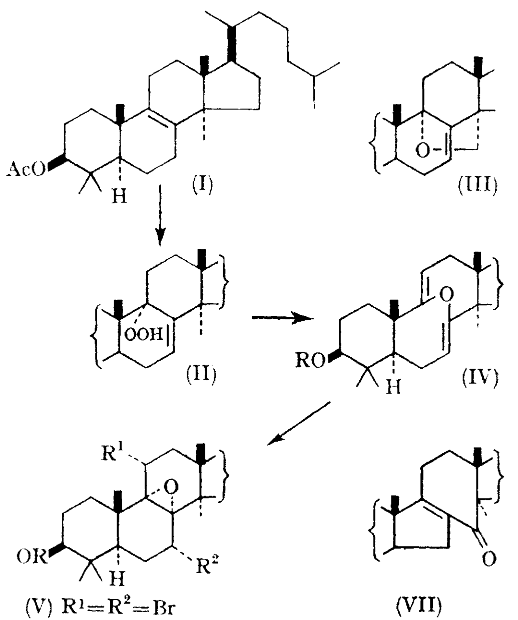
Photosensitised Oxidation of 3β-Acetoxylanost-8-ene

By J. E. FOX, A. I. SCOTT,* and D. W. YOUNG
(*The Chemical Laboratory, University of Sussex, Brighton* BN1 9QJ)

ONE of a series of experiments designed to simulate[1] the oxidative removal of angular methyl groups in the enzymic conversion of lanosterol into cholesterol[2] concerned the attempted formation of the 9α-hydroperoxide of lanost-7-ene (II) using the method developed by Schenck.[3] The lability of the products of this reaction led to an examination of the formation of the corresponding 9α-*p*-nitrobenzenepersulphonate *in situ* and its subsequent collapse to products such as (III).[4] However, the reaction underwent a different but interesting course as discussed below.

Oxygen was bubbled through a pyridine solution of 3*β*-acetoxylanost-8-ene (I) under irradiation with fluorescent light (40 w) in the presence of hæmatoporphyrin and *p*-nitrobenzenesulphonyl chloride. Chromatographic purification of the resultant mixture afforded six products. These were 3*β*-acetoxylanosta-7,9(11)-diene,[5] 3*β*-acetoxylanost-8-en-7-one,[6] 3*β*-acetoxy-(7α,8α)-[7] and -(7*β*,8*β*)-epoxylanost-9(11)-ene,† 3*β*-acetoxylanost-8-ene-7α-hydroperoxide† and a novel *ether* $C_{32}H_{52}O_3$, m.p. 144°, $[\alpha]_D$ + 164°, which we formulate as (IV; R = Ac). Hydrolysis to the alcohol (IV; R = H) caused the expected shift of the 3α-H from τ 5·4 (poorly resolved) to τ 6·7. Two significant proton resonances were observed at (a) τ 5·22 as a quartet with characteristic ABX pattern—A, τ 8·04; B, τ 7·64, and X, τ 5·22. J_{AX} 5; J_{BX} 8; J_{AB} 14 c./sec. and (b) τ 5·47 (triplet, J 3·5 c./sec.) constant with structure (IV; R = H). Bromination of (IV; R = Ac) afforded the epoxy-dibromide (V) whose structure and stereochemistry was earlier proved by *X*-ray diffraction analysis.[8] The formation of (V) by a concerted transannular reaction of the divinyl ether finds analogy in the recently reported reactions of the cyclodeca-1,6-diene system.[9] Similarly treatment of (IV; R = Ac) with boron trifluoride in acetic acid closed the 8,9-bond to form 3*β*,11-diacetoxy-8α,9α-epoxylanostane (VI) τ 7·96, 8·03 (2 × acetate CH_3) τ 4·72, 5·60 (2 × CHOAc)† together with the known enone (VII).[10]



(V) R¹=R²=Br
(VI) R¹=OAc;R²=H

These experiments define the constitution of the ether (IV; R = Ac). Its formation may be rationalised through the intermediacy of the 9α-hydroperoxide of 3*β*-acetoxylanost-7-ene (II) which is of interest as a model intermediate for the oxidative removal of the C-14-methyl group. However under the present conditions the Criegee

---

† Satisfactory analytical, spectroscopic, and degradative data were obtained for the structural assignments of these new compounds for which details will be given in the full Paper.

rearrangement[11] is preferred to the desired insertion reaction previously demonstrated in the case of heterolysis of the *p*-nitrobenzenesulphonate of 1,3,3-trimethylcyclohexyl hydroperoxide.[4]

(*Received, September 7th*, 1967; *Com.* 960.)

---

[1] *Cf.* J. Fried, J. W. Brown, and M. Applebaum, *Tetrahedron Letters*, 1965, 849; D. H. R. Barton, T. J. Bentley, and J. F. McGhie, *ibid.*, p. 2497; J. Fried, J. W. Brown, and L. Borkenhager, *ibid.*, p. 2499; C. W. Shoppe, J. C. Coll, N. W. Hughes, and R. E. Lack, *ibid.*, pp. 3249, 5235; *J. Chem. Soc.* (*C*), 1966, 2359; D. H. R. Barton, A. Hameed, and J. F. McGhie, *Tetrahedron Letters*, 1965, 4343.

[2] R. B. Clayton, *Quart. Rev.*, 1965, **19**, 168.

[3] G. Schenck, *Angew. Chem.*, 1957, **69**, 579.

[4] *Cf.* E. J. Corey and R. W. White, *J. Amer. Chem. Soc.*, 1958, **80**, 6686; R. A. Sneen and N. P. Matheny, *ibid.*, 1964, **86**, 5503.

[5] L. Ruzicka, R. Denes, and O. Jeger, *Helv. Chim. Acta*, 1946, **29**, 204.

[6] D. H. R. Barton, J. S. Fawcett, and B. R. Thomas, *J. Chem. Soc.*, 1951, 3147.

[7] M. V. Mijovic, W. Voser, H. Heusser, and O. Jeger, *Helv. Chim. Acta*, 1952, **35**, 964.

[8] J. K. Fawcett and J. Trotter, *J. Chem. Soc.* (*B*), 1966, 174.

[9] R. M. Gipson, H. W. Guin, S. H. Simonsen, C. G. Skinner, and W. Shive, *J. Amer. Chem. Soc.*, 1966, **88**, 5366.

[10] G. Snatzke and A. Nisar, *Annalen*, 1965, **683**, 159, and refs. cited.

[11] R. Criegee, *Ber.*, 1944, **77**, 722; G. O. Schenck and K. H. Schulte-Elte, *Annalen*, 1958, **618**, 185.