Problem R-06i (C_{20}H_{30}O_{5}Si)
270 MHz $^1$H NMR Spectrum in CDCl$_3$
Source: W. R. Parker/Burke (Reich digitized hard copy)

![NMR Spectrum Image]
Problem R-06I. This problem requires you to make a complete assignment of the signals of a compound (structure shown below), so that you can determine the stereochemistry of the two substituents on the dioxolane ring. Use the form: $\delta 5.2$, dq, $J = 13.5, 7.3$ Hz or AB of ABX$_3$, $J_{AB} = 12$ Hz, $J_{AX} = J_{BX} = 7$ Hz, $\delta_A = 4.36, \delta_B = 4.42$ ppm. Please show your assignments by placing the appropriate letters clearly on the expanded multiplets in the spectrum.

(a) Assign the signals of protons A and B. What kind of pattern do these protons form? Do an approximate first order analysis (give shifts, pattern and approximate couplings).

A:

B:

(b) Consider the signals for protons C and D. What kind of patterns are observed? Report shifts and couplings below (first order analysis is OK). How did you distinguish them from each other?

C:

D:

(c) Assign the protons H and I. Report shifts, multiplicity and coupling below.

H:

I:

(d) Below report on the crucial signals for E, F and G. Indicate multiplicity and coupling constants. Circle the structure with the correct stereochemistry and explain your reasoning below.

E:

F:

G:
**Problem R-06I.** This problem requires you to make a complete assignment of the signals of a compound (structure shown below), so that you can determine the stereochemistry of the two substituents on the dioxolane ring. Use the form: \( \delta = 5.2, \text{dq, } J = 13.5, 7.3 \text{ Hz or AB of ABX}_3, J_{AB} = 12 \text{ Hz, } J_{AX} = J_{BX} = 7 \text{ Hz, } \delta_A = 4.36, \delta_B = 4.42 \text{ ppm.} \) Please show your assignments by placing the appropriate letters clearly on the expanded multiplets in the spectrum.

![Structure of the compound](image)

(a) Assign the signals of protons A and B. What kind of pattern do these protons form? Do an approximate first order analysis (give shifts, pattern and approximate couplings).

\[
\begin{align*}
\text{A and B are a CH}_2-\text{CH}_2 \text{ system, expect both to be diastereotopic (MNXY pattern)} \\
\text{A: } & 0.77, 0.82 \delta, \text{MNXY, } 2J_{MN} = 14, 3J_{MX} = 3J_{NY} = 6, 3J_{MY} = 3J_{NX} = 10 \text{ Hz} \\
\text{B: } & 3.43 \delta, \text{MNXY, td, } J = 10, 7 \quad (2J_{XY} = 10, 3J_{XM} = 10, 3J_{YN} = 7 \text{ Hz}) \quad \text{(An AB system where both A and B are are split into a dd, with } J = 10, 6) \\
\end{align*}
\]

(b) Consider the signals for protons C and D. What kind of patterns are observed? Report shifts and couplings below (first order analysis is OK). How did you distinguish them from each other?

\[
\begin{align*}
\text{Both C and D will be diastereotopic (AB quartets), D next to ketone will have larger } J_{AB} \\
\text{C: } & 4.58, \text{d, } J = 7; \quad 4.72, \text{d, } J = 7 \quad (J_{AB} = 7 \text{ Hz, expect smaller } 2J \text{ coupling here, } \pi-\text{donor, } \sigma-\text{acceptor}) \\
\text{One shift -1} \\
\text{D: } & 4.33, \text{d, } J = 18; \quad 4.48, \text{d, } J = 18 \quad (J_{AB} = 18 \text{ Hz, } \alpha-\text{keto increases } 2J \text{ coupling, } \pi-\text{acceptor}) \\
\text{One shift -1} \\
\end{align*}
\]

(c) Assign the protons H and I. Report shifts, multiplicity and coupling below.

\[
\begin{align*}
\text{H: } & \delta 5.43, \text{ddq, } J = 15, 8, 2 \text{ Hz} \quad (3J_{HI} = 15, 3J_{HG} = 8, 4J_{HMe} = 2 \text{ Hz}) \\
\text{I: } & \delta 5.86, \text{dq, } J = 15, 7 \text{ Hz} \quad (3J_{IH} = 15, 3J_{IHe} = 7.5 \text{ Hz}) \\
\text{Swap H/I -2} \\
\end{align*}
\]

(d) Below report on the crucial signals for E, F and G. Indicate multiplicity and coupling constants. Circle the structure with the correct stereochemistry and explain your reasoning below.

\[
\begin{align*}
\text{E: } & \delta 4.82, \text{d, } J = 4 \text{ Hz} \quad (3J_{EF} = 4 \text{ Hz}) \\
\text{F: } & \delta 3.84, \text{dd, } J = 8, 4 \text{ Hz} \quad (3J_{FE} = 4 \text{ Hz, } 3J_{FG} = 8 \text{ Hz}) \quad \text{(Swap G/H -3)} \\
\text{G: } & \delta 4.65, \text{t, } J = 7.5 \text{ Hz} \quad (3J_{GH} = 3J_{GF} = 7.6 \text{ Hz}) \\
\text{The G-I long range coupling is not resolved} \\
\end{align*}
\]

6 **Stereochem, justification**

\[
\begin{align*}
\text{No J value -2} \\
\text{The large } J_{FG} \text{ of 8 Hz requires them to be diaxial (note that ax-ax couplings, and } 3J \text{ couplings in general, are reduced when O-substituents are present)} \\
\end{align*}
\]
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