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**Chapter Three, Problem A** 

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

Example A

C<sub>12</sub>H<sub>22</sub>O<sub>2</sub>

IR: 2926, 2856, 1728, 1645, 1436, 1197, 1175, 819 cm<sup>-1</sup>

<sup>13</sup> C NMR	<sup>1</sup> H NMR
166.5, s 29.0, t	6.14, dt, 1H, J = 7.5, 11.5 Hz
150.7, d 28.9, t	5.68, d, 1H, J = 11.5 Hz
119.0, d 28.8, t	3.61, s, 3H
50.6, q 22.5, t	2.57, dt, 2H, J = 7.5, 7.4 Hz
31.7, t 13.9, q	1.35, m, 2H
29.3, t	1.18, m, 10H
29.1, t	0.80, m, 3H

**Worksheet, step two:** We need to find out the source of the IHD. From the <sup>13</sup>C data, there is a signal at 166.5, 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  $\alpha$  shift next to the carbonyl is + 20, and the  $\alpha$  shift for the carbon attached to the sp<sup>3</sup> 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	diverting provident and the
CH <sub>3</sub>	+ 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 <sub>2</sub>	+ 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 <sub>2</sub>	+ 29	+24	+11	+10	-5
NH <sub>3</sub>	+ 26	+24	+ 8	+ 6	-5
NHR	+ 37	+31	+ 8	+ 6	4
NR <sub>2</sub>	+ 42		+ 6		-3
NR <sub>3</sub>	+ 31		+ 5		-7
NO <sub>2</sub>	+ 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 <sup>13</sup>C data for the problem, it seems likely that the carbon attached to the sp<sup>3</sup> hybridized O has three H's, 50.6, q The  $\alpha$  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 3.6 for such a methyl. In fact, we observe this at 3.61, s, 3H.

lable n.1 conti	nue	20																								
M = methyl																										
8 M = methylene																										
<ul> <li>M = methine</li> </ul>													δ													
.4	.2	5.	8.0	6.	4 .2	2 4	1.8	8.6	5.4	4 .:	2 3	3.3	8 . (	5.4	4.2	2 2	2.8	. 6	5.4	ŧ.:	2	1.1	8.	6.	4.	2 0
M—OPh		Γ		:		00	1																			Π
M—OC(==O)R		:				00		1																		
M—OC(=O)Ph						3	1																			
M-OC(=O)CF <sub>3</sub>					00		I																			$\square$
M—OTs*			•				0	1																		
MC(==0)H		T												•	þ											

There is still another IHD to account for. From 150.7, d and 119.0, d, there is clearly an alkene. Further, while 119, d is close to the normal range, 150.7, d is larger than the normal range. This suggests an alkene polarized by an electron-withdrawing group, in this case the carbonyl of the ester. We can confirm this by considering the chemical shifts of the alkene H's. From the text, the starting point is 5.28, with the increments

Table H.1 continued

## from Table H6 added.

See Figure 5.10 for more information											
		Ζ				Ζ					
SUBSTITUENT R	GEM	CIS	TRANS	SUBSTITUENT R	GEM	CIS	TRANS	,			
—Н	0	0	0	Н							
Alkyl	0.44	-0.26	-0.29		1.03	0.97	1.21				
—Alkyl-ring <sup>a</sup>	0.71	-0.33	-0.30	0-0							
CH <sub>2</sub> 0,CH <sub>2</sub> I	0.67	-0.02	-0.07	Ν							
-CH <sub>2</sub> S	0.53	-0.15	-0.15	6-0							
CH2Cl,CH2Br	0.72	0.12	0.07	C ≡0	1.37	0.93	0.35				
-CH <sub>2</sub> N	0.66	-0.05	-0.23	CI							
$-C \equiv C$	0.50	0.35	0.10	-C = 0	1.10	1.41	0.99				
—C≡N	0.23	0.78	0.58	-OR, R:aliph	1.18	-1.06	-1.28				
C==C	0.98	-0.04	-0.21	OR, R:conj <sup>b</sup>	1.14	-0.65	-1.05				
C==C conj <sup>b</sup>	1.26	0.08	-0.01	-OCOR	2.09	-0.40	-0.67				
C==0	1.10	1.13	0.81	-Aromatic	1.35	0.37	-0.10				
-C=O conj <sup>b</sup>	1.06	1.01	0.95	Cl	1.00	0.19	0.03				
-COOH	1.00	1.35	0.74	—Br	1.04	0.40	0.55				
-				R							
COOH conj <sup>b</sup>	0.69	0.97	0.39	N R: alipł	n 0.69	-1.19	-1.31				
				R							
600D	0.04		0.54	_N n "	0.00	0.72	0.01				
COOR	0.84	1.15	0.56	R:conj	2.30	-0.73	-0.81				
—COOR conj <sup>b</sup>	0.68	1.02	0.33	IX.							

See Figure 3.10 for more information

Table H.6 Calculation of <sup>1</sup>H NMR Chemical Shifts for Alkenes

From the calculations, it is clear that the chemical shifts are predicted to be different for the two geometric isomers. The calculated values for the Z alkene come closer to the data for the unknown.



We can confirm this by observing the coupling constant, 11.5 Hz, shared by the two alkene H's. From Table H2 (next page), a typical value for a Z alkene is 10 Hz, for an E alkene 17 Hz.

Table H.2	continued
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TYPE	J <sub>ab</sub> (Hz)	Job TYPICAL	TYPE		J <sub>ab</sub> (Hz)	Jab TYPICAL
د <sup>۲</sup>			CH <sub>a</sub> —C≡C —CH <sub>a</sub> —C≡	СНь ≡С—СНь—	23 - 23	
(cis or trans)	cis 4-12 trans 2-10		H <sub>a</sub> H <sub>b</sub>	<		6
H <sub>a</sub>	cis 7–13		H <sub>a</sub>	$\leq^{H_b}$		4
(cis or trans)	trans 4—9			$<^{H_b}$		2.5
CH <sub>a</sub> -OH <sub>b</sub> (no exchanged)	ge) 4-10	5				
Сн <sub>а</sub> —Сн <sub>ь</sub>	1–3	2–3	Ha	J (ortho) J (meta) J (para)	6–10 1–3 0–1	9 3 ~0
с=сн <sub>а</sub> -сн <sub>ь</sub>	58	6		I(2-3)	(5-6)	5
H <sub>a</sub> c=c <sub>H<sub>b</sub></sub>	12–18	17	$5 \begin{pmatrix} 4 \\ 5 \\ 6 \end{pmatrix} $	J (3-4) J (2-4) J (3-5) J (2-5) J (2-6)	(7-9) (1-2) (1-2) (0-1) (0-1)	8 1.5 1.5 1
$> = < +_{H_b}$	0–3	02	4 3	J (2–3) J (3–4)	1.3-2.0 3.1-3.8	18 3.6
	6–12	10	s Com	J (2-4) J (2-5)	00 12	~0 1.5

Worksheet, Step 3: There are no more heteroatoms.

**Worksheet, Step 4c:** All that remains to complete the structure are seven  $CH_2$ 's and a  $CH_3$ , 0.80, m, 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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