Photolysis Products from 4α- and 4β-Hydroxysantonenes

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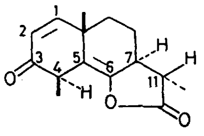
Summary Photolysis of 4β- and 4α-hydroxysantonenes gives in addition to the corresponding hydroxyphotosantonenes, a further photolysis product of the photosantonenes, and a common *C*-acetyl compound derived by a 1,2-shift of the 3-carbonyl group.



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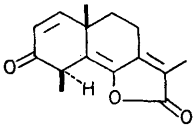

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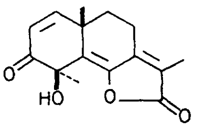

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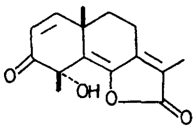

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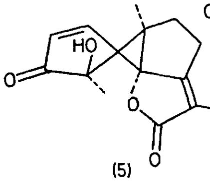

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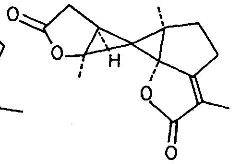

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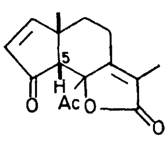

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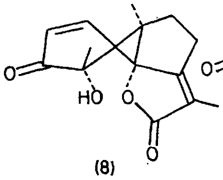

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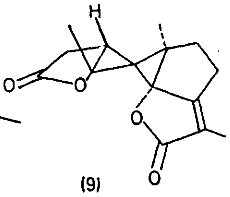

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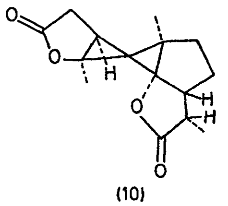

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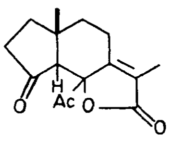

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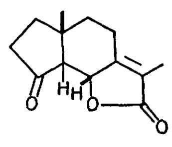

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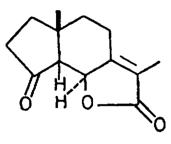

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We have recently discussed the structures of the photolysis products of 4α-(*H*)-pyrosantonin (**1**)[1] and santonene (**2**).[2] The compounds formed are those expected from 1,5-dien-3-one systems.[3] We now report on the photolysis of the 4-hydroxysantonenes (**3**) and (**4**). The 4β-hydroxy isomer (**3**) gives the hydroxyphotosantonene (**5**), but also a further photolysis product (**6**), and a *C*-acetyl derivative (**7**). The 4α-hydroxy isomer (**4**) gives the hydroxyphotosantonene (**8**), a further photolysis product (**9**), and the same *C*-acetyl derivative (**7**).

The structure of the hydroxyphotosantonenes (**5**) and (**8**)† follows from their u.v., i.r., and n.m.r. spectra. In particular, the 4-methyl signal of (**5**) is at τ 8·84, shielded by the 7(11)-double bond.[2] The 4-methyl signal in (**8**) is at the normal position (τ 8·5), but changing solvent from deuteriochloroform to pyridine causes a shielding of the 11-methyl, as expected if pyridine complexes with the 4α-hydroxy group.

The two further photolysis products (**6**) and (**9**)† possess very similar spectral properties. Their u.v. spectra suggest that the chromophore containing an αβ-unsaturated lactone conjugated to a cyclopropane ring is still present. They lack the cyclopentenone chromophore, and in its place they show an i.r. peak characteristic of a pentanolide. The ^{13}C n.m.r. spectrum of (**6**) shows the presence of two lactone carbonyls and only one double bond. The ^{1}H n.m.r. spectrum indicates the presence of three methyl groups. In (**6**), the 4-methyl signal (τ 8·45) is shielded by the αβ-unsaturated lactone system, and lies at high field, while the 10-methyl is deshielded by the saturated lactone (τ 8·57).

We can identify the signals of the 2-methylene (AB) and 1-methine (X) protons by carrying out the photolysis of (**5**) and (**8**) in [$^{2}H_{1}$]-methanol. In (**6**) the 2-methylene protons

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† For convenience, the numbering of these compounds follows that of the parent santonene.

appear as a double doublet at τ 7·1 (J_{AB} 18 Hz, J_{AX} 6 Hz, J_{BX} 2 Hz) and the 1-methine as a double doublet at τ 7·95. In the deuteriated protoproduct, the 2-proton appears as a triplet. The corresponding 2-methylene signal in (**9**) appears as a doublet at τ 7·14 (J 4 Hz), indicating that the 2-protons must be accidentally equivalent. In this case,[4] the coupling constant is the average of J_{AX} and J_{BX}. Deuteriation causes a collapse of the doublet to half its size (J 3·5 Hz).

Of the two isomers, (**6**) and (**9**), only (**6**) can be hydrogenated (Pt). The product (**10**) is not labile in boiling methanol and hence the new lactone ring is not *trans*-fused to the cyclopentane ring.[1] *cis*-Ring fusion can only be formed if the β-face is absorbed on the catalyst surface. Models show that adsorption on the β-face is possible in (**6**), but not in (**9**). The addition of hydrogen, following absorption on the unhindered α face in (**6**) or (**9**), must be impossible because the products would be extremely strained *trans*-fused lactones. We are aware of no other case where hydrogenation is inhibited, not because of steric hindrance to adsorption, but because the products formed would be very unstable.

The photoproduct (**7**) common to both 4β- and 4α-hydroxy santonenes is the sole product when acetophenone is used as sensitiser. It contains an $\alpha\beta$-unsaturated pentenone system (u.v., i.r., and n.m.r. spectra) an $\alpha\beta$-unsaturated lactone (u.v. and i.r. spectra) and an acetyl group. The singlet at τ 6·88 (5H) rules out the alternative structure with the acetyl group at the 5-position. Hydrogenation gives a dihydro derivative (**11**) which can also be obtained by photolysis of dihydro 4α- and 4β-hydroxy santonenes in the presence of acetophenone. Mild basic hydrolysis of (**11**) gives the deacetyl compounds (**12**) and (**13**), whose stereochemistry is assigned on the basis of their n.m.r. spectra[2,6] and also of the c.d. spectra[7] of the borohydride reduction products. This is the first example of a light-induced 1,2-acyl shift in a 1,5-dien-3-one system [*cf.* ref. 3(c)].

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

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

[3] (a) B. Nann, O. Gravel, R. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 1963, **46**, 2473; (b) B. Nann, H. Wehrli, K. Schaffner, and O. Jeger, *ibid.*, 1965, **48**, 1680; (c) S. Domb and K. Schaffner, *ibid.*, 1970, **53**, 1765.

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

[5] K. N. Houk, D. J. Northington, and R. E. Duke, *J. Amer. Chem. Soc.*, 1972, **94**, 6233; *cf.* D. I. Schuster, G. R. Underwood, and T. P. Knudson, *J. Amer. Chem. Soc.*, 1971, **93**, 4304 and references therein.

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

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