

## Peroxide–Diene Oxygen Transfer Reactions induced by Titanium Tetrachloride

By Derek H. R. Barton and Richard K. Haynes,\* Chemistry Department, Imperial College, London SW7 2AY

Catalysis of the reaction between triplet oxygen and ergosteryl acetate (I) by titanium tetrachloride unexpectedly affords 6 $\alpha$ -chloro-5-hydroxy-5 $\alpha$ -ergosta-7,22-dien-3 $\beta$ -yl acetate (III). This chlorohydrin is produced by a reaction between equimolar amounts of the 5,8-peroxide (II) and the acetate (I), the generality and mechanism of which are discussed briefly.

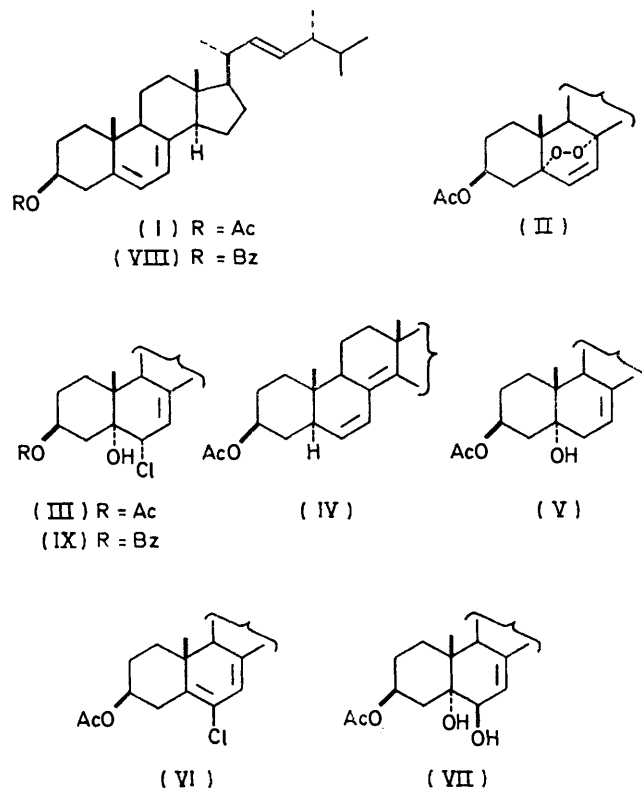
DURING experiments on the Lewis-acid-catalysed conversion of ergosteryl acetate (I) into the 5,8-peroxide (II) by reaction with triplet oxygen,<sup>1</sup> titanium tetrachloride was found to be a relatively inferior catalyst. With 0.2 mol. equiv. of titanium salt in dichloromethane at  $-80^{\circ}\text{C}$ , irradiation with a tungsten lamp for 3 h was required to complete the reaction. There was no reaction in the dark. In contrast, the use of 1–2 mol. equiv. of titanium tetrachloride under the same conditions gave a rapid *dark* reaction with formation of some *endo*-peroxide (II) and a new compound (III) (40–70%),  $\text{C}_{30}\text{H}_{47}\text{ClO}_3$ . Under irradiation the yield of (III) was not markedly altered. The best yields were obtained by using dilute solutions. A small amount of 5 $\alpha$ -ergosta-6,8(14),22-trien-3 $\beta$ -yl acetate (IV) was also formed.

The new compound was identified as 6 $\alpha$ -chloro-5-hydroxy-5 $\alpha$ -ergosta-7,22-dien-3 $\beta$ -yl acetate (III) on the basis of the following evidence. The i.r. spectrum showed the presence of a hydrogen-bonded hydroxy-group. This was clearly tertiary since the compound was unchanged on attempted acetylation and oxidation. The  $^1\text{H}$  n.m.r. spectrum indicated that attack had taken place at the 5,6-double bond: the signals at  $\tau$  7.45 and 7.6 due to 4 $\alpha$ - and 4 $\beta$ -protons, respectively, were no longer present. Signals at  $\tau$  5.36 and 4.87 were consistent with a 6 $\beta$ -H and a C-7 vinylic proton. The mass spectrum had peaks at  $m/e$  490 ( $M^+$ ), 472 ( $M^+ - \text{H}_2\text{O}$ ), 454 ( $M^+ - \text{HCl}$ ), 436 ( $M^+ - \text{HCl} - \text{H}_2\text{O}$ ), 376 (base peak,  $M^+ - \text{HCl} - \text{H}_2\text{O} - \text{AcOH}$ ), and 251 ( $M^+ - \text{HCl} - \text{H}_2\text{O} - \text{AcOH} - \text{C}_9\text{H}_{17}$ ). There was no maximum above 220 nm in the u.v. spectrum.

Reduction with chromium(II) smoothly gave back ergosteryl acetate (I). Reduction with lithium aluminium hydride followed by reacetylation gave in good yield the known<sup>2</sup> 5-hydroxy-5 $\alpha$ -ergosta-7,22-dien-3 $\beta$ -yl acetate (V). The chlorohydrin (III) was readily dehydrated by pyridine–thionyl chloride to give 6-chloro-ergosteryl acetate (VI), which had all the appropriate spectral characteristics.

<sup>1</sup> D. H. R. Barton, R. K. Haynes, P. D. Magnus, and I. D. Menzies, *J.C.S. Chem. Comm.*, 1974, 511; preceding paper.

The new compound (III) was also obtained in low yield by treatment of 5,6 $\beta$ -dihydroxy-5 $\alpha$ -ergosta-7,22-dien-3 $\beta$ -yl acetate (VII)<sup>3</sup> with thionyl chloride in methylene chloride.



These data established the structure (III); the only doubtful point was the configuration of the chlorine at C-6. This is assigned as  $\alpha$  mainly on the basis of the hydrogen bonding shown by the i.r. spectrum.<sup>4</sup> The optical rotation is also more consistent with a 6 $\alpha$ - than with a 6 $\beta$ -configuration.<sup>3</sup> The smooth dehydration

<sup>2</sup> G. F. Laws, *J. Chem. Soc.*, 1953, 4185.

<sup>3</sup> G. H. Alt and D. H. R. Barton, *J. Chem. Soc.*, 1954, 1356.

<sup>4</sup> A. Nickon, *J. Amer. Chem. Soc.*, 1957, 79, 243.

(diaxial elimination) to 6-chloroergosteryl acetate also indicates a  $6\alpha$ -chloro-configuration.

Apart from titanium tetrachloride, of the large number of Lewis acids examined as catalysts for triplet oxygenation of (I), only chromyl chloride gave chlorohydrin (III). Under oxygen in the dark at  $-80^\circ$  chromyl chloride gave the *endo*-peroxide (II) (43%) and the chlorohydrin (III) (23%). Under argon only the chlorohydrin (III) (41%) was formed. Thus, with chromyl chloride the chlorohydrin (III) is produced by a conventional thermal reaction. The addition of chromyl chloride to olefins normally affords products with *trans*-stereochemistry.<sup>5</sup> The ergosterol diene system, however, affords an allylic chlorohydrin so that there is opportunity for a more complex mechanism. Indeed, the epoxidation of ergosteryl acetate gives both  $5\alpha,6\alpha$ -(*cis*-) and  $5\alpha,6\beta$ -(*trans*)diols.<sup>3</sup>

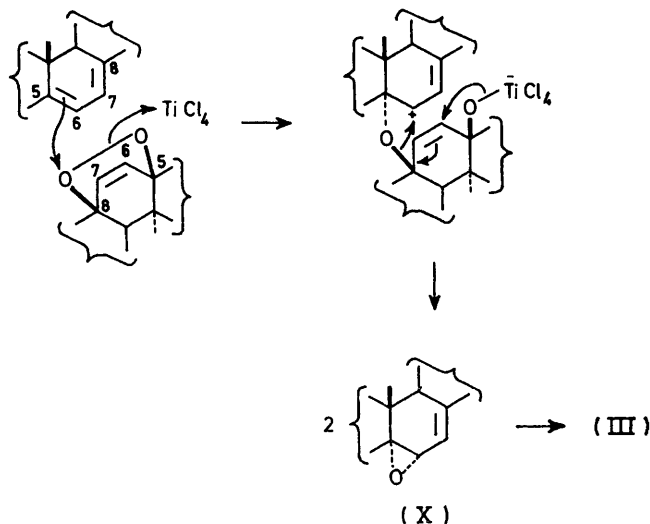
With the structure of the chlorohydrin (III) established, it remains to consider the mechanism of its formation. It does not arise from the *endo*-peroxide (II) alone which, in the absence of ergosteryl acetate (I) is stable at  $-80^\circ\text{C}$  under the experimental conditions. Ergosteryl acetate itself, in the absence of oxygen, is converted at  $-80^\circ\text{C}$  into a complex mixture containing high-melting dehydro-dimers which are different from the known photodimers<sup>6</sup> since they are higher-melting. This experiment shows that ergosteryl acetate can reduce titanium tetrachloride. A mechanism for chlorohydrin formation might, therefore, involve ergosteryl acetate (I) reducing titanium tetrachloride and the resulting titanium(III) reducing in turn the *endo*-peroxide (II). This hypothesis was tested by adding an excess of titanium tetrachloride at  $-80^\circ\text{C}$  in the absence of oxygen to an equimolar mixture of compounds (I) and (II). The chlorohydrin (III) was indeed formed but in such a high yield (99% based on only one component reacting) that it is clear that the chlorohydrin must arise from the interaction of (I) with (II) to give, in principle, two molar proportions of (III). Furthermore t.l.c. during the reaction showed that (I) and (II) diminished at the same rate as (III) appeared.

That (I) and (II) are both involved in the formation of (III) was confirmed when a 'mixed' experiment with ergosteryl benzoate (VIII) and the acetate *endo*-peroxide (II) gave *both* the acetate (III) and the benzoate (IX) in approximately equimolecular amounts (64 and 70%, respectively). The benzoate chlorohydrin (IX) was also formed by treatment of ergosteryl benzoate (VIII) with titanium tetrachloride under oxygen in the usual way.

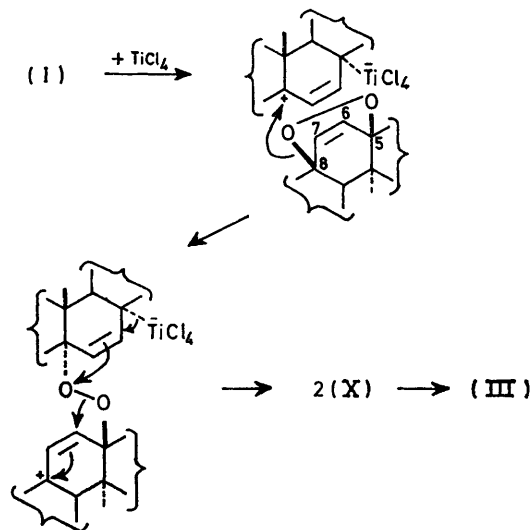
Finally, ergosteryl acetate (I), di-*t*-butyl peroxide, and titanium tetrachloride under anaerobic conditions also gave the chlorohydrin (III).

The mode of formation of the chlorohydrin (III) is intriguing. In principle, one can argue that either the titanium tetrachloride activates the *endo*-peroxide

(Scheme 1) or that it activates ergosteryl acetate (Scheme 2). In both of these Schemes the  $5\alpha,6\alpha$ -epoxide is written as an intermediate. It is known that such an epoxide opens easily to give  $5\alpha,6\alpha$ - and  $5\alpha,6\beta$ -disubstituted compounds.<sup>3</sup> Activation of peroxide systems with Lewis acids to promote electrophilic attack on aromatic systems is also known.<sup>7</sup> Thus, in Scheme 1 the ability



SCHEME 1



SCHEME 2

of titanium tetrachloride to promote oxygen transfer from *endo*-peroxide to diene with subsequent chlorohydrin formation can be attributed to the molecular affinity of titanium for oxygen, and the lability of the titanium-chlorine bond.<sup>8</sup> However, of the many Lewis acids investigated, titanium tetrachloride also appears

<sup>7</sup> M. E. Kurz and G. J. Johnson, *J. Org. Chem.*, 1971, **36**, 3184; and references cited therein.

<sup>8</sup> R. Colton and J. H. Canterford, 'Halides of the Transition Elements. Halides of the First Row Transition Elements,' Wiley-Interscience, London, 1969, p. 47, and references cited therein.

<sup>5</sup> S. J. Cristol and K. R. Eilar, *J. Amer. Chem. Soc.*, 1950, **72**, 4353; H. L. Slates, and N. L. Wendler, *ibid.*, 1956, **78**, 3749.

<sup>6</sup> P. J. Flanagan and J. B. Thomson, *Tetrahedron Letters*, 1965, 1671.

unique in its behaviour towards ergosteryl acetate and in its ability to effect oxygen transfer. Consequently, the formalism of Scheme 2 must also be considered. Further investigation of the scope and mechanism of this interesting process will be reported in due course (by R. K. H.).

#### EXPERIMENTAL

Dichloromethane was stirred for 24 h with concentrated sulphuric acid, washed with water and saturated sodium hydrogen carbonate solution, dried over calcium chloride, and distilled under argon from calcium hydride. Immediately prior to use, the dichloromethane was redistilled under argon from phosphorus pentoxide directly into the calibrated reaction vessel. Titanium tetrachloride, b.p. 134–136°, was distilled under argon and solutions in dichloromethane (10 ml) were made up in a nitrogen-flushed dry box.

Light petroleum refers to the fraction of b.p. 60–80°. Optical rotations were recorded for solutions in CHCl<sub>3</sub>. U.v. spectra were obtained with a Unicam SP 800B spectrometer, i.r. spectra with a Perkin-Elmer 257 spectrometer, and n.m.r. spectra with a Varian T-60 instrument for solutions in CDCl<sub>3</sub>. Mass spectra were recorded on an A.E.I. MS9 spectrometer. T.l.c. was carried out with silica gel G (Merck) plates developed in 9 : 1 light petroleum-ethyl acetate. Spots were located by spraying with concentrated sulphuric acid.

*6 $\alpha$ -Chloro-5-hydroxy-5 $\alpha$ -ergosta-7,22-dien-3 $\beta$ -yl Acetate (III) from Ergosteryl Acetate (I) with Titanium Tetrachloride and Oxygen.*—(a) Under dry oxygen, a solution (100 ml) of the acetate (I) (200 mg,  $4.6 \times 10^{-4}$  mol) in dichloromethane was cooled, with stirring, to  $-80^\circ\text{C}$ , and in the dark, freshly prepared titanium tetrachloride solution [173 mg,  $9.2 \times 10^{-4}$  mol in dichloromethane (1.0 ml)] was added all at once. A deep purple solution was formed, which after *ca.* 2 min assumed an intense bright orange colour. After 5 min, the mixture was poured into water, and washed thoroughly with aqueous sodium hydrogen carbonate. Filtration through anhydrous sodium sulphate, addition of a few drops of pyridine to the filtrate, and evaporation under reduced pressure at room temperature gave a pale green residue. Trituration with light petroleum gave the chlorohydrin (III) as a white powder. Concentration of the mother liquors furnished more *chlorohydrin* (III) (total 131 mg, 73%). Recrystallised from ethyl acetate, this formed fine white needles, m.p. 192–194° (subl. 170–180°),  $[\alpha]_D^{22} + 43.25^\circ$  (*c* 0.80),  $\nu_{\max}$  (CCl<sub>4</sub>) (3 570m, 3 450w, 2 960s, 2 880m, 1 733s, 1 468s, 1 374s, 1 250s, 1 175m, 1 053s, and 995m cm<sup>-1</sup>,  $\tau$  4.75 (2 H, m, 22- and 23-H), 4.87 (1 H, m,  $W_{\frac{1}{2}}$  8 Hz, 7-H), 5.08 (1 H, m,  $W_{\frac{1}{2}}$  *ca.* 18 Hz, 3 $\alpha$ -H), 5.36 (1 H, m,  $W_{\frac{1}{2}}$  8 Hz, 6 $\beta$ -H), and 7.98 (3 H, s, 3 $\beta$ -OAc),  $M^+$  490 (Found: C, 73.5; H, 9.6; Cl, 7.85. C<sub>30</sub>H<sub>47</sub>ClO<sub>3</sub> requires C, 73.35; H, 9.65; Cl, 7.2%). The mother liquors were subjected to preparative layer chromatography (p.l.c.) on alumina in 9 : 1 light petroleum-ethyl acetate to isolate the peroxide (II) (14 mg, 7%).

(b) The above experiment was repeated under irradiation from a 500 W tungsten lamp. The chlorohydrin (III) (133 mg, 74%) and peroxide (II) (34 mg, 18%) were isolated.

*Characterisation of the Chlorohydrin (III).*—The chlorohydrin (III) was recovered (80%) on attempted acetylation (acetic anhydride-pyridine for 12 h at room temperature)

and from attempted oxidation (92% recovery) with chromium trioxide-pyridine in dichloromethane for 35 min.

The chlorohydrin (III) (49 mg), chromium(II) acetate (108 mg, 6 equiv.), ethylenediamine (1 ml), and water (1 ml) in deoxygenated dimethylformamide (10 ml) were stirred under argon at 60 °C for 6 h and then at room temperature for 14 h. Water (50 ml) was added and a brown semicrystalline precipitate was filtered off. P.l.c. and recrystallisation from ether-methanol gave ergosteryl acetate (I) (23 mg, 53%) (m.p. and mixed m.p. and  $[\alpha]_D$ ).

The chlorohydrin (III) (98 mg) in dry tetrahydrofuran (10 ml) was added slowly to a stirred suspension of lithium aluminium hydride (12 mg) in dry tetrahydrofuran (5 ml) at room temperature under nitrogen. After refluxing for 3 h, the mixture was cooled to room temperature, and the excess of hydride was destroyed with 10 drops of saturated sodium sulphate solution. Celite was added to the stirred mixture, which was filtered through Celite. The filtrate was evaporated and the residue treated with acetic anhydride (0.5 ml) and pyridine (1 ml) at 0 °C for 24 h. Removal of solvent afforded the acetate (V) (69 mg, 76%) as needles (from acetone-methanol), m.p. 229–232° (lit.,<sup>2</sup> 230–232°).

Thionyl chloride (150 mg) in dichloromethane (6 ml) was added dropwise to compound (III) (125 mg) in dichloromethane (10 ml)-pyridine (2 ml) at  $-30^\circ\text{C}$ . The mixture was allowed to warm to 0 °C, and after 35 min at this temperature was poured into ether (25 ml). The solution was washed with water, 5% sulphuric acid, water, and aqueous sodium hydrogen carbonate, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to leave a pale yellow residue. Addition of methanol gave *6-chloroergosteryl acetate* (VI) (77 mg, 64%), m.p. (from methanol-acetone) 122–124°,  $[\alpha]_D^{22} - 57^\circ$  (*c* 0.61),  $\lambda_{\max}$  (cyclohexane) 295sh (log  $\epsilon$  *ca.* 3.6), 283.5 (3.89), 273 (3.91), and 265sh (*ca.* 3.8) nm,  $\nu_{\max}$  (CCl<sub>4</sub>) 2 968s, 2 880m, 1 743s, 1 685m, 1 523m, 1 378m, 1 240s, and 1 040s cm<sup>-1</sup>,  $\tau$  4.57 (1 H, m,  $W_{\frac{1}{2}}$  8 Hz, 7-H), 4.80 (2 H, m, 22- and 23-H), 5.38 (1 H, m,  $W_{\frac{1}{2}}$  22 Hz, 3 $\alpha$ -H), 6.76 (1 H, m,  $W_{\frac{1}{2}}$  *ca.* 12 Hz, 4 $\alpha$ -H), 7.03 (1 H, m,  $W_{\frac{1}{2}}$  *ca.* 16 Hz, 4 $\beta$ -H), and 7.97 (3 H, s, OAc),  $M^+$  472 (Found: C, 76.2; H, 9.75; Cl, 7.35. C<sub>30</sub>H<sub>45</sub>ClO<sub>2</sub> requires C, 76.15; H, 9.6; Cl, 7.5%).

*Alternative Preparations of the Chlorohydrin (III).*—(a) Chromyl chloride (30 mg, 1.7 equiv.) in dichloromethane (0.76 ml) was added to a stirred solution of the acetate (I) (50 mg) in dichloromethane (25 ml) under oxygen at  $-80^\circ\text{C}$ . An orange solution containing a dark brown precipitate was formed instantly. Ethanol (5 ml) was added to the mixture, which was then washed with water and aqueous sodium hydrogen carbonate. The organic phase was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to leave a white residue. T.l.c. of this indicated the presence of equal amounts of the peroxide (II) and the chlorohydrin (III) as well as polymeric material. Recrystallisation from a minimal volume of ether enabled compound (III) (13 mg, 23%) to be separated from the peroxide (II). P.l.c. of the mother liquors enabled (II) (23 mg, 43%) to be isolated.

(b) The above experiment was repeated with deoxygenated solutions under argon. No peroxide (II) was detected in the reaction mixture, from which the chlorohydrin (III) was isolated as described above (23 mg, 41%).

(c) 5,6 $\beta$ -Dihydroxy-5 $\alpha$ -ergosta-7,22-dien-3 $\beta$ -yl acetate (470 mg) in dichloromethane (25 ml) was treated at room temperature, with stirring, with thionyl chloride (350 mg) in dichloromethane (10 ml) added dropwise over 25 min. Work-up in the usual way followed by p.l.c. on alumina in

light petroleum-benzene-ethyl acetate (6:3:1) gave the chlorohydrin (III) (26 mg, 5%), m.p. and mixed m.p. 192–194°,  $[\alpha]_D^{22} + 43^\circ$  (*c* 0.23).

*Anaerobic Reactions of Titanium Tetrachloride.*—(a) *With ergosteryl acetate* (I). Experiment (a) above was repeated under argon; the same marked colour change of the reaction mixture took place. Work-up yielded a pale yellow residue, t.l.c. of which indicated the presence of u.v.-active material,  $R_F$  0.6 [as for (I)], u.v.-inactive material,  $R_F$  ca. 0.5 (corresponding to the subsequently isolated products), traces of a third more polar product, and polymeric material. The residue was extracted with ether to leave amorphous white material (30 mg). Addition of acetone to a solution of this material in chloroform precipitated an amorphous white solid (20 mg), which decomposed at 270–290° to a brown gum. The mother liquors were concentrated to yield a semi-crystalline precipitate (40 mg), m.p. 225–260° (with residual unmelted material),  $\tau$  4.63 (1 or 2 H, m,  $W_{\frac{1}{2}}$  ca. 6 Hz), 4.70 (4 H, m, 22- and 23-H), 5.20 (1 or 2 H, m,  $W_{\frac{1}{2}}$  ca. 7 Hz), 5.25 (2 H, m,  $W_{\frac{1}{2}}$  20 Hz, 3 $\alpha$ -H), 7.95 (6 H, s, 3 $\beta$ -OAc), and 7.4–9.6 (CH<sub>2</sub> and Me), *m/e* 892, 876, 874, and 437.

Addition of the peroxide (II) (1 equiv.) in deoxygenated dichloromethane to a reaction mixture prepared as above after 3 min resulted in formation of a small quantity of the chlorohydrin (III). No diminution in yield of the above products was detected in the reaction mixture by t.l.c.

(b) *With ergosteryl acetate peroxide* (II). With the peroxide (II) (100 mg) and conditions as above, a yellow-orange mixture was produced. After 3 min t.l.c. indicated the presence of unchanged peroxide (II) and a more polar product,  $R_F$  ca. 0.2 (ca. 10–20%). No chlorohydrin (III) was present. After 6 min, ergosteryl acetate (I) (100 mg) in deoxygenated chloroform (5 ml) was added, and chlorohydrin formation occurred instantaneously, with concomitant decrease in the quantity of (II), but not of the initially formed minor polar product, as shown by t.l.c. Repetition of the reaction under oxygen, but omitting addition of (I), also yielded a small amount of the above product. No chlorohydrin formation took place.

(c) *With ergosteryl acetate* (I) and *ergosteryl acetate peroxide* (II). Titanium tetrachloride [130 mg, 2.0 equiv. with respect to (II) in deoxygenated CH<sub>2</sub>Cl<sub>2</sub> (1.2 ml)] was added to a stirred solution of compounds (I) (152 mg) and (II) (152 mg) in dichloromethane under argon at –80 °C in the dark. The usual colour transformation took place, and t.l.c. indicated chlorohydrin (III) formation after 2 min. More titanium tetrachloride (65 mg) was added to convert residual (I). The mixture was worked up in the usual way to yield a pale yellow residue, which crystallised from ether-ethyl acetate to yield compound (III) {166 mg, 52% [calculated on the basis that 1 mol (II)  $\rightarrow$  2 mol (III)]}. The mother liquors contained peroxide (II), small amounts of chlorohydrin (III), u.v.-active material with  $R_F$  0.6 [that of (I)], and polymeric material.

(d) *With ergosteryl benzoate* (VIII) and *ergosteryl acetate*

*peroxide* (II). Titanium tetrachloride [485 mg, 4.0 equiv. with respect to (II)] in dichloromethane (3.4 ml) was added to a solution of the peroxide (II) (300 mg) and ergosteryl benzoate (VIII) (630 mg) in dichloromethane (200 ml) under argon at –80 °C in the dark. The mixture assumed a deep orange black colour, and t.l.c. after 3 min indicated clean formation of the acetate chlorohydrin (III) and benzoate chlorohydrin (IX) in equal quantities. Work-up as before gave a crystalline mixture (255 mg) of (III) and (IX) (from ethyl acetate-ether). By analysis of n.m.r. integrals of the benzoyl and 3 $\alpha$ , 6 $\beta$ , 7-, 22-, and 23-protons, the mixture was shown to consist of 35 mg of (III) and 225 mg of (IX). From the mother liquors were obtained further crops containing increasing quantities of (III). A final fraction (26 mg) was pure (III). In all, 440 mg of material was collected which n.m.r. analysis showed to consist of 200 mg of (III) [64%, calculated on the basis of complete reaction of (II)] and 240 mg of (IX) [70%, calculated on the basis that 300 mg of (II) react with 310 mg of (VIII) to yield 340 mg of (IX)]. Fractional crystallisation of the first fraction from ethyl acetate yielded 6 $\alpha$ -chloro-5-hydroxy-5 $\alpha$ -ergosta-7,22-dien-3 $\beta$ -yl benzoate (IX) as prisms, m.p. 190–192° (decomp., with gas evolution commencing at ca. 180°),  $[\alpha]_D^{22} + 27.9^\circ$  (*c* 0.93),  $\nu_{\max}$  (CCl<sub>4</sub>) 3 564m, 3 418w, 2 950s, 2 870s, 1 725s, 1 453m, 1 372w, 1 272s, 1 177m, 1 120m, 1 070w, 1 030w, 963w, and 708w cm<sup>-1</sup>,  $\tau$  (CDCl<sub>3</sub>) 1.82–2.69 (5 H, m, PhCO), 4.64 (1 H, m,  $W_{\frac{1}{2}}$  ca. 18 Hz, 3 $\alpha$ -H), 4.80 (2 H, m, 22- and 23-H), 4.92 (1 H, m,  $W_{\frac{1}{2}}$  ca. 8 Hz, 7-H), and 5.32 (1 H, m,  $W_{\frac{1}{2}}$  8 Hz, 6 $\beta$ -H),  $M^+$  552 (Found: C, 75.8; H, 8.65; Cl, 6.7. C<sub>35</sub>H<sub>49</sub>ClO<sub>3</sub> requires C, 76.0; H, 8.95; Cl, 6.4%).

T.l.c. of the mother liquors on silver-nitrate-impregnated silica gel in 13:7 light petroleum-benzene indicated the presence of unchanged ergosteryl benzoate (VIII) and ergosteryl acetate peroxide (II), and a second u.v.-active material [possibly 5 $\alpha$ -ergosta-6,8(14),22-trien-3 $\beta$ -yl benzoate]. No trace of ergosteryl acetate (I) was detected.

The benzoate chlorohydrin (IX) was also obtained by treatment of (VIII) (320 mg) in dichloromethane (120 ml) at –80 °C with titanium tetrachloride (243 mg, 2.0 equiv.) under dry oxygen. The chlorohydrin (IX) was formed rapidly (ca. 3 min) and was the major product (t.l.c.). Traces of starting material, a more polar product, and polymeric material were also present. Work-up in the usual way afforded crude (IX) (255 mg, 72%), which was recrystallised from ethyl acetate (yield 140 mg., 40%).

*Formation of the Chlorohydrin* (III) *from Ergosteryl Acetate* (I) and *Di-*t*-butyl Peroxide*.—Titanium tetrachloride [440 mg, 3.0 equiv. with respect to (I)] in dichloromethane (2.5 ml) was added to the acetate (I) (380 mg) and di-*t*-butyl peroxide [635 mg, 5.0 equiv. with respect to (I)] in dichloromethane at –80 °C under argon. The usual colour transformation from purple to orange was observed. After 5 min, the mixture was worked up in the usual way to yield the chlorohydrin (III) (130 mg, 31%).

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