Chemistry 216

Second Examination

June 17, 2010

Professor Masato Koreeda
(120 min, 120 points)

Name ______________________
Please Print

Signature ______________________

Student ID # ______________________

Please CHECK OFF your lab section.

sectn #	GSI
______130	Rebecca Chota
______131	Junsi Gu
______132	Rui Huang
______133	Natalie Vandeven
______134	Deidra Gerlach
______135	Shaoon Rahman
______136	Soojeong Kim
______137	Emily Nelson
______138	Anthony Grillo
______139	Wen Wen

This exam has 13 pages including this cover page. The last five pages include a periodic table, tables of characteristic IR frequencies, representative H-1 and C-13 NMR chemical shifts, and H-1/H-1 coupling constants and a table of pKa values for representative acids.

I	14	
II	6	
III	11	
IV	14	
V	5	
VI	25	
VII	20	
VIII	12	
IX	13	
TOTAL	**120**	

I. (14 points) The Grignard reagent C_6H_5-MgBr is prepared from bromobenzene (C_6H_5-Br) and Mg. Answer in the boxes below the following questions.

(1) (2 points) Is the carbon atom associated with the bromine atom in bromobenzene electrophilic or nucleophilic?

electrophilic	nucleophilic

[circle one]

(2) (2 points) Is the carbon atom associated with magnesium in the Grignard reagent electrophilic or nucleophilic?

electrophilic	nucleophilic

[circle one]

(3) (2 points) Is the magnesium atom oxidized or reduced during the formation of the Grignard reagent?

oxidized	reduced

[circle one]

(4) (4 points) Explain why the Grignard reaction has to be carried out in an anhydrous solvent.

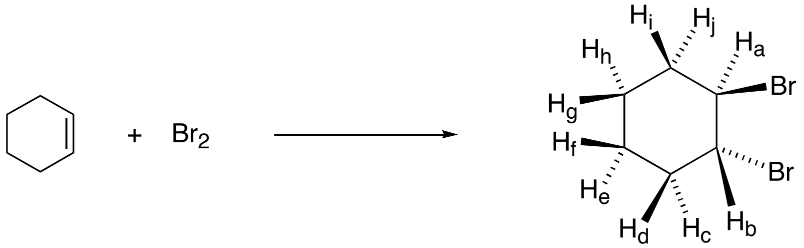
(5) (4 points) Write the conjugate carbon acid (i.e., C-H) of the C_6H_5–MgBr and explain why Grignard reagents are strong bases.

structure:	explanation:

II. (6 points) Ethanol [CH_3CH_2OH] is often present in technical-grade diethyl ether. If this grade of diethyl ether were used, what effect, if any, would the ethanol have on a Grignard reagent used? Explain through the use of a chemical equation using C_6H_5–MgBr as an example.

explanation based upon the reaction mechansim:

III. (11 points) Treatment of cyclohexene with bromine produces *trans*-1,2-dibromocyclohexane as a racemate. In spite of its simple structure, it shows quite complex spectra, particularly the ^{1}H NMR spectrum.



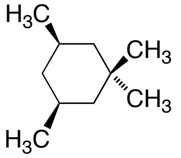
(1) (2 points) How many different ^{13}C NMR peaks would you expect from this dibromide? ________

(2) (9 points) Identify the indicated pairs of hydrogens in the dibromide as (i) homotopic, (ii) enantiotopic, or (iii) diastereotopic Hs. Write the answers as (i), (ii), or (iii).

H_a and H_b ________ H_c and H_d ________ H_e and H_f ________
H_g and H_h ________ H_i and H_j ________ H_c and H_i ________
H_d and H_j ________ H_e and H_g ________ H_f and H_h ________

IV. (14 points) Show how many peaks you would expect to observe in the proton-decoupled ^{13}C NMR spectra of the following compounds. Indicate your answers in each of the boxes provided.

(1)



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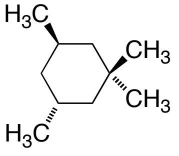

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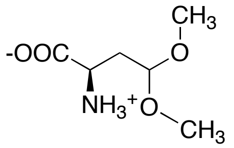
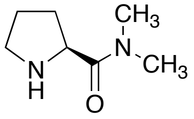
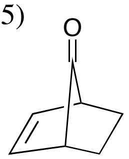


(4)

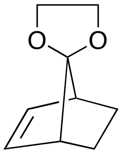


(room temperature)

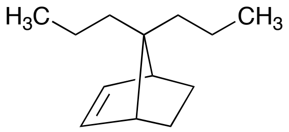
(5)



(6)



(7)

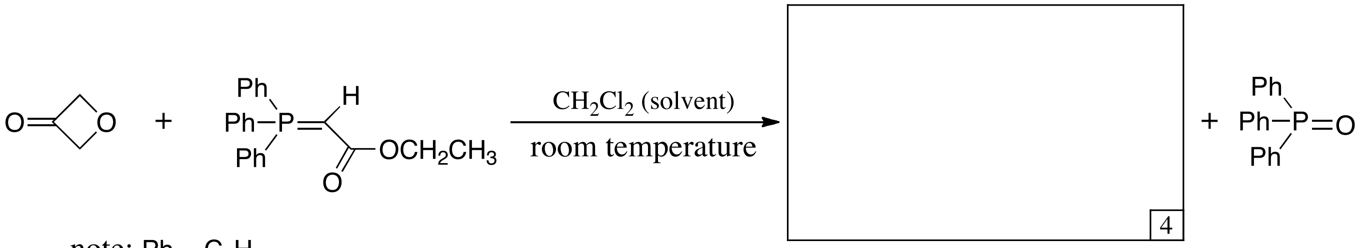


V. (5 points) The pK_a value of the NH of CH_3NH_2 is about 35. In contrast, the pK_a value of NH of urea [$(H_2N)_2C=O$] is about 12. Provide an explanation in the box below as to why the NH of urea is considerably more acidic than that of methylamine. If your explanation involves the resonance concept, make sure to draw a relevant resonance structure(s).

5

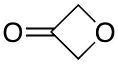
VI. (25 points) For each of the following two reactions, draw in the box the structure of the expected product from the reaction shown and provide in the box a reasonable step-by-step mechanism using the curved-arrow convention that accounts for its formation. You need not show the mechanism for the protonation step in (2).

(1) (11 points) [*J. Am. Chem. Soc.* **2010**, in press]



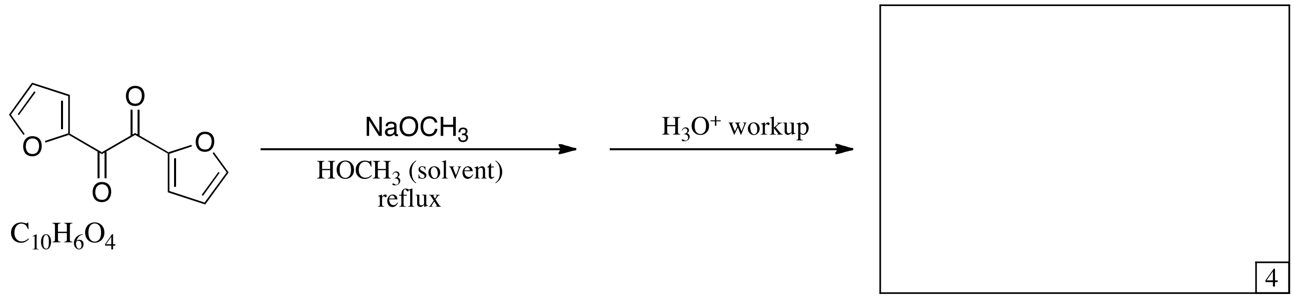
note: Ph = C_6H_5

Mechanism:



$\boxed{7}$

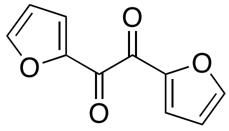
(2) (14 points)



$C_{10}H_6O_4$

$C_{11}H_{10}O_5$

Mechanism:

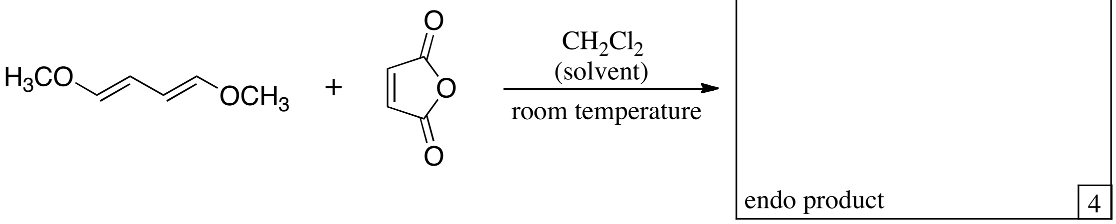


$\boxed{10}$

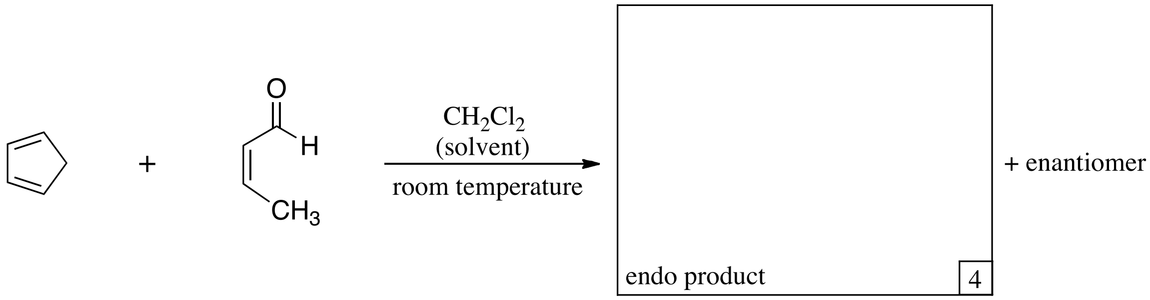
Name_______________________

VII. (20 points) For each of the following reactions, draw in the box provided the structure of the expected product.

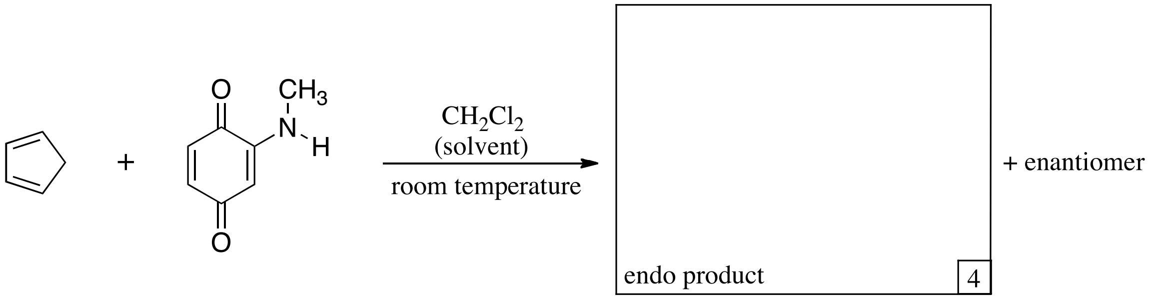
(1)



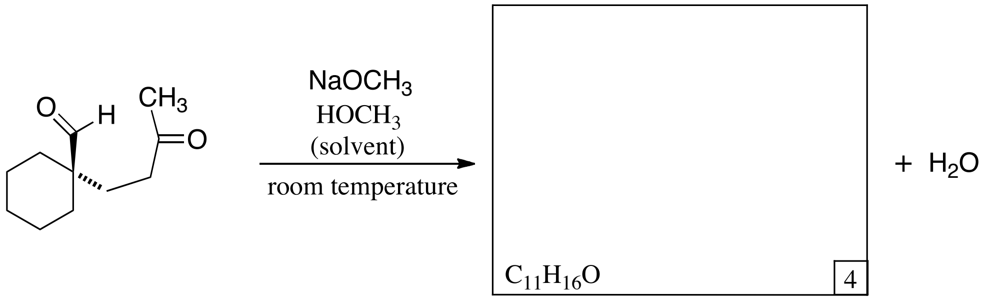
(2)



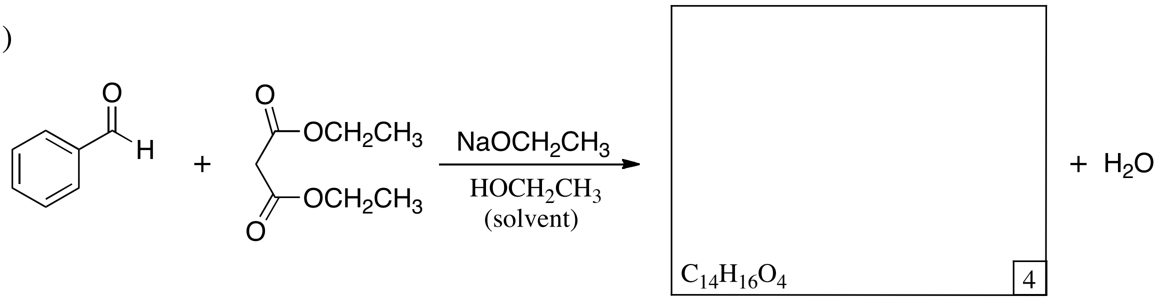
(3)



(4)

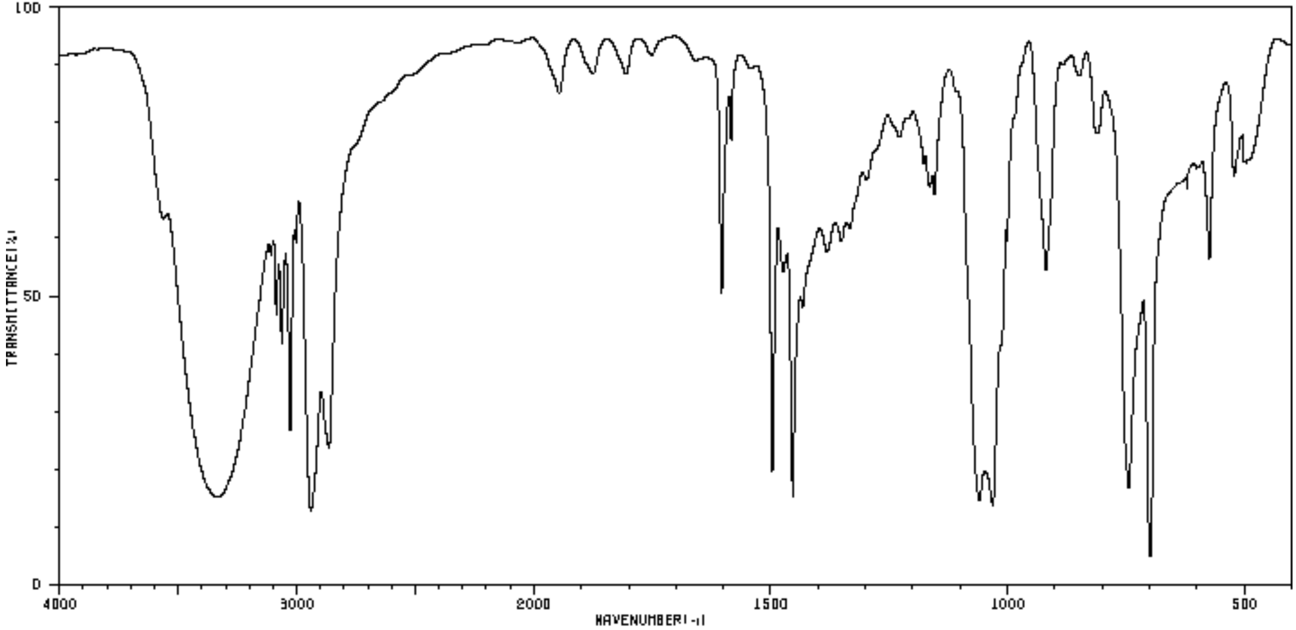


(5)

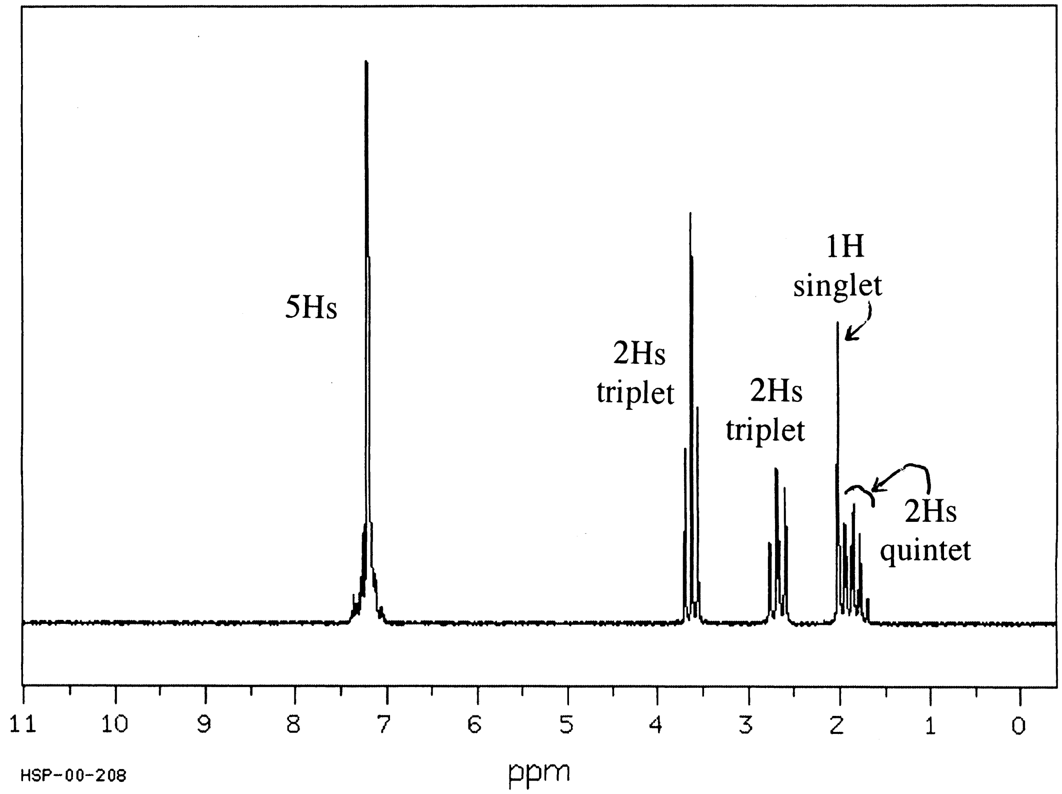


VIII. (12 points) On the basis of its spectroscopic information provided below, answer the questions given on page 7 and draw the structure of the compound ($C_9H_{12}O$) in the box on page 7.

IR (liquid film)



^1H NMR spectrum in $CDCl_3$



^{13}C NMR data (in $CDCl_3$): δ 32.06, 34.15, 61.85, 125.79, 128.35, 128.39, and 141.91 ppm

VIII. (continued)

(1) (1 points) What is (are) the unit(s) of unsaturation of this compound? _____________

(2) (1 point) Does this compound have a benzene ring? Yes No (circle the one that applies)

(3) (1 point) What does the IR spectrum tell you in terms of the presence of an *O*-containing functional group in this molecule? _____________

(4) (4 points) What is the structure of this compound? (no partial)

4

(5) (5 points) Draw in the box below the structure you showed above and assign all ^{1}H peaks in the 1 – 4 ppm range and the ^{13}C peak at 61.85 ppm to the corresponding H and C nuclei in the proposed structure.

5

IX. (13 points) On the basis of its spectroscopic information provided below, answer the questions given on page 8 and draw the structure of the compound ($C_7H_{14}O$) in the box on page 8.

$C_7H_{14}O$: IR (liquid film) 2958 - 2872 (several strong peaks), 1719 cm^{-1} (strong).

^{1}H NMR ($CDCl_3$) δ 0.890 (d, 6H, *J* = 7.1 Hz), 1.359 (quartet, 2H, *J* = 7.1 Hz), 1.435 (nonet,* 1H, *J* = 7.1 Hz), 2.137 (s, 3H), and 2.418 (t, 2H, *J* = 7.1 Hz)

^{13}C NMR ($CDCl_3$) δ 22.36, 27.73, 29.79, 32.72, 41.82, 209.22 ppm

note: *nine peaks

IX. (continued)

(1) (1 points) What is (are) the unit(s) of unsaturation of this compound? _____________

(2) (1 point) What do the IR spectral data tell you in terms of the presence of an *O*-containing functional group in this molecule? _____________

(3) (1 points) What do the ^{13}C NMR spectral data tell you in terms of the presence of an *O*-containing functional group in this molecule? _____________

(4) (4 points) What is the structure of this compound? (no partial)

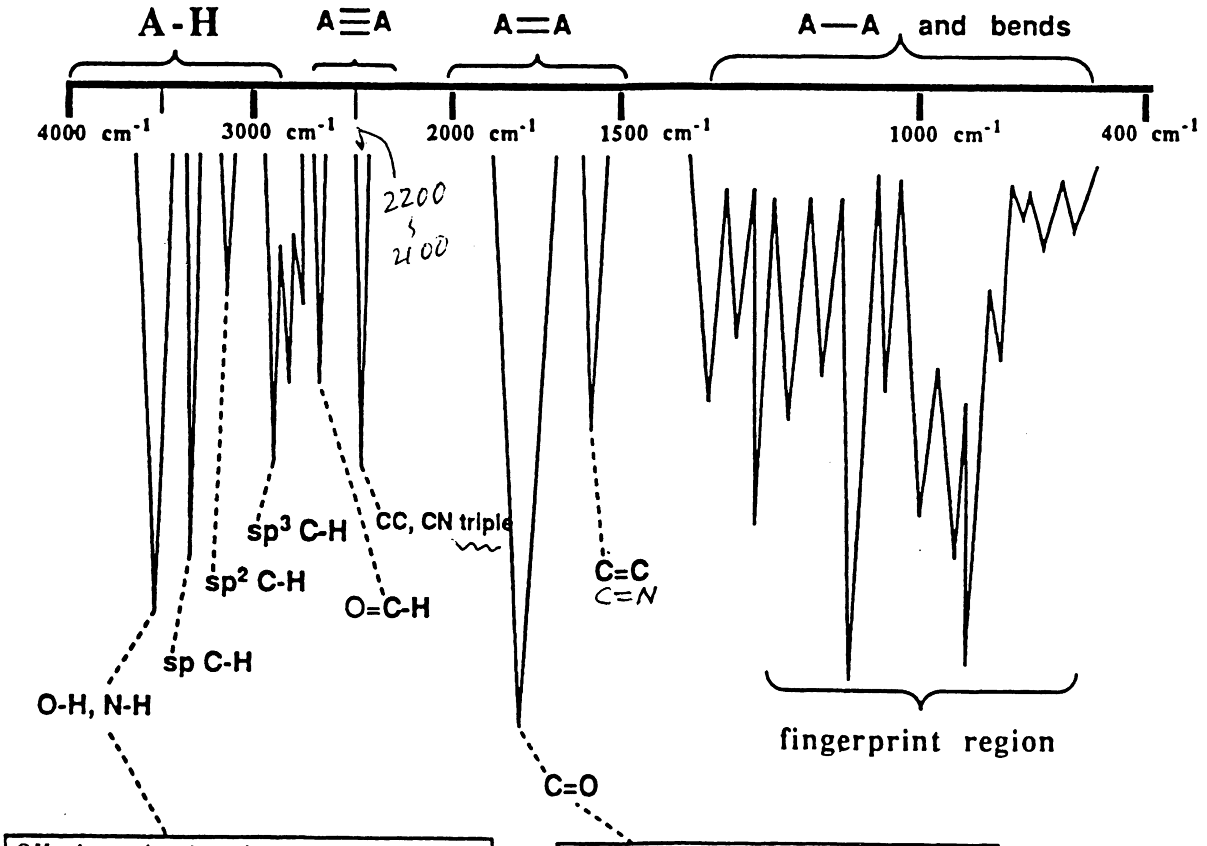
4

(5) (6 points) Draw in the box below the structure you showed above and assign all ^{1}H peaks and the ^{13}C peak at 209.22 ppm to the corresponding H and C nuclei in the proposed structure.

6

PERIOD	GROUP 1A	2A													3A	4A	5A	6A	7A	
1	1 H 1.008																			2 He 4.003
2	3 Li 6.941	4 Be 9.012													5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31													13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96		22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	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 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91		40 Zr 91.22	41 Nb 92.91	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 127.6	53 I 126.9	54 Xe 131.3
6	56 Cs 132.9	56 Ba 137.3	57 La 138.9	58-71 LANTH-ANIDES	72 Hf 178.5	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 197.0	80 Hg 200.6		81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra 226.0	89 Ac 227.0	90-103 ACTIN-IDES	104 (261)	105 (262)	106 (263)													

LANTHANIDE SERIES	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	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 173.0	71 Lu 175.0
ACTANIDE SERIES	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	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 (260)



OH absorption broadens and moves to lower υ when H-bonded:

non-H-bond: sharp, 3600 cm^{-1}

H-bond alcohol: broad, 3500-3200 cm^{-1}

H-bond acid: very broad, 3300-2800 cm^{-1}

carbonyl absorption frequencies roughly follow observed reactivity trends for carbonyl compounds:

acid halide > anhydride > ester > aldehyde > ketone, acid > amide

conjugation lowers υ by ca. 20 cm^{-1}

TABLE 10.2 Characteristic Infrared Absorption Frequencies

Bond Type	Stretching, cm^{-1}	Bending, cm^{-1}
C—H alkanes	2960–2850 (*s*)	1470–1350 (*s*)
C—H alkenes	3080–3020 (*m*)	1000–675 (*s*)
C—H aromatic	3100–3000 (*v*)	870–675 (*v*)
C—H aldehyde	2900, 2700 (*m*, 2 bands)	
C—H alkyne	3300 (*s*)	
C≡C alkyne	2260–2100 (*v*)	
C≡N nitrile	2260–2220 (*v*)	
C=C alkene	1680–1620 (*v*)	
C=C aromatic	1600–1450 (*v*)	
C=O ketone	1725–1705 (*s*)	
C=O aldehyde	1740–1720 (*s*)	
C=O α,β-unsaturated ketone	1685–1665 (*s*)	
C=O aryl ketone	1700–1680 (*s*)	
C=O ester	1750–1735 (*s*)	
C=O acid	1725–1700 (*s*)	
C=O amide	1690–1650 (*s*)	
O—H alcohols (not hydrogen bonded)	3650–3590 (*v*)	
O—H alcohols (hydrogen bonded)	3600–3200 (*s*, broad)	1620–1590 (*v*)
O—H acids	3000–2500 (*s*, broad)	1655–1510 (*s*)
N—H amines	3500–3300 (*m*)	
N—H amides	3400-3200 (*m*)	
C—O alcohols, ethers, esters	1300–1000 (*s*)	
C—N amines, alkyl	1220–1020 (*w*)	
C—N amines, aromatic	1360–1250 (*s*)	
NO_2 nitro	1560–1515 (*s*) 1385–1345 (*s*)	

s = strong absorption *w* = weak absorption
m = medium absorption *v* = variable absorption

TABLE 11.1 Typical Chemical Shifts for Types of Hydrogen Atoms, Seen in Proton Magnetic Resonance Spectra

Type of Hydrogen Atom	δ*	Type of Hydrogen Atom	δ*
RCH_3	0.9	$R_2C{=}CH_2$	5.0
RCH_2R acyclic	1.3	$RCH{=}CR_2$	5.3
cyclic	1.5	ArH	7.3
R_3CH	1.5–2.0	$R\overset{O}{\overset{\|}{C}}H$	9.7
$R_2C{=}\underset{R'}{\underset{\mid}{C}}CH_3$	1.8		
		RNH_2	1–3
$R\overset{O}{\overset{\|}{C}}CH_3$	2.0–2.3	$ArNH_2$	3–5
$ArCH_3$	2.3	$R\overset{O}{\overset{\|}{C}}NHR$	5–9
$RC{\equiv}CH$	2.5	ROH	1–5
$RNHCH_3$	2–3	ArOH	4–7
$RCH_2X(X{=}Cl, Br, I)$	3.5		
$ROCH_3$, $R\overset{O}{\overset{\|}{C}}OCH_3$	3.8	$R\overset{O}{\overset{\|}{C}}OH$	10–13

*The chemical shift values are given in ppm relative to tetramethylsilane at δ 0.00 and are for the hydrogen atoms shown in boldface in the formulas. The values for hydrogen atoms on oxygen and nitrogen are highly dependent on solvent, concentration, and temperature.

TABLE 11.3 Coupling Constants Seen in Proton Magnetic Resonance Spectra

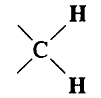
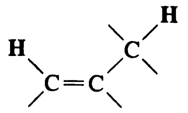
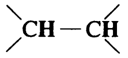
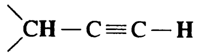
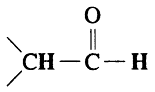
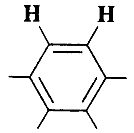
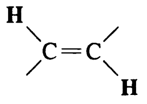
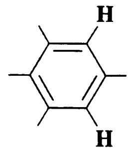
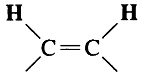
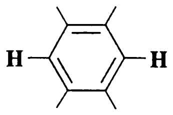
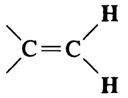
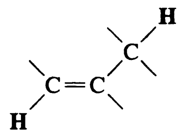
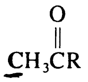
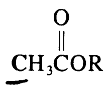
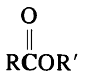
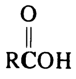
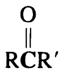
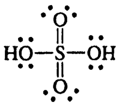
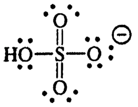
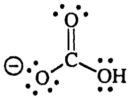
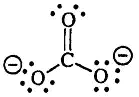
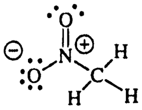
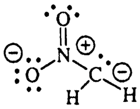
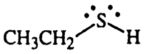
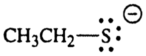
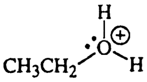
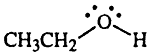
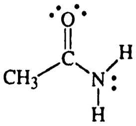
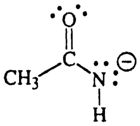
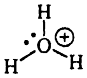
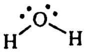
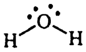
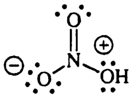
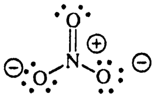
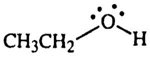
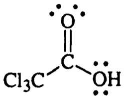
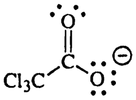
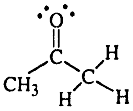
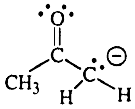
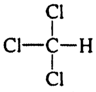
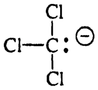
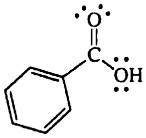
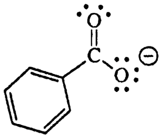
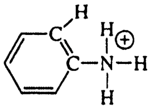
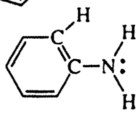
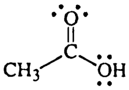
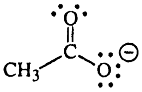
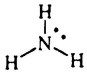
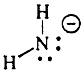
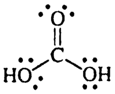
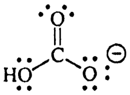
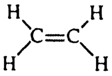
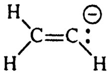
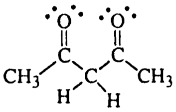
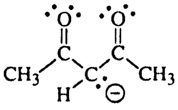
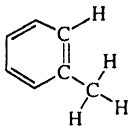
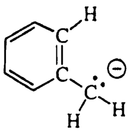
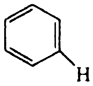
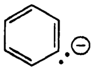
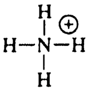
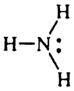
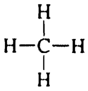
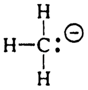
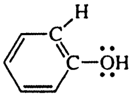
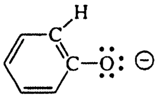
Type of Hydrogen Atoms	J, Hz	Type of Hydrogen Atoms	J, Hz
	12–15		0–3
	6–8		2–3
	2–3		6–10
	12–18		1–3
	6–12		0–1
	0–2		
	0–3		

TABLE 11.4 Chemical Shifts for Carbon Atoms in Carbon-13 Nuclear Magnetic Resonance Spectra

Type of Carbon Atom	δ*	Type of Carbon Atom	δ*
$RCH_2\underline{C}H_3$	13–16	$RCH{=}\underline{C}H_2$	115–120
$R\underline{C}H_2CH_3$	16–25	$R\underline{C}H{=}CH_2$	125–140
$R_3\underline{C}H$	25–38	$RC{\equiv}N$	117–125
 $\underline{C}H_3\overset{O}{\overset{\|}{C}}R$	~30	ArH	125–150
 $\underline{C}H_3\overset{O}{\overset{\|}{C}}OR$	~20	 $R\overset{O}{\overset{\|}{C}}OR'$	170–175
RCH_2Cl	40–45	 $R\overset{O}{\overset{\|}{C}}OH$	177–185
RCH_2Br	28–35	 $R\overset{O}{\overset{\|}{C}}H$	190–200
RCH_2NH_2	37–45	 $R\overset{O}{\overset{\|}{C}}R'$	205–220
RCH_2OH	50–64		
$RC{\equiv}\underline{C}H$	67–70		
$R\underline{C}{\equiv}CH$	74–85		

*The chemical shift values are given in ppm relative to tetramethylsilane at δ 0.00 and are for the carbon atoms shown in boldface in the formulas.

ACID	pK_a	CONJUGATE BASE	ACID	pK_a	CONJUGATE BASE
(Strongest Acid)		*(Weakest Base)*			
	–9			10.2	
$H-I$	–9	$I^{\ominus}$		10.2	
$H-Cl$	–7	$Cl^{\ominus}$		10.5	
	–2.4			15.0	
	–1.7			15.7	$H-O^{\ominus}$
	–1.3			17	$CH_3CH_2-O^{\ominus}$
	0.64			19	
$H-F$	3.2	$F^{\ominus}$		20	
	4.2		$H-C\equiv C-H$	26	$H-C\equiv C^{\ominus}$
	4.6		H_2	35	$H^{\ominus}$
	4.8			36	
	6.5			36	
	9.2			41	
$H-C\equiv N$	9.1	$^{\ominus}C\equiv N$		43	
	9.4			49	
	10.0				
			(Weakest Acid)		*(Strongest Base)*