# Photolytic Production of Vitamin D. The Preparative Value of a Photo-sensitiser

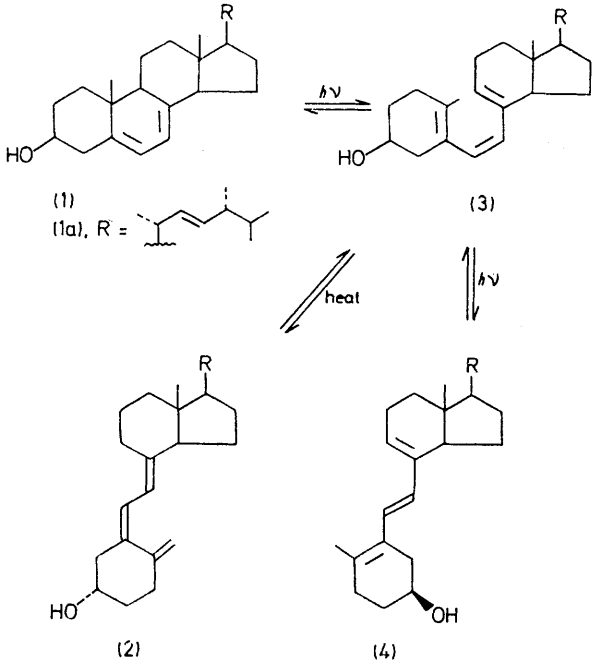
By STEPHEN C. EYLEY and DUDLEY H. WILLIAMS*
(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

*Summary* Fluorenone, previously known to sensitise photolytic interconversion of previtamin D and tachysterol trimethylsilyl ethers, is used in a convenient and practical method of increasing the yield of vitamin D from the provitamin.

THE conversion of provitamin D (**1**) into the vitamin (**2**) is of importance not only in the commercial preparation of the vitamin, but more particularly in syntheses of biologically active metabolites[1] and analogues of the vitamin *via* suitable hydroxylated provitamin intermediates. The yield of previtamin D (**3**), and hence the vitamin, obtained from irradiation of the provitamin is limited[2] by the photolytic conversion of the previtamin into tachysterol (**4**), the major photoproduct in the 'quasi' photostationary state. We report the use of a triplet sensitiser to make previtamin D (**3**) indirectly the major product of the photolysis.

Irradiation (using a Hanovia medium pressure mercury vapour lamp) of ergosterol, provitamin $D_2$ (**1a**, R = $C_9H_{17}$), in ether at 0 °C under $O_2$-free $N_2$ for 15 min resulted in *ca.* 75% conversion. T.l.c. indicated the presence of (**1a**), tachysterol$_2$, and previtamin $D_2$ in the approximate proportions 1:2:1. Previtamin $D_2$, and tachysterol$_2$, were separated from ergosterol and the small amount of over-irradiation products by preparative t.l.c.[3] The mixture was heated in ethanol to rearrange the previtamin to the vitamin. Tachysterol was separated from the vitamin as the Diels–alder adduct with maleic anhydride. Chromatography afforded the vitamin as an oil (11%, assuming $\epsilon$ 18,300 at $\lambda$ 265 nm). Crystallisation gave vitamin $D_2$ 9%, m.p. 115—116 °C (lit.[4] 114·5—117 °C).

Fluorenone has been shown to sensitise photolytic interconversion of previtamin D and tachysterol trimethylsilyl ethers, quantum yields having been determined.[5] Irradiation of (**1a**, R = $C_9H_{17}$) for 1 h in the presence of fluorenone (1 mol. equiv.) gave no photo-products as evidenced by t.l.c. which would readily detect 1% of previtamin D or tachysterol. However, addition of fluorenone to a photolysis mixture obtained as described earlier, followed by a second 15 min irradiation at 0 °C under $N_2$ gave a reaction mixture containing previtamin $D_2$ as the major component. Thermal equilibration of the previtamin and vitamin, and isolation of vitamin $D_2$ in the same manner as employed for the unsensitised reaction gave the vitamin as an oil (35%, by quantitative u.v. spectroscopy), which in turn afforded crystalline vitamin $D_2$ (28%). Fluorenone did not interfere with the chromatographic procedures. Ergosterol (27%) was recovered from the irradiation mixture. Yields of vitamin $D_2$ quoted represent isolated yields, and are not corrected for recovered starting material.




Thus, incorporation of a second, sensitised irradiation into the reaction sequence provides a convenient and practical method of increasing the yield of vitamin D from the provitamin by a factor of approximately three.

We thank the S.R.C. for financial support.

(*Received, 4th August* 1975; *Com.* 889.)

[1] H. K. Schnoes and H. F. DeLuca, *Vitamins and Hormones*, 1974, **32**, 385.
[2] M. P. Rappoldt and E. Havinga, *Rec. Trav. chim.*, 1960, **79**, 369.
[3] D. R. Crump, D. H. Williams, and B. Pelc, *J.C.S. Perkin I*, 1973, 2731.
[4] A. Windaus, O. Linsert, A. Lüttringhaus, and G. Weidlich, *Annalen*, 1932, **492**, 226.
[5] A. E. C. Snoeren, M. R. Daha, J. Lugtenburg, and E. Havinga, *Rec. Trav. chim.*, 1970, **89**, 261.