sition-state bond to carbon, the α-d effect would be expected to be reduced to about 1.07 and the β-d_3 effect to about 1.00.[15]

In our view the mechanism involves first the formation of the unrearranged tight ion pair which can undergo substitution, elimination, rearrangement, or return. Since the rearrangement rate is retarded, in comparison with the pinacolyl analogue, relatively larger yields of unrearranged products are found, and internal return becomes more competitive. Furthermore, in the less nucleophilic fluorinated alcohol solvents, attack on the unrearranged ion is slower than in the ethanol solvents, leading to relatively more internal return and larger proportions of rearrangement.

What cannot be sorted out definitively from the isotope effects are the following: (a) The extent of internal return in the ethanolic solvents, because the majority of the product is unrearranged substitution and the isotope effects are not strongly influenced by internal return under these circumstances; (b) whether reverse rearrangement of the tertiary ion is faster than its reaction with solvent to form the rearranged substitution product. A steady-state treatment of this mechanism using expected values for the single-step isotope effects[16] gives a satisfactory fit to the data and suggests that in the fluorinated alcohol solvents the reverse rearrangement is competitive and that internal return dominates further reaction by factors between 1 and 3. The details of this analysis will be published along with additional results on other secondary adamantyl carbinyl esters.

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Registry No. 1-(1-Adamantyl)ethanol *p*-bromobenzenesulfonate, 80206-36-6; 1-(1-adamantyl)ethanol pentamethylbenzenesulfonate, 80206-37-7.

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(15) Calculations in ref 11 show that replacing an α chlorine by carbon has very little effect on a CH/CD fractionation factor. As shown in ref 1, the maximum isotope effect for a chlorine leaving group is about 1.15 while the maximum for a sulfonate leaving group is about 1.23. It follows that the effect on an initial state fractionation factor caused by replacing α oxygen by α carbon is about 1.23/1.15 or 1.07. β substituents have little effect on α CH/CD fractionation factors as long as the β carbon does not have a vacant orbital.

(16) Shiner, V. J., Jr.; Nollen, D. A.; Humski, K. *J. Org. Chem.* **1979**, *44*, 2108-2115.

Wavelength-Controlled Production of Previtamin D_3[†]

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The photochemical conversion of provitamin D (7-dehydrocholesterol, 7-DHC) to previtamin D (P_3), thermally converted to vitamin D_3 at 37 °C, has been studied, in detail, because of the importance of yield maximization in the commercial production of the vitamin[1] (see Scheme I). Generally, the maximization of the yield has been achieved by control of the extent of the irradiation and the wavelength and/or the multiplicity of the excitation source. In one such study,[2] 254-nm light was used to prepare a mixture of 25% 7-DHC, 25% P_3, and 50% tachysterol$_3$ (T_3). This mixture, in turn, was irradiated at 0 °C in the presence of fluorenone (1 mol equiv) to sensitize the conversion of T_3 to P_3 and the P_3 converted to D_3 by a thermal reaction to give an overall yield of D_3 of 28–35%.[2,3]

In another study,[4-6] it has been shown that employment of light of 295-nm wavelength gives the maximum yield of P_3, i.e., 31–

Table I. Molecular Extinction Coefficients of Irradiation Products

λ, nm	ε 7-DHC	 P_3	 T_3	 L_3
254	4500	7250	11 450	4130
300	1250	930	11 250	1320
330	25	105	2 940	30
340	20	40	242	25
350	10	25	100	20

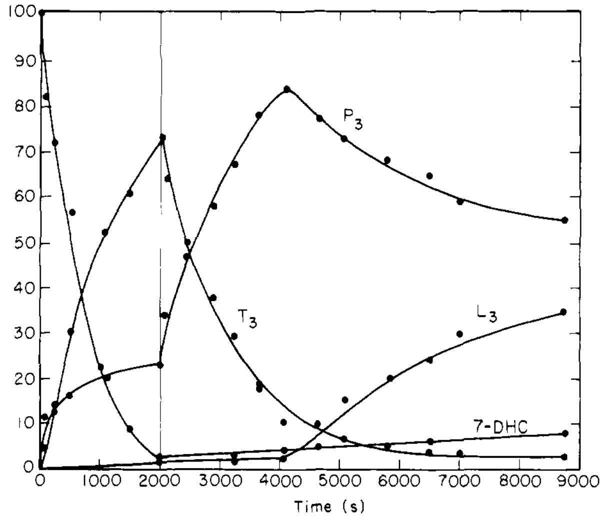

Figure 1. Reaction profile of irradiation of 7-DHC at 254 and then 350 nm.

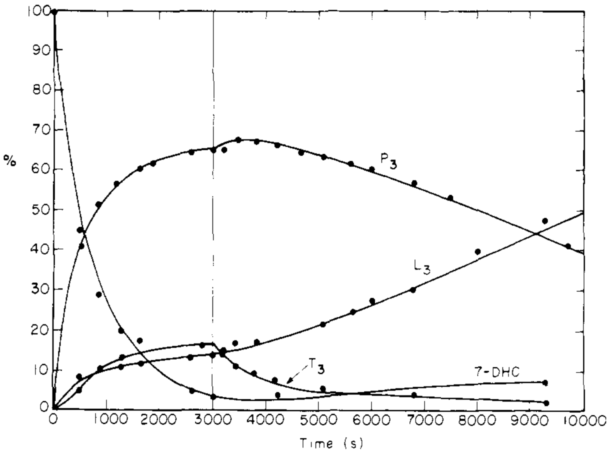

Figure 2. Reaction profile of irradiation of 7-DHC at 300 and then 350 nm.

[†] This paper is dedicated to Holger Erdmann on the occasion of his 80th birthday.

(1) For general reviews of the photochemistry related to 7-DHC, see: (a) Dauben, W. G.; McInnis, E. L.; Michno, D. M. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 81–129. (b) Jacobs, H. J. J.; Havinga, E. "Advances in Photochemistry"; Pitts, J. N., Jr., Hammond, G. S., Gollnick, K., Eds.; Interscience Publishers: New York, 1979; Vol. 11, pp 305–373. (c) Norman, A. W. "Vitamin D"; Academic Press: New York, 1979.

(2) Eyley, S. C.; Williams, D. H. *J. Chem. Soc., Chem. Commun.* **1975**, 858.

(3) Snoeren, A. E. C.; Daha, M. R.; Lugtenburg, J.; Havinga, E. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 261.

(4) (a) Kobayashi, T.; Yasumura, M. *J. Nutr. Sci. Vitaminol.* **1973**, *19*, 123. (b) Sato, T.; Yamachuchi, H.; Ogata, Y.; Kunii, T.; Kagei, K.; Katsui, G.; Toyoshima, S.; Yasumura, M.; Kobayashi, T. *Ibid.* **1980**, *26*, 545.

(5) Barton, D. H. R.; Hesse, R. H.; Pechet, M. M.; Rizzardo, E. *J. Am. Chem. Soc.* **1973**, *95*, 2748.

(6) Pfoertner, K.; Weber, J. P. *Helv. Chim. Acta* **1972**, *55*, 921. Pfoertner, K. *Ibid.* **1972**, *55*, 937.

(7) For the irradiations at 254, 300, and 350 nm, a RPR-100 Rayonet Photochemical Reactor was used with GE-G8T5, RPR-3000A, or RPR-3500A lamps, respectively. All irradiations of 7-DHC were run in nitrogen degassed ethyl ether (sodium/benzophenone) at <5 °C (quartz Dewar, Cryocool probe). The method of analysis was the standard HPLC chromatography (see: Holic, M. F.; MacLaughlin, J. A.; Doppelt, S. H. *Science (Washington, D.C.)* **1981**, *211*, 5907).

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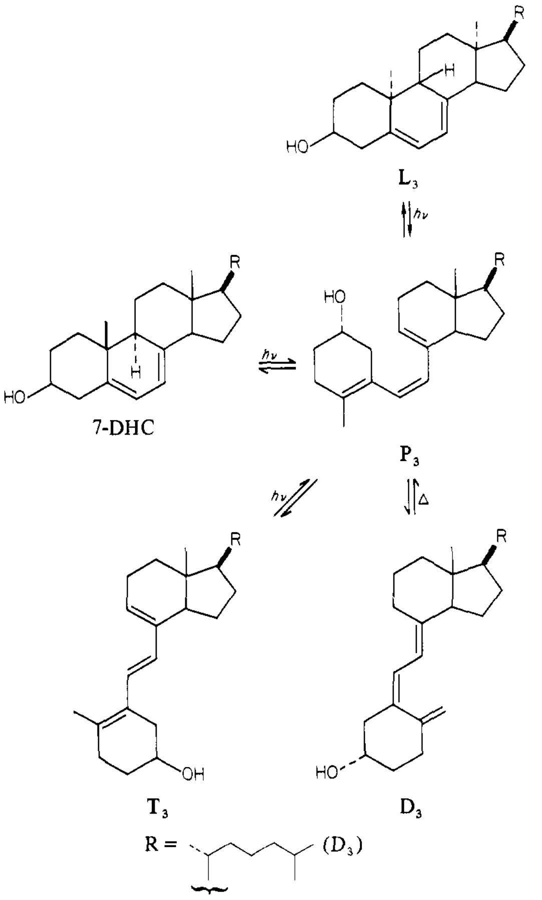
Scheme I



33%.[4a] Although such irradiations were not carried to the 295-nm quasi-photostationary state at 0 °C, the calculated composition of which is 1% 7-DHC, 70% P_3, 26% T_3, and 3% L_3,[8] the yield of P_3 seemed low.

In order to maximize the yield of new vitamin D analogues being prepared in this laboratory, a careful study of the irradiation process has been undertaken. From an examination of the spectral data of the four major irradiation products of the quasi-photostationary state shown in Table I, it was evident that a two-step direct irradiation, first using light of 254 or 300 nm followed by light of ≥330 nm should accomplish this goal. We should like to present the results of our study which shows an 83% yield of P_3 (HPLC) at 95% conversion of 7-DHC. After acceptance of this paper a selected study was reported by Malatesta et al.[13]

The reaction profiles of 7-DHC irradiated initially at 254 or 300 nm to the quasi-photostationary state and the resulting mixture then irradiated at 350 nm are shown in Figures 1 and 2.[7]

At 254 nm, under the standard irradiation conditions, the quasi-photostationary state was reached after 2000 s of reaction time, the major product (~75%) being T_3. The composition of the reaction mixture is in excellent agreement with the values calculated on the basis of the molar extinction coefficient of the products and the quantum yields for the various interconversions (T_3, 70.8%; P_3, 23.5%; L_3, 3.4%; 7-DHC, 2.3%).[8] When this mixture was then irradiated at 350 nm, a rapid change occurred to yield a mixture of 83% P_3, 11% T_3, 2% L_3, and 4% 7-DHC. Continued irradiation brought about further changes, mainly, the formation of L_3 at the expense of P_3.

A similar experiment using 300-nm light as the initial excitation source under the standard irradiation conditions again gave a quasi-photostationary state after 3000 s of reaction time, but under these conditions the major product (~65%) is P_3. The composition of the reaction mixture is in good agreement with the calculated values, the variations probably being due to the more broad band of the so-called 300-nm Rayonet light source.[8] When this mixture was then irradiated at 350 nm, again a change occurred to yield L_3 at the expense of P_3 but no initial increase in P_3.

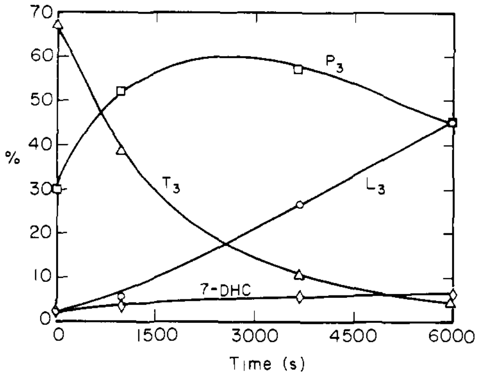


Figure 3. Irradiation of T_3 mixture at 355 nm (YAG laser).

The efficiency of the transformation of T_3 to P_3 using the broad band 350-nm Rayonet lamp was further studied in order to see if the light at the lower wavelength end of the excitation band played an important role. The quasi-photostationary state mixture of products prepared from 7-DHC with 254-nm light was irradiated with 355-nm light from a YAG laser;[9] the results are shown in Figure 3. It is seen that the same general results are found but the buildup of P_3 reaches only 60%, the formation of L_3 being more efficient at the early stage of the irradiation. These results are in line with the recent findings[10] that the ring closure of P_3 to L_3 is more efficient at higher wavelengths and that cis–trans isomerization of P_3 to T_3 is less efficient at higher wavelengths.[11]

Thus, it is found that if 7-DHC is first irradiated at 0 °C with 254-nm light to give a quasi-photostationary state of 7-DHC, P_3, T_3, and L_3 and this mixture then irradiated (0 °C) with 350-nm light, a maximum of 83% P_3 (HPLC yield) at 95% conversion of 7-DHC is possible. It is critical, however, to monitor the reaction closely since the formation of L_3 at the expense of P_3 becomes a competing, and eventually the main, process.

This two-step direct irradiation procedure has been applied to the conversion of 7-DHC to D_3 on a preparative scale. The irradiation of 7-DHC at 0 °C with 254-nm light gave 6% 7-DHC, 28% P_3, 64% T_3, and 2% L_3 (HPLC), and this mixture upon irradiation with 350-nm light gave 8% 7-DHC, 73% P_3, 9% T_3, and 10% L_3 (HPLC). The final irradiation mixture was separated by medium-pressure liquid chromatography (MPLC) at 0 °C to give P_3 in 66% yield. The isolated P_3 was thermally equilibrated in refluxing ethanol to give D_3 and P_3 in a 83:17 ratio (HPLC), and the vitamin was isolated (MPLC) in 50% yield.

Application of this two-step procedure to the formation of the biologically important 1α-hydroxyvitamin D from 1α-hydroxy-7-dehydrocholesterol[12] gives, qualitatively, similar results.

Acknowledgment. This investigation was supported by PHS Grant 00709, National Institute of Arthritis, Metabolism, and Digestive Diseases, U. S. Public Health Service. The laser study was partially supported by the National Science Foundation Grant CHE 79-16250 awarded to the University of California at Berkeley in collaboration with Stanford University.

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(8) Havinga, E.; deKock, R. J.; Rappoldt, M. P. *Tetrahedron* **1960**, *11*, 276. The calculated values quoted in this present manuscript differ from those quoted in the reference since a corrected reaction scheme has been used.

(9) For 355-nm light, the third harmonic of a Quanta Ray Nd-YAG laser was used (10 pps, 10 ns/pulse, 60 mJ/pulse, 0.8-cm beam diameter) and the measured average power was 0.4 W. A 1.5-mL ethereal solution of 7-DHC (9.21×10^{-5} M) in a sealed, suprasil, 1-cm cuvette, cooled to <5 °C on a thermostatically cooled magnetic stirrer, was initially irradiated at 254 nm to prepare the starting mixture.

(10) Jacobs, H. J. C.; Gielen, J. W. J.; Havinga, E. *Tetrahedron Lett.* **1981**, 4013.

(11) These findings along with the data in Table I strongly suggest that light of 330-nm wavelength would be the wavelength of choice for maximum formation of P_3.

(12) This material was kindly supplied by Dr. M. P. Rappoldt of Duphar B.V., Weesp, Holland.

(13) Malatesta, V.; Willis, C.; Hackett, P. A. *J. Am. Chem. Soc.* **1981**, *103*, 6781.