The Chemistry of Santonene. Part XI.[1] Products of Photolysis of 4-Hydroxysantonene and its 4-Epimer, their Structures, and Some Pyrolysis Studies [2]

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Photolysis of 4-hydroxysantonene [4-hydroxy-3-oxo-4α*H*-eudesma-1,5,7(11)-trien-12,6-olactone] (3) affords the A-nor-6-acetyl compound (4) (triplet state intermediate), 4-hydroxyphotosantonene {a spiro(bicyclo[3.1.0]-hexane)-6,1'-cyclopentane} (5) (singlet state) and a dilactone (6a) {a rearrangement product of (5) having a spiro(bicyclo[3.1.0]hexane)-6,1'-cyclopropane skeleton}. Photolysis of 4-hydroxy-4β*H*-santonene (7) affords the same A-nor-6-acetyl compound (4), 4-hydroxy-4β*H*-photosantonene (8), and a dilactone (9a). The structure of the A-nor-6-acetyl compound follows from its conversion [by hydrogenation to (13) followed by removal of the 6-acetyl group with base] into the epimeric lactones (14) and (15). The n.m.r. and c.d. spectra of the 3-alcohols derived from (14) and (15) support the suggested stereochemistry of (4). Photolysis of 1,2-dihydro-4-hydroxy-santonene and its 4-epimer in the presence of acetophenone gives the dihydro-A-nor-6-acetyl compound (13). The structures of the hydroxy-photocompounds follow from comparison of their spectra with those of the photo-santonenes and photopyrosantonins.

The dilactones are formed from the hydroxyphotosantonenes *via* hydroxy-keten intermediates. Pyrolysis of the dilactones leads to a 'Woodward-Hoffman forbidden rupture of the spiropentane skeleton, to give compounds containing a methylenecyclobutane system.

THE photolysis of steroidal 1,5-dien-3-ones (1) has been extensively studied by Jeger, Schaffner, and their co-workers.[3,4] They have shown that the products possess the general structure (2). We have shown that the photolyses of 4α*H*-pyrosantonin [5] and santonene [6] follow similar pathways. We wished to investigate the photolysis products from 4-hydroxysantonene and its epimer [7] as it was possible that the presence of the hydroxy-group

[1] Part X, A. Fröhlich, K. Ishikawa, and T. B. H. McMurry, *J.C.S. Perkin I*, 1975, 726.

[2] Preliminary communication, D. S. R. East, T. B. H. McMurry, and R. R. Talekar, *J.C.S. Chem. Comm.*, 1974, 450.

[3] B. Nann, O. Gravel, R. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 1973, **46**, 2473; B. Nann, H. Wehrli, K. Schaffner, and O. Jeger, *ibid.*, 1965, **48**, 1680.

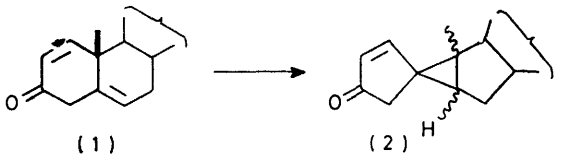
[4] S. Domb and K. Schaffner, *Helv. Chim. Acta*, 1970, **53**, 1765.

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

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

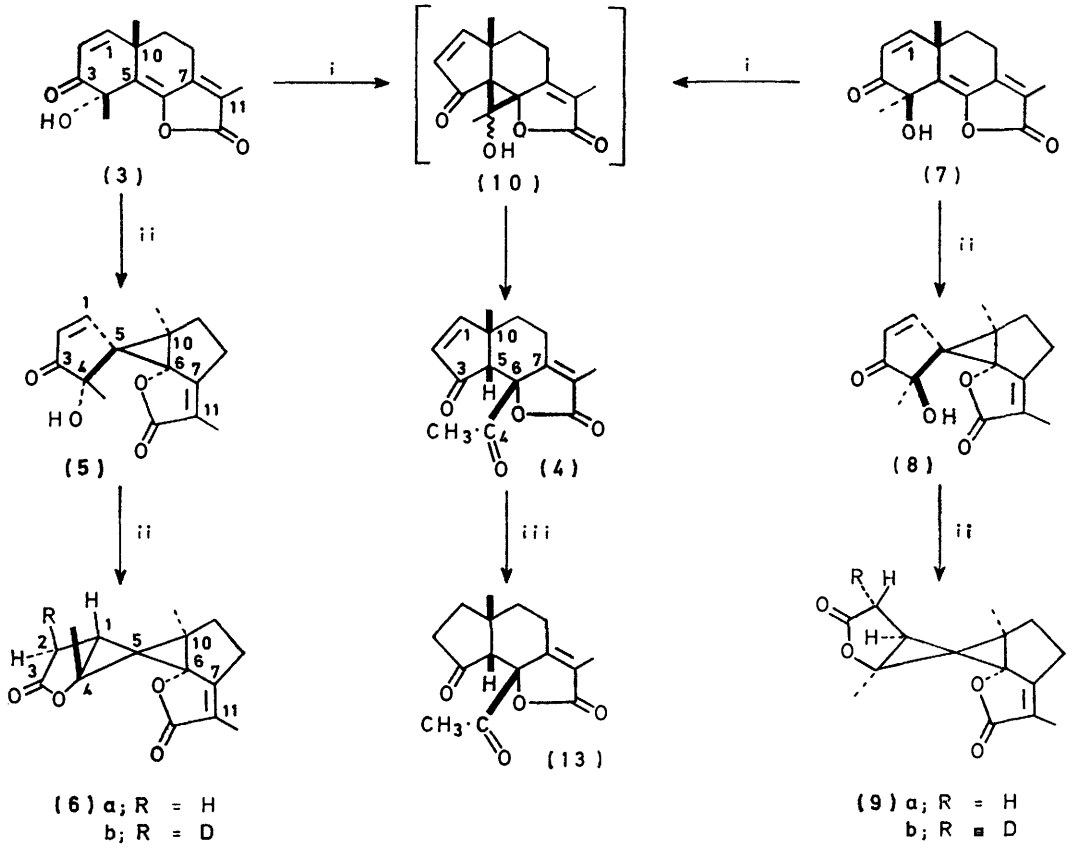
[7] T. B. H. McMurry and R. C. Mollan, *J. Chem. Soc.* (*C*), 1969, 1619.

might modify the reaction pathways. This possibility has been realised in two respects.



(1) (2)

First, photolysis of 4-hydroxysantonene (3) affords a *C*-acetyl compound (4) in addition to a 'normal' photolysis product, 4-hydroxyphotosantonene (5). Secondly, the photoproduct (5), under the conditions of which acts as a triplet quencher.[8] The acetyl compound arises by a 1,2-acyl shift (oxa-di-π-methane) to give the cyclopropanol (10), which rearranges to the *C*-acetyl compound. This reaction is apparently the only known example of a photochemically induced 1,2-acyl shift in a $\Delta^{1,5}$-3-one system (*cf.* ref. 4), though such shifts have been observed in other systems.[9] The structure of compound (4) was confirmed by spectral data. The n.m.r. spectrum suggests the presence of one tertiary methyl, a methyl on an αβ-unsaturated lactone unit, a methyl next to carbonyl, and two olefinic cyclopentenone protons. A one-proton singlet at τ 6.84 attributed to >CH·CO– is not observed when the photolysis is carried



(3) (10) (7) (5) (4) (8) (13)

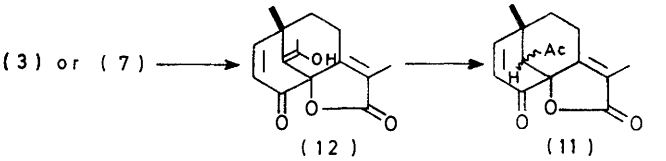
(6) a; R = H
b; R = D

(9) a; R = H
b; R = D

i, *via* triplet state; ii, *via* singlet state; iii, H_2–Pcl

the experiment, undergoes further transformation to give the dilactone (6a). Photolysis of the 4β-hydroxy-isomer (7) affords the same *C*-acetyl compound (4), 4-hydroxy-4β*H*-photosantonene (8), and a transformation product, (9a), of (8). Photolysis of the hydroxyphotosantonenes (5) and (8) affords the respective transformation products (6a) and (9a).

The *C*-acetyl compound (4) is the sole product when the photolysis is carried out in the presence of acetophenone or 2-acetylnaphthalene, and so must be formed from the triplet excited state. It is not formed when the photolysis is carried out in the presence of ferrocene, out in the presence of methan[^{2}H]ol. An i.r. peak at 1 710 cm^{-1} (characteristic of a cyclopentenone) and a



(3) or (7) (12) (11)

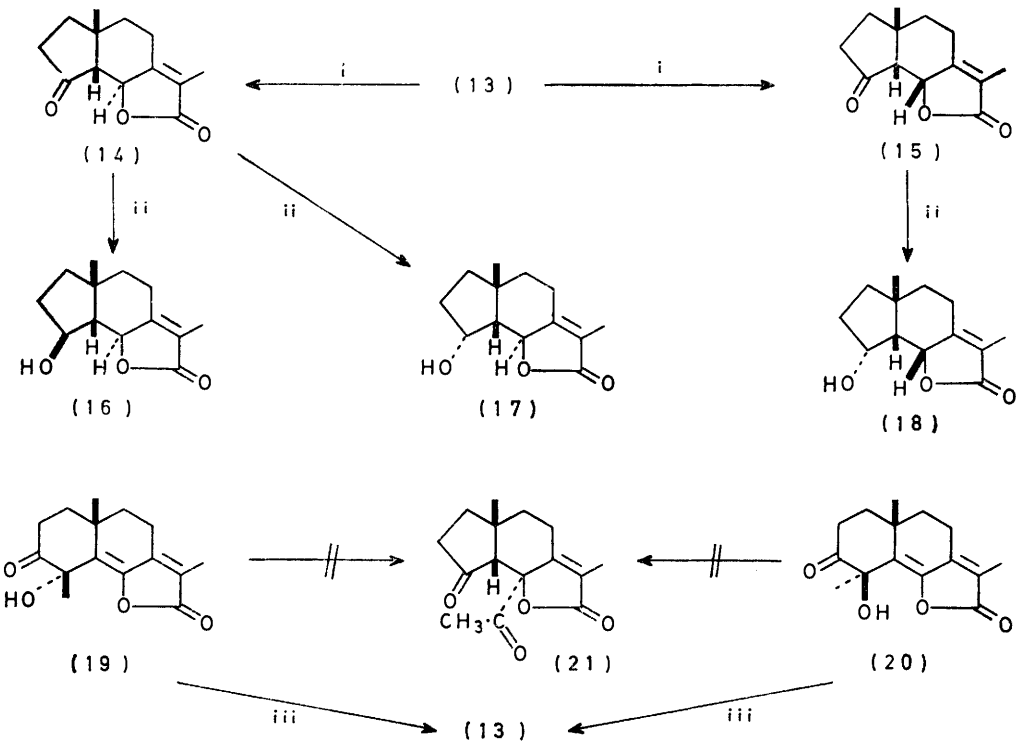
peak at 1 735 cm^{-1} in the spectrum of the dihydro-derivative (13) (see later) rules out the alternative structure (11) derived from either 4-hydroxysantonene by a 1,3-acyl shift *via* the enolic intermediate (12). This alternative is also excluded by the degradative experiments described later.

[8] R. E. Bozak, *Adv. Photochem.*, 1971, **8**, 227.
[9] T. Sazaki, K. Kanematsu, K. Hayakawa, and A. Kondo, *J. Org. Chem.*, 1973, **38**, 4100.

Hydrogenation of compound (4) affords a dihydro-derivative (13), the n.m.r. spectrum of which lacks the vinyl proton signals but otherwise parallels that of the precursor (4). The cyclopentanone carbonyl group gives rise to an i.r. peak at 1 735 cm^{-1}. When compound (13) is treated with dilute base, it is converted into a mixture of two isomeric compounds (14) and (15). The n.m.r. spectra of both lack the acetyl methyl signal. In its place there is a signal at τ 5.38 for (14) and at τ 5.15 for (15). The γ-protons in related $\alpha\beta$-unsaturated lactones [6,10] absorb in the same area. Both signals are doublets. This demonstrates that the *C*-acetyl group in (4) and (13) is attached to C-6,† and that there is a methine proton at C-5.

We now have to assign the stereochemistry at C-5 and -6 of (4) and its degradation products. The 5β-configuration (*cis*-AB-ring fusion) in (4) is suggested by a nuclear Overhauser effect (n.O.e.) experiment in which the 5-proton signal is increased in intensity by 16% (at 60 MHz) when the 10-methyl frequency is irradiated. We assume that this stable *cis*-ring fusion is preserved in all degradation products described, and can provide some evidence for this assumption.

The 6-acetyl group is also β-oriented. This follows from the position of the 10-methyl n.m.r. signal (τ 8.61). We now have a series of 6α- and β-substituted 7(11)-enolactones in which ring B is either five- or six-membered.[6,7,11,12] The n.m.r. spectra of the 6α-substituted compounds show the 10-methyl signal at higher field (generally τ 8.9—9.1) than those of the 6β-substituted compounds (generally τ 8.5—8.80). In the former case the angular methyl group lies in the shielding zone of the 7-enolactone group. We have confirmed that this method can be used to give the correct assignment of configuration at the 6-position by c.d. measurements on derivatives of the deacetyl compounds (14) and (15). Reduction of compound (14) with borohydride affords two hydroxy-compounds, (16) and (17), in approximately equal proportions, whereas similar reduction of (15) affords only one compound (18). The two deacetyl compounds (14) and (15) show 10-methyl signals at τ 8.98 and 8.65, respectively. The corresponding signals in the spectra of (16) and (17) occur at τ 8.92 and 9.08, whereas that in the spectrum of (18) occurs at τ 8.81. Application of our n.m.r. method predicts that (14), (16), and (17) have a 6α-proton, whereas (15) and (18) possess a 6β-proton.



i, OMe^-; ii, BH_4^-; iii, *hν*, sensitizer

The unsaturated lactone rule devised by Beecham [13] predicts that compounds (16) and (17) should have negative c.d. peaks around 250 nm, caused by the $n \longrightarrow \pi^*$ transition of the lactone carbonyl group, whereas (18) should show a similar but positive peak. This behaviour was in fact observed. We would expect to be able to apply Beecham's rule to compounds (14) and

† We employ the same numbering system for the photoproducts as we do for the hydroxysantonenes.

[10] T. B. H. McMurry and D. F. Rane, *J. Chem. Soc.* (*C*), 1970, 2012.

[11] D. S. R. East, T. B. H. McMurry, and R. C. Mollan, *J. Chem. Soc.* (*C*), 1970, 2008.

[12] T. B. H. McMurry and R. R. Talekar, following paper.

[13] A. F. Beecham, *Tetrahedron*, 1972, **28**, 5543.

(15), but in these cases, the ketone $n \longrightarrow \pi^*$ peak lies very close to the lactone peaks, and we would not like to make predictions based on the spectra. More recently, the sign of the $\pi \longrightarrow \pi^*$ band in unsaturated lactones has been correlated with their stereochemistry.[14] Application of this rule to our compounds predicts the same stereochemistry as Beecham's method. In an earlier paper [6] we assigned a peak at *ca.* 260 nm to an unsaturated lactone $\pi \longrightarrow \pi^*$ transition in dihydrophotosantonenes. This should have been assigned to a $n \longrightarrow \pi^*$ transition.

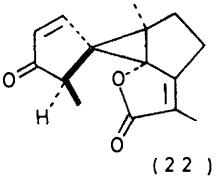
The borohydride reductions also support a 5β*H*-configuration in the various products derived from (4). Models suggest that if H-5 in (14) were α-oriented then reduction would take place only from the α-side, affording one product. We obtain two. If H-5 in (15) were α-oriented, two products might be expected. We obtain one. We assign the structures (16) and (17) as indicated, as the 6-proton signal in the n.m.r. spectrum of (17) lies at lower field than the corresponding signal in the spectra of the other isomers. This is to be expected as H-6 is deshielded by the 3α-hydroxy-group. Furthermore only in (17) does the 6-proton signal shift on changing solvent from chloroform to pyridine (τ 4.95 to 4.54).

Photolysis of 1,2-dihydro-4-hydroxysantonene (19) and its 4β-hydroxy-isomer (20) in the presence of acetophenone affords the dihydro-acetyl compound (13). This reaction must proceed *via* a triplet excited state, involving an oxa-di-π-methane (1,2-acyl shift) rearrangement. No products formed by a 1,3-acyl shift were found (*cf.* ref. 15). There are plenty of analogies for this reaction in the steroid field.[16,17] Earlier evidence suggested that whereas the dihydro-4α-hydroxy-isomer existed mainly in a conformation with ring A in a distorted 'chair' form, the preferred conformation of ring A in the dihydro-4β-hydroxy-isomer was a distorted 'boat'.[11,18] There is no sign that the 4β-isomer reacts through a boat conformation,† as this should give rise to a product (21) with the acetyl group α-oriented. It was recognised [11] that the compounds exist in an equilibrium mixture of various conformers. It may be that the chair conformation of ring A in (20) is the more reactive; alternatively, in the excited triplet state, the chair conformation may be the more stable, though it is not in the ground state.[20]

The two hydroxysantonenes (5) and (8) are formed from singlet excited states, and their further rearrangement to the dilactones (6a) and (9a) also proceeds *via* singlet excited states. This follows from quenching experiments. Our initial experiments employed penta-1,3-diene as quencher, but were unsuccessful, as the diene formed adducts with either reactants or products, which were not investigated further. However, in the presence of ferrocene [8] the only products from the photolyses of the hydroxysantonenes were the hydroxyphotosantonenes and their rearrangement products. The photochemical rearrangement of (8) to (9a) did not occur in the presence of acetophenone. Previous examples of the 'normal' rearrangement appeared to proceed *via* triplet excited states.[3-6]

The structures of the two hydroxyphotosantonenes are supported by their u.v. and i.r. spectra, which resemble the corresponding spectra of photosantonene (22).[6] In the n.m.r. spectra, the 4-methyl signal of (8) occurs at τ 8.84, considerably higher than the corresponding signal of (5) at τ 8.50. This can be explained if the 4-methyl group of (8) lies in the shielding zone of the unsaturated lactone. In the corresponding 4-hydroxyphotosantonene (5), change of solvent from chloroform to pyridine causes a considerable upfield shift of the 11-methyl signal, which can be explained if the hydroxy-group lies close to the 11-methyl group. This suggests that the stereochemistry of the 5-position is as shown, and is identical in both hydroxy-photoproducts (5) and (8).

Both hydroxyphotosantonenes, (5) and (8), afford dihydro-derivatives, (23) and (24) respectively. The 4-methyl signal for (23) is at higher field than that for (5), whereas the corresponding signal for (24) is very close to that for (8). This confirms the shielding of the 4α-methyl group by the unsaturated lactone in (24) and (8). Surprisingly, the hydroxyphotosantonenes, (5) and (8), are stable at 200 °C, whereas slow interconversion of the



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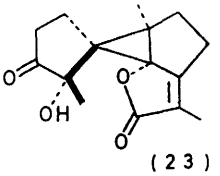

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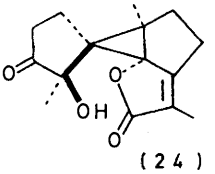


(24)

photosantonenes occurs at room temperature.[6] Similarly the hydroxy-dihydro-derivatives, (23) and (24), are stable in boiling toluene, again in contrast to the corresponding dihydrophotosantonenes.

The u.v. spectra of the dilactones (6a) and (9a) show

† Compounds related to (10) with α- and β-oriented cyclopropane rings have been isolated (or give rise to further products) from the photolysis of 4-acetoxy- [12] and 4-methoxy-santonenes.[19] Similar behaviour had already been found in the related steroid series.[16]

[14] I. Uchida and K. Kuriyama, *Tetrahedron Letters*, 1974, 3761.

[15] K. G. Hancock, J. T. Lau, and P. L. Wylie, *Tetrahedron Letters*, 1974, 4149.

[16] 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.

[17] K. Kojima, K. Sakai, and K. Tanabe, *Tetrahedron Letters*, 1969, 1925; H. Sato, K. Nakanishi, J. Hayashi, and Y. Nakadaira, *Tetrahedron*, 1973, **29**, 273.

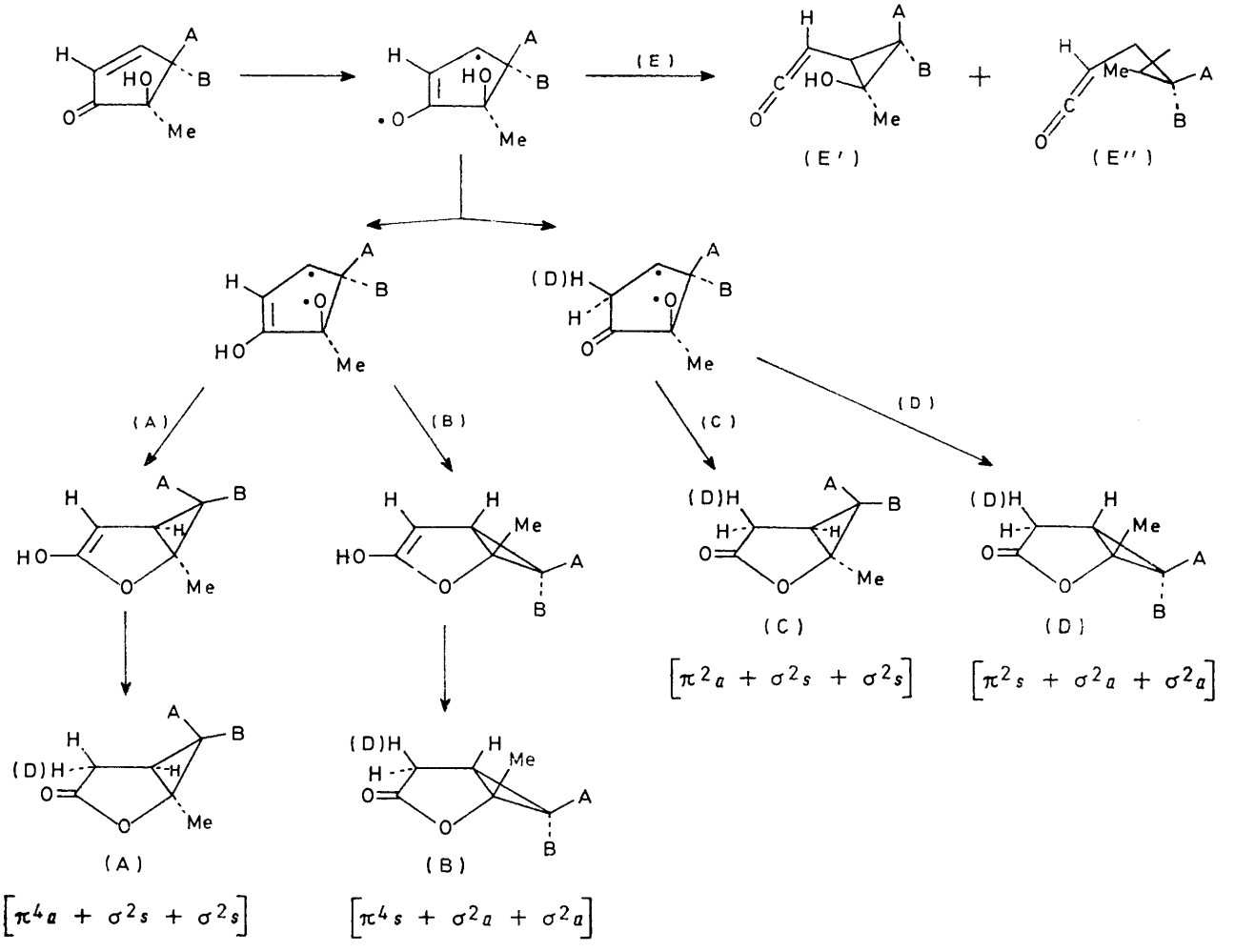
[18] L. Bartlett, P. M. Scopes, T. B. H. McMurry, and R. C. Mollan, *J. Chem. Soc.* (*C*), 1969, 1088.

[19] T. B. H. McMurry and S. Mihashi, unpublished results.

[20] F. D. Lewis and R. W. Johnston, *J. Amer. Chem. Soc.*, 1972, **94**, 8914.

peaks at 255 nm, characteristic of an αβ-unsaturated lactone or a cyclopentenone conjugated with a cyclopropane ring. The i.r. spectra confirm the presence of the unsaturated lactone (1 748 and 1 754 cm^{-1}, respectively) but the hydroxy- and cyclopentenone bands are missing in both cases. In their place, peaks around 1 775 cm^{-1} appear, characteristic of a saturated five-membered lactone carbonyl group. The presence of an unsaturated lactone system in both compounds is confirmed by the ^1H n.m.r. spectra, which show peaks at τ 8.12 assigned to the 11-methyl group; in addition, each shows two signal for compound (6a) derived from 4-hydroxyphotosantonene is at the normal position (τ 8.27). This confirms the stereochemistry shown for the dilactones.

We can identify the n.m.r. signals of the 2-methylene (AB) and 1-methine (X) protons in (6a) and (9a) by carrying out the photolysis of the hydroxyphotosantonenes in methan[^2H]ol. In the spectrum of (9a) the 2-methylene protons appear as the AB portion of an ABX system at τ 7.1 (J_{AB} 18, J_{AX} 6, J_{BX} 2 Hz) and the 1-proton as a double doublet at τ 7.95. In the monodeuteriated analogue (9b) the 2-proton signal is broad,



SCHEME 1

other angular methyl groups. The absence of the cyclopentenone vinyl protons and the hydroxy-group is also demonstrated. The ^{13}C n.m.r. spectrum of (9a) shows the presence of two lactone carbonyl groups (δ 166.7 and 175.0 p.p.m. from Me_4Si) and one C=C system.

These results suggest that the photorearrangement involves only the hydroxycyclopentenone ring, and lead to the structures (6a) and (9a). Compound (9a) derived from 4-hydroxy-4β*H*-photosantonene shows the 4-methyl n.m.r. signal at τ 8.44 as this group is in the shielding zone of the αβ-unsaturated lactone, whereas the corresponding as the proton is still coupled to the 1-methine proton and also to the 2-deuterium. The 1-methine signal has collapsed to a broad singlet. These n.m.r. spectral features bear resemblance to those of photoparthenin,[21] which has a similar lactone system, though the cyclopropyl proton in the latter resonates at higher field.

In the case of the photoproduct (6a), the 2-methylene signal appears as a doublet at τ 7.14 (J 4 Hz), indicating that the 2-protons must be accidentally equivalent, the

[21] J. Kagan, S. P. Singh, K. Warden, and D. A. Harrison, *Tetrahedron Letters*, 1971, 1849.

coupling constant being the average of J_{AX} and J_{BX}.[21,22] In accord with this, the 1-methine signal is a triplet (τ 7.90, J 4 Hz). The corresponding deuteriated derivative shows a 2-proton signal (1 H) as a doublet (J 3.5 Hz, coupled to deuterium), and the 1-methine signal becomes a broad singlet.

Models (which have to be flexible) suggest that the torsion angles between the 2α- and β-protons and the 1-methine proton are *ca.* 20 and 85° in (6a) and (9a), but there may be distortion in the former case because of repulsion between the two lactone rings. In both cases, the deuterium adds from the less hindered side to give (6b) and (9b), the torsion angle between the remaining 2-methylene proton and the methine proton being close to 90°.

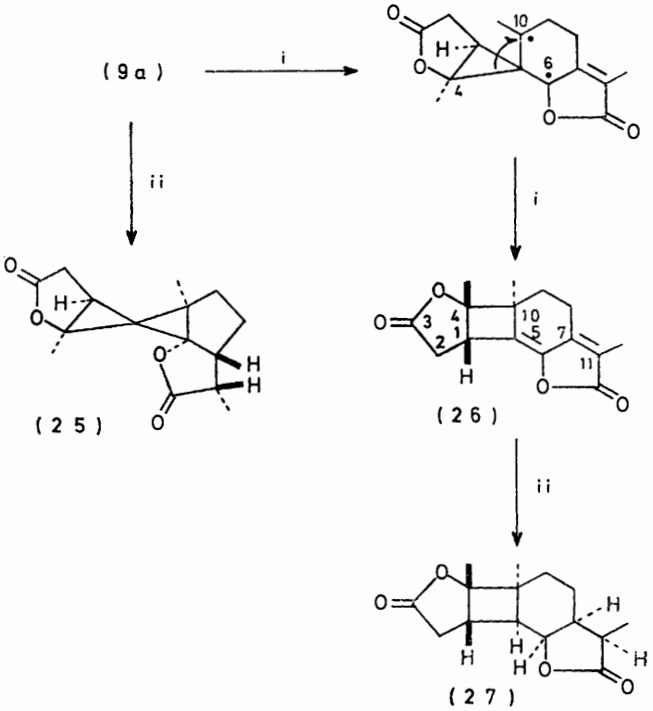
The two dilactones differ in one remarkable respect. Compound (9a), but not (6a), can be hydrogenated over platinum to give a dihydro-derivative (25). As this derivative is stable in refluxing methanol, it cannot contain a *trans*-fused lactone group.[5] Addition of hydrogen on the unhindered α-face of either lactone would lead to the extremely strained *trans*-fused lactones. Addition from the unhindered β-face in (9a) would lead to a *cis*-fused lactone. The β-face in (6a) is very hindered, as it is protected by the other lactone ring. This is apparently the first example to be reported where hydrogenation does not occur, not because of steric hindrance to absorption (on the α-face), but because the products are very unstable.

The hydroxycyclopentenone ⟶ cyclopropanelactone rearrangement implicit in the conversion of (5) into (6a), and of (8) into (9a) also occurs with some simple 5-hydroxycyclopentenones.[23] Examination of the mechanism suggests that there are four possible pathways (Scheme 1) for a concerted reaction. Of these, paths (A) and (D) are forbidden.*,[24] In addition paths (B) and (D) fail to explain the stereochemistry of the rearrangements, and path (C) fails to explain the stereochemistry of the deuterium addition. We are reduced* to considering pathways through a cyclopropanol ketene (path E).[25] Allowed reactions can lead to alcohols (E′) and (E″); however we cannot detect any product derived from cyclopropanols of type (E″). It may be that the hydroxy-group forms a hydrogen bond with the incipient keten carbonyl in the transition state leading to (E′), thus stabilising this route.

Pyrolysis of the β-dilactone (9a) (200 °C for 1 min) leads to a single isomer (26), which shows a peak in the u.v. at 291 nm, characteristic of the αβ,γδ-dienolactone. The i.r. spectrum shows the presence of a saturated five-membered lactone ring, as well as the unsaturated lactone. The ^{1}H N.m.r. spectrum shows the presence of three methyl groups, two angular (τ 8.69 and 8.45), and the third the 11-methyl group attached to a double bond (τ 8.09). There is a further 1-proton signal (broad doublet) at τ 6.40 (J 8 Hz) which we have identified as due to the 1-proton, coupled unequally to the 2-methylene protons.

Hydrogenation (over Pt) of compound (26) affords a tetrahydro-derivative (27), which possesses two saturated lactone rings. The 11-methyl signal in the n.m.r. becomes a doublet, but the other two methyl signals remain singlets. The doublet at τ 6.40 disappears but there is a triplet at τ 5.18 characteristic of >CHO·CO coupled equally to two other protons.

As spiropentanes are known to rearrange to methylenecyclobutanes,[26] the structures (26) and (27) seem logical for the pyrolysis product and its tetrahydro-derivative. The weakest bond in the β-dilactone is the 6,10-bond, and breaking it gives rise to a stable 6,10-diradical (Scheme 2). Migration of the 4,5-bond to the



SCHEME 2 i, heat at 200 °C for 1 min; ii, H_2–Pt

10-position leads to (26). Because of the constraint imposed by the rings fused to the spiropentane, the rearrangement cannot proceed *via* an allowed concerted pathway,[26] and probably involves diradicals.

Pyrolysis of the α-dilactone (6a) follows a more complex pathway. The first product formed (28) has a u.v. maximum at 221 nm, but it rearranges to a mixture of an isomer (29), $\lambda_{max.}$ 283 nm, and the enantiomer (30) of the pyrolysis product (26). This explains our observ-

* It is possible that the reaction can proceed *via* a $[_\pi 4_a + _\sigma 2_a + _\sigma 2_s]$ process, in which the O–H bond is used antarafacially. However models suggest that the transition state for this process is unlikely.

[22] L. M. Jackman and S. Sternhell, 'Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 1969, 2nd edn., p. 132.

[23] G. Gowda and T. B. H. McMurry, unpublished results.

[24] R. B. Woodward and R. Hoffman, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.

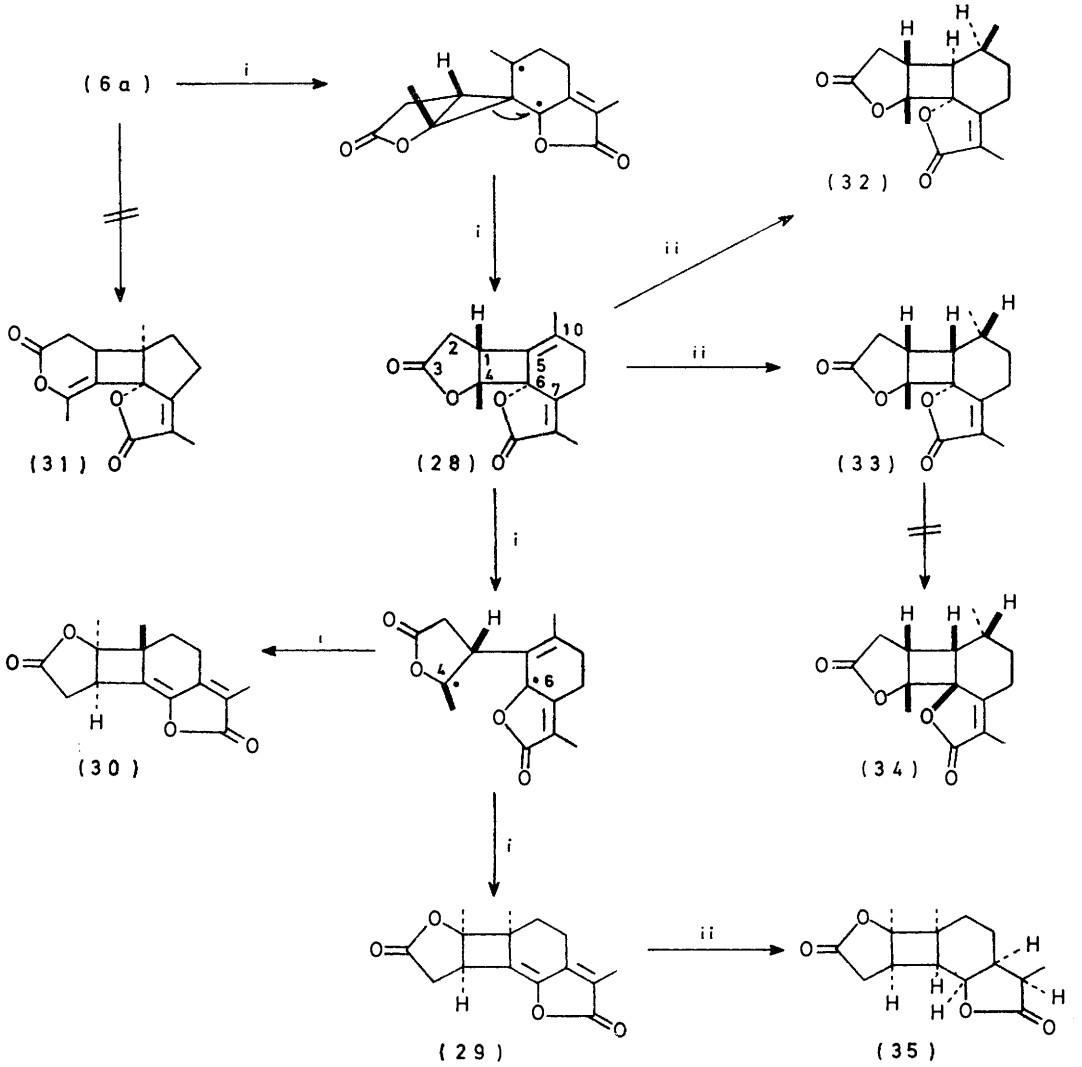
[25] W. C. Agosta and A. B. Smith, *J. Amer. Chem. Soc.*, 1971, **93**, 5513.

[26] J. J. Gajewski and L. T. Burka, *J. Amer. Chem. Soc.*, 1972, **94**, 8865.

ation that the mass spectra of both dilactones (6a) and (9a) are identical. Hydrogenation of (28) over palladium or platinum affords a mixture of two dihydro-derivatives (n.m.r.), which we have been unable to separate. Both seem to possess the 11-methyl group attached to a double bond (n.m.r.), and the presence of the chromophore is confirmed by the u.v. spectrum. Two other methyl signals occur at τ 8.43 and 8.61 (sum equivalent to one methyl) and the third methyl signal is a broad doublet at τ 9.08. There is no peak in the n.m.r. spectrum characteristic of –CHMe·O·CO–. This rules out structures of type (31) for the pyrolysis product itself.

The two products can be assigned structures based on the addition of hydrogen to the α- and the β-face of the 5,10-double bond. In the former case the product will have the structure (32); in the latter the initial product would be (33), with the very strained *trans*-bicyclo[4.2.0]-octane partial structure,[27,28] but (33) could rearrange to (34), *via* a 4,6-diradical. However, (33) is to be preferred as the 4-methyl signal is well shielded. Models show that of the three structures (32)—(34) only (34) possesses a 4-methyl group which does not lie over the αβ-unsaturated lactone. The pyrolysis product (29) affords a tetrahydro-derivative (35) on hydrogenation, the n.m.r. spectrum of which agrees with the suggested structure.

We can rationalise this pyrolysis pathway if we assume that once again the 6,10-bond breaks first. In this case, however, the 4,5-bond migrates to the 6- rather than the 10-position. The transition state for the latter migration would have two methyl groups eclipsed. Pyrolysis at higher temperatures causes cleavage of the 4,6-bond to give a stable diradical (Scheme 2). Migration of C-4 over the β-face of the cyclohexene ring affords (29), and over the α-face, involving inversion at the 10-position, affords (30). The two pyrolysis products (26) and (29) possess very similar n.m.r. and c.d. spectra.



SCHEME 3 i, heat; ii, H_2–Pt

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EXPERIMENTAL

For general experimental details, see Part VIII.[5] Specific rotations were measured for solutions in ethanol unless otherwise stated. The 11-methyl n.m.r. signal for most of these compounds can be easily recognised as a broad signal, the broadening being caused by a small homoallylic coupling with one or both of the 8-methylene protons. In some compounds this coupling can be resolved. We indicate this broadening by placing b after the τ value.

Photolysis of 4-Hydroxysantonene.—4-Hydroxysantonene (3) (2.4 g) in tetrahydrofuran (15 ml) and dry ether (400 ml) were irradiated for 6 h. The solvent was evaporated off and the residue chromatographed over silica (200 g) (elution with light petroleum–ether) to afford in order 4-hydroxyphotosantonene (5) (180 mg) as an oil, $[\alpha]_D^{25}$ +74° (*c* 0.3 in $CHCl_3$), M^+ 260, $\nu_{max.}$ 3 400, 1 755, 1 715, 1 678, and 1 575 cm^{-1}, u.v. plateau between 239 and 258 nm (log ε 3.85), c.d. (MeOH) 345, 268, 232, and 227 nm (Δε −0.59, +13.4, −15.5, and −17.7), τ 8.60 (10-Me), 8.50 (4β-Me), 8.18b (11-Me), 3.74 (d, *J* 6 Hz, 2-H), and 2.45 (d, *J* 6 Hz, 1-H); the *α-dilactone* (6a) (200 mg) as needles (from ethyl acetate–light petroleum), m.p. 193—194° $[\alpha]_D^{21}$ −68.7° (*c* 0.1) (Found: C, 68.7; H, 6.1. $C_{15}H_{16}O_4$ requires C, 69.2; H, 6.2%), $\nu_{max.}$ 1 775, 1 748, and 1 675 cm^{-1}, $\lambda_{max.}$ 257 nm (log ε 4.01), c.d. 277, 235, and 212 nm (Δε −2.2, −10.2, and +5.9), τ 8.68 (10-Me), 8.27 (4-Me), 8.12b (11-Me), 7.9 (t, *J* 4 Hz, 1-H), and 7.14 (d, *J* 4 Hz, 2-H_2); the *acetyl compound* (4) (400 mg) as needles (from ethyl acetate–light petroleum), m.p. 169—170°, $[\alpha]_D^{22}$ +254° (*c* 0.15) (Found: C, 69.4; H, 6.2%), $\nu_{max.}$ 1 750, 1 720, 1 710, 1 675, and 1 595 cm^{-1}, $\lambda_{max.}$ 225 nm (log ε 4.23), c.d. 338, 296, 242, and 212 nm (Δε −0.7, +9.3, +10.9, and −35.4), τ 8.61 (10-Me), 8.20b (11-Me), 7.93 (Ac), 6.84 (5-H), 3.97 (d, *J* 6 Hz, 2-H), and 2.66 (d, *J* 6 Hz, 1-H); and starting material (300 mg), m.p. and mixed m.p. 160—161°.

Photolysis of 4-*Hydroxy*-4βH-*santonene* (7).—4-Hydroxy-4β*H*-santonene (7) (2.25 g) in tetrahydrofuran (15 ml) and dry ether (400 ml) were irradiated for 4 h. The solvent was removed, and the residue chromatographed over silica (200 g) (elution with light petroleum–ether) to afford, in order, the β-*dilactone* (9a) (250 mg) as needles (from ethyl acetate–light petroleum), m.p. 133—134°, $[\alpha]_D^{20}$ −120° (*c* 0.1) (Found: C, 68.9; H, 6.0%), $\nu_{max.}$ 1 778, 1 750, and 1 675 cm^{-1}, $\lambda_{max.}$ 254 nm (log ε 4.14), c.d. 270, 238, and 212 nm (Δε −3.8, −12.1, and +10.35), τ 8.57 (10-Me), 8.44 (4-Me), 8.12b (11-Me), 7.95 (dd, *J* 6 and 2 Hz, 1-H), and 7.1 (m, 2-H_2); 4-*hydroxy*-4βH-*photosantonene* (8) (135 mg) as needles (from light petroleum–ethyl acetate), m.p. 210—212°, $[\alpha]_D^{24}$ +126.6° (*c* 0.15) (Found: C, 69.0; H, 6.1%), $\nu_{max.}$ 3 425, 1 755, 1 715, 1 675, and 1 575 cm^{-1}, $\lambda_{max.}$ 257 nm (log ε 4.12), c.d. 344, 267, and 236 nm (Δε +4.75, +10.50, and −3.40), τ 8.84 (4-Me), 8.59 (10-Me), 8.10b (11-Me), 3.70 (d, *J* 6 Hz, 2-H), and 2.34 (d, *J* 6 Hz, 1-H); and the acetyl compound (4) (475 mg), m.p. and mixed m.p. 169—170°.

Sensitisation and Quenching Experiments.—(*a*) 4-Hydroxysantonene (3) (250 mg), acetophenone (5 g), and benzene (200 ml) were irradiated for 4 h. Removal of the solvent and chromatography of the residue gave the acetyl compound (4) (113 mg), m.p. and mixed m.p. 169—170°.

(*b*) Similar treatment of 4-hydroxy-4β*H*-santonene (250 mg) afforded the β-dilactone (4 mg), m.p. and mixed m.p. 133—134°, and the acetyl compound (4) (105 mg), m.p. and mixed m.p. 169—170°.

(*c*) 4-Hydroxysantonene (3) (300 mg), ferrocene (1 g), tetrahydrofuran (5 ml), and ether (30 ml) were irradiated (200 W lamp) for 15 h. The products separated by column chromatography were 4-hydroxyphotosantonene (5) (15 mg) and the α-dilactone (6a) (40 mg), both identified by their i.r. spectra, m.p. and mixed m.p.

(*d*) Similar photolysis of 4-hydroxy-4β*H*-santonene (300 mg) afforded the β-dilactone (9a) (50 mg) and 4-hydroxy-4β*H*-photosantonene (10 mg).

The 1,2-*Dihydro-acetyl Compound* (13).—The acetyl compound (4) (300 mg), 10% palladium–charcoal (150 mg), and ethyl acetate (25 ml) were stirred in hydrogen until 1 mol. equiv. was absorbed (1 h). Removal of the catalyst and the solvent afforded the *dihydro-derivative* (13) (275 mg) as needles (from ethyl acetate–light petroleum), m.p. 131—132°, $[\alpha]_D^{22}$ +128° (*c* 0.15) (Found: C, 69.1; H, 7.1. $C_{15}H_{18}O_4$ requires C, 68.7; H, 6.9%), $\nu_{max.}$ 1 760, 1 735, 1 718, and 1 675 cm^{-1}, $\lambda_{max.}$ 223 nm (log ε 3.94), c.d. 296, 250, and 229 nm (Δε +5.9, +4.4, and −6.63), τ 8.81 (10-Me), 8.14b (11-Me), 7.87 (Ac), and 6.98 (5-H).

The Deacetyl Compounds (14) *and* (15).—Sodium methoxide (19 mg) in methanol (2 ml) was added to compound (13) (250 mg) in methanol (15 ml), under nitrogen, and the mixture was set aside at room temperature for 4 h. The solution was then acidified with acetic acid, and the solvent was removed *in vacuo*. The product was dissolved in ethyl acetate and washed with water. Chromatography of the mixture over silica afforded, in order, the 6αH-*compound* (14) (150 mg) as plates (from chloroform–light petroleum), m.p. 128—130°, $[\alpha]_D^{20}$ −19.2° (*c* 0.2) (Found: C, 70.8; H, 7.6. $C_{13}H_{16}O_3$ requires C, 70.9; H, 7.3%), $\nu_{max.}$ 1 750 and 1 680 cm^{-1}, $\lambda_{max.}$ 222 nm (log ε 3.97), c.d. 325, 314, 290, and 227 nm (Δε −0.15, −0.13, +0.13, and +8.13), τ 8.98 (10-Me), 8.18b (11-Me), 5.38 (d, *J* 8 Hz, 6-H); and the 6βH-*compound* (15) (30 mg) as rhombs (from ether–light petroleum), m.p. 107—109°, $[\alpha]_D^{23}$ −63.7° (*c* 0.075) (Found: C, 70.7; H, 7.3%), $\nu_{max.}$ 1 752 and 1 685 cm^{-1}, $\lambda_{max.}$ 223 nm (log ε 4.1), c.d. 298 and 223 nm (Δε +3.77 and −15.0), τ 8.65 (10-Me), 8.22b (11-Me), and 5.15 (d, *J* 8 Hz, 6-H).

Reductions with Borohydride.—(a) *The* 6αH-3-*ketone* (14). The ketone (14) (100 mg), sodium borohydride (15 mg), and methanol (15 ml) were set aside for 3 h. The mixture was acidified with dilute hydrochloric acid, and the solvent removed. The residue was extracted with ethyl acetate, and the product separated by preparative t.l.c. to give the 3α-*hydroxy-compound* (17) (40 mg) as rhombs (from ether–light petroleum), m.p. 82—84°, $[\alpha]_D^{24}$ +40.0° (*c* 0.08) (Found: C, 70.0; H, 8.4. $C_{13}H_{18}O_3$ requires C, 70.2; H, 8.2%), $\nu_{max.}$ 1 740 and 1 675 cm^{-1}, $\lambda_{max.}$ 223 nm (log ε 4.08) c.d. 248 and 219 nm (Δε −0.63 and +11.6), τ 9.08 (10-Me), 8.20b (11-Me), 4.95 (d, *J* 9 Hz, 6-H), and 5.58 (m, 3-H); and the 3β-*hydroxy-compound* (16) (35 mg) as needles (from chloroform–light petroleum), m.p. 128—130°, $[\alpha]_D^{24}$ +74.0° (*c* 0.1) (Found: C, 70.1; H, 8.5%), $\nu_{max.}$ 1 745 and 1 680 cm^{-1}, $\lambda_{max.}$ 222 nm (log ε 4.2), c.d. 250 and 220 nm (Δε −0.67 and +14.15), τ 8.92 (10-Me), 8.20b (11-Me), 5.47 (d, *J* 9 Hz, 6-H), and 5.58 (m, 3-H).

(b) *The* 6βH-3-*ketone*. The ketone (40 mg), sodium borohydride (7 mg), and methanol (15 ml) were set aside for 3 h at room temperature. The product was purified by preparative t.l.c. to afford the 3α-*hydroxy-compound* (18) (25 mg) as needles (from chloroform–light petroleum), m.p. 166—168°, $[\alpha]_D^{24}$ −180.0° (*c* 0.1) (Found: C, 69.9; H, 8.1%), $\nu_{max.}$ 1 740 and 1 675 cm^{-1}, $\lambda_{max.}$ 226 nm (log ε 4.12), c.d. 253 and 223 nm (Δε +0.54 and −12.8), τ 8.81 (10-Me), 8.23b (11-Me), 5.05 (d, *J* 8.0 Hz, 6-H), and 5.42 (m, 3-H).

Photolysis of 1,2-*Dihydro*-4-*hydroxysantonene* (19).—1,2-Dihydro-4-hydroxysantonene (19) (250 mg) and acetophenone (5 g) in dry benzene (250 ml) were irradiated for **6 h** to give the dihydro-acetyl compound (13) (120 mg), $[\alpha]_D^{25}$ +128°, m.p. and mixed m.p. 130—132°.

Photolysis of 1,2-*Dihydro*-4-*hydroxy*-4β*H*-*santonene* (20).—1,2-Dihydro-4-hydroxy-4β*H*-santonene (20) (250 mg) and acetophenone (5 g) in benzene (250 ml) were irradiated for 6 h to give the dihydro-acetyl compound, m.p. and mixed m.p. 130—132°.

Hydrogenation Experiments.—(a) 1,2-*Dihydro*-4-*hydroxyphotosantonene* (23). 4-Hydroxyphotosantonene (5) (25 mg) and palladium–charcoal (10%; 16 mg) in ethyl acetate (15 ml) were stirred in hydrogen until 1 mol. equiv. was absorbed. The product was the *dihydro-derivative* (23) (18 mg), needles (from ethyl acetate–light petroleum), m.p. 148—150°, $[\alpha]_D^{24}$ +26.2° (*c* 0.075) (Found: C, 68.7; H, 6.9%), $\nu_{max.}$ 3 420, 1 750, 1 720, and 1 670 cm^{-1}, $\lambda_{max.}$ 258 nm (log ε 3.92), c.d. 303, 257, and 220 nm (Δε +3.46, −0.99, and −10.4), τ 8.65 (10-Me and 4-Me) and 8.18b (11-Me).

(b) Similar hydrogenation of 4-hydroxy-4β*H*-photosantonene (8) (30 mg) afforded the *dihydro-derivative* (24) (20 mg) as needles (from ethyl acetate–light petroleum), m.p. 204—206°, $[\alpha]_D^{20}$ −208° (*c* 0.4) (Found: C, 69.1; H, 6.6%), $\nu_{max.}$ 3 500, 1 745, 1 720, and 1 670 cm^{-1}, $\lambda_{max.}$ 258 nm (log ε 4.12), c.d. 303, 262, and 230 nm (Δε −8.10, +5.28, and −11.5), τ 8.68 (10-Me), 8.86 (4-Me), and 8.14b (11-Me).

(c) The *dihydro*-β-*dilactone* (25). The β-dilactone (9a) (50 mg), platinum oxide (50 mg), and ethyl acetate (15 ml) were stirred in hydrogen until no more was absorbed. The product was the *dihydro-derivative* (25) (45 mg), needles (from dichloromethane–light petroleum), m.p. 180—182°, $[\alpha]_D^{24}$ +100.0° (*c* 0.05) (Found: C, 69.1; H, 6.65. $C_{15}H_{18}O_4$ requires C, 68.7; H, 6.9%), $\nu_{max.}$ 1 780 cm^{-1}, τ 8.71 (10-Me), 8.76 (d, *J* 10 Hz, 11-Me), and 8.30 (4-Me).

(d) Under similar conditions, the α-dilactone was not reduced.

Pyrolysis Experiments.—(a) *The pyro*-β-*dilactone* (26). The β-dilactone (9a) (50 mg) was heated in a thin-walled tube under nitrogen for 1 min at 200 °C. The single product (t.l.c.), isolated by preparative t.l.c., was the *pyro*-β-*dilactone* (26), needles (from chloroform–light petroleum), m.p. 288—290° (decomp.), $[\alpha]_D^{21}$ −141.7° (*c* 0.12) (Found: C, 69.2; H, 6.2%), $\nu_{max.}$ 1 775, 1 765, 1 710, and 1 635 cm^{-1}, $\lambda_{max.}$ 290 nm (log ε 4.19), c.d. 299 and 260 nm (Δε −10.5 and +9.9), τ 8.69 (10-Me), 8.45 (4-Me), 8.09b (11-Me), and 6.40 (m, 1-H).

(b) *The pyro*-α-*dilactones* (28)—(30). The α-dilactone (6a) (2 × 50 mg) was heated in a thin-walled tube under nitrogen at 200 °C for 5 min. T.l.c. showed three products which were separated by preparative t.l.c. (ethyl acetate–ether, 5 : 95) to afford the *pyro*-α-*dilactone* (30) (10 mg) as needles (from ethyl acetate–light petroleum), m.p. 278—280° (decomp), $[\alpha]_D^{20}$ +140.6° (*c* 0.06), c.d. 294 and 258 nm (Δε +11.5 and −9.82), i.r., u.v., and n.m.r. spectra identical with those of the pyro-β-dilactone (26); the *pyro*-α-*dilactone* (29) (45 mg), needles (from chloroform–light petroleum), m.p. 155—156°, $[\alpha]_D^{22}$ +175° (*c* 0.05) (Found: C, 69.0; H, 6.3%), $\nu_{max.}$ 1 775, 1 750, and 1 665 cm^{-1}, $\lambda_{max.}$ 283 nm (log ε 4.24), c.d. 293, 258, and 223 nm (Δε −6.0, +15.4, and +7.0), τ 8.63 (10-Me), 8.49 (4-Me), 8.12b (11-Me), and 6.18 (d, *J* 8 Hz, 1-H); and the *pyro*-α-*dilactone* (28) (30 mg), needles (from chloroform–light petroleum), m.p. 190—192°, $[\alpha]_D^{25}$ −30.5° (*c* 0.075) (Found: C, 69.1; H, 6.5%), $\nu_{max.}$ 1 778, 1 750, and 1 660 cm^{-1}, $\lambda_{max.}$ 221 nm (log ε 4.19), c.d. 242 and 216 nm (Δε −8.26 and +13.9), τ 8.48 (10-Me), 8.18 (4-Me), 8.12b (11-Me), and 6.62 (m, 1-H).

(c) Pyrolysis of the α-dilactone for shorter periods led to increased yields of the pyro-α-dilactone (28) and to less consumption of starting material.

(d) The pyro-α-dilactone (28) (10 mg) was heated in a thin-walled tube under nitrogen at 200 °C for 5 min. The products, separated by preparative t.l.c., were the pyro-α-dilactones (29) and (30) (4 and 3 mg).

Hydrogenation Experiments.—(a) *The tetrahydropyro*-β-*dilactone* (27). The pyro-β-dilactone (26) (30 mg) and platinum oxide (30 mg) in ethyl acetate (15 ml) were stirred in hydrogen until no more was absorbed. The product was purified to give the *tetrahydropyro*-β-*dilactone* (27) (25 mg), rhombs (from chloroform–light petroleum), m.p. 206—208°, $[\alpha]_D^{23}$ −42.5° (*c* 0.08) (Found: C, 67.8; H, 7.6. $C_{15}H_{20}O_4$ requires C, 68.2; H, 7.6%), $\nu_{max.}$ 1 760 cm^{-1}, τ 8.88 (10-Me), 8.65 (4-Me), 8.80 (d, *J* 8 Hz, 11-Me), and 5.18 (t, *J* 7 Hz, 6-H).

(b) *The tetrahydropyro*-α-*dilactone* (35). The pyro-α-dilactone (29) (30 mg) and platinum oxide (30 mg) in ethyl acetate (15 ml) were stirred in hydrogen until no more was absorbed. The product, separated by preparative t.l.c., was the *tetrahydropyro*-α-*dilactone* (35) (20 mg), rhombs (from chloroform–light petroleum), m.p. 160—162°, $[\alpha]_D^{20}$ −32.0° (*c* 0.125) (Found: C, 64.3; H, 7.3. $C_{15}H_{20}O_4,H_2O$ requires C, 63.8; H, 7.7%), $\nu_{max.}$ 1 770 cm^{-1}, τ 8.76 (10-Me), 8.80 (d, *J* 8 Hz, 11-Me), and 8.64 (4-Me), and 5.35 (t, *J* 5 Hz, 6-H).

(c) *The dihydropyro*-α-*dilactones* (32) *and* (33). The pyro-α-dilactone (28) (30 mg) and platinum oxide (30 mg) in ethyl acetate (15 ml) were stirred in hydrogen until no more was absorbed. The product, isolated by preparative t.l.c., was a mixture of dihydro-derivatives (20 mg), rhombs (from chloroform–light petroleum), m.p. 100—122° (Found: C, 68.7; H, 6.9%), $\nu_{max.}$ 1 770, 1 755, and 1 665 cm^{-1}, $\lambda_{max.}$ 231 nm (log ε 4.16), τ 9.08 (d, *J* 6 Hz, 10-Me), 8.61 [4-Me in (34)], 8.43 [4-Me in (33)], and 8.17b (11-Me).

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