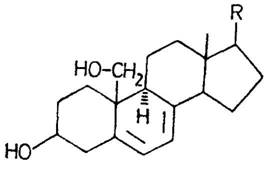
Photochemical Decomposition of 19-Hydroxy-7-dehydrocholesterol. *X*-Ray Crystallographic Study of 19-Norcholesta-5(10),6-dien-3β-yl Acetate

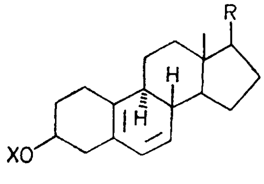
By HERBERT PAAREN and ROBERT M. MORIARTY*
(*Department of Chemistry, University of Illinois, Chicago Circle Campus, Illinois* 60680)
and JUDITH FLIPPEN
(*Naval Research Laboratory, Washington, D.C.* 20390)

Summary Irradiation of the title compound proceeds with loss of the C(10) hydroxymethyl group to yield 19-norcholesta-5(10),6-dien-3β-ol; the *X*-ray structure of the corresponding acetate was determined.

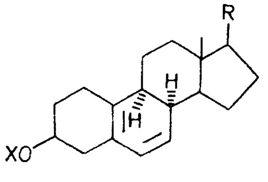
RECENTLY we found that the irradiation of 19-acetoxy-7-dehydrocholesterol proceeded in a manner entirely analogous to that of the vitamin itself.[1] We report now that irradiation (125 W Hanovia 8A36; quartz filter; 15 min) of the related 19-alcohol (**1**)† proceeds in a different way yielding (**2a**) m.p. 91·0—91·5 °C [$\lambda_{\max}$ 266 nm (ϵ 4400)] and (**3**) (oil, homogeneous on t.l.c.; which result from loss of the C(10) functionality.‡



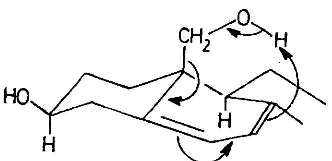
(1)



(2)



(3)
a; X = H
b; X = Ac



(4)

19-Norcholesta-5(10),6-diene-3β-ol (**2a**) is a primary photoproduct, while the diene (**3a**) is derived from (**2a**) in a secondary photochemical reaction. The dienes (**2a**) and (**3a**) formed the acetates (**2b**), m.p. 94—95 °C, and (**3b**) (oil), both of which upon dehydrogenation yielded the same known ring B aromatic compound.[2]

A discussion of the mechanism of formation of (**2a**) and (**3a**) requires knowledge of the stereochemistry of the BC-ring juncture. Since both compounds possess a skewed homoannular *cisoid* diene, c.d. should be useful in establishing the stereochemistry. Thus in (**2a**) as drawn (8-β, 9-α) the ring B-diene exists as a conformationally rigid right-handed helix. Application of the 'diene rule' leads to prediction of a positive Cotton effect;[3] however, a negative curve was observed [$\lambda_{\max}$ 266 nm (ϵ 4400), $\Delta\epsilon$ −5·70 (266 nm)]. Because of this contradiction[4] we solved the structure of (**2a**) by an *X*-ray diffraction study of the acetate derivative which crystallized in the monoclinic space group, $P2_1$ with $a = 14{\cdot}437(7)$, $b = 7{\cdot}731(5)$, $c = 12{\cdot}477(7)$ Å; $\beta = 117{\cdot}2(1)°$; $Z = 2$; $D_c = 1{\cdot}11$ g cm^{-3}. 1437 independent reflections were collected on an automatic diffractometer ($2\theta_{\max} = 126{\cdot}5°$, Cu-$K_\alpha$ radiation, Ni filter) using the θ–2θ scanning technique. The structure was solved by the symbolic addition procedure for non-centrosymmetric crystals.[5] In the early stages of the structure determination it was difficult to distinguish the enantiomorphs, since both appeared as superimposed structures in the *E*-maps owing to the fact that the atoms of the central six-membered ring (B) as well as C(3), C(4), C(14), and C(15) were related by an approximate centre of symmetry (non-crystallographic) in the middle of ring B.

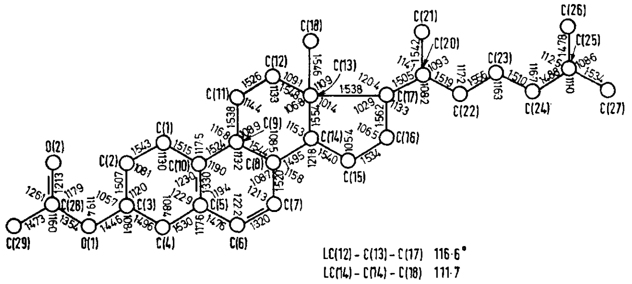


FIGURE. Bond angles and bond distances for cholest-5(10),6-diene-3β-yl acetate (**2b**).

Full-matrix least-squares refinement[7] on the full set of data led to a final *R* factor of 0·054 (R_w 0·065). Hydrogen atoms were included at calculated positions and used in the final cycles of refinement as constant parameters.§ Bond lengths and angles (Figure) lie within the range of values usually found in steroids. However, the unsaturation present in ring B has caused some distortions in the conformations of the six-membered rings. Ring A is in an envelope conformation and ring B has adopted a half-boat conformation. The C ring is basically in a normal chair conformation, but some of the torsion angles lie outside the expected range of 55—60° for such conformations.

To study the mechanism of the reaction, the C(3) and C(19) O-deuterio analogue of (**1**) was converted into (**2b**) and the product was shown to contain one deuterium atom

---

† Prepared from cholest-5-en-7-one-3,19-diol diacetate by the modified Bamford-Stevens reaction;[1] m.p. 178—179 °C.

‡ Compounds (**2a**) and (**3a**) could be separated by chromatography. Spectral data showed the presence of the diene and the molecular weights were determined by mass spectrometry.

§ A list of calculated and observed structure factors and calculated hydrogen co-ordinates can be obtained from the author.

bound to carbon (by high-resolution mass spectra). Since the *X*-ray data fix the C(8) hydrogen as axial (β), and the incorporation of deuterium points to an intramolecular process, the rearrangements depicted in (**4**) would be the most straightforward path for the photofragmentation. This eight-electron photoreaction is allowed in a concerted manner. A somewhat related photofragmentation has been observed in the case of certain 14-hydroxy-20-oxo-Δ^{16}-steroids.[8] Although the stereochemistry of the BC ring juncture in the isomeric (**3a**) is undetermined, it is probably *cis* (either α or β) and this compound probably results from photochemical opening of the diene in (**2a**) to the 9,10-seco-triene which recloses in a thermal (disrotatory way) establishing the *cis* stereochemistry.[9]

(*Received*, 3*rd November* 1975; *Com.* 1232.)

---

[1] R. M. Moriarty, H. Paaren, and J. Gilmore, *J.C.S. Chem. Comm.*, 1974, 927.

[2] A. van der Gen, J. Lakeman, M. A. M. P. Gras, and H. O. Huisman, *Tetrahedron*, 1964, 2521.

[3] For leading references see E. Charney, J. M. Edwards, U. Weiss, and H. Ziffer, *Tetrahedron*, 1972, **28**, 973.

[4] This point will be discussed in a future communication.

[5] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

[7] W. R. Busing, K. O. Martin, H. A. Levy, R. D. Ellison, W. C. Hamilton, J. A. Ibers, C. K. Johnson, and W. E. Thiesien, ORXFL 53, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1971.

[8] F. Marti, H. Wehrli, and O. Jeger, *Helv. Chim. Acta*, 1973, **56**, 1078.

[9] W. R. Roth and B. Peltzer, *Angew. Chem. Internat. Edn.*, 1964, **3**, 440; E. Havinga, R. K. deKock, and M. P. Rappoldt, *Tetrahedron* 1960, **11**, 276; The 5(10),6-diene has been encountered in other steroidal examples, *e.g.*, J. Kalvoda and G. Anner, *Helv. Chim. Acta*, 1967, **50**, 269; F. S. Alvarez and A. N. Watt, *J. Org. Chem.*, 1972, **37**, 3725.