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Chapter Three, Problem C

Worksheet, step one: In this case, the IHD = 7. All the H's are attached to carbon

C16H20O2

IR: 2922, 1673, 1245, 755, 692 cm⁻¹

MS: 244 (M+, 43), 151 (42), 121 (16), 109 (100)

¹³ C NMR		¹ H NMR
199.8, s	32.3, t	7.24 - 7.29, 2H, m
158.7, s	32.1, t	6.86 - 6.94, 3H, m
144.6, d	26.2, t	6.70, 1H, t, J = 4.5 Hz
135.4, s	15.6, q	3.93, 2H, t, J = 6.2 Hz
129.3, d (2))	2.55, 1H, dd, J = 11.4, 8.2 Hz
120.5, d		2.44, 1H, m
114.2, d (2))	2.10, 3H, m
67.4, t		1.80, 2H, m
44.4, t		1.77, 3H, s
35.3, d		1.52, 2H, m

Worksheet, step two: With an IHD of at least 4 and signals in the ¹H spectrum around 7, we should suspect a benzene derivative. From 7.24-7.29, 2H, m and 6.86-6.94, 3H, m, there are five H's on the benzene ring, so there is just one substituent. From Table H4, 6.86-6.94, 3H, m teaches us that one of the O's is directly attached to the benzene ring. This is confirmed by Table C12. We then use Table C12 to calculate the chemical shifts for the benzene carbons.



We are left with 199.8, s, 144.6, d, and 135.4, s not yet accounted for. The 199.8, s is a ketone, and the 144.6, d, and 135.4, s are each alkenes. The chemical shift of 144.6, d is greater than the normal range, so we know that the alkene is polarized by being directly

attached to the carbonyl. Of the two possible substructures, only the one on the left would have its doublet at greater than the normal range. The alkene H is also downfield, 6.70, 1H, t, J=4.5, so we know that there are two H's on carbon next to the alkene.



From the generic ¹³C chemical shifts for ketone (see problem 1A), we observe that the carbon on the other side of the ketone is 44.4, t, so a $-CH_2$ -. From Table H1, these H's should come at about 2.4.



We see that we have 2.55, 1H, dd, J = 11.4, 8.2 Hz. From this, we know that there is one H on the carbon next to this $-CH_2$ -, and that the H's on the $-CH_2$ - do not have the same chemical shift. If they do not have the same chemical shift, they should share a large coupling constant, in this case probably 11.4 Hz. This is called a *geminal* coupling constant (see Table H2). So, we can expand our picture.



Worksheet, Step 3: There is one ether oxygen. One end is attached to the benzene ring. From the generic chemical shifts for sp³ hybridized carbons attached to ether O, it appears that the other end is a $-CH_2$ -, at 67.4, t.

Generic Chemical Shifts: Ether



From Table H1, the $-CH_2$ -O - attached to a benzene ring should come at about 4.05. Indeed, we have 3.93, 2H, t, J = 6.2 Hz. So we know that next to the $-OCH_2$ - is another $-CH_2$ -.









Worksheet, Step 4c: In addition to the two fragments above, we count that we have two more $-CH_2$ -'s, and we know that we have a ring.

Worksheet, Step 5: In addition to the methyl group attached to the alkene, we know that we have one branch point, 35.3, d, and one group at the end of the pendant chain, the $-CH_2$ - CH_2 -OPh, where Ph is a shorthand way of writing a benzene ring. There are two ways to put this together, in cartoon form. The cartoon on the right cannot be correct. *Any* size ring with only one substituent would have to have symmetry, and there is no symmetry in the data.



Given the total number of $-CH_2$ -'s, there are two possibilities.



The mass spec fragmentation matches the structure on the right.



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