Problem R-06D \((\text{C}_{13}\text{H}_{18}\text{O}_3)\)

200 MHz \(^1\text{H}\) NMR spectrum in CDCl\(_3\)

Source: Yuntao Song, Chuck Heap-Burke (Reich digitized hard copy 28-10)

![200 MHz \(^1\text{H}\) NMR spectrum in CDCl\(_3\)](image)

Problem R-06D \((\text{C}_{13}\text{H}_{18}\text{O}_3)\)

75 MHz \(^{13}\text{C}\) NMR spectrum in CDCl\(_3\)

Source: Yuntao Song (Chuck Heap-SDB) 28-10

![75 MHz \(^{13}\text{C}\) NMR spectrum in CDCl\(_3\)](image)
Problem R-06D \((\text{C}_{13}\text{H}_{18}\text{O}_3)\). Determine the structure (or part structure) of R-06D from the \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra provided. The compound contains a \(\text{Ph-CH}_2\text{-O-CH}_2\text{-O-}\) group.

(a) DBE __________ 

(b) Interpret the \(^{13}\text{C}\) NMR spectrum. Use the Normal and DEPT-135 spectra to help in the analysis. Identify what kind of carbon each signal corresponds to and write possible part structures (you may wish to examine all the data before completing this section).

Type of C (e.g. sp\(^3\) CH\(_2\)) and/or part structures (e.g. N-CH\(_2\))

16.69

69.70

76.36

77.68

93.85

117.09

127.68

127.77

128.36

137.01

137.38
(c) When D$_2$O was added to the sample, the signal B disappeared and D became a clean triplet. What does this tell you about these peaks?

(d) What can you learn from the signals A and C (part structures)?

(e) Analyze the 1-proton multiplet H at $\delta$ 5.9 (shown below). Draw a coupling tree on the multiplet below, and report coupling constants (in the standard form: e.g., $\delta$ 3.9, tq, $J = 12$, 4 Hz, 1H). Show any part structure you could obtain from the signal. You may use first-order analysis.

(f) Analyze the signals labeled G (two protons at $\delta$ 5.3), reproduced below. Show couplings with (coupling tree) and report J values and a part structure. You may use first order analysis.

(g) Assign the signals E and F and explain their appearance. What kind of multiplets are these? Do an accurate calculation of the chemical shifts and couplings for multiplet E (frequencies are given on the spectrum).

(h) Draw the structure of $\textbf{R-06D}$. If more than one structure is possible, show them, and circle the one you think fits the data best and give your reasons for choosing it. Place labels on the protons (A, B, C etc) to identify their NMR signals.
Problem R-06D (C\textsubscript{13}H\textsubscript{18}O\textsubscript{3})
200 MHz \textsuperscript{1}H NMR spectrum in CDCl\textsubscript{3}
Source: Yuntao Song (Chuck Heap-Burke) 28-10
Problem R-06D \((\text{C}_{13}\text{H}_{18}\text{O}_{3})\). Determine the structure (or part structure) of R-06D from the \(^1\text{H}\) and \(\text{C}^{13}\) NMR spectra provided. The compound contains a Ph-CH\(_2\)-O-CH\(_2\)-O- group.

1. (a) DBE 5

   Ph has 4 DBE, thus one double bond/ring in rest of molecule

   (b) Interpret the \(\text{C}^{13}\) NMR spectrum. Use the Normal and DEPT-135 spectra to help in the analysis. Identify what kind of carbon each signal corresponds to and write possible part structures (you may wish to examine all the data before completing this section).

<table>
<thead>
<tr>
<th>Type of C (e.g. sp(^3) CH(_2)) and/or part structures (e.g. N-CH(_2))</th>
<th>16.69</th>
<th>69.70</th>
<th>76.36</th>
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<th>117.09</th>
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<tbody>
<tr>
<td>(\text{CH}_3)</td>
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<td>(\text{CH}-\text{O})</td>
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<td>(\text{CH}-\text{O})</td>
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<td>(\text{CH}_2)-\text{O} (possibly C=CH(_2))</td>
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<td>(\text{CH}_2)=C</td>
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</table>

Only 17 C-H protons apparent in C-13, so most be OH
(c) When D₂O was added to the sample, the signal B disappeared and D became a clean triplet. What does this tell you about these peaks?

B is an OH signal, and it is coupled to a CH coupled to two other protons

Most common error - failure to consider second structure

(d) What can you learn from the signals A and C (part structures)?

A is probably a CH₃-CH₂ group, C is coupled to it, and to one additional proton

\[ A: 1.18, \text{ d, } J 7 \text{ Hz} \]
\[ C: 3.69, \text{ pentet, } J = 6 \text{ Hz} \]

(e) Analyze the 1-proton multiplet H at \( \delta 5.9 \) (shown below). Draw a coupling tree on the multiplet below, and report coupling constants (in the standard form: e.g., \( \delta 3.9, \text{ tq, } J = 12, 4 \text{ Hz, } 1H \)). Show any part structure you could obtain from the signal. You may use first-order analysis.

\[ \delta 5.89, \text{ ddd, } J = 17, 10, 7 \text{ Hz} \]

This is a very characteristic multiplet of a proton coupled cis (10 Hz) and trans (17 Hz) across a double bond, plus one additional coupling (7 Hz)

(f) Analyze the signals labeled G (two protons at \( \delta 5.3 \)), reproduced below. Show couplings with (coupling tree) and report J values and a part structure. You may use first order analysis.

G are the two terminal =CH₂ protons, one coupled cis (10 Hz), the other trans (17 Hz) the additional splittings are the 2J between them, and a long range coupling

\[ H: 5.22, \text{ dt, } J = 10, 1.5 \text{ or ddd, } J = 10, 1.5, 1 \]
\[ G: 5.36, \text{ dt, } J = 16.5, 1.5 \]

(g) Assign the signals E and F and explain their appearance. What kind of multiplets are these? Do an accurate calculation of the chemical shifts and couplings for multiplet E (frequencies are given on the spectrum).

Both E and F are AB quartets, corresponding to the diastereotopic O-CH₂-O (F) and Ph-CH₂-O (E) groups of the BOM protecting group. Molecule must have an asymmetric center.

\[ J_{AB} = 11.4 \text{ Hz} \quad C = 928.3 \text{ Hz} \quad \Delta \nu_{AB} = 10.7 \text{ Hz} \quad \nu_A = 923.0 \quad \nu_B = 933.6 \quad -1 \text{ for no } \delta \]
\[ \delta_A = 4.62 \quad \delta_B = 4.67 \quad -2 \text{ for not diving } \nu_{AB} \text{ by 2} \]

(h) Draw the structure of **R-06D**. If more than one structure is possible, show them, and circle the one you think fits the data best and give your reasons for choosing it. Place labels on the protons (A, B, C etc) to identify their NMR signals.

2 points for assignment

Stereochemistry not easily assignable

+ about 10 other structures
Problem R-06D (C₁₃H₁₈O₃)
200 MHz ¹H NMR spectrum in CDCl₃
Source: Yuntao Song, Chuck Heap-Burke (Reich digitized hard copy 28-10) g