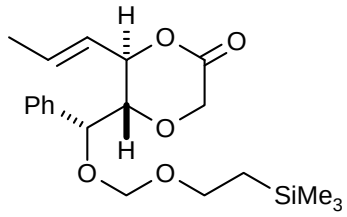
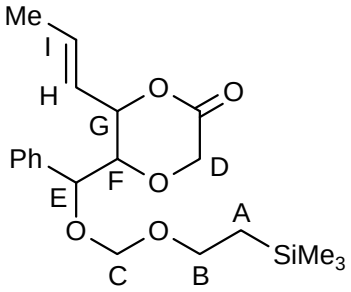
Problem R-06l ($C_{20}H_{30}O_5Si$)
270 MHz ^{1}H NMR Spectrum in $CDCl_3$
Source: W. R. Parker/Burke (Reich digitized hard copy) g



PLT ex-2-2006-07-gq.plt

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: δ 5.2, dq, J = 13.5, 7.3 Hz *or* AB of ABX_3, J_{AB} =12 Hz, $J_{AX} = J_{BX}$ = 7 Hz, δ_A = 4.36, δ_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:

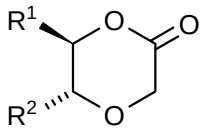
(c) Assign the protons **H** and **I**. Report shifts, multiplicity and coupling below.

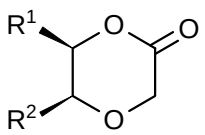
H:

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:

30

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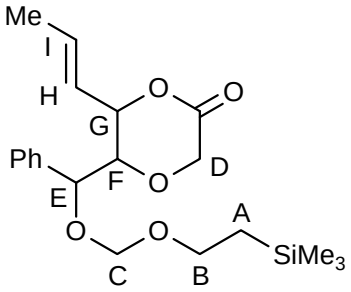

(a) Assign the signals of protons **A** and **B**. What kind of pattern do these protons form? Do an approximate first order analysis (give shifts, pattern and approximate couplings).

A and B are a CH_2-CH_2 system, expect both to be diastereotopic (MNXY pattern)

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A: 0.77, 0.82 δ, MNXY, $^2J_{MN}$ = 14, $^3J_{MX} = {}^3J_{NY}$ = 6, $^3J_{MY} = {}^3J_{NX}$ = 10 Hz

(An AB system where both A and B are are split into a dd, with J = 10, 6)

3

B: 3.43 δ, MNXY, td, J = 10, 7 ($^2J_{XY}$ = 10, $^3J_{XM}$ = 10, $^3J_{XN}$ = 7 Hz)

3.65 δ, MNXY, td, J = 10, 7 ($^2J_{XY}$ = 10, $^3J_{YN}$ = 10, $^3J_{YM}$ = 7 Hz)

(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?

Both C and D will be diastereotopic (AB quartets), D next to ketone will have larger J_{AB}

6

C: 4.58, d, J =7; 4.72, d, J = 7 (J_{AB} = 7 Hz, expect smaller ^2J coupling here, π-donor, σ-acceptor)

One shift -1

D: 4.33, d, J = 18; 4.48, d, J =18 (J_{AB} = 18 Hz, α-keto increases ^2J coupling, π-acceptor)

One shift -1

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

H: δ 5.43, ddq, J = 15, 8, 2 Hz ($^3J_{HI}$ = 15, $^3J_{HG}$ = 8, $^4J_{H\text{-}Me}$ = 2 Hz)

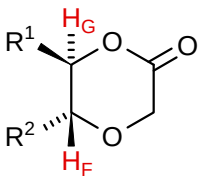
4

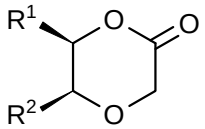
I: δ 5.86, dq, J = 15, 7 Hz ($^3J_{IH}$ = 15, $^3J_{I\text{-}Me}$ = 7.5 Hz)

Swap H/I -2

(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: δ 4.82, d, J = 4 Hz ($^3J_{EF}$ = 4 Hz)





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F: δ 3.84, dd, J = 8, 4 Hz ($^3J_{FE}$ = 4 Hz, $^3J_{FG}$ = 8 Hz)

Swap G/H -3

G: δ 4.65, t, J = 7.5 Hz ($^3J_{GH} = {}^3J_{GF}$ = 7.6 Hz)

The G-I long range coupling is not resolved

The large J_{FG} of 8 Hz requires them to be diaxial (note that ax-ax couplings, and ^3J couplings in general, are reduced when O-substituents are present)

6 Stereochem, justification

No J value -2

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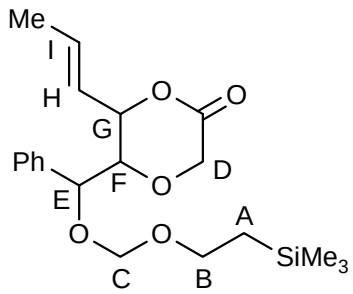

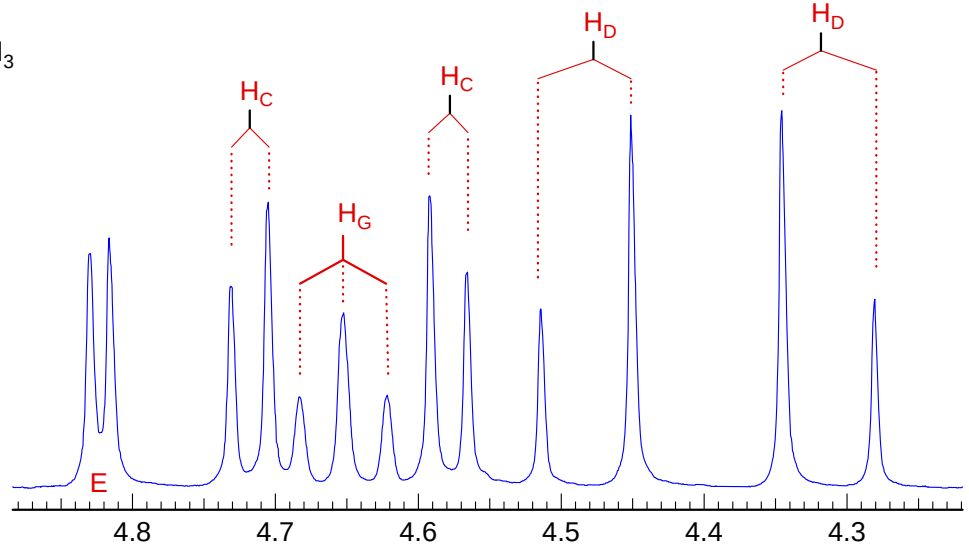

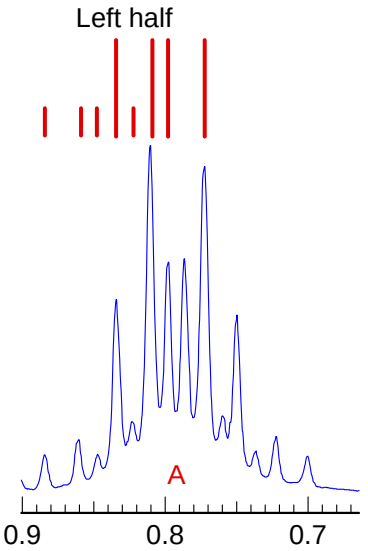

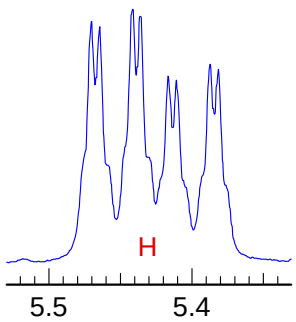

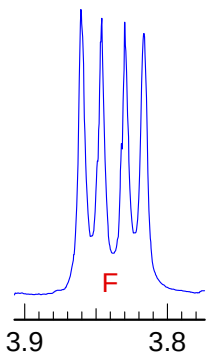

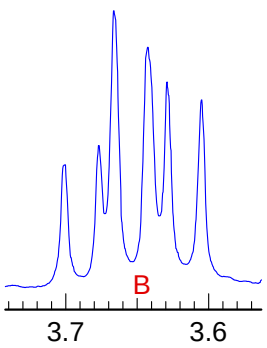

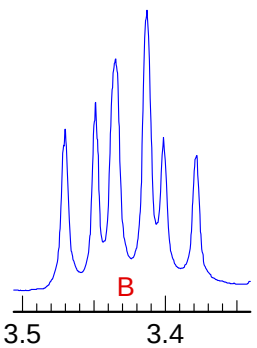

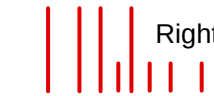

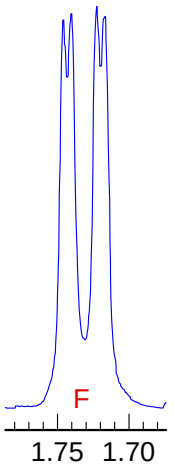

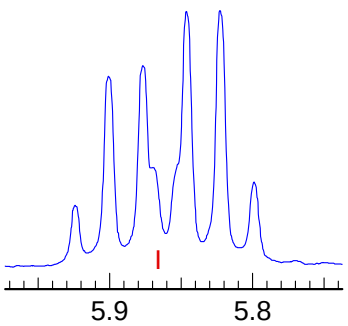

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