

## The Chemistry of Santonene. Part X.<sup>1</sup> Products of the Action of Phosphorus Pentachloride on Santonin

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Reaction of santonin (1) with phosphorus(v) chloride affords 3-chloroeudesma-1,3,5,7(11)-tetraen-12,6-olactone (2) and 1 $\alpha$ ,2 $\beta$ ,3-trichloroeudesma-3,5,7(11)-trien-12,6-olactone (4). In (4), the 2 $\beta$ -chlorine is easily replaced by other groups with retention of configuration. Under more forcing conditions, 14-substituted 3-chloroeudesma-1,3,5,7(11)-tetraen-12,6-olactone derivatives (12) are obtained. The trichloro-triene (4) loses hydrogen chloride when treated with strong base to give 1,3-dichloroeudesma-1,3,5,7(11)-tetraen-12,6-olactone (6), and loses chlorine when treated with iodide in dimethylformamide to give (2). Hydrogenation of either (2) or (4) affords 3-chloroeudesma-3,5,7(11)-trien-12,6-olactone (5).

Our interest in the action of phosphorus trichloride in acetic acid on santonin (1) and related compounds<sup>2</sup> led us to investigate the action of phosphorus halides either as neat reagent or in an inert solvent on santonin.<sup>3</sup> The starting point of our investigation was the eighty-year-old report<sup>4</sup> that santonin with phosphorus pentachloride in chloroform afforded a trichloride, C<sub>15</sub>H<sub>15</sub>Cl<sub>3</sub>O<sub>2</sub>. When we reinvestigated this reaction, we found that two products were formed, a monochloride, C<sub>15</sub>H<sub>15</sub>ClO<sub>2</sub>, and the trichloride, C<sub>15</sub>H<sub>15</sub>Cl<sub>3</sub>O<sub>2</sub>. The monochloride is a precursor of the trichloride, as shown by the fact that the former is formed in greater yield when 2 mol. equiv. of the pentachloride are used at room temperature, whereas the latter is the main product when an excess of pentachloride is used at 60°. Moreover, reaction of the monochloride with phosphorus pentachloride in chloroform affords the trichloride.

The monochloride (2) has spectral properties very similar to those of 3-*O*-methyl- (3a) and 3-*O*-acetyl-santonene (3b).<sup>5</sup> In particular, the u.v. maximum at 382 nm is characteristic of a tetraenolide, and the n.m.r. spectrum shows the presence of an angular

methyl group, two methyls attached to olefinic bonds, and two olefinic protons.

The trichloride (4) possesses a u.v. maximum at 329 nm characteristic of the trienolide (5)<sup>2</sup> and it lacks the two olefinic proton signals in the n.m.r. spectrum. In their place are a doublet at  $\tau$  5.68 and a multiplet at  $\tau$  5.0 assignable to the 1- and 2-protons, respectively. The former chemical shift ( $\tau$  5.68) is similar to those of the 1-protons in a series of 1-halogeno-compounds; indeed, this confirms the halogen position in the latter series.<sup>2</sup> The 2-proton is coupled with the 1-proton ( $J$  2 Hz; torsion angle *ca.* 60°) and also with the 4-methyl group.

We now have to determine the configuration of the 1- and 2-chloro-substituents. Wyman *et al.*<sup>6</sup> have shown that olefins react with phosphorus pentachloride to give dichloro-compounds derived entirely, or almost entirely, by *trans*-addition to the double bond. This is believed to proceed by ionisation of the phosphorus pentachloride into PCl<sub>4</sub><sup>+</sup> and PCl<sub>6</sub><sup>-</sup>.<sup>7</sup> A *trans*-diaxial assignment of chlorine atoms in our case is confirmed by nuclear Overhauser effect measurements: irradiation at the 10-methyl frequency causes an enhancement of

<sup>1</sup> Part IX, D. S. R. East, K. Ishikawa, and T. B. H. McMurry, *J.C.S. Perkin I*, 1973, 2563.

<sup>2</sup> T. B. H. McMurry and D. F. Rane, *J. Chem. Soc. (C)*, 1971, 3851.

<sup>3</sup> Preliminary communication, A. Fröhlich, K. Ishikawa, and T. B. H. McMurry, *Tetrahedron Letters*, 1973, 995.

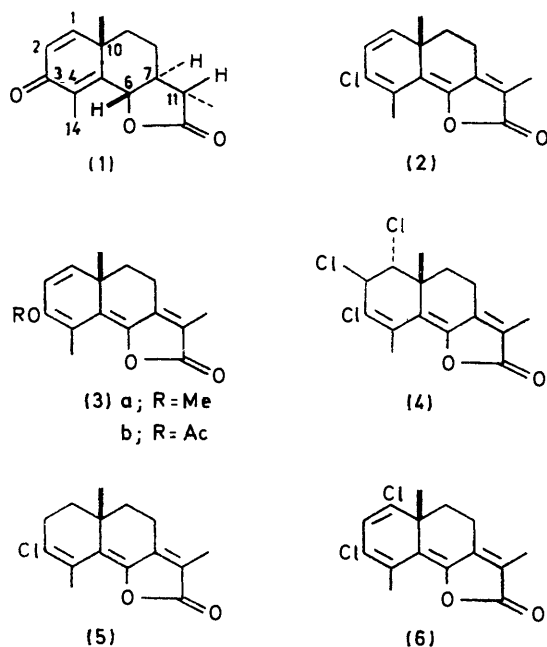
<sup>4</sup> J. Klein, *Ber.*, 1892, **25**, 3317; 1893, **26**, 982.

<sup>5</sup> T. B. H. McMurry and R. C. Mollan, *J. Chem. Soc. (C)*, 1967, 1813.

<sup>6</sup> D. P. Wyman, J. Y. C. Wang, and W. R. Freeman, *J. Org. Chem.*, 1963, **28**, 3173.

<sup>7</sup> D. S. Payne, *J. Chem. Soc.*, 1953, 1052.

the 1-proton signal (16% at 60 MHz), while the 2-proton signal remains unchanged, suggesting that the 1-hydrogen is  $\beta$ - and the 2-hydrogen  $\alpha$ -oriented. Furthermore,



comparison of the 10-methyl n.m.r. signal of the trichloride with the corresponding signal of the monochloro-triene (5)<sup>2</sup> supports this conclusion. The 2- $\beta$ -chloro-substituent deshields the methyl group, shifting the signal from  $\tau$  8.90 to 8.50.

The coupling between the 4-methyl group and the 2-proton is 1.5 Hz, which seems to be too large to be accounted for by the torsion angle required for a  $2\alpha$ -proton.<sup>8</sup> However, similar coupling constants are found for both  $2\alpha$ - and  $2\beta$ -protons with a 4-methyl group in related systems.

The trichloride does not lose hydrogen chloride easily, e.g. when treated with pyridine, but treatment with triethylamine in pyridine at 95°, or with diazabicyclooctane or 1,5-diazabicyclo[4.3.0]non-5-ene<sup>9</sup> in toluene at room temperature, gives the 1,4-dichlorotetraene (6).

In a nuclear Overhauser effect experiment, irradiation at the frequency of the 10-methyl group in (6) causes no increase in the size of the vinyl proton signal, indicating that this proton is in the 2-position. This is also confirmed by the chemical shift of the 2-proton ( $\tau$  4.02), to be expected for CH linked to two CCl groups.

Treatment of the trichloride with iodide in acetone, or preferably in dimethylformamide, causes elimination of the 1- and 2-chlorine atoms to give (2). While ideally we should compare the rate of elimination with that of an isomeric 1,2-dichloride, this result also suggests that the two chlorines are *trans*-diaxial.<sup>10</sup>

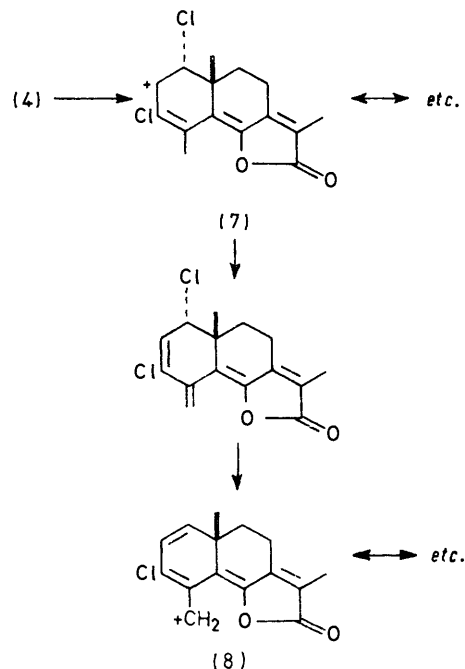
\* The carbocations can be conveniently so described, though the positive charge must be distributed over the whole  $\pi$ -system.

<sup>8</sup> L. M. Jackman and S. Sternhell, 'Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 2nd edn., 1969, p. 325.

Hydrogenation of either the trichloride (4) or the monochloride (2) over palladium-charcoal gave, among other, unidentified products, the chloro-triene (5), thus confirming the carbon skeleton. The chemistry of the trichloride (4) is dominated by the very ready formation of the 2-carbocation\* (7), and its further transformation under more forcing conditions into the 14-carbocation\* (8). A reasonable pathway is shown in the Scheme. We employed various conditions to generate the carbocations, but mostly used trifluoroacetic acid solution, or silver ion in methylene chloride. In the former case, the 2-cation is formed rapidly but it rearranges slowly to the 14-cation. In the latter case, reaction with 1 mol. equiv. of silver tetrafluoroborate at room temperature gives mostly the 2-cation, whereas reaction with 2 mol. equiv. at higher temperatures gives the 14-cation.

We can detect the cations indirectly by trapping with various nucleophiles. For example, formation of the 2-cation (a) in the presence of water affords the 2 $\beta$ -hydroxy-compound (9a), (b) in the presence of acetate affords the 2 $\beta$ -acetoxy-compound (9b), and (c) in the presence of anisole gives the *p*-methoxyphenyl derivatives (9c and d).

The 2-chloro-substituent is replaced by other groups with retention of configuration. This is understandable



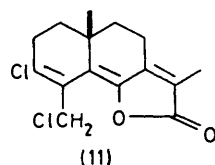
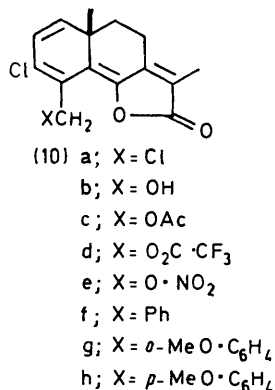
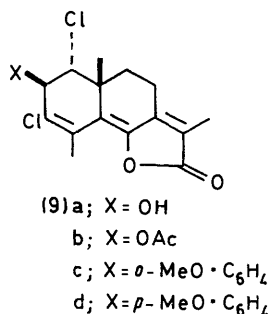
SCHEME

if the 1 $\alpha$ -chlorine atom acts as a 'neighbouring group.' The n.m.r. spectra of the products all show significant similarities, especially in the deshielding of the 10-methyl group and the size of the 2-H,4-Me coupling.

<sup>9</sup> H. Oediger, H.-J. Kabbe, F. Möller, and K. Eiter, *Chem. Ber.*, 1966, **99**, 2012.

<sup>10</sup> D. H. R. Barton and E. Miller, *J. Amer. Chem. Soc.*, 1950, **72**, 1066.

Moreover, the use of europium shift reagents shows that the proton nearest to the 2-hydroxy-group is the 2-proton, followed by the 1-proton and the 10- and 4-methyl groups. The hydroxy-compound (9a) forms the acetate (9b) and it can also be reconverted into the trichloride (4).



The 14-cation can be trapped by chloride, hydroxide, acetate, trifluoroacetate, and nitrate ions to give compounds (10a–e) respectively and also by benzene to give (10f). In the case of anisole we could only obtain the *o*-methoxyphenyl derivative (10g) in a pure state, but the n.m.r. spectrum of fractionally crystallised material showed fractions containing the *p*-methoxyphenyl derivative (10h). The 14-methylene protons in these products are diastereotopic. Though the asymmetric centre in the molecule is not close,<sup>11</sup> an AB quartet is observed in the n.m.r. spectra (deuteriochloroform) of (10a) and (10g). Europium shift reagent studies on the 14-hydroxy-compound confirm that, apart from the 14-methylene group no other protons lie close to the hydroxy-group.

Hydrogenation of the 3,14-dichloro-tetraene (10a) over palladium-charcoal affords the 3,14-dichloro-triene (11) (uptake 1 mol. equiv.) and the 3-chloro-triene (5) (uptake 2 mol. equiv.).

#### EXPERIMENTAL

For general instructions, see Part VIII,<sup>12</sup> but specific rotations were measured for solutions in ethanol.

**Reaction of Santonin with Phosphorus Pentachloride.**—(a) *With 2 mol. equiv.* Santonin (1) (3 g) and phosphorus pentachloride (5 g) in purified chloroform (75 ml) were stirred at room temperature for 2 h. The mixture was poured into water and the chloroform layer extracted with sodium hydrogen carbonate solution, washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated. The n.m.r. spectrum of the resulting solid (2.6 g) showed it to contain the monochloro-tetraene (2) and the trichloro-triene (4) in the ratio 5:2 (see below). Chromatography of the

solid (1 g) over fine silica gave 3-chloro-eudesma-1,3,5,7(11)-tetraen-12,6-olactone (2) (200 mg) as rhombs, m.p. 110–111°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> –1510° (*c* 0.15) (Found: C, 68.6; H, 5.8; Cl, 13.7. C<sub>15</sub>H<sub>15</sub>ClO<sub>2</sub> requires C, 68.8; H, 6.0; Cl, 13.7%),  $\nu_{\max}$  1740, 1620, 1280, and 1018 cm<sup>-1</sup>,  $\lambda_{\max}$  382 and 268 nm (log  $\epsilon$  4.22 and 3.90),  $\tau$  8.72 (10-Me), 8.05br (11-Me), 7.60br (4-Me), 4.35 (d, *J* 9 Hz, 1-H), and 4.02 (d, *J* 9 Hz, 2-H).

(b) *With 4 mol. equiv.* Santonin (3 g) and phosphorus pentachloride (10 g) in purified chloroform (75 ml) were refluxed for 2 h. The mixture was worked up as above to give a solid (2.5 g), which was recrystallised from ethyl acetate to give 1 $\alpha$ ,2 $\beta$ ,3-trichloro-eudesma-3,5,7(11)-trien-12,6-olactone (4) (2.0 g) as cubes, m.p. 178–180° (decomp.), [ $\alpha$ ]<sub>D</sub><sup>20</sup> –246° (*c* 0.67) (Found: C, 54.1; H, 4.6; Cl, 31.7. C<sub>15</sub>H<sub>15</sub>Cl<sub>3</sub>O<sub>2</sub> requires C, 54.0; H, 4.5; Cl, 31.9%),  $\nu_{\max}$  1750, 1625, 1005, and 725 cm<sup>-1</sup>,  $\lambda_{\max}$  329 nm (log  $\epsilon$  4.39),  $\tau$  8.50 (10-Me), 8.08br (11-Me), 7.55 (d, *J* 2 Hz, 4-Me), 5.68 (d, *J* 2 Hz, 1-H), and 5.0 (m, 2-H).

**Conversion of the Chloro-tetraene (2) into the Trichloro-triene (4).**—The chloro-tetraene (2) (100 mg), phosphorus pentachloride (350 mg), and purified chloroform (12 ml) were refluxed for 1 h. The mixture was worked up as before to give the trichloro-triene (4), m.p. and mixed m.p. 178–180° (decomp.). Similar results were obtained using chlorine in chloroform and also antimony pentachloride.

**Dechlorination of the Trichloride (4).**—The trichloro-triene (4) (20 mg), sodium iodide (200 mg), and dimethylformamide (5 ml) were heated at 95° for 5 min. The mixture was poured into water and extracted with ether. The extract was washed with sodium thiosulphate solution and water, and dried. The product was purified by preparative t.l.c. to give the chloro-tetraene (2) (10 mg), m.p. and mixed m.p. 110°.

**Dehydrochlorination of the Trichloride (4).**—(a) The trichloro-triene (4) (400 mg), 1,5-diazabicyclo[4.3.0]non-5-ene (1 ml), and toluene (5 ml) were stirred at 20° for 60 min; the mixture was then diluted with ether and shaken with 15% hydrochloric acid. The organic layer was dried and evaporated to leave a yellow solid (300 mg), which was crystallised from hexane-ether to give 1,3-dichloro-eudesma-1,3,5,7(11)-tetraen-12,6-olactone (6) (200 mg) as leaflets, m.p. 83–84°, [ $\alpha$ ]<sub>D</sub><sup>22</sup> –1320° (*c* 0.18) (Found: C, 60.9; H, 4.8; Cl, 24.15. C<sub>15</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>2</sub> requires C, 60.6; H, 4.7; Cl, 23.9%),  $\nu_{\max}$  1770, 1623, and 1505 cm<sup>-1</sup>,  $\lambda_{\max}$  383 and 273 nm (log  $\epsilon$  4.23 and 4.10),  $\tau$  8.72 (10-Me), 8.05br (11-Me), 7.60br (4-Me), and 4.02br (2-H).

(b) The above experiment was repeated but the mixture was heated at 95° for 3 min, giving the same product. Similar results were obtained using triethylamine in pyridine at 95° or diazabicyclo-octane in toluene at 95°.

**Hydrogenation Experiments.**—(a) The trichloro-triene (50 mg), palladium-charcoal (5%; 50 mg), and ethyl acetate (20 ml) were stirred in hydrogen until 1 mol. equiv. had been absorbed. Removal of catalyst and solvent left a solid, which was purified by preparative t.l.c. to afford the 3-chloro-triene (5) (25 mg) as needles, m.p. and mixed m.p. 119–120°.

(b) The chloro-tetraene (50 mg) under the same conditions also gave the chloro-triene (5) (25 mg).

**1 $\alpha$ ,3-Dichloro-2 $\beta$ -hydroxyeudesma-3,5,7(11)-trien-12,6-olactone (9a).**—The trichloride (200 mg), silver acetate (120 mg), trifluoroacetic acid (5 ml), and water (1 ml)

<sup>11</sup> G. M. Whitesides, J. J. Grocki, D. Holtz, H. Steinberg, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1965, **87**, 1058; G. M. Whitesides, D. Holtz, and J. D. Roberts, *ibid.*, 1964, **86**, 2628.

<sup>12</sup> K. Ishikawa and T. B. H. McMurry, *J.C.S. Perkin I*, 1973, 914.

were stirred for 5 min and the mixture was diluted with ether (10 ml). The silver chloride was removed and the mixture poured into water. The organic layer was separated, washed with sodium hydrogen carbonate solution and water, dried, and evaporated. The product was crystallised from ether–light petroleum to give the 2 $\beta$ -hydroxy-compound (9a) (120 mg) as platelets, m.p. 178–179° (decomp.),  $[\alpha]_D^{25} -246^\circ$  (*c* 0.11),  $\nu_{\max}$ . 3450, 1740, 1630, 1590, and 1285  $\text{cm}^{-1}$ ,  $\lambda_{\max}$ . 330 nm (log  $\epsilon$  4.43),  $\tau$  8.60 (10-Me), 8.05br (11-Me), 7.59 (d, *J* 1.5 Hz, 4-Me), 5.82 (d, *J* 2 Hz, 1-H), and 5.27 (m, 2-H).

*Conversion of the Hydroxy-dichloride (9a) into the Trichloride (4).*—The hydroxy-dichloride (45 mg), phosphorus pentachloride (25 mg), and purified chloroform (10 ml) were stirred at room temperature for 30 min. The mixture was worked up as described above, to give the trichloride (10 mg), m.p. and mixed m.p. 178–179°.

Similar results were obtained using thionyl chloride in chloroform, and triphenyl phosphine–carbon tetrachloride.<sup>13</sup>

2 $\beta$ -Acetoxy-1 $\alpha$ ,3-dichloro-*eudesma*-3,5,7(11)-*trien*-12,6-*olactone* (9b).—(a) The trichloro-compound (4) (50 mg), silver acetate (25 mg), and acetic acid (15 ml) were stirred at room temperature for 5 min. The mixture was worked up as before to give the 2 $\beta$ -acetoxy-compound (45 mg) as needles (from hexane–ether), m.p. 179–181° (decomp.),  $[\alpha]_D^{22} -307^\circ$  (*c* 0.14) (Found: C, 57.45; H, 4.8; Cl, 19.6.  $\text{C}_{17}\text{H}_{16}\text{Cl}_2\text{O}_4$  requires C, 57.2; H, 5.1; Cl, 19.85%).  $\nu_{\max}$ . 1740, 1220, and 1010  $\text{cm}^{-1}$ ,  $\lambda_{\max}$ . 326 (log  $\epsilon$  4.54),  $\tau$  8.67 (10-Me), 8.09br (11-Me), 7.89 (OAc), 7.62 (d, *J* 1 Hz, 4-Me), 6.03 (d, *J* 2 Hz, 1-H), and 4.35 (m, 2-H).

(b) The hydroxy-dichloride (9a) (45 mg), acetic acid (1 ml), and trifluoroacetic anhydride (0.15 ml) were heated at 95° for 1 h. The product, separated by preparative t.l.c., was the acetoxy-dichloride (15 mg), m.p. and mixed m.p. 179–181°.

1 $\alpha$ ,3-Dichloro-2 $\beta$ -(*o*- and *p*-methoxyphenyl)*eudesma*-3,5,7(11)-*trien*-12,6-*olactones* (9c and d).—Silver tetrafluoroborate (240 mg) in anisole (25 ml) was added slowly to the trichloride (4) (400 mg) in anisole (50 ml), and the mixture was stirred for 1 h at room temperature. The products were separated by careful preparative t.l.c. (methylene chloride–light petroleum) to give, as the first fraction, the 2-(*o*-methoxyphenyl) derivative (9c) as needles (from ether–light petroleum), m.p. 234–236°,  $[\alpha]_D^{22} -27^\circ$  (*c* 0.19) (Found: C, 65.25; H, 5.4; Cl, 17.7.  $\text{C}_{22}\text{H}_{22}\text{Cl}_2\text{O}_3$  requires C, 65.2; H, 5.5; Cl, 17.45%),  $\nu_{\max}$ . 1770, 1750, 1635, 1615, and 750  $\text{cm}^{-1}$ ,  $\lambda_{\max}$ . 332 nm (log  $\epsilon$  4.50),  $\tau$  9.07 (10-Me), 8.10br (11-Me), 7.47 (d, *J* 1.6 Hz, 4-Me), 6.08 (OMe), 5.57 (1-H), 5.34 (2-H), and 3.0 (m, aromatic).

The second fraction was purified by further preparative t.l.c. and crystallised from ether–light petroleum to give the 2-(*p*-methoxyphenyl) derivative (9d) as leaflets, m.p. 217–225° (decomp.),  $[\alpha]_D^{21} -95^\circ$  (*c* 0.21) (Found: C, 65.25; H, 5.55; Cl, 17.6%),  $\nu_{\max}$ . 1750, 1630, 1602, 1582, and 830  $\text{cm}^{-1}$ ,  $\lambda_{\max}$ . 326 (log  $\epsilon$  4.5),  $\tau$  9.14 (10-Me), 8.12br (s, 11-Me), 7.49 (d, *J* 1 Hz, 4-Me), 6.25 (OMe), 5.68 (1-H), 5.55 (m, 2-H), and 3.0 (dd, *J* 9 Hz, aromatic).

3,14-Dichloro-*eudesma*-1,3,5,7(11)-*tetraen*-12,6-*olactone* (10a).—The trichloro-triene (4) (500 mg), trifluoroacetic acid (5 ml), and chloroform (4 ml) were refluxed for 1.5 h. The product was crystallised from ether–light petroleum to give the dichloride (10a) (210 mg) as leaflets, m.p. 124–126°,  $[\alpha]_D^{21} -995^\circ$  (*c* 0.26) (Found: C, 60.5; H, 4.7; Cl, 23.7%),  $\nu_{\max}$ . 1760, 1640, 1540, and 780  $\text{cm}^{-1}$ ,  $\lambda_{\max}$ . 376 and 272 nm (log  $\epsilon$  4.18 and 3.98),  $\tau$  8.76 (10-Me), 8.10br

(11-Me), 5.16 (dd, *J* 13 Hz, 14-H<sub>2</sub>), and 4.12 (ABq, *J* 10 Hz, 1- and 2-H).

3-Chloro-14-hydroxy-*eudesma*-1,3,5,7(11)-*tetraen*-12,6-*olactone* (10b).—(a) The 3,14-dichloride (10a) (200 mg), silver acetate (110 mg), trifluoroacetic acid (2 ml), and water (1 ml) were refluxed for 10 min. The product was separated by preparative t.l.c. to give the hydroxy-compound (10b) (180 mg) as cubes (from ether–light petroleum), m.p. 164–166°,  $[\alpha]_D^{21} -1370^\circ$  (*c* 0.16), (Found: C, 63.9; H, 5.4; Cl, 12.65.  $\text{C}_{15}\text{H}_{15}\text{ClO}_3$  requires C, 63.7; H, 5.4; Cl, 12.7%),  $\nu_{\max}$ . 3350br, 1760, 1630, and 1520  $\text{cm}^{-1}$ ,  $\lambda_{\max}$ . 376 and 266 nm (log  $\epsilon$  4.2 and 3.6),  $\tau$  8.76 (10-Me), 8.11 (11-Me), 5.32br (14-H<sub>2</sub>), and 4.17 (ABq, *J* 10 Hz, 1- and 2-H).

(b) Similar treatment of the trichloride (4) afforded a mixture from which, by preparative t.l.c., both the 2-hydroxy-compound (9a) and the 14-hydroxy-compound were obtained.

14-Acetoxy-3-chloro-*eudesma*-1,3,5,7(11)-*tetraen*-12,6-*olactone* (10c).—The dichloro-tetraene (10a) (240 mg), acetic acid (30 ml), acetic anhydride (3 ml), and silver acetate (140 mg) were heated at 95° for 1 h, and then stirred for 12 h at room temperature. The product was purified by preparative t.l.c. to give the acetate (10c) (90 mg) as rods, m.p. 110–112°,  $[\alpha]_D^{22} -1065^\circ$  (*c* 0.16) (Found: C, 64.1; H, 5.6; Cl, 11.3.  $\text{C}_{17}\text{H}_{17}\text{ClO}_4$  requires C, 63.7; H, 5.5; Cl, 11.05%),  $\nu_{\max}$ . 1745, 1710, 1630, and 1220  $\text{cm}^{-1}$ ,  $\lambda_{\max}$ . 372 and 285 nm (log  $\epsilon$  4.19 and 3.97),  $\tau$  8.75 (10-Me), 8.10 (11-Me), 7.97 (OAc), 4.78 (14-H<sub>2</sub>), and 4.08 (ABq, *J* 10 Hz, 1- and 2-H).

3-Chloro-14-trifluoroacetoxy-*eudesma*-1,3,5,7(11)-*tetraen*-12,6-*olactone* (10d).—The dichlorotetraene (10a) (50 mg), silver tetrafluoroborate (25 mg), dry trifluoroacetic acid (1 ml), and trifluoroacetic anhydride (1 ml) were stirred for 5 min at room temperature. The silver chloride and solvent were removed, and the product was crystallised from cyclohexane to give the trifluoroacetate (10d) as leaflets (25 mg), m.p. 139–141°,  $[\alpha]_D^{22} -1040^\circ$  (*c* 0.12) (Found: C, 54.3; H, 4.2.  $\text{C}_{17}\text{H}_{14}\text{ClF}_3\text{O}_4$  requires C, 54.7; H, 3.8%),  $\nu_{\max}$ . 1782, 1748, and 1645  $\text{cm}^{-1}$ ,  $\lambda_{\max}$ . 372 and 270 (log  $\epsilon$  4.24 and 3.98),  $\tau$  8.75 (10-Me), 8.09 (11-Me), 4.44 (14-H<sub>2</sub>), and 4.05 (ABq, *J* 10 Hz, 1- and 2-H).

3-Chloro-14-nitro-oxy-*eudesma*-1,3,5,7(11)-*tetraen*-12,6-*olactone* (12e).—The dichloride (10a) (100 mg), silver nitrate (60 mg), and acetonitrile (10 ml) were stirred at room temperature for 24 h. The product was isolated and crystallised from ether–light petroleum to give the nitrate (12e) (50 mg) as leaflets, m.p. 151–152°,  $[\alpha]_D^{21} -1185^\circ$  (*c* 0.195) (Found: C, 56.2; H, 4.4; Cl, 11.0; N, 4.3.  $\text{C}_{15}\text{H}_{14}\text{ClNO}_3$  requires C, 55.8; H, 4.4; Cl, 11.0; N, 4.3%),  $\nu_{\max}$ . 1740, 1620, and 1280  $\text{cm}^{-1}$ ,  $\lambda_{\max}$ . 374 and 267 nm (log  $\epsilon$  4.2 and 3.9),  $\tau$  8.75 (10-Me), 8.09br (4-Me), 4.31br (14-H<sub>2</sub>), and 4.05 (ABq, *J* 10 Hz, 1- and 2-H).

3-Chloro-14-phenyl-*eudesma*-1,3,5,7(11)-*tetraen*-12,6-*olactone* (10f).—The trichloride (4) (50 mg), silver tetrafluoroborate (30 mg), and benzene (5 ml) were stirred at room temperature for 1 h, and the mixture was then refluxed for 10 min. The product was purified by preparative t.l.c. and crystallised from ether–light petroleum to afford the phenyl adduct (30 mg) as leaflets, m.p. 171–172°,  $[\alpha]_D^{21} -828^\circ$  (*c* 0.20) (Found: C, 74.4; H, 5.4; Cl, 10.1.  $\text{C}_{21}\text{H}_{17}\text{ClO}_2$  requires C, 74.9; H, 5.1; Cl, 10.5%),  $\nu_{\max}$ . 1740, 1625, and 1530  $\text{cm}^{-1}$ ,  $\lambda_{\max}$ . 377 and 266 nm (log  $\epsilon$  4.24 and

<sup>13</sup> I. M. Downie, J. B. Holmes, and J. B. Lee, *Chem. and Ind.*, 1966, 900.

4.16),  $\tau$  8.95 (10-Me), 8.15br (11-Me), 5.70br (14-H<sub>2</sub>), 4.1 (ABq, *J* 10 Hz, 1- and 2-H), and 2.75 (aromatic H).

3-Chloro-14-(*o*-methoxyphenyl)eudesma-1,3,5,7(11)-tetraen-12,6-olactone (10g).—The trichloride (4) (200 mg), silver tetrafluoroborate (240 mg), and anisole (40 ml) were heated at 95° for 45 min. The products were separated by preparative t.l.c. to give, as the first fraction, the 14-(*o*-methoxyphenyl) derivative (10g) (90 mg) as rhombs (from ether-light petroleum), m.p. 127—129°,  $[\alpha]_D^{22}$  -1345° (*c* 0.19) (Found: C, 71.8; H, 6.0; Cl, 10.15. C<sub>22</sub>H<sub>21</sub>ClO<sub>3</sub> requires C, 71.6; H, 6.2; Cl, 9.6%),  $\nu_{\max}$  1742, 1628, 1535, and 740 cm<sup>-1</sup>,  $\lambda_{\max}$  379 and 270 (log  $\epsilon$  4.19 and 3.98),  $\tau$  8.84 (10-Me), 8.19 (11-Me), 6.15 (OMe), 5.78 (ABq, *J* 16 Hz, 14-H<sub>2</sub>), 4.14 (ABq, *J* 9 Hz, 1- and 2-H), and 3.1 (m, aromatic H).

The second fraction contained some of the 14-(*p*-methoxyphenyl) compound (10h) (n.m.r. spectra) but this could not be obtained pure.

Hydrogenation of the 3,14-Dichlorotetraene (10a).—(a) 3,14-Dichloroeudesma-3,5,7(11)-trien-12,6-olactone (11).

The dichloro-tetraene (50 mg), palladium-charcoal (50 mg), and ethyl acetate (25 ml) were stirred in hydrogen until 1 mol. equiv. had been absorbed. The product was purified by preparative t.l.c. to give the dichloro-triene (11) (25 mg) as cubes (from ether-light petroleum), m.p. 116—118°,  $[\alpha]_D^{21}$  -157° (*c* 0.17) (Found: C, 61.6; H, 5.0; Cl, 23.9. C<sub>15</sub>H<sub>16</sub>Cl<sub>2</sub>O<sub>2</sub> requires C, 60.8; H, 5.4; Cl, 23.7%),  $\nu_{\max}$  1745 and 1632 cm<sup>-1</sup>,  $\lambda_{\max}$  325 nm (log  $\epsilon$  4.51),  $\tau$  8.91 (10-Me), 8.18 (11-Me), and 5.28 (ABq, *J* 11 Hz, 14-H<sub>2</sub>).

(b) 3-Chloroeudesma-3,5,7(11)-trien-12,6-olactone. Hydrogenation of (10a) (50 mg) as above but until 2 mol. equiv. of hydrogen had been absorbed afforded the 3-chlorotriene (5) (25 mg), m.p. and mixed m.p. 119—121°.

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