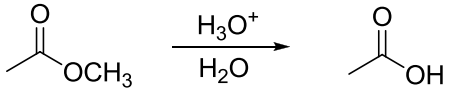
a)



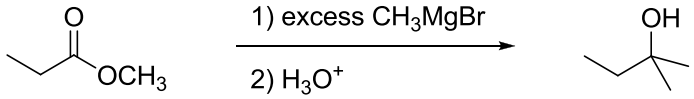
b)



c)



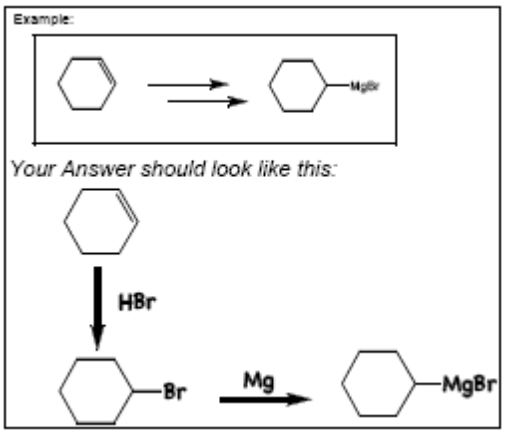
d)



Extra space for Question 16

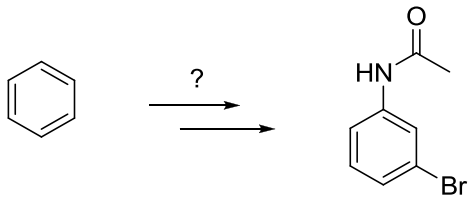
Multistep Synthesis (10 points)

17. Choose **one** of the following four synthesis problems. Show how you can synthesize the product on the right from the indicated starting material on the left. You can show a retrosynthesis for partial credit, but full credit requires writing out a sequence of forward reactions (see box at right for an example).

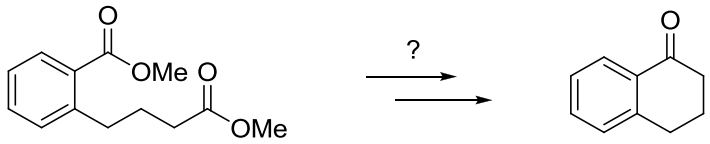


If you work on more than one problem, clearly indicate which one you want graded for credit (otherwise your first answer will be graded).

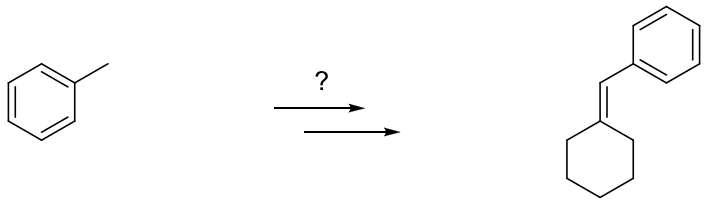
a)



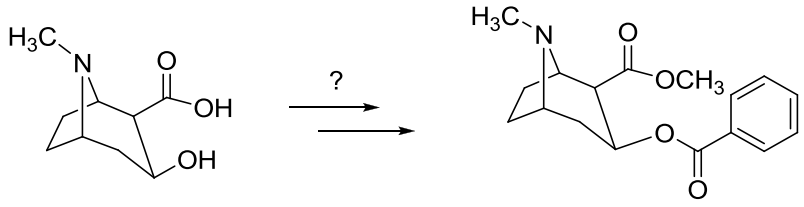
b)



c)



d)



cocaine

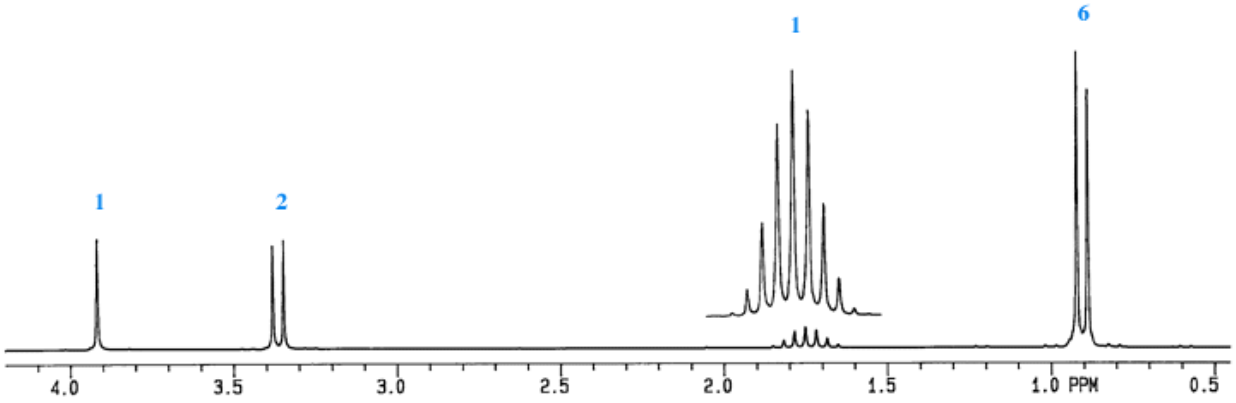
Extra space for Question 17

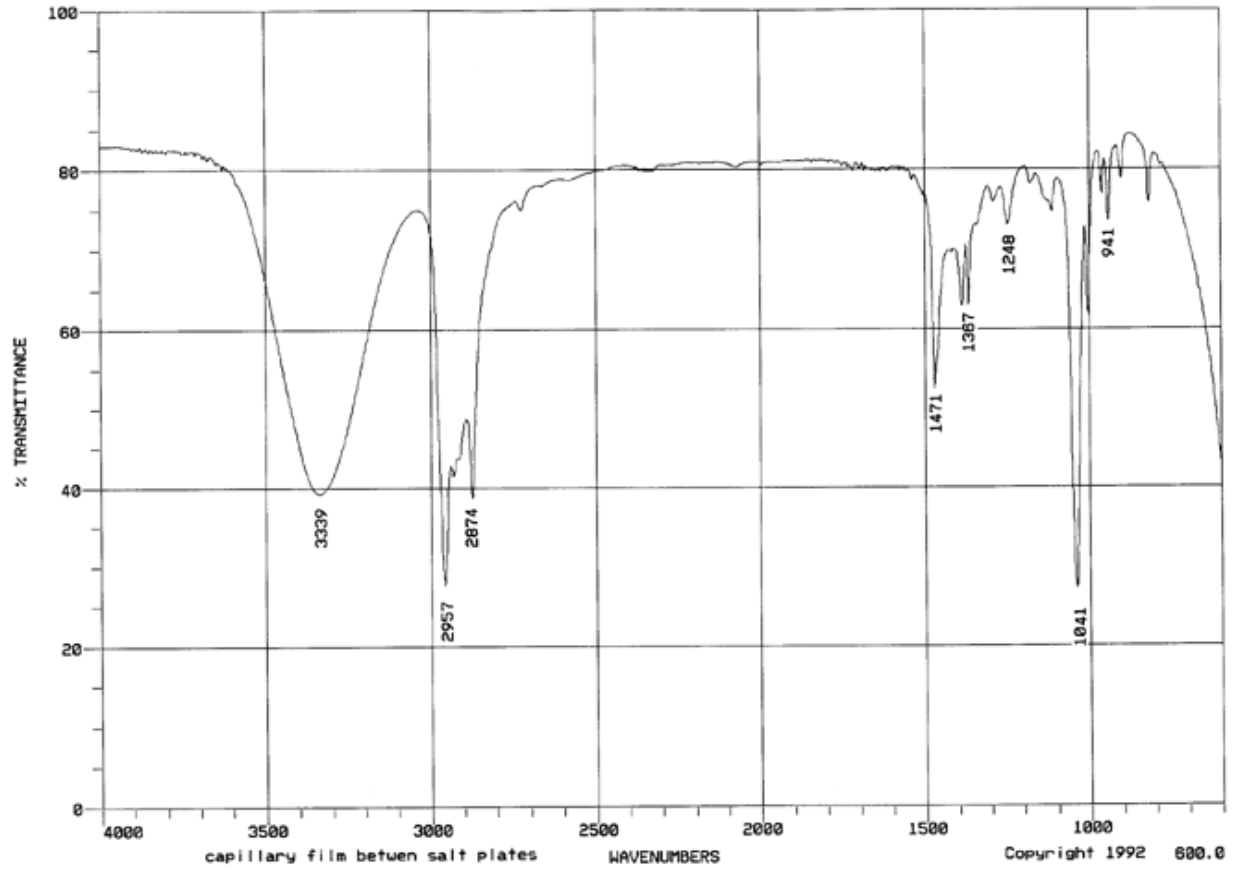
Part IV: Spectroscopic Analysis of an Unknown Compound (10 points)

18. The ^{1}H NMR and IR spectra for a compound with the formula $C_4H_{10}O$ are shown on the following page. The numbers above each signal on the NMR correspond to their integration. Note the expansion of the signal at ca.1.75 ppm that is provided for clarity. Also: the signal at 3.9 ppm disappears when the sample is shaken with a drop of D_2O.

The ^{13}C NMR (not shown) has 3 signals (at 69.6, 30.8, and 18.8 ppm).

Using the space below to show your work, identify the structure of the compound. Use the ^{1}H NMR data to construct a table (chemical shift, integration, multiplicity, assignment) to identify structural fragments, then arrive at the structure. **You are being graded on your analysis**. Any use of the degrees of unsaturation, IR, ^{13}C NMR, or explanation of the D_2O test, will be considered for extra credit.


1
6
1
2
4.0
3.5
3.0
2.5
2.0
1.5
1.0 PPM
0.5


% TRANSMITTANCE
100
80
60
40
20
0
3339
2957
2874
1471
1367
1248
941
1041
4000
3500
3000
2500
2000
1500
1000
capillary film betwen salt plates
WAVENUMBERS
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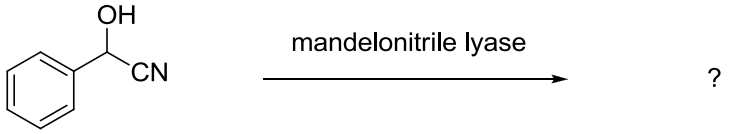
600.0

Extra Credit! (20 points)

Some mice from the field behind my property have moved into my house. The following questions pertain to mouse pheromones and pesticides.

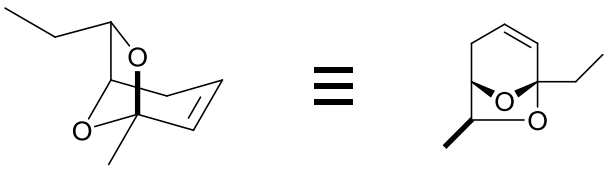
19. (2 points) I mentioned in one class that some millipedes use mandelonitrile as a chemical weapon. The enzyme mandelonitrile lyase breaks mandelonitrile down to simpler compounds. One of them is a poison that is produced in large enough amounts to kill a mouse.



What toxin is formed? (Hint: what class of compounds does mandelonitrile belong to, and how are they synthesized? If you know that, then you should know what the toxin is.)

Questions 20-21 involve pheromones found in mouse urine.

20. (3 points) 2,3-dehydro-*exo*-brevicomin is a component found in male mouse urine and is believed to trigger puberty acceleration in female mice. Two representations of this compound are shown below:

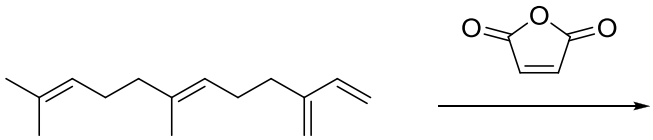


2,3-dehydro-*exo*-brevicomin

In theory, this compound could be hydrolyzed in aqueous acid to provide a carbonyl-containing compound. Draw the structure of this hydrolysis product.

21. (3 points) α-farnesene is another compound, formed in the male's preputial gland, and believed to have a similar effect on females. It is also a component of hops, which are used to preserve and give flavor to beer. α-farnesene tends to decompose, in part because it is a good diene for Diels-Alder reactions.

Show the product of the following Diels-Alder reaction:



α-farnesene

22. (12 points) Warfarin and related derivatives ("super-warfarins") are blood thinners that are often used for pest control. The following chemical steps are taken from a synthesis of the super-warfarin brodifacoum. Provide reagents for each of the indicated steps (the reaction arrows with boxes around them):

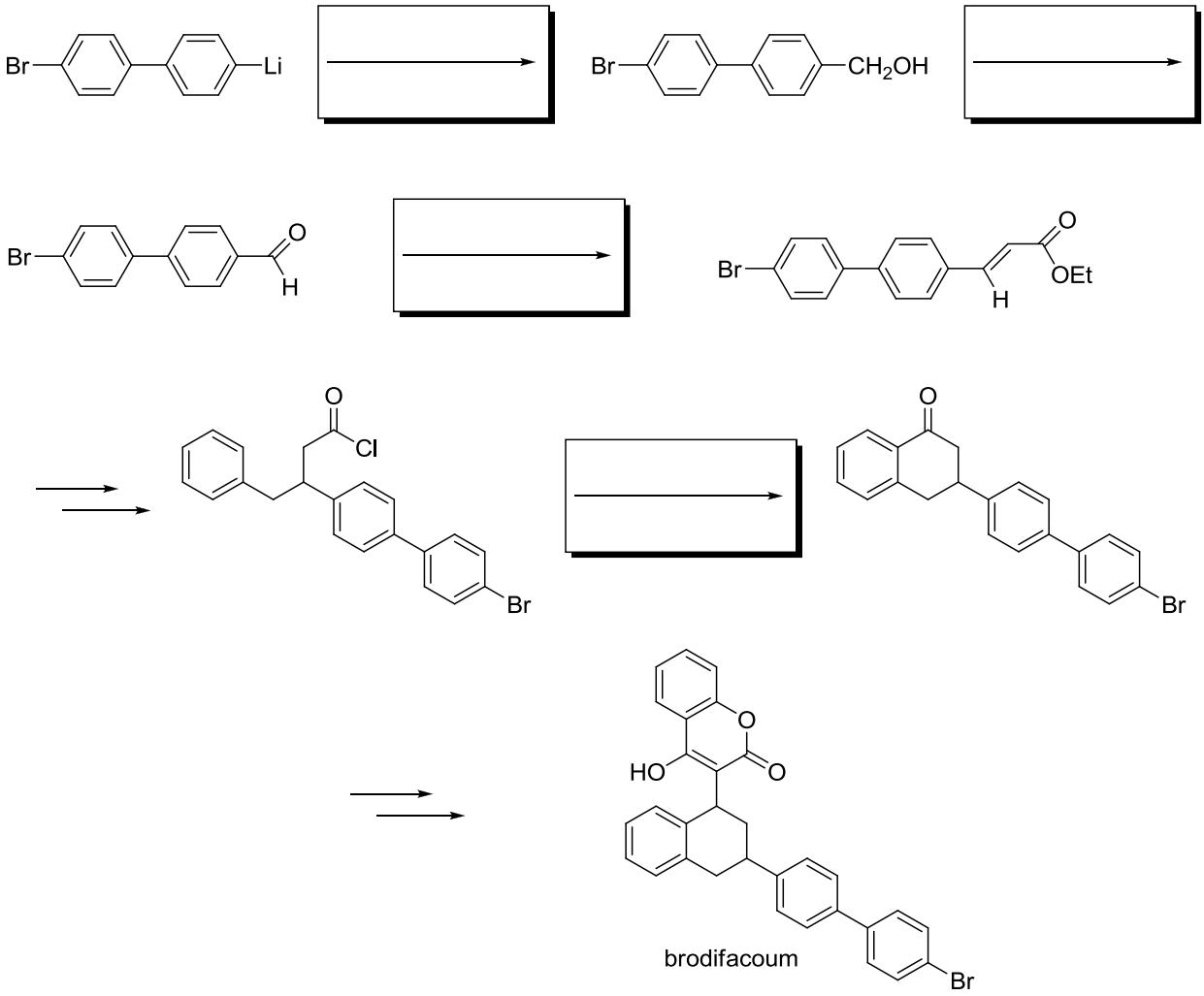


TABLE 15.5 Some ^{13}C Chemical Shifts

Type of Carbon	Chemical Shift (δ)[a]	Type of Carbon	Chemical Shift (δ)[a]
Alkanes		Alcohols, ethers	
Methyl	0–30	C–O	50–90
Methylene	15–55	Amines	
Methine	25–55	C–N	40–60
Quaternary	30–40	Halogens	
Alkenes		C–F	70–90
C=C	80–145	C–Cl	25–50
Alkynes		C–Br	10–40
C≡C	70–90	C–I	−20–10
Aromatics	110–170	Carbonyls, C=O	
Benzene	128.7	$R_2C=O$	190–220
		RXC=O (X = O or N)	150–180

[a]The chemical shift δ is in parts per million (ppm) from TMS.

TABLE 15.4 Chemical Shifts of Various Hydrogens[a,b]

Hydrogen	δ (ppm)
CH_3	0.8–1.0
CH_2	1.2–1.5
CH	1.4–1.7
C=C–CH (allylic hydrogens)	1.8–2.3
O=C–CH	2.0–2.5
Ph–CH (benzylic hydrogens)	2.3–2.8
≡C–H	2.5
R_2N–CH	2.0–3.0
I–CH	2.8–3.3
Br–CH	2.8–3.5
Cl–CH	3.1–3.8
F–CH	4.1–4.7
O–CH	3.1–3.8
$=CH_2$ (terminal alkene)	5.0
C=CH (internal alkene)	4.5–5.5
Ph–H (aromatic hydrogens)	7.0–7.5
O=CH (aldehyde hydrogens)	9.0–10.0
RCOOH	10–13

[a]These values are approximate. There will surely be examples that lie outside the ranges indicated. Use them as guidelines, not "etched in stone" inviolable numbers.

[b]Watch out for loose talk. For example, "aromatic hydrogen" means a hydrogen attached to a benzene ring.

Some Useful IR Stretching Frequencies

Bond	Frequency (cm^{-1})	Intensity
O-H (alcohol)	3650-3200	Strong, broad
O-H (carboxylic acid)	3300-2500	Strong, **very** broad
N-H	3500-3300	Medium, broad
C-H	3300-2700	Medium
C≡N	2260-2220	Medium
C≡C	2260-2100	Medium to weak
C=O	1780-1650	Strong
C-O	1250-1050	strong