standard deviations (4 pages). Ordering information is given on any current masthead page.

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(21) Reaction of 0.107 mmol of **1** with 0.214 mmol of PPh_3 in CH_3CN yielded $Ir(NO)L_3$ (75% isolated) and $C_3H_5PPh_3^+P_6^-$ (65%). Reaction of 0.135 mmol of **3** with 0.270 mmol of PPh_3 gave $Rh(NO)L_3$ (81%) and $C_3H_5PPh_3^+BF_4^-$ (85%). Products were characterized by comparisons with authentic samples. Reactions with pyridine and these complexes in CH_3CN yielded 30–40% $M(NO)L_3$ as a precipitate. Quantitative conversion of allyl to $[C_3H_5\text{-}NC_5H_5]^+$ was observed via ^1H NMR.

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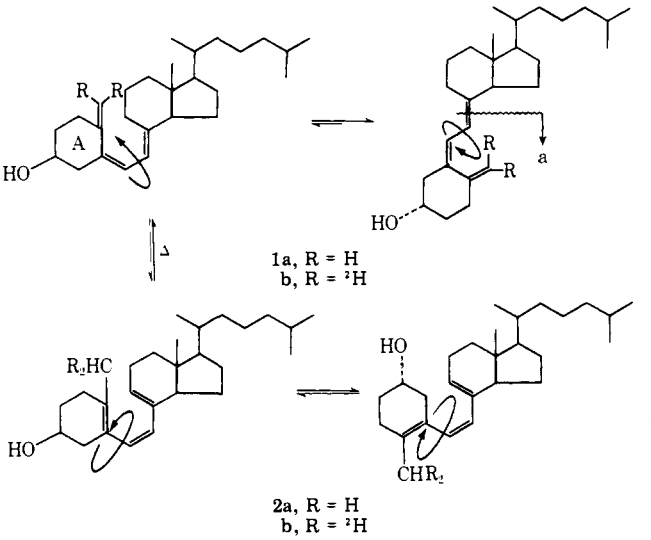
Use of ^2H NMR and Mass Spectrometry for the Investigation of the Vitamin D_3–Previtamin D_3 Equilibrium

Sir:

Vitamin D_3 is formed biogenetically from 7-dehydrocholesterol by irradiation followed by isomerization of the resulting previtamin D_3.[1] Establishment of the intramolecular and uncatalyzed nature of the isomerization[2] led to the postulate that it occurs by antrafacial, sigmatropic 1,7-hydrogen migration.[3] This migration may take place from two diastereomeric conformations of the *cis*-1,3,5-trienes, but, as expected for a biological process, only one should be preferred. However, Akhtar and Gibbons[4] suggested the absence of such preference on thermal equilibration of previtamin, claiming tritium scrambling between the 19, 9α, and 9β positions of the vitamin after 2-h heating of the C-19-tritium-labeled previtamin.

Scheme I. Thermal equilibrium previtamin D–vitamin D



We prepared [19,19-^2H]vitamin D_3 (**1b**) by reacting the dimethylene ketone analogue of vitamin D_3 with triphenylphosphine [^2H]methylene.[5] The integration of the two signals of C-19 protons (at 4.7 and 4.9 ppm)[6] indicated that **1b** was ~80% d_2-isotopically pure. Heating of **1b** in isooctane at 80 °C for 2 h results in a 80:20 equilibrium mixture of vitamin D_3 (**1**) and previtamin D_3 (**2**)[2] (Scheme I). Surprisingly we have observed that the ^1H NMR spectra of the vitamin before and after thermal equilibration were practically identical. In addition, the spectrum of the isolated previtamin was consistent with the structure in which all the deuterium was at C-19, the signal intensity of the vinylic proton at C-9 (at 5.50 ppm) corresponding to a full proton. It appears that the vitamin D_3–previtamin D_3 equilibrium was attained by 1,7-protium migration rather than by deuterium migration.

Deuterium migration from C-19 to C-9 could only be detected after prolonged heating. Thus, after 14 h at 80 °C, the ^1H NMR of **1b** showed an increase of ~40% in the intensity of the signals due to protons at C-19 and a decreased intensity of the signal at 2.7 ppm which was assigned by Wing et al.[6b,7] to the 9β proton. However, it was difficult to decide whether changes occurred in the 9α proton signals (centered at 1.68 ppm[7]) since it was overlapped by other protons.[8] The ^1H NMR spectrum of previtamin D_3 (**2b**) also changed on prolonged heating, the signal intensity of the C-9 vinylic proton decreasing considerably.

The intramolecular isotope exchange rate could be monitored by mass spectrometry of **1b**, based on the finding that the characteristic abundant ion a[5,9] which includes ring A, C-6, and C-7 of the molecular ion contained the major part of its original label (Table I). We have heated the labeled vitamin D_3 (**1b**) for different periods of time and have determined the deuterium distribution in the molecular ion (*m/e* 384–386), and in the ion a (*m/e* 136–138) regions.[10,11] Table I shows that, while the isotopic composition of the molecular ion of **1b** remains practically unchanged during the 14-h heating, the number of deuterium atoms retained at C-19 decreased gradually. Complete distribution of the deuterium label be-

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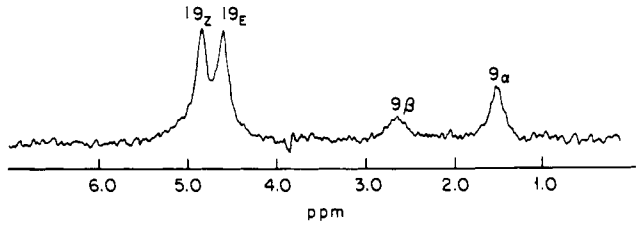

Figure 1. 41.4-MHz ^2H NMR spectrum of [19,19-^2H]vitamin D_3 (**1b**), after 14-h heating at 80 °C.

Table I. Mass Spectrometry of C-19-Deuterated Vitamin D_3 (**1b**). Deuterium Distribution in Fragment a (*m/e* 136-138) at Various Periods of Heating at 80 °C[a]

time, h	ion a deuterium content, %				deuterium label retained in ion a, %[b]
	d_0	d_1	d_2	atoms	
0	9	30	61	1.51[c]	100
2	12	38	50	1.38	91
4	14	45	41	1.27	84
6	16	49	35	1.19	79
8	23	53	24	1.01	66
14	27	52	21	0.94[d]	62

[a] The percentage are corrected for the ^{13}C isotope; estimated error was 7% of the value quoted. [b] Relative to the labeled fragment a, derived from nonequilibrated vitamin D_3. [c] Deuterium content in molecular ion, percent: d_0, 5; d_1, 24; d_2, 71; atoms, 1.66. [d] Deuterium content in molecular ion, percent: d_0, 8; d_1, 24; d_2, 68; atoms, 1.60.

tween C-19 and C-9 was not reached even after 14-h heating.

From the change of distribution of d_0, d_1, and d_2 in the ion a on heating, we have calculated the approximate isotope exchange rate, and found it to be 2.6×10^{-5} s^{-1}, which can be related to the rate of the deuterium transfer from C-19 of **2b** to C-9 of **1b.** Considering that the corresponding rate of protium migration was found to be 1.2×10^{-3} s^{-1},[2] the isotope effect k_H/k_D is ~45.[13]

To establish whether a kinetic preference exists in the previtamin-vitamin reaction, we have measured the ^2H NMR spectra of the deuterium-labeled vitamin **1b.** We have observed two signals whose chemical shifts at 4.7 and 4.9 ppm were identical with those of the protons at C-19 in the ^1H NMR spectrum of the unlabeled vitamin **1a.**[6] After heating for 14 h at 80 °C and separating the vitamin from the reaction mixture, two additional signals appeared at 1.68 and 2.70 ppm, the former identified as the deuteron at C-9α and the latter as the deuteron at C-9β[6b,7] (Figure 1). The integration ratio of the two signals was found to be ~2:1, indicating a preference for deuterium migration to the 9α position.[14] This preference was also observed in the ^2H NMR spectrum after 2-h heating which revealed, in addition to the signals due to ^2H at C-19, also a weak signal at 1.68 ppm of ^2H at C-9α, while the signal due to H at C-9β was undetectable.

It seems reasonable to assume that the transition state for the vitamin D_3-previtamin D_3 isomerization has a preferred conformation, in which the cis-1,3,5-triene system of the two compounds is twisted in a right-handed sense, ring A lying below the plane of the C/D rings.[15]

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(15) Since both the vitamin and the previtamin are at room temperature in the thermodynamically more stable 6,7 and 5,6 s-trans conformation, respectively, they have to undergo a right-handed rotation about these bonds to adopt such a conformation. This right-handed twist may be energetically preferred to the alternative left-handed twist.

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A Structural Model for the Photosynthetic Reaction Center

Sir:

We describe here the synthesis and characterization of the solution conformation of a molecule which brings into close proximity the principal molecular components believed to participate in the initial photoinduced electron-transfer reaction of photosynthesis. Comparison of the spectroscopic properties of the anion and cation radicals of bacteriochlorophyll and bacteriopheophytin (metal-free bacteriochlorophyll) with optical transients elicited from bacterial photosynthetic reaction centers has led to the widely accepted view that bacteriopheophytin serves as the first electron acceptor following photoexcitation.[1] The photoexcited electron donor has been shown to consist of a pair of bacteriochlorophylls[2] whose detailed structure remains elusive, though the subject of extensive speculation and modeling.[3] The identity of participants in green plant and algal photosynthesis is much less certain owing to the complication of two photosystems and unavailability of simple, low molecular weight reaction centers. In spite of this, an increasing body of evidence is developing which suggests intermediate transient electron acceptors in both photosystem I and II,[4,5] and pheophytin and chlorophyll monomers are very reasonable candidates.[5] The central question which then emerges is the nature of the spatial relationship among these components which facilitates efficient forward electron transfer, and synthetic model compounds can provide the first steps toward an answer.

The covalently linked array of metal-containing and metal-free pyrochlorophyll macrocycles[6] shown in Figure 1

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