Final Exam
Chemistry 345
Professor Gellman
13 May 2010

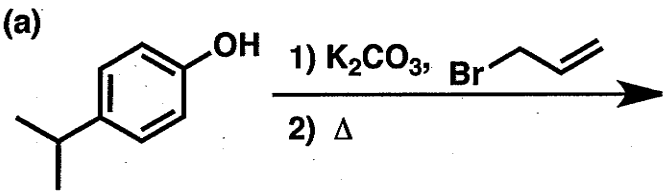
Last Name _____

First Name _____

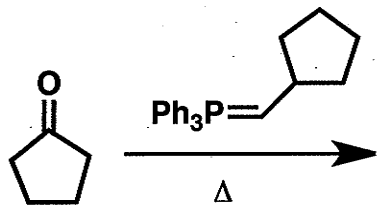
General Instructions:
(i) Use scratch paper at back of exam to work out answers; final answers must be recorded at the proper place on the exam itself for credit.
(ii) Print your name on each page.

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

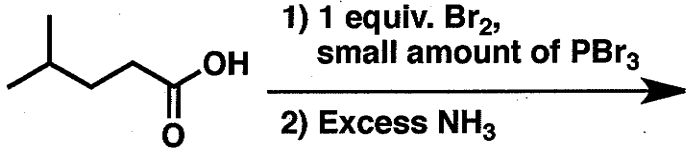
(a)



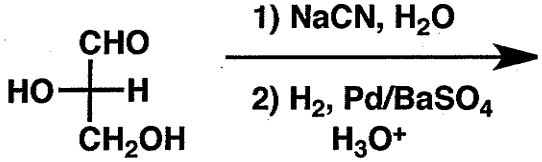
(b)



(c)



(d)



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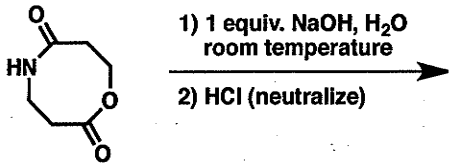
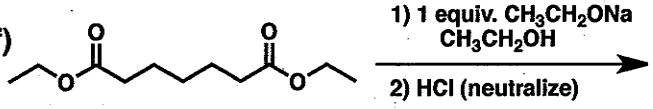
1. (cont.)

Name _____

(e)



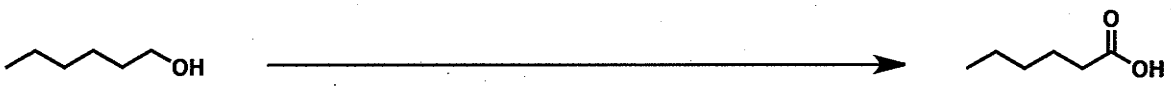
(f)



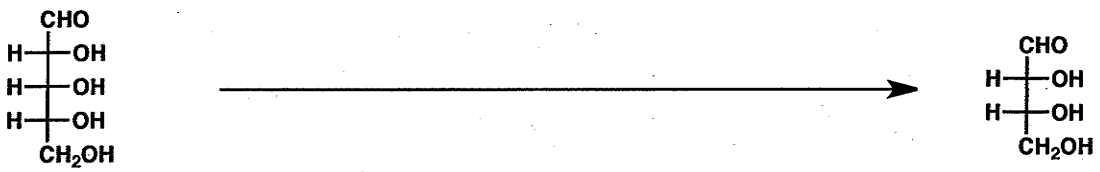
[Note: In the IR region 1700 - 1800 cm^{-1}, the starting material has a single strong signal at 1745 cm^{-1}, but the product has two signals, at 1745 cm^{-1} and 1725 cm^{-1}.]

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.

(a)



(b)



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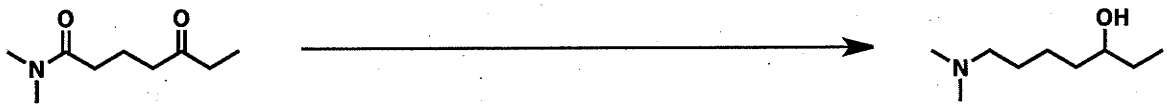
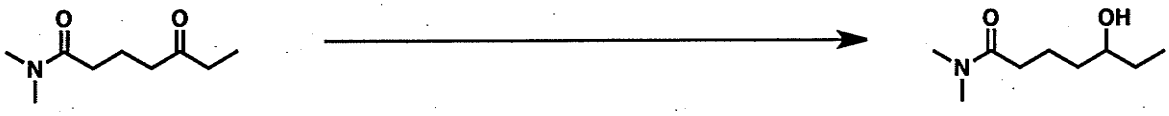
Name _____

2. (cont.)

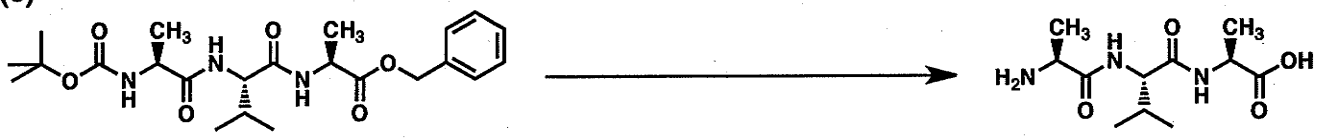
(c)



(d)



(e)



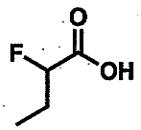
(f)

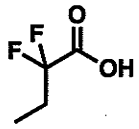
(g)

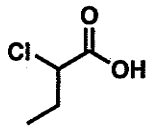
Name _____

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

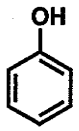
(a)

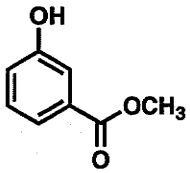


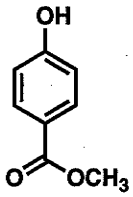




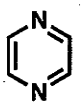
(b)

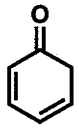


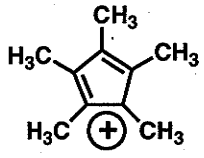


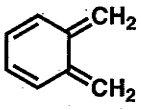


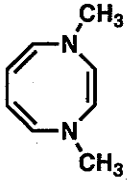
4. (12 points) Among the species shown below, CIRCLE those that you would expect to benefit from aromatic stabilization.

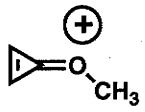






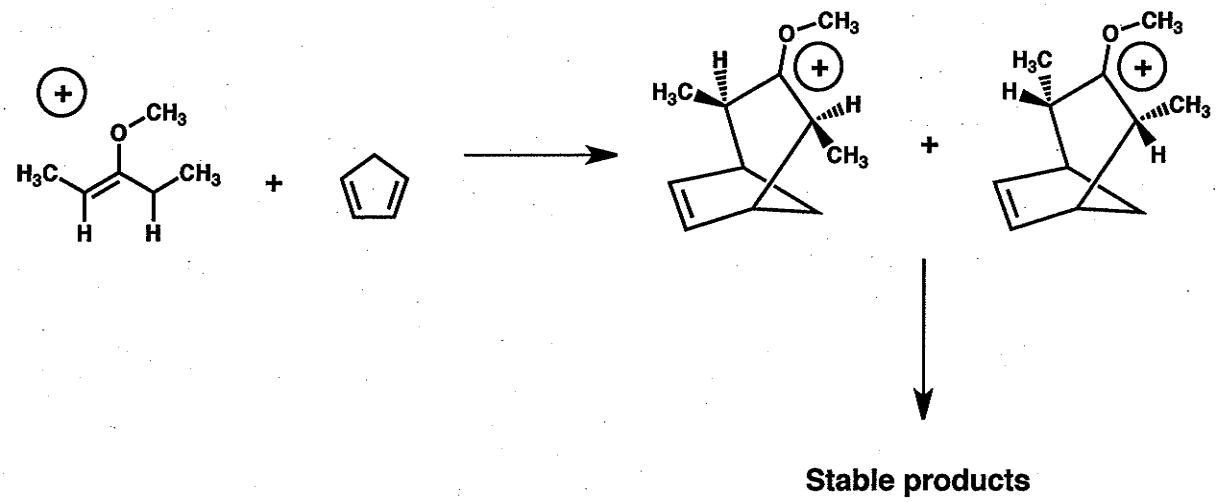






Name _____

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).

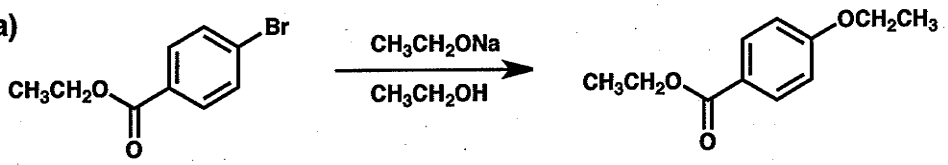


Stable products

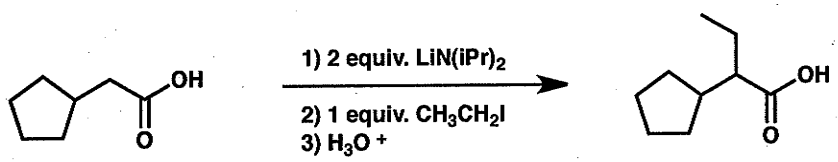
Name _____

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

(a)

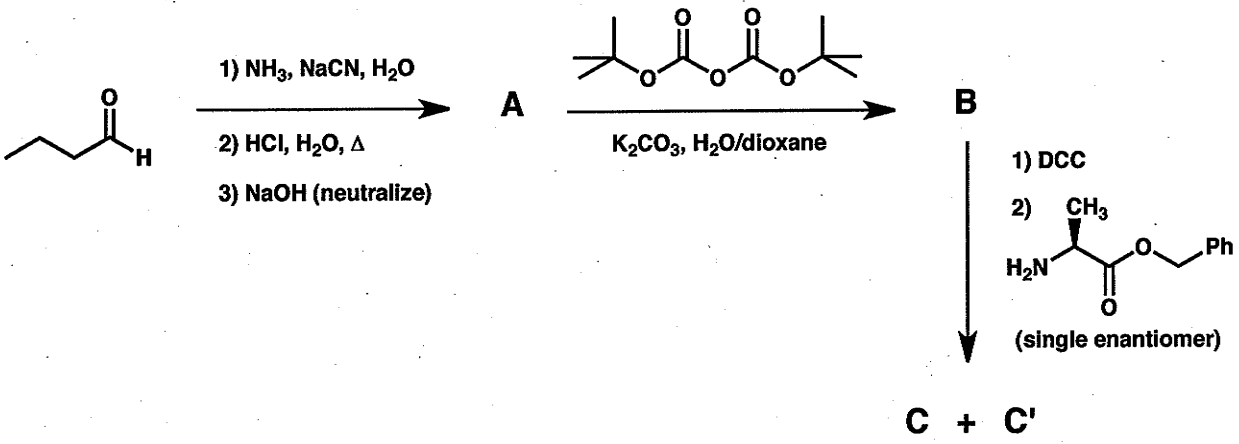


(b)



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.

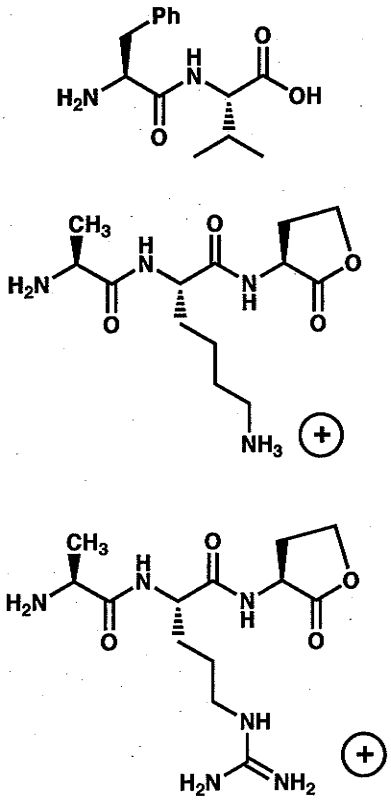
Draw the Fischer projection of D-erythrose.

Draw the Fischer projection of X.

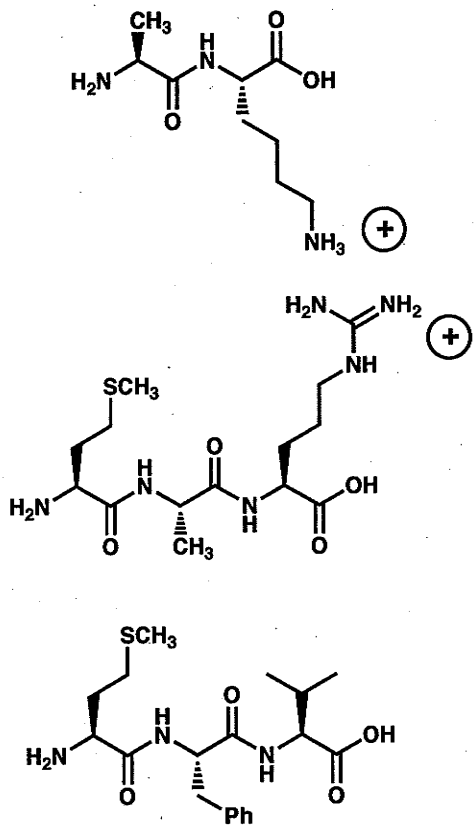
Name _____

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:



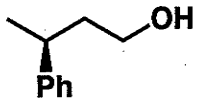
Fragments from degradation with trypsin:



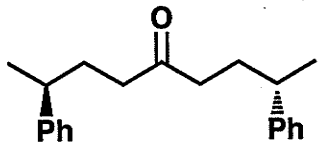
Peptide Z =

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 = 

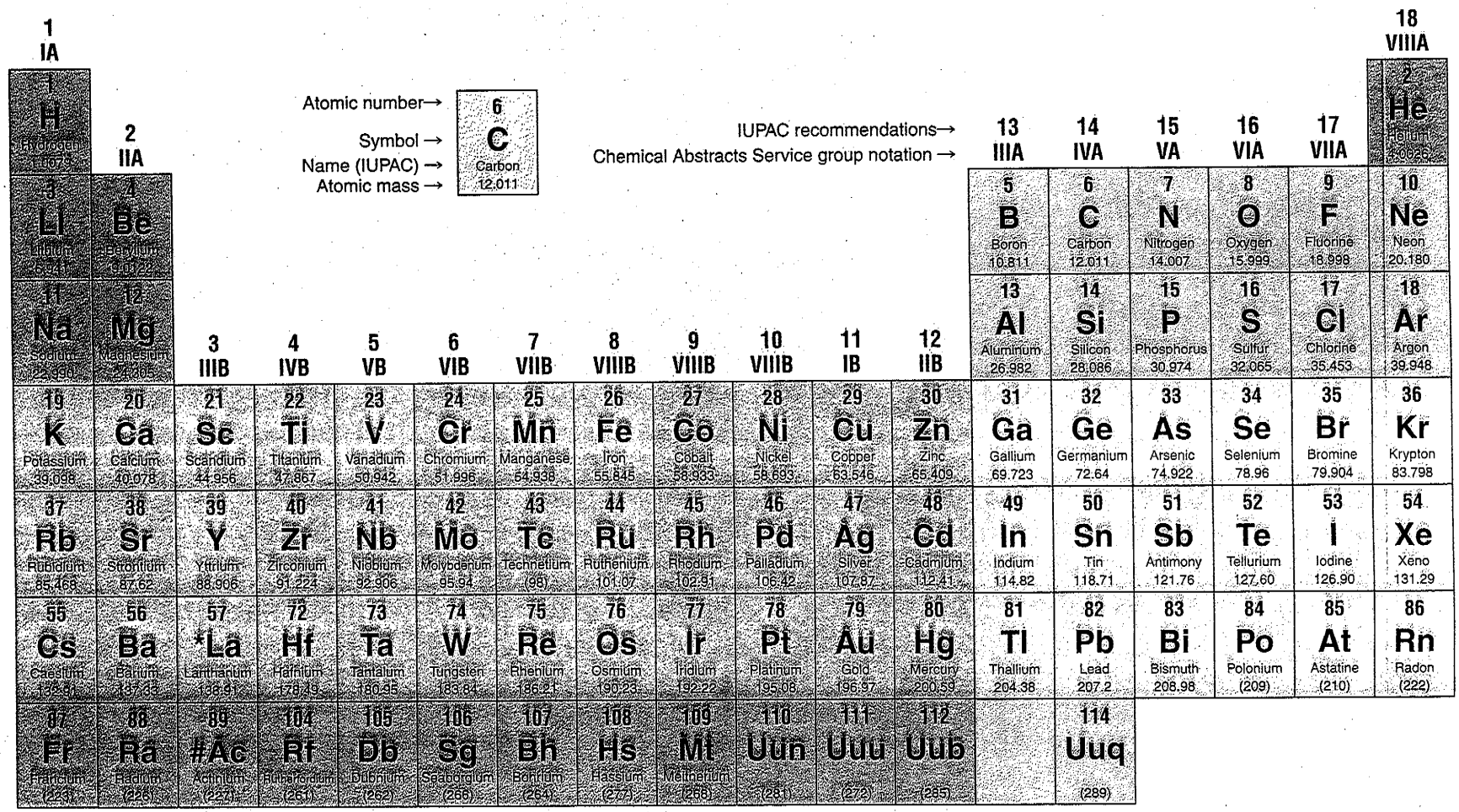
(single enantiomer)

Target = 

Name _____

Problem	Score
1	/ 39
2	/ 45
3	/ 8
4	/ 12
5	/ 10
6	/ 18
7	/ 20
8	/ 20
9	/ 12
10	/ 16
Total:	/ 200

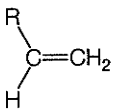
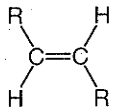
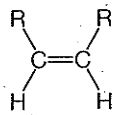
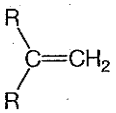
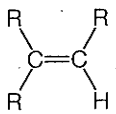
Periodic Table of the Elements



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.

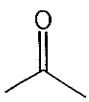
Table 15.3 gives the general positions of absorptions of a variety of functional groups, and once again we come to the question of memorization. Should one learn this chart by heart? Personally, I think not. It is important to know that this kind of general correlation exists, and you should have a rough 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)
	995–985 915–905	s (out-of-plane bend)
	980–960	s (out-of-plane bend)
	730–665	s (out-of-plane bend) (br, variable)
	895–885	s (out-of-plane bend)
	840–790	m (out-of-plane bend)

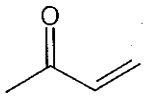
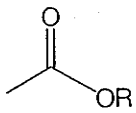
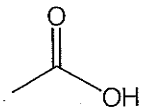
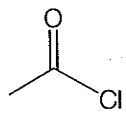
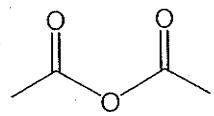
(continued)

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			
 C=O	1730–1700 (higher in strained cyclic molecules)	s	(stretch)

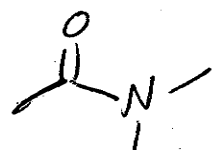
(continued)

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)

[a]**CAUTION!** 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}.

[b]Medium = m, strong = s, weak = w, broad = br.

Amides  1620–1680 cm^{-1} s (stretch)