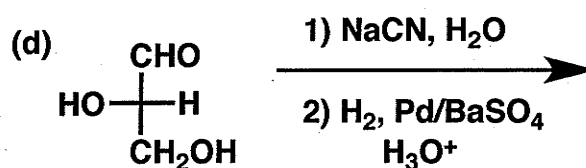
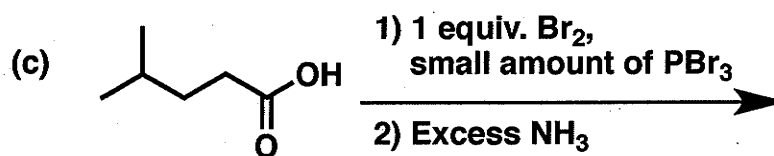
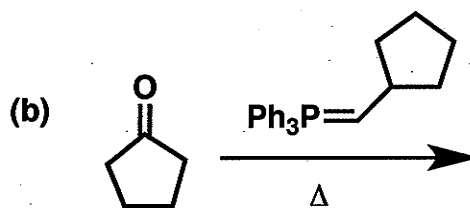
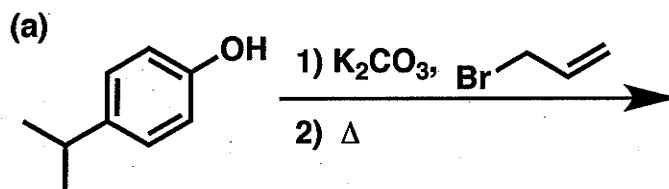


General Instructions:

- (i) Use scratch paper at back of exam to work out answers; final answers must be recorded at the proper place on the exam itself for credit.
- (ii) Print your name on each page.

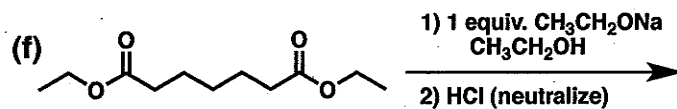
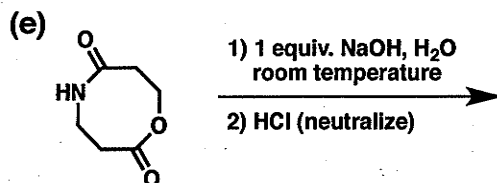
1. (39 points) Show the major product or products expected from each reaction:



-- cont. on next page --

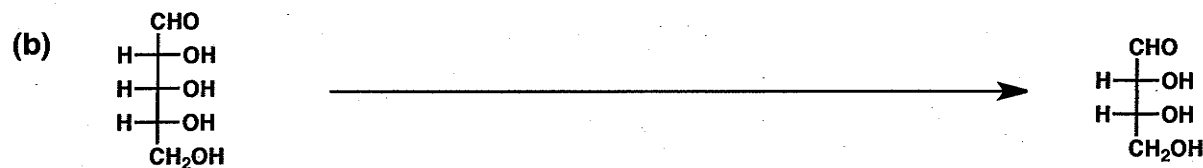
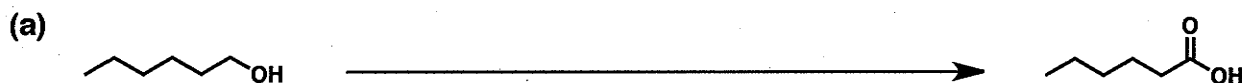
Name _____

1. (cont.)



[Note: In the IR region 1700 - 1800 cm⁻¹, the starting material has a single strong signal at 1745 cm⁻¹, but the product has two signals, at 1745 cm⁻¹ and 1725 cm⁻¹.]

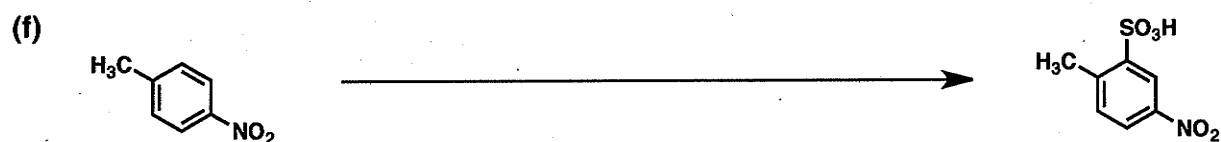
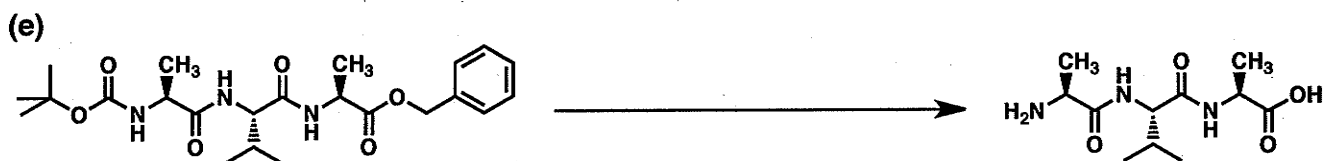
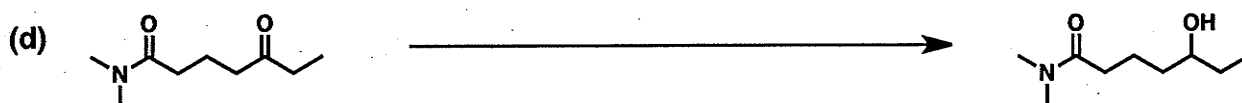
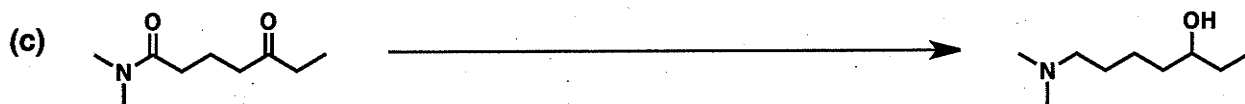
2. (45 points) Show the reagents and other organic molecules required to convert the starting material to the indicated product. Be sure to differentiate clearly between distinct steps, by using "1)", "2)", etc.



(cont. on next page)

Name _____

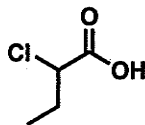
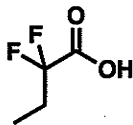
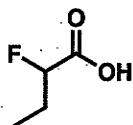
2. (cont.)



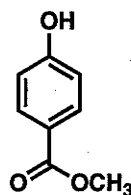
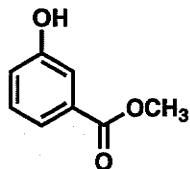
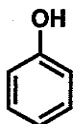
Name _____

3. (8 points) For each set of compounds below, rank the molecules, left to right, from lowest pK_a to highest pK_a (i.e., your answer should have the form $X < Y < Z$).

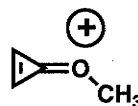
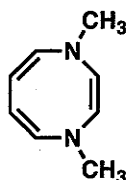
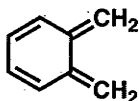
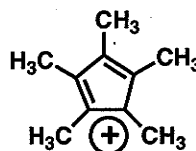
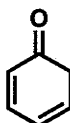
(a)



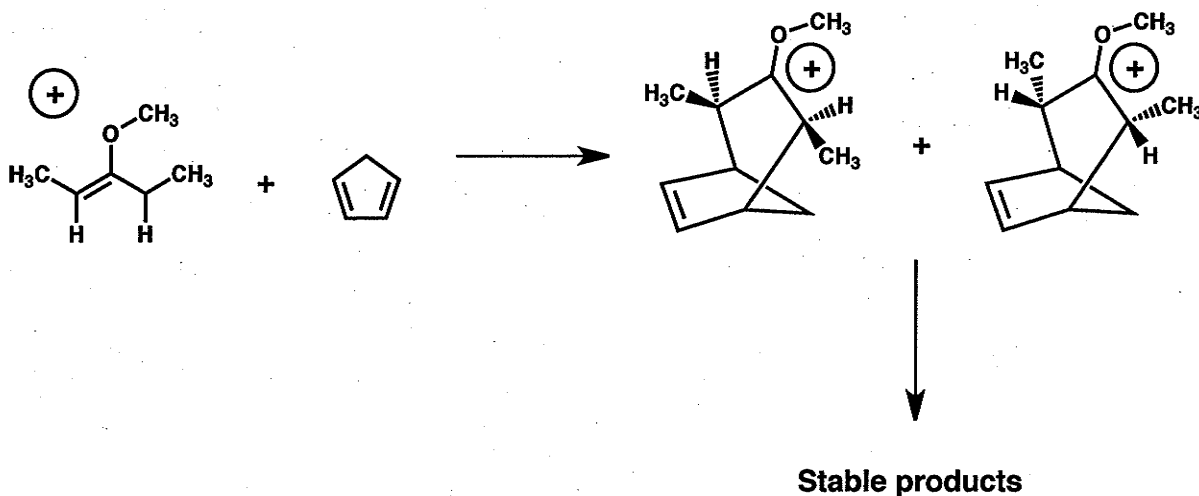
(b)



4. (12 points) Among the species shown below, CIRCLE those that you would expect to benefit from aromatic stabilization.

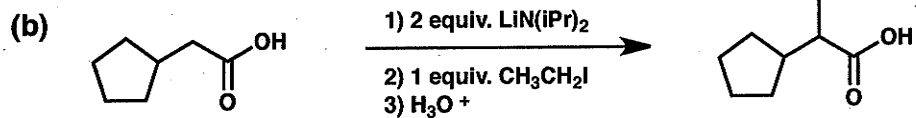
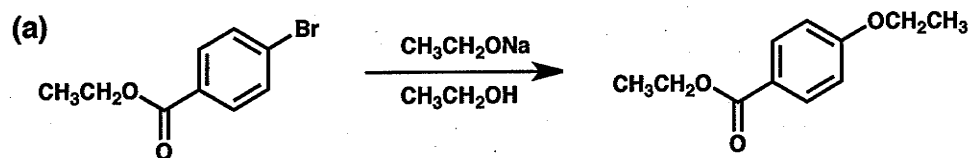


5. (10 points) The cation shown on the left below would be expected to react with cyclopentadiene to form the two isomeric bicyclic cations shown on the right (these intermediate would then go on to form more stable species). Provide a molecular orbital rationale for the expectation that these specific bicyclic cations would form (and not isomers with *trans* methyl groups).



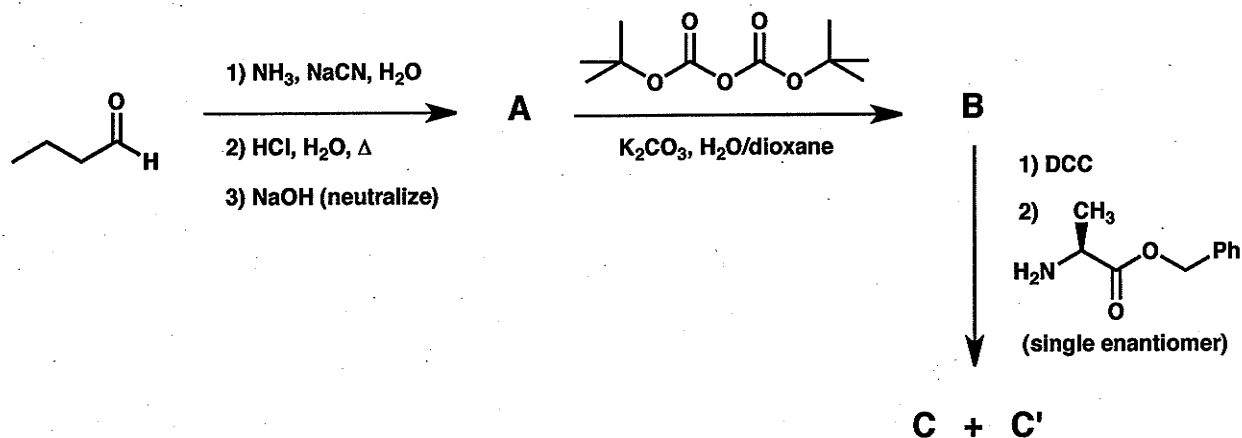
Name _____

6. (18 points) Draw a mechanism (curved arrows) for the reaction shown below.



Name _____

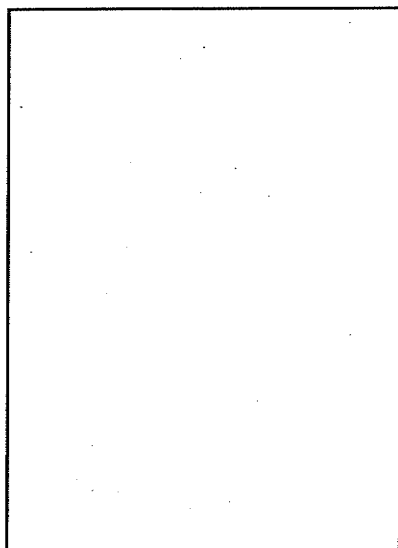
7. (20 points) When the aldehyde shown below is subjected to the sequential reaction conditions indicated, A is formed. Further reactions, as shown, generate B and then a final product that turns out to have two chromatographically separable and isomeric components, C and C'. Give the structures of A, B, C and C'.



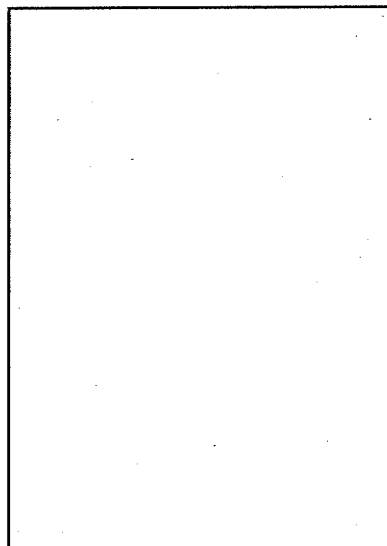
Name _____

8. (20 points)

(a) Draw the Fischer projection of D-glucose (open chain form; not cyclic).

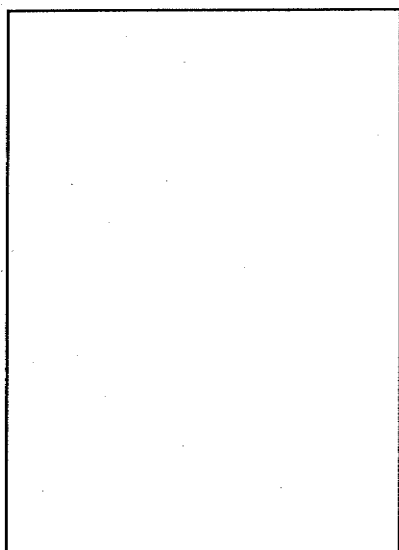


(b) Mannose is the 2-epimer of glucose. Draw the Fischer projection of L-mannose (open chain form; not cyclic).

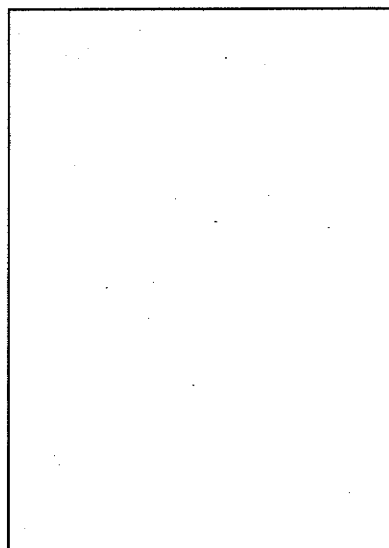


(c) Compound X is an aldohexose. When X is treated with 3 equivalents of PhNHNH_2 in acetic acid, the osazone formed is different from the osazone obtained from D-glucose or D-mannose (these two give the same osazone). However, when X is subjected to two cycles of the Wohl degradation process, the resulting aldotetrose, D-erythrose, is the same as the aldotetrose generated from two cycles of Wohl degradation of D-glucose or D-mannose.

Draw the Fischer projection of D-erythrose.

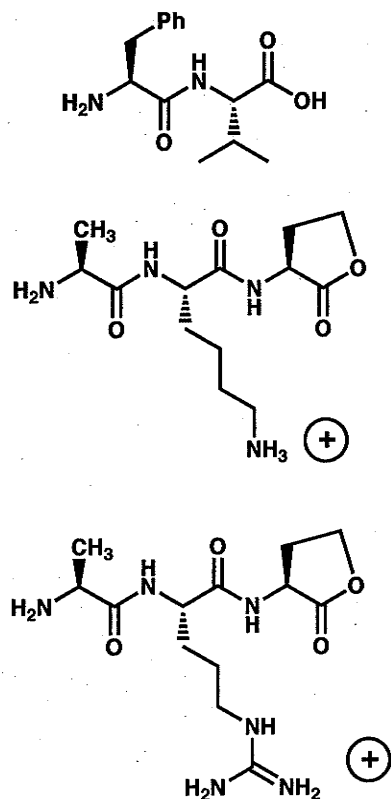


Draw the Fischer projection of X.

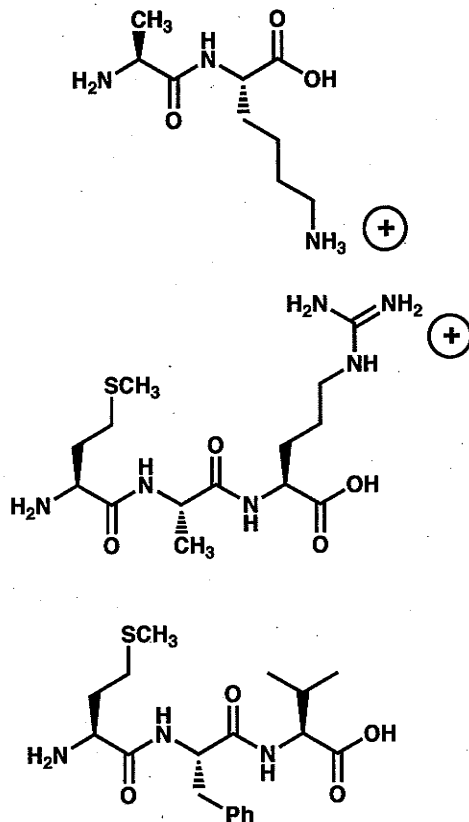


9. (12 points) When peptide Z is treated with CNBr, three short fragments are generated, as shown below. When peptide Z is instead treated with the enzyme trypsin, a different set of three short fragments is generated, as shown. Based on this information, what is peptide Z?

Fragments from degradation with CNBr:



Fragments from degradation with trypsin:

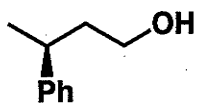


Peptide Z =

Name _____

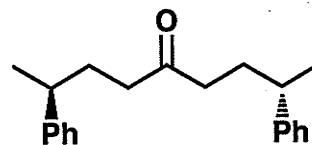
10. (16 points) Propose a synthesis of the target molecule shown below from the indicated starting material. You may use other reagents that contain no more than one carbon atom.

Starting Material =



(single enantiomer)

Target =



<u>Problem</u>	<u>Score</u>
1	/ 39
2	/ 45
3	/ 8
4	/ 12
5	/ 10
6	/ 18
7	/ 20
8	/ 20
9	/ 12
10	/ 16

Total:**/ 200**

PERIODIC TABLE OF THE ELEMENTS

1
IA

2
IIA

Atomic number →
Symbol →
Name (IUPAC) →
Atomic mass →

6
C
Carbon
(12.011)

IUPAC recommendations →
Chemical Abstracts Service group notation →

18
VIIIA

IUPAC recommendations →																		IUPAC recommendations →																	
Atomic number →																		Atomic number →																	
Symbol →																		Symbol →																	
Name (IUPAC) →																		Name (IUPAC) →																	
Atomic mass →																		Atomic mass →																	
C Carbon 12.011																		C Carbon 12.011																	
13 III A																		13 III A																	
14 IV A																		14 IV A																	
15 V A																		15 V A																	
16 VI A																		16 VI A																	
17 VII A																		17 VII A																	
18																		18																	
19 K Potassium 39.098																		19 K Potassium 39.098																	
20 Ca Calcium 40.078																		20 Ca Calcium 40.078																	
21 Sc Scandium 44.956																		21 Sc Scandium 44.956																	
22 Ti Titanium 47.867																		22 Ti Titanium 47.867																	
23 V Vanadium 50.942																		23 V Vanadium 50.942																	
24 Cr Chromium 51.996																		24 Cr Chromium 51.996																	
25 Mn Manganese 54.938																		25 Mn Manganese 54.938																	
26 Fe Iron 55.845																		26 Fe Iron 55.845																	
27 Co Cobalt 58.933																		27 Co Cobalt 58.933																	
28 Ni Nickel 58.693																		28 Ni Nickel 58.693																	
29 Cu Copper 63.546																		29 Cu Copper 63.546																	
30 Zn Zinc 65.409																		30 Zn Zinc 65.409																	
31 Ga Gallium 69.723																		31 Ga Gallium 69.723																	
32 Ge Germanium 72.64																		32 Ge Germanium 72.64																	
33 As Arsenic 74.922																		33 As Arsenic 74.922																	
34 Se Selenium 78.96																		34 Se Selenium 78.96																	
35 Br Bromine 79.904																		35 Br Bromine 79.904																	
36 Kr Krypton 83.798																		36 Kr Krypton 83.798																	
37 Rb Rubidium 85.468																		37 Rb Rubidium 85.468																	
38 Sr Strontium 87.62																		38 Sr Strontium 87.62																	
39 Y Yttrium 88.906																		39 Y Yttrium 88.906																	
40 Zr Zirconium 91.224																		40 Zr Zirconium 91.224																	
41 Nb Niobium 92.906																		41 Nb Niobium 92.906																	
42 Mo Molybdenum 95.94																		42 Mo Molybdenum 95.94																	
43 Tc Technetium (98)																		43 Tc Technetium (98)																	
44 Ru Ruthenium 101.07																		44 Ru Ruthenium 101.07																	
45 Rh Rhodium 102.91																		45 Rh Rhodium 102.91																	
46 Pd Palladium 106.42																		46 Pd Palladium 106.42																	
47 Ag Silver 107.87																		47 Ag Silver 107.87																	
48 Cd Cadmium 112.41																		48 Cd Cadmium 112.41																	
49 In Indium 114.82																		49 In Indium 114.82																	
50 Sn Tin 118.71																		50 Sn Tin 118.71																	
51 Sb Antimony 121.76																		51 Sb Antimony 121.76																	
52 Te Tellurium 127.60																		52 Te Tellurium 127.60																	
53 I Iodine 126.90																		53 I Iodine 126.90																	
54 Xe Xenon 131.29																		54 Xe Xenon 131.29																	
55 Cs Cesium 132.91																		55 Cs Cesium 132.91																	
56 Ba Barium 137.33																		56 Ba Barium 137.33																	
57 La Lanthanum 138.91																		57 La Lanthanum 138.91																	
58 Ce Cerium 140.12																		58 Ce Cerium 140.12																	
59 Pr Praseodymium 140.91																		59 Pr Praseodymium 140.91																	
60 Nd Neodymium 144.24																		60 Nd Neodymium 144.24																	
61 Pm Promethium (145)																		61 Pm Promethium (145)																	
62 Sm Samarium 150.36																		62 Sm Samarium 150.36																	
63 Eu Europium 151.96																		63 Eu Europium 151.96																	
64 Gd Gadolinium 157.25																		64 Gd Gadolinium 157.25																	
65 Tb Terbium 158.93																		65 Tb Terbium 158.93																	
66 Dy Dysprosium 162.50																		66 Dy Dysprosium 162.50																	
67 Ho Holmium 164.93																		67 Ho Holmium 164.93																	
68 Er Erbium 167.26																		68 Er Erbium 167.26																	
69 Tm Thulium 168.93																		69 Tm Thulium 168.93																	
70 Yb Ytterbium 173.04																		70 Yb Ytterbium 173.04																	
71 Lu Lutetium 174.97																		71 Lu Lutetium 174.97																	
72 Hf Hafnium 178.49																		72 Hf Hafnium 178.49																	
73 Ta Tantalum 180.95																		73 Ta Tantalum 180.95																	
74 W Tungsten 183.84																		74 W Tungsten 183.84																	
75 Re Rhenium 186.21																		75 Re Rhenium 186.21																	
76 Os Osmium 190.23																		76 Os Osmium 190.23																	
77 Ir Iridium 192.22																		77 Ir Iridium 192.22																	
78 Pt Platinum 195.08																		78 Pt Platinum 195.08																	
79 Au Gold 196.97																		79 Au Gold 196.97																	
80 Hg Mercury 200.59																		80 Hg Mercury 200.59																	
81 Tl Thallium 204.38																		81 Tl Thallium 204.38																	
82 Pb Lead 207.2																		82 Pb Lead 207.2																	
83 Bi Bismuth 208.98																		83 Bi Bismuth 208.98																	
84 Po Polonium (209)																		84 Po Polonium (209)																	
85 At Astatine (210)																		85 At Astatine (210)																	
86 Rn Radon (222)																		86 Rn Radon (222)																	
87 Fr Francium (223)																		87 Fr Francium (223)																	
88 Ra Radium (226)																		88 Ra Radium (226)																	
89 Ac Actinium (227)																		89 Ac Actinium (227)																	
90 Th Thorium (232)																		90 Th Thorium (232)																	
91 Pa Protactinium (231)																		91 Pa Protactinium (231)																	
92 U Uranium (238)																		92 U Uranium (238)																	
93 Np Neptunium (237)																		93 Np Neptunium (237)																	
94 Pu Plutonium (244)																		94 Pu Plutonium (244)																	
95 Am Americium (243)																		95 Am Americium (243)																	
96 Cm Curium (247)																		96 Cm Curium (247)																	
97 Bk Berkelium (247)																		97 Bk Berkelium (247)																	
98 Cf Californium (251)																		98 Cf Californium (251)																	
99 Es Einsteinium (252)																		99 Es Einsteinium (252)																	
100 Fm Fermium (257)																		100 Fm Fermium (257)																	
101 Md Mendelevium (258)																		101 Md Mendelevium (258)																	
102 No Nobelium (259)																		102 No Nobelium (259)																	
103 Lr Lawrencium (262)																		103 Lr Lawrencium (262)																	
104 Rf Rutherfordium (261)																		104 Rf Rutherfordium (261)																	
105 Db Dubnium (262)																		105 Db Dubnium (262)																	
106 Sg Seaborgium (266)																		106 Sg Seaborgium (266)																	
107 Bh Bohrium (264)																		107 Bh Bohrium (264)																	
108 Hs Hassium (277)																		108 Hs Hassium (277)																	
109 Mt Meitnerium (268)																		109 Mt Meitnerium (268)																	
110 Uu Ununium (281)																		110 Uu Ununium (281)																	
111 Uu Ununium (272)																		111 Uu Ununium (272)																	
112 Uu Ununium (285)																		112 Uu Ununium (285)																	
114 Uu Ununium (289)																		114 Uu Ununium (289)																	

*Lanthanide Series

Actinide Series

Although this complexity may seem confusing at first, it is usually possible to gain a lot of information about the groups present in a molecule, even if we cannot assign all the bands, or draw a complete structure of the sample molecule. It is a great help in structure assignment to know what types of bonds are present in a molecule. There is also an important side benefit to these complicated IR spectra. The very complexity of the spectrum means that IR spectra of quite similar molecules are different. Each spectrum serves as a fingerprint of the molecule. If two IR spectra are identical (not similar—my old boss insisted on there being no difference greater than the width of the pen line drawn by the recorder) the compounds must be the same.

Table 15.3 gives the general positions of absorptions of a variety of functional groups, and once again we come to the question of memorization. Should one learn this chart by heart? Personally, I think not. It is important to know that this kind of general correlation exists, and you should have a rough idea of where some important functional groups absorb. If you come to use IR often, you will automatically learn the relevant details of the chart, as you work out what the signals in your IR spectra tell you.

TABLE 15.3 Typical Infrared Absorptions of Functional Groups^a

Functional Group	Position (cm ⁻¹)	Intensity ^b
Alkanes		
C—H	2980–2850	m-s (stretch)
C—C	1480–1420	m (bend)
Alkenes		
=C—H	3150–3000	m (stretch)
C=C	1680–1620	m-w (stretch)
(conj) C=C	1630–1600	m-w (stretch)
$\begin{array}{c} \text{R} \\ \\ \text{C}=\text{CH}_2 \\ \\ \text{H} \end{array}$	995–985 915–905	s (out-of-plane bend)
$\begin{array}{c} \text{R} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{R} \end{array}$	980–960	s (out-of-plane bend)
$\begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$	730–665	s (out-of-plane bend) (br, variable)
$\begin{array}{c} \text{R} \\ \\ \text{C}=\text{CH}_2 \\ \\ \text{R} \end{array}$	895–885	s (out-of-plane bend)
$\begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{H} \end{array}$	840–790	m (out-of-plane bend)

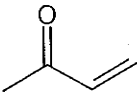
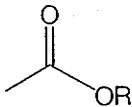
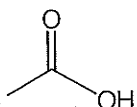
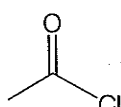
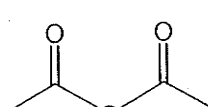
(continued)

TABLE 15.3 Typical Infrared Absorptions of Functional Groups^a (Continued)

Functional Group	Position (cm ⁻¹)	Intensity ^b
Alkynes		
≡C-H	3350-3300	s (stretch)
C≡C	2260-2100	m-w (stretch)
Alcohols		
O-H		
free	3650-3580	m (stretch)
hydrogen bonded	3550-3300	br, s (stretch)
C-O	1260-1000	s (stretch)
	1150-1050	
Amines		
N-H	3500-3100 (two bands for primary amines, one band for secondary amines)	br, m (stretch)
C-N	~1200	m (stretch)
Aromatic compounds		
≡C-H	3080-3020	m-w (stretch)
C=C	1600-1580	m-w (stretch)
C-H		
mono	770-730	s (out of plane bend)
	710-690	
ortho	770-735	s (out-of-plane bend)
meta	900-860	m (out of plane bend)
	810-750	s (out-of-plane bend)
	725-680	m (out-of-plane bend)
para	860-800	s (out-of-plane bend)
Carbonyl compounds aldehydes, ketones		
	1730-1700 (higher in strained cyclic molecules)	s (stretch)

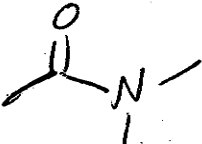
(continued)

TABLE 15.3 Typical Infrared Absorptions of Functional Groups^a (Continued)

Functional Group	Position (cm ⁻¹)	Intensity ^b
Carbonyl compounds aldehydes, ketones		
	1680-1660	s (stretch)
C-H (aldehydes)	2900-2700 (two bands)	w (stretch)
Esters		
	1750-1735 1300-1000	s (C=O) (stretch) s (C-O) (stretch)
Acids		
	1730-1700 3200-2800	s (C=O) (stretch) s, br (O-H) (stretch)
Acid chlorides		
	1820-1770	s (C=O) (stretch)
Anhydrides		
	1820-1750 (two bands) 1150-1000	s (C=O) (stretch) s (C-O) (stretch)
Imines		
C=N	1680-1640	m (stretch)
Cyanides (nitriles)		
C≡N	~2250	s (stretch)

^aCAUTION! There certainly is some subjectivity in this table, and the values represent average positions for "normal" compounds. Conjugation generally lowers double-bond stretching vibrations by about 20 cm⁻¹.

^bMedium = m, strong = s, weak = w, broad = br.

Amides  1620-1680 cm⁻¹ s (stretch)

