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## **Chapter Three, Problem B**

**Worksheet, step one:** In this case, the IHD = 4. All the H's are attached to carbon. [As originally published, this problem incorrectly said " $O_2$ ", and the (3) was missing from the 31.4, q.]

C11H16O

IR: 2980, 1615, 1585, 1470, 1370, 1305, 1188, 1040, 835 cm<sup>-1</sup>

13 <sub>C NMR</sub>	<sup>1</sup> H NMR
157.3, s	1.27, s, 9H
143.1, s	3.67, s, 3H
126.0, d (2)	6.80, d, J = 8.5 Hz, 2H
113.3, d (2)	7.25, d, J = 8.5 Hz, 2H
54.8, q	
33.9, s	
31.4, q (3)	

**Worksheet, step two:** With an IHD of 4 and signals in the <sup>1</sup>H spectrum around 7, we should suspect a benzene derivative. That (three alkenes, one ring) accounts for all the IHD. From 6.80, d, J = 8.5 Hz, 2H and 7.25, d, J = 8.5 Hz, 2H, there are four H's on the benzene ring, so there must be two substituents. From the symmetry, they must be 1,4 on the ring. It remains to determine the nature of X and Y.



**Worksheet, Step 3:** There is one oxygen. From Table C11, the  $\alpha$  shift for ether O is + 58. The generic chemical shifts for sp<sup>3</sup> hybridized carbons attached to ether O are then calculated to be:

## **Generic Chemical Shifts: Ether**



Inspecting the data, this appears to be a methyl ether, 54.8, q. The other end of the ether does not appear, so it may not be  $sp^3$  hybridized. Could it be  $sp^2$  hybridized, one of the benzene carbons? From Table H1, the methyl ether attached to a benzene ring should come at about 3.85, s, 3H. Indeed, we have 3.67, s, 3H.

		-																									
M = methyl																											
8 M = methylene																											
<ul> <li>M = methine</li> </ul>													δ														
.4	.2 .5	5.8	3.6	.4	.2	4	.8	3.6	5.	4 .	2 .	3.	8.	6.	4.	2 2	2.	8.	6.4	4.	2	1.	8	.6	.4	.2	_0
M—OPh				:		0	J																				
M—OC(==O)R		:				0		1																			
M—OC(=O)Ph	:				ç	}	I					Γ															
$M - OC = O)CF_3$		Γ			0		I																				
M—OTs*			:				00	۱					Γ	Γ													
M - C = OH														•	ģ							Γ	Γ				

Table H.1 continued

There are three more Tables that are useful for benzene derivatives. The first is C12.

Table C.12 Incremental Shifts of the Aromatic Carbon Atoms of Monosubstituted Benzenes (ppm from Benzene at 128.5 ppm. + Downfield, – Upfield). Carbon Atoms of Substituents ppm from TMS\*

	C-1				COF	SUBSTITUENT
SUBSTITUENT	(ATTACHMEN	D C-2	C-3	C-4	(ppm	from TMS)
Η	0.0	0.0	0.0	0.0		
CH <sub>3</sub>	9.3	+0.7	-0.1	-2.9	21.3	
CH <sub>2</sub> CH <sub>3</sub>	+15.6	-0.5	0.0	-2.6	29.2 (CI	H <sub>2</sub> ), 15.8 (CH <sub>3</sub> )
CH(CH <sub>3</sub> ) <sub>2</sub>	+20.1	-2.0	0.0	-2.5	34.4 (Cł	I), 24.1 (CH <sub>3</sub> )
C(CH <sub>3</sub> ) <sub>3</sub>	+22.2	-3.4	-0.4	-3.1	34.5 (C)	, 31.4 (CH <sub>3</sub> )
CH=CH <sub>2</sub>	+9.1	-2.4	+0.2	-0.5	137.1 (C	H), 113.3 (CH
C=CH	-5.8	+6.9	+0.1	+0.4	84.0 (C)	, 77.8 (CH)
C <sub>6</sub> H <sub>5</sub>	+12.1	-1.8	-0.1	-1.6		
CH <sub>2</sub> OH	+13.3	-0.8	-0.6	-0.4	64.5	
CH <sub>2</sub> OCCH <sub>3</sub>	+7.7	$\sim 0.0$	$\sim 0.0$	~0.0	20.7 (CI	I <sub>3</sub> ), 66.1 (CH <sub>2</sub> ),
					170.5	(C=0)
OH	+26.6	-12.7	+1.6	-7.3		I
OCH <sub>3</sub>	+31.4	-14.4	+1.0	-7.7	54.1	

Our current partial structure has a  $CH_3O$ - at one end of the benzene ring, and an alkyl group at the other. We can see that C-1 of the ring, where the oxygen is attached, should come at about 128.5 + 31.4 = 159.9, s, and we have in our data 157.3, s.



Table H2 and H4 are also useful. From Table H2, the coupling constant between the H's on the benzene ring should be about 8 Hz. In the data, we observe 8.5 Hz. Note that meta coupling, though small, is real and is usually observed. In this case, there is no meta coupling because the H's that are meta to each other have the same chemical shift, and so do not couple to each other.

TYPE	Ja	6 (Hz)	Jao TYPICAL	TYPE		J <sub>ab</sub> (Hz)	J <sub>ob</sub> TYPIC	CAL
رد <sup>H</sup>				CH <sub>a</sub> —C≡C —CH <sub>a</sub> —C≡	сн, ≡с—сн,—	2–3 2–3		
(cis or trans)	cis trans	4–12 2–10		H <sub>a</sub> H <sub>b</sub>	<		6	
<sup>S</sup>	cis trans	7-13		H <sub>a</sub>	$\leq^{H_b}$		4	
(cis or trans)					$<^{H_b}$		2.5	
$CH_a - OH_b$ (no exchan	ige)	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>b</sub>		58	6		J (2–3)	(56)	5	
H <sub>a</sub> c=c <sub>H<sub>b</sub></sub>		12–18	17	$5 \frac{4}{6} \frac{3}{2}$	J (3-4) J (2-4) J (3-5) J (2-5) I (2-6)	(7-9) (1-2) (1-2) (0-1)	8 1.5 1.5 1	i.
$c = c \begin{pmatrix} H_a \\ H_b \end{pmatrix}$		0–3	0–2	4 3	J (2-3) J (3-4)	1.3-2.0 3.1-3.8	18 3.6	
		6-12	10	5 0 2	J (2-4) J (2-5)	00 12	~0 1.5	

Table H.2 continued

Table H4 teaches the chemical shift of H's attached to the benzene ring. Looking at the upper part of the Table, alkyl groups do not change the initial value of 7.2 very much. At the bottom of the part of the Table shown (there is more in the text), it is apparent that H ortho and para to the substituent we have, a  $CH_3O_{-}$ , should be shifted upfield, while the H's meta to  $CH_3O_{-}$ ,would be shifted slightly downfield. That is what we observe in the data, with one set of benzene H's at 6.80, and the other at 7.25.

	9	.8	.6	.4	ŧ.	2	8.8	8.6	5.	4 .:	2	7.	8.6	5.4	4.;	2 (	6		ð	5
Benzene	Γ	Τ	Τ							:										
CH <sub>3</sub> (omp)											:									
CH <sub>3</sub> CH <sub>2</sub> (omp)	Τ	Τ									:									
(CH <sub>3</sub> ) <sub>2</sub> CH (omp)		T									:									
(CH3)3C o, m, p										:	::									
$C = CH_2 (omp)$										:										
C≡CH o, (mp)									:	:										
Phenyl o, m, p									:	:	:									
CF <sub>3</sub> (omp)	Τ								:											
CH <sub>2</sub> Cl (omp)	Τ									:										
CHCl <sub>2</sub> (omp)		Τ								:										
CCl <sub>3</sub> o, (mp)						:			:											
CH <sub>2</sub> OH (omp)											:									
CH <sub>2</sub> OR (omp)										:										
CH <sub>2</sub> OC(=O)CH <sub>3</sub> (omp)										:										
CH <sub>2</sub> NH <sub>2</sub> (omp)										:										
Fm, p, o										:		:								
Cl (omp)	Τ															1				
Br o, (pm)	Τ								:											
I o, p, m								:			:									
OH m, p, o											:	:	:							
OR m, (op)	Τ	T								:		:								
	-	-				-							1		L	<b>—</b>				

Table H.4 Chemical Shifts of Protons on Monosubstituted Benzene Rings

**Worksheet, Step 4a:** All that remains to complete the structure are three  $CH_3$ 's and a C with no H's. From the symmetry 31.4, q (3) and 1.27, s, 9H, all three methyls are attached to one carbon.

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



We can now use Table C12 (above) to calculate "precise" chemical shifts of the benzene C's. There are four different C's. For each, we start with the base value of 128.5, then add the shift due to each of the two substituents.



We can then put the data in tabular form, to compare it to the data for the unknown. For some problems, this will be the only way to distinguish between positional isomers.

Calculated	Actual
156.8, s	157.3, s
143.0, s	143.1, s
126.1, d (2)	126.0, d (2)
113.7, d (2)	113.3, d (2)

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