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Chapter Two, Problem B

Worksheet, step one: In this case, the IHD = 1. All the H's are attached to carbon.

Example B

 $C_{10}H_{20}O_2$

¹³ C NMR	¹ H NMR
177.0, s	0.89, t, J = 7.3 Hz, 3H
64.4, t	1.26, d, J = 6.5 Hz, 6H
34.1, d	1.4, m, 6H
31.6, t	1.64, m, 2H
28.8, t	2.52, m, 1H
25.7, t	4.05, t, J = 7.1 Hz, 2H
22.6, t	
19.1, q (2)	
14.0, q	

Worksheet, step two: We need to find out the source of the IHD. From the ¹³C data, there is a signal at 177, which is a singlet. From the summary on the worksheet, we know that this is in the carbonyl range. Referring to Table C9, we find that this is a

Table C.9 Shift Positions for the C=O Group and Other Carbon Atoms of Carboxylic Acids, Esters, Lactones, Chlorides, Anhydrides, Amides, Carbamates, and Nitriles (ppm from TMS)



carboxylic acid derivative. More specifically, since the only other heteroatom is another O, and all the H's are attached to carbon, we know that we have an ester.

Note that the ester is an usual functional group in that it has an alkyl chain at each end, so we need to do generic chemical shifts for each end. Consulting Table C11, we observe that the α shift next to the carbonyl is + 20, and the α shift for the carbon attached to the sp³ hybridized O is + 51.

Table C.11 Incremental Substituent Effects (ppm) on Replacement of H by Y in Alkanes

	Ý fi Term				
	c	x	ſ	3	γ
Y ·	TERMINAL	INTERNAL	TERMINAL	INTERNAL	the three memory
CH ₃	+ 9	+ 9	+ 6	+ 6	-2
$CH = CH_2$	+ 20		+ 6		-0.5
C CH	+ 4.5		+ 5.5		-3.5
COOH	+21	+16	+3	+ 2	-2
COO-	+ 25	+20	+5	+ 3	-2
COOR	+20	+17	+3	+ 2	-2
COCI	+ 33	28		+ 2	
CONH ₂	+ 22		+ 2.5		-0.5
COR	+ 30	+24	+ 1	+ 1	-2
CHO	+ 31		0		-2
Phenyl	+ 23	+17	+ 9	+ 7	-2
OH	+ 48	+41	+10	+ 8	-5
OR	+ 58	+51	+ 8	+ 5	-4
OCOR	+ 51	+45	+ 6	+ 5	-3
NH ₂	+ 29	+24	+11	+10	-5
NH ₃	+ 26	+24	+ 8	+ 6	-5
NHR	+ 37	+31	+ 8	+ 6	4
NR ₂	+ 42		+ 6		-3
NR ₃	+ 31		+ 5		-7
NO ₂	+ 63	+57	+ 4	+ 4	
CN	+ 4	+ 1	+ 3	+ 3	-3
SH	+ 11	+11	+12	+11	$^{-4}$
SR	+20		+ 7		-3
F	+ 68	+63	+ 9	+ 6	-4
Cl	+ 31	+32	+11	+10	-4
Br	+ 20	+25	+11	+10	-3
I	<u>,</u> − , 6	+ 4	+11	+12	-1

It follows that there will be two tables of generic chemical shifts for the ester functional group, that look like this. Inspecting the ¹³C data for the problem, it seems likely that the carbon attached to the sp³ hybridized O has two H's, 64.4, t. The α shift next to the carbonyl of + 20 is not enough to make the carbon stand out from the crowd.

Generic Chemical Shifts: Ester



Following up on the carbon attached to the sp³ hybridized O, from Table H1, we predict a chemical shift of about 4.1 for such a methylene. In fact, we observe this at 4.05, t, J=7.1 Hz, 2H. Since it is a triplet, there must be two H's on the adjacent H also.

Table H.1 contin	nue	d																							
M = methyl																									
8 M = methylene																									
 M = methine 												δ													
.4	.2 5	.8	.6.	4 .:	2 4	1.8	8.0	5.4	4 .:	2 3	3.8	3 .6	5.4	4 .2	2 2	8	.6	.4	1.1	2 1	1.8	ŝ	5 A	.2	2 0
M—OPh			:		00	1																			
M-OC(==O)R		•			00		1																		
M-OC(=O)Ph	•				Ş	1																			
M-OC(=O)CF ₃				0		I																			
M-OTs*						0	1																		
M - C = 0H								T					•	5											

Although the C next to an ester carbonyl does not stand out in the ¹³C spectrum, it does in the ¹H spectrum. Again referring to Table H1, we have a choice of a methyl at 2.0 (3H), a methylene at 2.25 (2H), or a methine at 2.5 (1H). Of the three, the one that fits the data is 2.52, m, 1H.



Combing all of this information, we have a beginning for the structure.



Worksheet, Step 3: There are no more heteroatoms.

Worksheet, Step 4a: There is a pair of methyl groups that have the same chemical shift, so they are symmetrical. There is no other symmetry in the data, so the two methyl groups must be attached to the same carbon. They appear as a doublet in the ¹H spectrum (1.26, d, J=6.5 Hz. 6H), so they are attached to a carbon with one H. They must be attached to the carbon adjacent to the carbonyl, since there is no other doublet in the ¹³C spectrum. So, our picture is gathering details.

Worksheet, Step 4c: All that remains to complete the structure are three more CH_2 's and a CH_3 , 0.89, t, J=7.3 Hz, 3H, at the end of the alkyl chain.

Worksheet, Step 5: We have all the pieces, and there is only one way to put them together.



Referring again to Table C10 (next page), we can understand the chemical shift for the C next to the ester carbonyl. The starting hydrocarbon is the C-2 of propane, at 16. Adding the α *internal* shift from Table C11 (above) for ester carbonyl of +17 gives us 33, d (observed 34.1, d).

COMPOUND	C-1	C-2	C-3	C-4	C-5
Methane	-2.3		 A DESCRIPTION OF DESCRIPTION OF DESCRIPTION 	san an ann an Alaine ann an Alaine ann an Anna	
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2		
Pentane	13.9	22.8	34.7	22.8	13.9
Hexane	14.1	23.1	32.2	32.2	23.1
Heptane	14.1	23.2	32.6	29.7	32.6
Octane	14.2	23.2	32.6	29.9	29.9
Nonane	14.2	23.3	32.6	30.0	30.3
Decane	14.2	23.2	32.6	31.1	30.5
Isobutane	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Isohexane	22.7	28.0	42.0	20.9	14.3
Neopentane	31.7	28.1			
2,2-Dimethylbutane	29.1	30.6	36.9	8.9	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH ₃)	
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
2,3-Dimethylpentane	7.0	25.3	36.3	(14.6, 3-CH ₃)	

Table C.10 The 13 C Shifts for Some Linear and Branched-Chain Alkanes (ppm from TMS)

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