Organic Structure Elucidation - A Workbook of Unknowns

www.nd.edu/~smithgrp/structure/workbook.html

Answers and Spectroscopic Assignments
Problems 1-8

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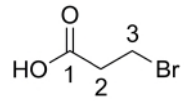
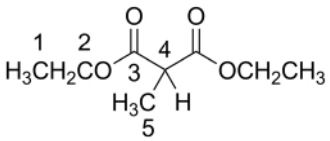
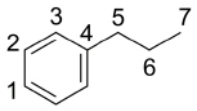
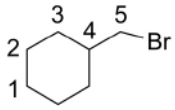
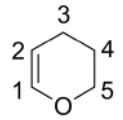
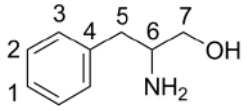
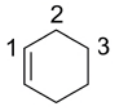
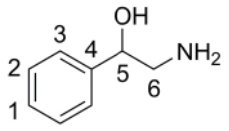
Spectroscopic Technique	Signal/Information	Comments
Problem 1		
Formula	$C_3H_5BrO_2$, UN=1	1 double bond
Mass Spectrum (m/z)	152, 154 (M^+, $[M+2]^+$)	Br present (1:1)
	135, 137 (M-17)	M–OH
	107, 109 (M-45)	M–COOH
	73 (M-79)	M–Br
IR (cm^{-1})	3067 (broad)	COOH
	1717	C=O stretch (acid)
^1H NMR (ppm)	>9 (exchanges)	COOH
	3.45 (t)	H3
	3.0 (t)	H2
^{13}C NMR (ppm)	178 (s)	C1
	24.3 (t)	C3
	38.6 (t)	C2
		 3-Bromopropionic acid
Problem 2		
Formula	$C_8H_{14}O_4$, UN=2	2 double bonds
Mass Spectrum (m/z)	174 (M)	
	146	M–CH_2=CH_2 (McLafferty Rgt)
	129 (M-45)	M–OCH_2CH_3
	101 (M-73)	M–$COOCH_2CH_3$
IR (cm^{-1})	2986	C(sp^3)-H stretch
	1749	C=O stretch (ester)
^1H NMR (ppm)	4.17 (m)	H2 (diastereotopic)
	3.39 (q)	H4
	1.39 (d)	H5
	1.24 (t)	H1
^{13}C NMR (ppm)	170	C3
	61	C2
	46	C4
	13.9, 13.5	C1
		C5
		 Diethyl methylmalonate

Problem 3		
Formula	C_9H_{12} UN=4	Phenyl ring
Mass Spectrum (m/z)	120 (M^+) 105 (M-15) 91 (M-29)	 M–CH_3 M–CH_2CH_3 (tropylium ion)
IR (cm^{-1})	3027, 3062 2865, 2900	C(*sp²*)-H stretch (aryl) C(*sp³*)-H stretch (alkyl)
^{1}H NMR (ppm)	7.35 (m) 2.64 (t) 1.71 (sextet) 1.02 (t)	H1, H2, H3 H5 H6 H7
^{13}C NMR (ppm)	142.6 128.4, 128.1 125.5 38.0 24.5 13.8	C4 C2, C3 C1 C5 C6 C7
		 Propylbenzene
Problem 4		
Formula	$C_7H_{13}Br$ UN=1	1 ring
Mass Spectrum (m/z)	176, 178 (M^+, $[M+2]^+$) 97 (M-79) 83 (M-93)	Br present (1:1) M–Br M–CH_2Br (cyclohexyl ring)
IR (cm^{-1})	2938, 2849 1445	C(*sp³*)-H stretches (alkyl) CH_2 bend
^{1}H NMR (ppm)	3.27 (d) 1.86 - 1.63 (m) 1.25 - 0.98 (m)	H5 H1-H4 H1-H4
^{13}C NMR (ppm)	40.8, 40.0 31.7, 26.1, 25.8	C4, C5 C1, C2, C3
		 Cyclohexylmethyl bromide
Problem 5		
Formula	C_5H_8O, UN=2	1 ring and 1 double bond
Mass Spectrum (m/z)	84 (M^+) 55 (M-29) 28 (M-56)	 M–C_2H_5 (Retro Diels-Alder) Ethene cation (Retro Diels-Alder)
IR (cm^{-1})	3063 2860, 2937	C(*sp²*)-H stretch C(*sp³*)-H stretches

	1644 1070, 1238	C=C stretch C-O stretches
^{1}H NMR (ppm)	6.35 (dt) 4.66 (m) 3.97 (t) 1.98 (q) 1.84	H1 H2 H5 H3 H4
^{13}C NMR (ppm)	144.0 101.7 65.7 22.7, 19.4	C1 C2 C5 C3, C4
		 3,4-Dihydro-2H-pyran
Problem 6 Formula	$C_9H_{13}NO$ UN=4	Aryl ring
Mass Spectrum (m/z)	152 (MH^+) 120 (M-31) 91 (M-60) 60 (M-91)	 M–CH_2OH M–$CH_2CH(NH_2)CH_2OH$ (tropylium ion) M–$PhCH_3$
IR (cm^{-1})	3352, 3298 2800-3100 3075 2823 1581	Amine N-H stretches OH stretch C(sp^2)-H stretch C(sp^3)-H stretch Amine N-H bend
^{1}H NMR (ppm)	7.37-7.25 (m) 5.2 (1H, exchanges) 3.69 (dd), 3.47 (dd) 3.18 (sp) 2.85 (dd), 2.58 (dd) 2.1 (2H, exchanges)	H1- H3 OH H7 (diastereotopic) H6 H5 (diastereotopic) NH_2
^{13}C NMR (ppm)	138.6 129.1, 128.3 126.3 66.2 54.1 40.8	C4 C2, C3 C1 C7 C6 C5
		 2-Amino-3-phenylpropanol

Problem 7		
Formula	C_6H_{10}, UN = 2	1 ring and 1 double bond
Mass Spectrum (m/z)	82 (M^+)	
	67 (M-15)	M–CH_3 (Rearrangement)
	54 (M-28)	M–ethene (Retro Diels-Alder)
	28 (M-54)	M–1,3-butadiene (Retro Diels-Alder)
IR (cm^{-1})	3064	C(sp^2)-H stretch
	2780, 2985	C(sp^3)-H stretches
	1692	C=C stretch
^{1}H NMR (ppm)	5.66 (s)	H1
	1.99 (m)	H2
	1.61 (quintet)	H3
^{13}C NMR (ppm)	127	C1
	25.1	C2
	22.6	C3
		 Cyclohexene
Problem 8		
Formula	$C_8H_{11}NO$, UN =4	Phenyl ring
Mass Spectrum (m/z)	138 (MH^+)	
	120 (M-18)	M–H_2O
	107 (M-31)	M–CH_3NH_2 (hydroxyl tropylium ion)
	77 (M-61)	M–$CH_2(OH)CH_2NH_2$
	30 (M-108)	M–$PhCH_2OH$ [$CH_2NH_2^+$]
IR (cm^{-1})	2500-3500	O--H--N stretch
	3358	Amine N-H stretch
	1598	Amine N-H bend
^{1}H NMR (ppm)	7.36 (m)	H1-H3
	5.2 (exchanges)	OH
	4.35 (dd)	H5
	2.59 (dd), 2.51 (dd)	H6 (diastereotopic)
	1.3 (broad)	NH_2
^{13}C NMR (ppm)	142.7	C4
	128.3, 125.8	C2, C3
	127.4	C1
	74.1	C5
	49.2	C6
		 2-Amino-1-phenylethanol