The Chemistry of Santonene. Part XII.[1] Photolysis of 4-Acetoxysantonene and its 4-Epimer: an Example of Photodecarboxylation of Acetates

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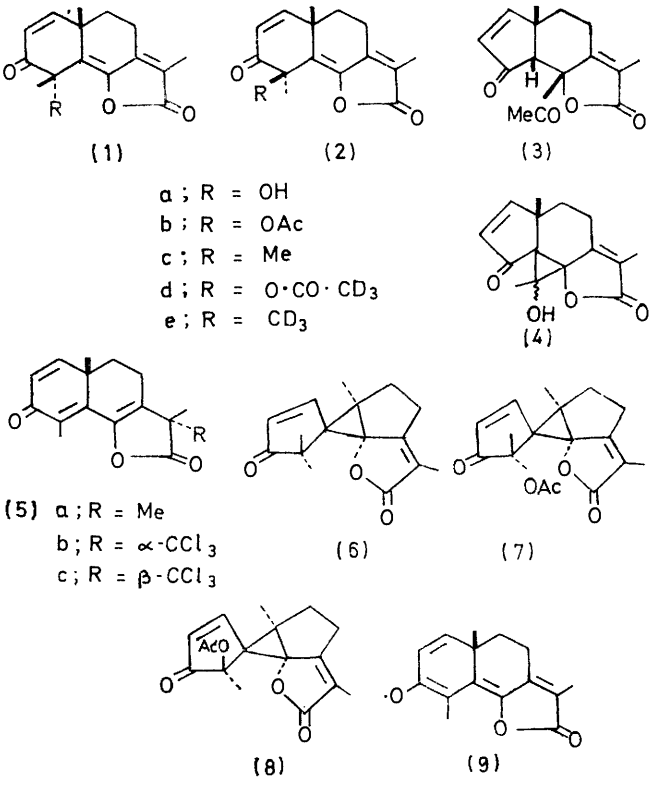
Photolysis of 4-acetoxysantonene [4-acetoxy-3-oxo-4α*H*-eudesma-1,5,7(11)-trien-12,6-olactone] (1b) or its 4-epimer (2b) affords a mixture of 4-methylsantonene (1c) and its 11-methyl-$\Delta^{1,4,6}$-isomer (5a), 4-methylphotosantonene (6), and, in methanol, the corresponding 4-acetoxyphotosantonene (7) or its 4-epimer (8). The reaction is believed to proceed *via* santonenyl and acetoxyl radicals, of which the latter undergo decarboxylation and recombine intermolecularly with the santonenyl radicals. The decarboxylation proceeds *via* a triplet state, whereas the 4-acetoxyphotosantonenes are formed *via* a singlet state.

Photolysis of 1,2-dihydro-4-acetoxysantonene (10a) or its 4-epimer (11a) affords 1,2-dihydro-4-methylsantonene (10b), its 11-methyl-$\Delta^{4,6}$-isomer (14), and both the 6α- and 6β-methyl-$\Delta^{4,7(11)}$-isomers (12) and (13). The $\Delta^{1,4,7(11)}$-isomer of 6β- (but not 6α-) acetoxysantonene affords traces of 4- and 11-methyl compounds. Photolysis of 1,2-dihydro-4-methylsantonene (10b) in the presence of a triplet sensitiser affords the stereoisomeric A-norcyclopropanes (18) and (19). The latter is unstable to acid, and rearranges to the 6-isopropenyl derivative (20).

PHOTOLYSIS of steroidal 1,5-dien-3-ones [2,3] and related systems [4,5] does not afford any product derived from an oxa-di-π-methane rearrangement *via* a triplet excited



state.[6] This type of rearrangement is characteristic of the triplet excited state of steroidal 5-en-3-ones.[7] In the preceding paper [1] we describe how 4-hydroxysantonene (1a) and its 4-epimer (2a) can undergo such a reaction *via* a triplet excited state, to give compound (3), presumably *via* (4). We decided to investigate the photoproducts of the acetates (1b) and (2b) to see whether we could obtain compounds corresponding to (4), and to determine their stereochemistry (*cf.* ref. 7*a*).

In the event, photolysis of either acetate (1b) or (2b) in benzene in the presence or absence of triplet sensitisers affords 4- and 11-methyl derivatives [(1c) and (5a)] and 4-methylphotosantonene (6). In the case of 4-acetoxy-4β*H*-santonene (2b), we were also able to obtain the 'normal' [2-5] photoproduct (8), in the absence of sensitiser. When the photolyses were carried out in methanol, no 11-substituted product was obtained, but both isomers afforded 4-methylsantonene and its photoproduct (6), and each gave the corresponding 'normal' acetoxyphotoproduct, (7) or (8). The product (6) was obtained from (1c) on photolysis.

When we photolysed (1b) or (2b) in benzene in the presence of ferrocene as a triplet quencher,[8] the reaction proceeded more slowly and the products (apart from unchanged starting material) consisted of the corresponding acetoxyphotosantonenes, and traces of ferrocene adducts with the santonene (not investigated further), but no methylsantonenes. These results suggest that the formation of the normal products (7) and (8) occur from the singlet excited state, but that the decarboxylation products are formed from a triplet state. We believe that the triplet state decomposes to give santonenyl (9) and acetoxyl radicals.† Decarboxylation of the acetoxyl radical [10] and recombination leads to *C*-methylated products. A few examples of the photochemical de-

† In an α-acetoxy-α′β′,βγ-dienone,[9] where formation of two radicals would be sterically inhibited, photolysis proceeds by another route.

[1] Part XI, D. S. R. East, T. B. H. McMurry, and R. R. Talekar, preceding paper.

[2] B. Nann, D. Gravel, P. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 1963, **46**, 2473; B. Nann, H. Wehrli, K. Schaffner, and O. Jeger, *ibid.*, 1965, **48**, 1680.

[3] S. Domb and K. Schaffner, *Helv. Chim. Acta*, 1970, **53**, 1765.

[4] K. Ishikawa and T. B. H. McMurry, *J.C.S. Perkin I*, 1973, 914.

[5] D. S. R. East, K. Ishikawa, and T. B. H. McMurry, *J.C.S. Perkin I*, 1973, 2563.

[6] K. N. Houk, D. J. Northington, and R. E. Duke, *J. Amer. Chem. Soc.*, 1972, **94**, 6233; D. I. Schuster, G. R. Underwood, and T. B. Knudsen, *ibid.*, 1971, **93**, 4304.

[7] (*a*) S. Domb, G. Bozzato, J. A. Saboz, and K. Schaffner, *Helv. Chim. Acta*, 1969, **52**, 2436; S. Domb and K. Schaffner, *ibid.*, 1970, **53**, 677; (*b*) K. Kojima, K. Sakai, and K. Tanabe, *Tetrahedron Letters*, 1969, 1925; H. Sato, K. Nakanishi, J. Hayashi, and Y. Nakadaira, *Tetrahedron*, 1973, **29**, 275.

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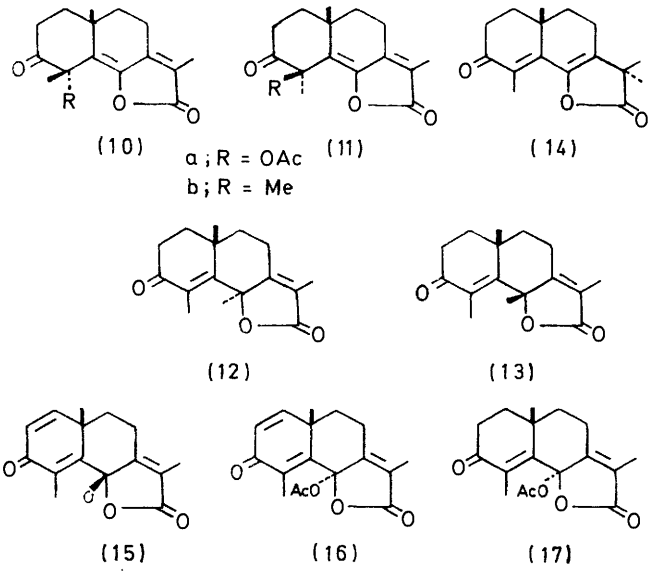
[9] J. Sazaki, K. Kanematsu, K. Hayakawa, and A. Kondo, *J. Org. Chem.*, 1973, **38**, 4100.

[10] L. Herk, M. Feld, and M. Szwarc, *J. Amer. Chem. Soc.*, 1961, **83**, 2998.

carboxylation of acetates [11,12] * and other esters [14] and lactones [15] have been reported, but a major product derived from *C*-methylation is obtained in only one case of acetate decarboxylation.[11] The reaction is also related to the photolyses of 3-benzyloxy-3,5-dienes,[16] and 3-trichloroacetoxy-3,5-dienes.[17] The latter involves a decarbonylation. In each case the alkyl radical initially generated is resonance-stabilised.

In our case, we detected no product derived from attack of the methyl radical on the 6-position of the santonenyl radical, nor any further photoproduct of these hypothetical products. However, photolysis of either of the 1,2-dihydro-compounds (10a) and (11a) in benzene in presence of acetophenone affords the $\Delta^{4,7(11)}$-isomers, 6α- and 6β-methyldihydrosantonenes (12) and (13), in addition to the 4-methyl and 11-methyl compounds (10b) and (14), the latter two being also prepared by hydrogenation of the corresponding methyl derivatives (1c) and (5a).



The $\Delta^{1,4,7(11)}$-isomer of 6β-acetoxysantonene (15) [but not the 6α-isomer (16)] readily affords a mixture of 4- and 11-methyl compounds, (1c) and (5a), as well as unidentified products. This difference may be related to the observation [15] that dihydro-6-*epi*-santonin with an axial C(6)–O bond undergoes photochemical decarboxylation, whereas dihydrosantonin [equatorial C(6)–O bond] does not. 6-Acetoxysantonene (16) does give other photoproducts but we have not yet investigated them further. On the other hand, 6-acetoxydihydrosantonene (17) does give the same mixture of methylated products as its 4-acetoxy-isomers.

These results suggest that in the dihydro-series, and by implication in the acetoxysantonene series itself, the reaction proceeds in an intermolecular fashion. We have confirmed this by two experiments. Photolysis of either trideuterioacetate (1d) or (2d) affords the same mixture of 4-trideuteriomethylsantonenes, in the ratio *ca.* 70 : 30. We believe that the major isomer is the 4α-trideuteriomethyl derivative (1e), formed by attack of the methyl radical on the less hindered side. Furthermore, if the photolysis of either (1b) or (2b) is carried out in benzene–chloroform, the products are the 11-trichloromethyl compounds (5b and c) in the ratio 1 : 1 and traces (unisolated) of other compound(s). The attacking species in this case is the larger trichloromethyl radical, generated by attack of methyl or acetoxyl radical on chloroform. It is not clear as to why attack does not take place at the 4-position from the α-side, though attack from the β-side would be clearly inhibited. At the 11-position electronic and steric factors should not distinguish between the α- and β-sides.

We can identify the various photolysis products by means of their spectral properties. The 4-substituted santonenes, *e.g.* (1c) and (2c), show a u.v. maximum at a similar position to that of santonene itself [18] and also the 4-hydroxy- and 4-acetoxy-santonenes.[19] The n.m.r. spectrum of 4-methylsantonene (1c) shows the two 4-methyl signals close together at τ 8.46 and 8.43. In the mixture of trideuteriated compounds (1e) and (2e), it is the former peak which shows the largest decrease in size as compared with the corresponding signal in (1c). This, if we accept the argument above, must be the 4α-methyl signal.

The dihydro-4-methyl compound (10b) has a u.v. spectrum similar to those of the 4-hydroxy- and 4-acetoxy-compounds [19] and its n.m.r. spectrum shows the signal of the two 4-methyl groups as a singlet (τ 8.52). The 10-methyl signal occurs at τ 8.93, suggesting that a ring A boat conformation may make a substantial contribution to any conformational equilibrium.[20] However, the c.d. spectrum resembles closely that of 4(α)-acetoxy- and hydroxy-santonenes [21] which have ring A in a chair conformation.[20,21] The compound probably exists in a conformational equilibrium in which the ring A chair form predominates. The 11-substituted santonenes possess a u.v. maximum at *ca.* 315 nm, characteristic of 11-acetoxysantonene.[19] The 11-methyl groups

* Aromatic *C*-methyl compounds are minor products in the photolysis of substituted acetophenone oxime *O*-acetates.[13]

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[13] K. H. Grellman and E. Tauer, personal communication; T. Matsuura, personal communication.
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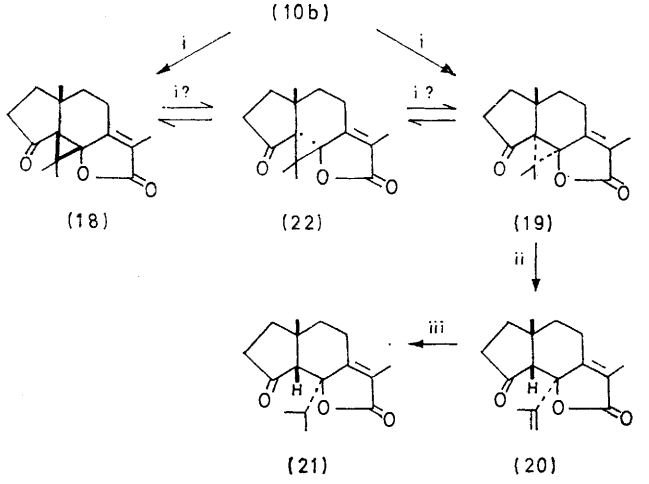
[16] J. T. Pinney and K. Schaffner, *Austral. J. Chem.*, 1968, **21**, 2265.
[17] J. Libman, M. Sprecher, and Y. Mazur, *J. Amer. Chem. Soc.*, 1969, **91**, 2062.
[18] T. B. H. McMurry and R. C. Mollan, *J. Chem. Soc.* (*C*), 1967, 1813.
[19] T. B. H. McMurry and R. C. Mollan, *J. Chem. Soc.* (*C*), 1969, 1619.
[20] D. S. R. East, T. B. H. McMurry, and R. C. Mollan, *J. Chem. Soc.* (*C*), 1970, 2008.
[21] L. Bartlett, P. M. Scopes, T. B. H. McMurry, and R. C. Mollan, *J. Chem. Soc.* (*C*), 1969, 1088.

are equivalent in 11-methylsantonene. In the 11-trichloromethyl santonenes (5b and c), we assign the lower field 10-methyl signal to the 11β-isomer.

The 'normal' photoproducts (7) and (8) possess the expected u.v. spectra and n.m.r. spectra. In particular, the 4-methyl group in 4-acetoxy-4β*H*-photosantonene (8) lies in the shielding zone of the unsaturated lactone, and consequently its n.m.r. signal is at high field (*cf.* refs 1, 4, and 5). The 4-acetoxy-group in (7) also resonates at a higher field than that in (8), for the same reason. We have been able to relate the 4-acetoxyphotosantonenes to the corresponding known 4-hydroxyphotosantonenes [1] by acetylation. In 4-methylphotosantonene (6), one of the 4-methyl groups is shielded and is consequently α-oriented. The 4-acetoxy- and 4-methyl-photosantonenes readily give 1,2-dihydro-derivatives on hydrogenation. Their n.m.r. spectra fit the same pattern.

1,2-Dihydro-4-methylsantonene (10b), on photolysis in the presence of acetophenone, affords two products (18) and (19). These can be separated by column chromatography but thick-layer chromatography causes the decomposition of (19) to (20). This rearrangement is also catalysed by trifluoroacetic acid.

The instability of (19), relative to (18), suggests that (19) possesses the strained *trans*-AB-ring fusion. While it is tempting to assign a peak at τ 9.15 in the n.m.r. spectrum of (19) to the 10-methyl group (*cf.* ref. 1), this is



i, *hν*, sensitizer; ii, H^+; iii, H_2–Pd

probably not correct. Models of (19) show that the α-cyclopropane ring flattens ring B, and hence the 10-methyl group lies outside the shielding zone of the unsaturated lactone. The peak at τ 9.15 can be assigned to the 4β-methyl group, which lies in the shielding zone of the 3-carbonyl, and the 10-methyl signal is at τ 8.62. These assignments are supported by observations on related compounds obtained by photolysis of 4-methoxy-4β*H*-santonene.[22]

Hydrogenation of compound (20) affords a dihydro-derivative (21), in which the side-chain methyl groups are diastereotopic. They show doublets in the n.m.r. spectrum at τ 9.32 and 8.95.

There are two possible explanations for the formation of the two products (18) and (19) from (10b). Compound (18) could be formed from the conformation in which ring A adopts the chair form and (19) from the conformation in which ring A is a boat.[7a,23] Alternatively, subsequent to the formation of (18) (or 19), a photochemical or thermal equilibrium between (18) and (19) could be established *via* the diradical (22). We have not distinguished between these possibilities.

EXPERIMENTAL

For general instructions see Part VIII [4] and Part XI.[1]

Photolysis of 4-Acetoxysantonene (1b).—4-Acetoxysantonene [19] (1 g) in dry benzene (400 ml) was irradiated for 4 h under nitrogen. The benzene was removed and the residue chromatographed over silica (120 g) (elution with ether–light petroleum) to afford, in order, *4-methylsantonene* (1c) (147 mg) as rhombs (from ethyl acetate–light petroleum), m.p. 103—105°, $[\alpha]_D^{24}$ +102° (*c* 0.50) (Found: C, 74.4; H, 7.0. $C_{16}H_{18}O_3$ requires C, 74.4; H, 7.0%), $\nu_{max.}$ 1 765, 1 744, 1 676, and 1 644 cm^{-1}, $\lambda_{max.}$ 287 and 223 nm (log ε 4.28 and 4.08), c.d. 292 and 244 nm (Δε +9.14 and −10.4), τ 8.65 (10-Me), 8.46 (4β-Me), 8.43 (4α-Me), 8.09b (11-Me), 3.90 (d, *J* 10 Hz, 2-H), and 3.30 (d, *J* 10 Hz, 1-H); *4-methylphotosantonene* (6) (20 mg) as needles (from ethyl acetate–light petroleum), m.p. 140—142°, $[\alpha]_D^{24}$ +136° (*c* 0.10) (Found: C, 74.0; H, 7.1%), $\nu_{max.}$ 1 745, 1 715, 1 670, and 1 580 cm^{-1}, $\lambda_{max.}$ 255 nm (log ε 4.22), c.d. 330, 267, and 237 nm (Δε +3.76, +20.3, and −39.4), τ 9.02 (4α-Me), 8.73 (4β-Me), 8.52 (10-Me), 8.10b (11-Me), 3.71 (d, *J* 6 Hz, 2-H), and 2.34 (d, *J* 6 Hz, 1-H); and *11-methyl-3-oxoeudesma-1,4,6-trien-12,6-olactone* (5a) (60 mg) as needles (from ethyl acetate–light petroleum), m.p. 108—110°, $[\alpha]_D^{24}$ +68° (*c* 0.085) (Found: C, 74.7; H, 7.25%), $\nu_{max.}$ 1 800, 1 645, 1 610, and 1 592 cm^{-1}, $\lambda_{max.}$ 317 and 238 nm (log ε 4.01 and 4.06), c.d. 380, 356, 303, 251, and 227 nm (Δε +1.79, +4.70, +1.02, −4.70, and −9.65), τ 8.75 (10-Me), 8.63 (11-Me_2), 7.80 (4-Me), 3.75 (d, *J* 10 Hz, 2-H), and 3.20 (d, *J* 10 Hz, 1-H).

Photolysis of 4-Acetoxy-4βH-santonene (2b).—Similar photolysis of 4-acetoxy-4,βH-santonene [19] (2.0 g) in benzene (400 ml) for 3 h and chromatography of the residue afforded 4-methylsantonene (1c) (245 mg), m.p. and mixed m.p. 103—105°, $[\alpha]_D^{24}$ +100° (*c* 0.05), 4-methylphotosantonene (6) (40 mg), m.p. and mixed m.p. 140—142°, $[\alpha]_D^{24}$ +134° (*c* 0.1), the 11-methyl-1,4,6-triene (5a) (170 mg), m.p. and mixed m.p. 108—110°, $[\alpha]_D^{24}$ +67° (*c* 0.085), and *4-acetoxy-4βH-photosantonene* (8) (30 mg) as plates (from chloroform–light petroleum), m.p. 228—230°, $[\alpha]_D^{19}$ +200° (*c* 0.06) (Found: C, 67.3; H, 6.3. $C_{17}H_{18}O_5$ requires C, 67.5; H, 6.0%), $\nu_{max.}$ 1 750, 1 725, 1 675, and 1 580 cm^{-1}, $\lambda_{max.}$ 254 nm (log ε 4.15), c.d. 329, 268, and 236 nm (Δε +10.6, +22.5, and −55.1), τ 8.60 (10-Me), 8.78 (4-Me), 8.10b (11-Me), 7.90 (OAc), 3.58 (d, *J* 6 Hz, 2-H), and 2.40 (d, *J* 6 Hz, 1-H).

Photolyses in Methanol.—(*a*) *4-Acetoxysantonene* (250 mg) gave 4-methylsantonene (20 mg), 4-methylphotosantonene (20 mg), and *4-acetoxyphotosantonene* (7) (12 mg) as needles (ethyl acetate–light petroleum), m.p. 218—220°, $[\alpha]_D^{21}$ +60° (*c* 0.07) (Found: C, 67.1; H, 6.1%), $\nu_{max.}$ 1 750, 1 720, 1 675, and 1 580 cm^{-1}, $\lambda_{max.}$ 245—257 nm (plateau, log ε 4.2), c.d. 326, 266, and 234 nm (Δε −3.65, +36.0, and −44.0),

[22] T. B. H. McMurry and S. Mihashi, unpublished results.
[23] *Cf.* F. D. Lewis and R. W. Johnson, *J. Amer. Chem. Soc.*, 1972, **94**, 8914.

τ 8.50 (10-Me), 8.45 (4-Me), 8.12b (11-Me), 8.15 (OAc), 3.63 (d, *J* Hz, 2-H), and 2.44 (d, *J* 6 Hz, 1-H).

(*b*) 4-Acetoxy-4β*H*-santonene (250 mg) afforded 4-methylsantonene (30 mg), 4-methylphotosantonene (20 mg), and 4-acetoxy-4,β*H*-photosantonene (10 mg).

Sensitisation and Quenching Experiments.—(*a*) 4-Acetoxysantonene (1 g), acetophenone (5 g), and benzene (400 ml) were irradiated for 2 h. Removal of the solvent and chromatography over silica (150 g) [elution with light petroleum–ether (50 : 50)] afforded 4-methylsantonene (185 mg), 4-methylphotosantonene (35 mg), and the 11-methyl-1,4,6-triene (5a) (75 mg).

(*b*) 4-Acetoxy-4β*H*-santonene (1 g), acetophenone (5 g), and benzene (400 ml) were irradiated for 1 h. Removal of the solvent and chromatography of the residue afforded 4-methylsantonene (192 mg), 4-methylphotosantonene (30 mg), and the 11-methyl-1,4,6-triene (5a) (70 mg).

(*c*) 4-Acetoxysantonene (300 mg), ferrocene (1 g), and methanol (400 ml) were irradiated for 7 h. Chromatography over silica (60 g) gave starting material (95 mg) and 4-acetoxyphotosantonene (30 mg).

(*d*) 4-Acetoxy-4β*H*-santonene (300 mg), ferrocene (1 g), and benzene (40 ml) were irradiated for 17 h. Chromatography afforded 4-acetoxy-4β*H*-photosantonene (30 mg) and starting material (80 mg).

Photolysis of 4-*Methylsantonene* (1c).—(*a*) 4-Methylsantonene (30 mg) and benzene (35 ml) were irradiated for 6 h. The product was purified by preparative t.l.c. to give 4-methylphotosantonene (6) (20 mg).

(*b*) 4-Methylsantonene (30 mg) and acetophenone (1 g) in benzene (35 ml) were irradiated for 3 h to give 4-methylphotosantonene (6) (20 mg).

Photolysis of 4-*Acetoxyphotosantonene and its Epimer.*—(*a*) 4-Acetoxyphotosantonene (30 mg) in benzene (35 ml) was irradiated for 6 h. Only starting material (22 mg) was isolated.

(*b*) 4-Acetoxy-4β*H*-photosantonene (30 mg) in benzene (35 ml) was irradiated for 6 h to give starting material (20 mg).

Photolysis of 4-*Acetoxy*-1,2-*dihydrosantonene* (10a).—4-Acetoxy-1,2-dihydrosantonene (10a) (1 g), acetophenone (5 g), and benzene (400 ml) were irradiated for 2 h. Removal of the solvent and chromatography of the residue over silica (100 g) [elution with light petroleum–ether (50 : 50)] gave, in order, 1,2-*dihydro*-4-*methylsantonene* (10b) (265 mg) as needles (from ethyl acetate–light petroleum), m.p. 108—110°, $[\alpha]_D^{22}$ +34.3° (*c* 0.15) (Found: C, 73.4; H, 7.8. $C_{16}H_{20}O_3$ requires C, 73.8; H, 7.7%), $\nu_{max.}$ 1 750, 1 710, and 1 645 cm^{-1}, $\lambda_{max.}$ 287 nm (log ε 4.35), c.d. 284, 255, 223, and 209 nm (Δε +3.0, −1.5, +0.6, and +1.7), τ 8.93 (10-Me), 8.53 (4-Me_2), and 8.12b (11-Me); 11-*methyl*-3-*oxoeudesma*-4,6-*dien*-12,6-*olactone* (14) (90 mg) as rhombs (from ethyl acetate–light petroleum), m.p. 126—128°, $[\alpha]_D^{26}$ +347.5° (*c* 0.08) (Found: C, 73.6; H, 8.0%), $\nu_{max.}$ 1 790, 1 655, 1 630, and 1 580 cm^{-1}, $\lambda_{max.}$ 305 nm (log ε 4.4), c.d. 370, 359, 346, 300, 235, and 211 nm (Δε +1.9, +2.7, +3.6, +6.5, +1.5, and −6.8), τ 8.81 (10-Me), 8.62 (11-Me_2), and 7.92 (4-Me); 1,2-*dihydro*-6α-*methylsantonene* (12) (13 mg) as needles (from ethyl acetate–light petroleum), m.p. 160—162°, $[\alpha]_D^{22}$ −100° (*c* 0.07) (Found: C, 74.0; H, 7.8%), $\nu_{max.}$ 1 745, 1 680, and 1 660 cm^{-1}, $\lambda_{max.}$ 237 nm (log ε 4.3), c.d. 344, 333, 243, and 198 nm (Δε +1.98, +2.32, −6.89, and −12.9), τ 8.98 (10-Me), 8.32 (6-Me), 8.15b (11-Me), and 7.93 (4-Me); and a 50% mixture (n.m.r.) of 1,2-dihydro-6α- and -6β-methylsantonene [(12) and (13)] (52 mg) as needles (from ethyl acetate–light petroleum), m.p. 115—125°. The physical constants for the 6β-methyl isomer are estimated as $[\alpha]_D^{20}$ +112° (*c* 0.13) (Found: C, 73.8; H, 7.65%), $\nu_{max.}$ 1 750, 1 685, and 1 665 cm^{-1}, $\lambda_{max.}$ 238 nm (log ε 4.3), τ 8.58 (10-Me), 8.32 (6β-Me), 8.15b (11-Me), and 7.93 (4-Me).

Photolysis of 4-*Acetoxy*-1,2-*dihydro*-4β*H*-*santonene* (11a).—Irradiation of 4-acetoxy-1,2-dihydro-4β*H*-santonene (2.4 g) and acetophenone (10 g) in benzene (400 ml) afforded, after chromatography, 1,2-dihydro-4-methylsantonene (170 mg), 11-methyl-4,6-diene (14) (225 mg), 1,2-dihydro-6α-methylsantonene (28 mg), and the mixture of 6α- and 6β-methyl compounds (120 mg).

Hydrogenation of 4-*Methylsantonene.*—4-Methylsantonene (1c) (30 mg), palladium–charcoal (10%; 30 mg), and ethyl acetate (15 ml) were stirred in hydrogen for 30 min. The product, isolated after removal of catalyst and solvent, was purified by preparative t.l.c. to give 1,2-dihydro-4-methylsantonene (10b) (20 mg), m.p. and mixed m.p. 108—110°.

Hydrogenation of 11-*Methyl*-3-*oxoeudesma*-1,4,6-*trien*-12,6-*olactone* (5a).—Compound (5a) (30 mg), palladium–charcoal (10%; 30 mg), and ethyl acetate (15 ml) were stirred in hydrogen for 1 h. The product, purified by preparative t.l.c., was the 1,2-dihydro-derivative (14) (20 mg), m.p. and mixed m.p. 126—128°.

Photolysis of 6β-*Acetoxysantonene.*—6β-Acetoxysantonene (15) (100 mg) in dry benzene (40 ml) was irradiated for 2 h. Chromatography on silica (50 g) gave a mixture (8 mg) of 4-methylsantonene, 4-methylphotosantonene, and the 11-methyl-1,4,6-triene (5a), identified by t.l.c. and n.m.r. spectrum.

Photolysis of 6α-*Acetoxy*-1,2-*dihydrosantonene* (17).—6α-Acetoxy-1,2-dihydrosantonene (300 mg) in dry benzene (400 ml) was irradiated for 3 h. The products, isolated by chromatography, were 1,2-dihydro-4-methylsantonene (80 mg), the 11-methyl-4,6-diene (14) (30 mg), 1,2-dihydro-6α-methylsantonene (5 mg), and the mixture of 6-methyl isomers (30 mg).

4-[$^2H_3$]*Acetoxysantonene* (1d).—4-Hydroxysantonene (1a) (1 g) and pyridine (5 ml) were cooled in ice and [$^2H_3$]acetyl chloride (1.5 ml) was added dropwise. The mixture was set aside for 15 h at room temperature. Chromatography of the crude product over silica (60 g) afforded the [$^2H_3$]acetate (1d) (640 mg), $\nu_{max.}$ 1 760, 1 730, 1 690, and 1 655 cm^{-1}. The n.m.r. spectrum was identical with that of the undeuteriated acetate except that the CH_3·CO signal was missing.

4-[$^2H_3$]*Acetoxy*-4β*H*-*santonene* (2d).—4-Hydroxy-4β*H*-santonene (2a) (1 g) under similar conditions afforded the corresponding [$^2H_3$]acetate (2d) (730 mg), $\nu_{max.}$ 1 758, 1 730, 1 695, and 1 655 cm^{-1}.

Photolysis of the Trideuterioacetates.—4-[$^2H_3$]Acetoxysantonene (250 mg) in dry benzene (400 ml) was irradiated for 3 h. The products, isolated after chromatography, were 4-[$^2H_3$]methylsantonene and its 4-epimer (30 mg), (1e) and (2e) in the ratio 70 : 30 (n.m.r.), 4-[$^2H_3$]methylphotosantonene, and its 4-epimer (13 mg), and the 11α- and 11β-[$^2H_3$]-methyl-1,4,6-trienes (14 mg). These compounds had physical constants nearly identical with those of the corresponding [^{1}H]-compounds, but the ^{1}H n.m.r. spectra showed a decrease in the appropriate signals.

Similar irradiation of 4-[$^2H_3$]acetoxy-4β*H*-santonene for 2.5 h afforded 4-[$^2H_3$]methylsantonene and its 4-epimer (30 mg), 4-[$^2H_3$] methylphotosantonene and its 4-epimer (10 mg), the 11α- and 11β-[$^2H_3$]methyl-1,4,6-trienes (12 mg), and [$^2H_3$]acetoxy-4β*H*-photosantonene (5 mg).

Photolysis in the Presence of Chloroform.—(a) 4-*Acetoxysantonene*. 4-Acetoxysantonene (200 mg), benzene (30 ml), and chloroform (5 ml) were irradiated for 12 h. The products were chromatographed over silica (60 g) to give 11β-*trichloromethyl*-3-*oxoeudesma*-1,4,6-*trien*-12,6-*olactone* (5c) (25 mg) as needles (from chloroform–light petroleum), m.p. 185—186°, $[\alpha]_D^{22}$ +80° (*c* 0.055) (Found: C, 52.7; H, 4.3; Cl, 29.55. $C_{16}H_{15}Cl_3O_3$ requires C, 53.1; H, 4.15; Cl, 29.5%), $\nu_{max.}$ ($CHCl_3$) 1 800, 1 655, and 1 620 cm^{-1}, $\lambda_{max.}$ 313, 250, and 227 nm (log ε 4.09, 3.94, and 3.87), c.d. 354, 259, and 228 nm (Δε +6.15, −4.7, and −10.4), τ 8.66 (10-Me), 8.18 (11-Me), 7.75 (4-Me), 3.73 (d, *J* 10 Hz, 2-H), and 3.20 (d, *J* 10 Hz, 1-H); and the 11α-*isomer* (5b) (20 mg) as needles (from chloroform–light petroleum), m.p. 210—212°, $[\alpha]_D^{23}$ +60.0° (*c* 0.05) (Found: C, 53.0; H, 4.2; Cl, 29.0%), $\nu_{max.}$ ($CHCl_3$) 1 798, 1 652, and 1 618 cm^{-1}, $\lambda_{max.}$ 310, 248, and 225 nm (log ε 4.05, 4.00, and 4.00), c.d. 355, 257, 231, and 200 nm (Δε +2.96, +1.18, −6.82, and +10.6), τ 8.78 (10-Me), 8.18 (11-Me), 7.82 (4-Me), 3.73 (d, *J* 10 Hz, 2-H), and 3.20 (d, *J* 10 Hz, 1-H).

(b) 4-*Acetoxy*-4βH-*santonene*. 4-Acetoxy-4β*H*-santonene (250 mg), benzene (35 ml), and chloroform (5 ml) were irradiated for 7 h. The products, separated by chromatography, were the 11β-trichloromethyl-1,4,6-triene (25 mg), the 11α-isomer (20 mg), and 4-acetoxy-4β*H*-photosantonene (10 mg).

4-*Acetoxyphotosantonene* (7).—4-Hydroxyphotosantonene (30 mg), pyridine (0.15 ml), and acetic anhydride (0.35 ml) were heated at 90 °C for 2 h. Removal of solvent and thick-layer chromatography afforded 4-acetoxyphotosantonene (7) (16 mg) as needles, m.p. and mixed m.p. 218—220°.

4-*Acetoxy*-4βH-*photosantonene* (8).—Similar acetylation of 4-hydroxy-4β*H*-photosantonene (30 mg) afforded 4-acetoxy-4β*H*-photosantonene (8) (20 mg) as plates, m.p. and mixed m.p. 228—230°.

4-*Acetoxy*-1,2-*dihydrophotosantonene*.— 4-Acetoxyphotosantonene (7) (20 mg), palladium–charcoal (10%; 100 mg), and ethyl acetate were stirred in hydrogen for 30 min. The product, after removal of catalyst and solvent, was purified by preparative t.l.c. to give the *dihydro-derivative* (15 mg) as needles (from ethyl acetate–light petroleum), m.p. 210—212°, $[\alpha]_D^{20}$ −60.0° (*c* 0.05) (Found: C, 66.9; H, 6.6. $C_{17}H_{20}O_5$ requires C, 67.1; H, 6.6%), $\nu_{max.}$ ($CHCl_3$) 1 745 and 1 675 cm^{-1}, $\lambda_{max.}$ 256 nm (log ε 4.14), c.d. 310, 285, 265, and 225 nm (Δε +0.46, −0.82, +2.29, and −11.40), τ 8.65 (10-Me), 8.55 (4-Me), and 8.15 (11-Me and OAc).

4-*Acetoxy*-1,2-*dihydro*-4βH-*photosantonene*.—Similar re-reduction of 4-acetoxy-4β*H*-photosantonene (8) (30 mg) afforded the *dihydro-derivative* (20 mg) as needles (from ethyl acetate–light petroleum), m.p. 156—158°, $[\alpha]_D^{22}$ −28.3° (*c* 0.06) (Found: C, 67.4; H, 6.9%), $\nu_{max.}$ ($CHCl_3$) 1 745 and 1 670 cm^{-1}, $\lambda_{max.}$ 256 nm (log ε 4.07), c.d. 290, 261, and 233 nm (Δε −7.0, +8.9, and −15.1), τ 8.75 (4- and 10-Me), 8.12b (11-Me), and 7.92 (OAc).

1,2-*Dihydro*-4-*methylphotosantonene*.—Similar reduction of 4-methylphotosantonene (6) (30 mg) afforded the dihydro-derivative (20 mg) as an oil, M^+ 260, $[\alpha]_D^{19}$ + 18° (*c* 0.1), $\nu_{max.}$ ($CHCl_3$) 1 740 and 1 670 cm^{-1}, $\lambda_{max.}$ 260 nm (log ε 4.1), τ 8.94 (4α-Me), 8.82 (4β-Me), 8.62 (10-Me), and 8.15b (11-Me).

Photolysis of 1,2-*Dihydro*-4-*methylsantonene*.—1,2-Dihydro-4-methylsantonene (200 mg), acetophenone (2 g) and benzene (400 ml) were irradiated for 3 h. The products, isolated after chromatography on silica (70 g), were the β-*cyclopropane* (18) (65 mg), needles (from ethyl acetate–light petroleum), m.p. 164—166°, $[\alpha]_D^{21}$ −80° (*c* 0.06) (Found: C, 73.5; H, 7.7%), $\nu_{max.}$ ($CHCl_3$) 1 740 and 1 640 cm^{-1}, $\lambda_{max.}$ 258 nm (log ε 4.07), c.d. 292, 272, 249, and 209 nm (Δε −1.9, −4.1, −8.6, and +18.7), τ 8.82 (10-Me), 8.53 and 8.28 (4-Me_2) and 8.12b (11-Me), and the α-*cyclopropane* (19) (55 mg) needles (from ethyl acetate–light petroleum), m.p. 115—116°, $[\alpha]_D^{21}$ −53.3° (*c* 0.06) (Found: C, 73.7; H, 7.4%), $\nu_{max.}$ 1 740 and 1 650 cm^{-1}, $\lambda_{max.}$ 247 nm (log ε 4.11), c.d. 292, 263, 239, and 207 nm (Δε +2.58, −3.45, +5.15, and −16.78), τ 9.15 (4β-Me), 8.62 (10-Me), 8.48 (4α-Me), and 8.15b (11-Me). During separation of the isomers by preparative t.l.c., the α-cyclopropane compound decomposed to give the 6α-*isopropenyl compound* (20) as needles (from chloroform–light petroleum), m.p. 124—125°, $[\alpha]_D^{21}$ −80° (*c* 0.05) (Found: C, 73.8; H, 7.7%), $\nu_{max.}$ ($CHCl_3$) 1 745 and 1 670 cm^{-1}, $\lambda_{max.}$ 222 nm (log ε 4.2), c.d. 298 and 213 nm (Δε +1.8 and −9.9), τ 8.9 (10-Me), 8.30 (CH_3–C=C), 8.12b (11-Me), and 5.2 and 4.9 (C=CH_2).

6α-*Isopropenyl*-3-*oxo*-A,14-*dinor*-5β-*eudesm*-7(11)-*en*-12,6-*olactone* (20).—The α-cyclopropane compound (50 mg) and trifluoroacetic acid (0.5 ml) were set aside for 15 min in an n.m.r. tube. The reaction was monitored by n.m.r. Removal of the solvent afforded the isopropenyl compound (20) (40 mg), m.p. and mixed m.p. 124—125°.

6α-*Isopropyl*-3-*oxo*-A,14-*dinor*-5β-*eudesm*-7(11)-*en*-12,6-*olactone* (21).—Compound (20) (35 mg), palladium–charcoal (10%; 20 mg), and ethyl acetate (10 ml) were stirred in hydrogen for 35 min. The product, purified by preparative t.l.c., was the *isopropyl compound* (21) (22 mg), needles (from chloroform–light petroleum), m.p. 148—150°, $[\alpha]_D^{25}$ −15.4° (*c* 0.05) (Found: C, 73.3; H, 8.3. $C_{16}H_{22}O_3$ requires C, 73.25; H, 8.45%), $\nu_{max.}$ 1 745 and 1 685 cm^{-1}, $\lambda_{max.}$ 223 nm (log ε 4.04), c.d. 310 and 229 (Δε −0.96 and +13.15), τ 9.02 (10-Me), 9.32 and 8.95 (both d, *J* 8 Hz, CMe_2), and 8.16b (11-Me).

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