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Chapter Two, Problem C

Worksheet, step one: In this case, the IHD = 2. All the H's are attached to carbon.

Example C

 $C_7H_{12}O_2$

IR: 2980, 2890, 1775, 1470, 1370, 1350, 1190, 1020, 980, 925 cm⁻¹

13C NMR	¹ H NMR
13.1, q	0.96, t, J = 6.8, 3H
17.9, t	1.4-1.9, m, 6H
27.3, t	2.4-2.6, m, 2H
28.1, t	4.5, m, 1H
36.9, t	
80.1, d	
176.6, s	

Worksheet, step two: We need to find out the source of the IHD. From the ¹³C data, there is a signal at 176.6, 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	α Y /	$\begin{array}{c c} Y \\ \gamma & \alpha & \gamma \\ \hline \beta & \beta \\ Internal \end{array}$	••• •	
	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 one H, 80.1, d 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 sp^3 hybridized O, from Table H1, we predict a chemical shift of about 4.5 for such a methine. In fact, we observe this at 4.5, 1H.

M = methyl																										
8 M = methylene																										
M = methine													δ													
	.4 .2	5	.8.	6.4	4 .:	2 4	4.8	3.6	5.	4 .:	2 3	3.8	8.6	.4	.2	2	8	.6	.4	.2	1	.8	.6	.4	.2	0
M—OPh		Τ		:		0	1																			
M - OC (= O)R		•				0		1																		
M—OC(=O)Ph		•		T		¢ ¢	1																			
$M - OC = O)CF_3$					00		ī																			
M—OTs*			•				0	1																		
M-C(==0)H														•<	2											

Table H.1 continued

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 2.4-2.6, m, 2H.

MC(=O)H						•	ξı						
MC(=0)R					:		0 0	I					
M-C(=O)Ph			+		00								
M-C(=0)OH						:	0	I					
M-C(=O)OR						•	0						
$M - C = O NR_2$							0						
		1				0							

There is still another IHD to account for. There are no alkenes, so this must be a ring. Could the ester be included in the ring, making it a lactone? As is discussed in the text, the carbonyl of a normal ester comes at 1735-1755 cm⁻¹, but the carbonyl stretch for a five-membered ring lactone comes at 1760-1780 cm⁻¹. Since we observe a carbonyl stretch at 1775 cm⁻¹, the ester must be part of the ring, and it must be a five-membered ring.

The methine where the sp^3 hybridized O is attached is a branch point, the only branch point in the structure. This gives us a partial structure.



Worksheet, Step 3: There are no more heteroatoms.

Worksheet, Step 4c: All that remains to complete the structure are two more CH_2 's and a CH_3 , 0.96, t, J=6.8 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.



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