Photochemical Transformations. X. Irradiation of a Fused Ring Homoannular Dienone Related to ψ-Santonin[1,2]

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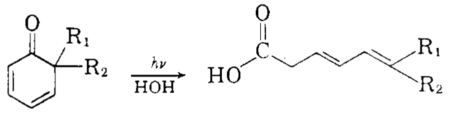
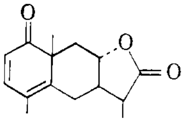
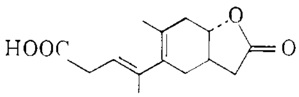
Received November 9, 1961

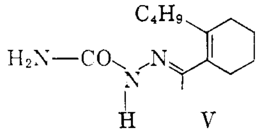
Barton and Quinkert[3] have found that on irradiation with ultraviolet light in the presence of a protic solvent *ortho*-type cyclohexadienones (I) undergo ring fission and yield β,γ:δ,ε-dienoic acid derivatives (II). In their study, these investigators studied a wide variety of monocyclic *ortho*-dienones and it was of interest to extend this interesting reaction to a fused ring system. In earlier work in this laboratory, the highly substituted fused ring *ortho*-dienone, $\Delta^{2,4}$-1-oxosantadiene-8α,12-olide (III),[4] derived from the sesquiterpene ψ-santonin, had been found to show instability toward light. The photochemical induced change in this fused ring *ortho*-dienone has now been studied.


I II

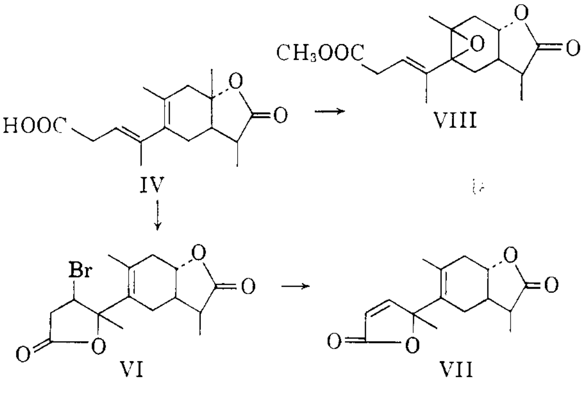
Irradiation of III in moist ether yielded an acid mixture from which a solid acid could be obtained in 50% yield. The remaining acidic oil which possessed spectral properties similar to those of the solid acid could not be induced to crystallize and apparently is a mixture of *cis* and *trans* isomers. Based upon the work of Barton and Quinkert,[3] the acid should possess the structure IV. The infrared spectrum of the solid product possessed bands at 1770 cm.$^{-1}$ and 1710 cm.$^{-1}$, characteristic of a γ-lactone and a carboxyl group. In the ultraviolet spectrum, there was no maximum down to 205 mμ, and at this wave length, the extinction coefficient was only 5900. Accepting the expected β,γ:δ,ε-dienic acid structure IV for the irradiation product, the absence of any absorption characteristic of a conjugated diene must be due to the almost complete inhibition of coplanarity of the two olefinic groupings. Examination of models of the expected structure IV clearly showed that the steric hindrance between the ring and the side chain was so severe that the olefinic bonds orient preferentially at right angles to one another. That such a steric inhibition to coplanarity of two unsaturated groups can effectively destroy conjugation has been found by Turner and Voitle,[5] who reported that the ultraviolet spectrum of the semicarbazone of 1-acetyl-2-butyl-Δ^1-cyclohexene (V), a compound of almost exact steric arrangements as IV, was identical with the spectrum of the semicarbazone of the related saturated ketone.


III


IV


V

To substantiate further structure IV for the irradiation product, the acid was hydrogenated and the oily tetrahydro derivative possessed an ultraviolet spectrum (ϵ_{210} 400) characteristic of a saturated compound. When treated with bromine in sodium bicarbonate solution, the acid IV readily formed a bromolactone (VI). The bromolactone possessed an intense single sharp band at 1775 cm.$^{-1}$, indicating the presence of only γ-lactones; thus, one end of the double bond which reacted must be γ to the carboxyl group. Upon dehydrobromination with collidine, the bromolactone yielded an α,β-unsaturated lactone VII (ν_{max} 1775, 1750 cm.$^{-1}$). The ultraviolet spectrum of VII showed an intense end absorption, and when the absorption of the bromolactone was subtracted from the spectrum of VII (to correct for the absorption of the other double bond), a maximum at 205 mμ (ε 8700) was found. The position of this maximum is characteristic of an α,β-unsaturated butenolide possessing no α or β substituents.[6]


IV VIII VI VII

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[1] For Paper IX, see W. G. Dauben and P. Baumann, *Tetrahedron Letters*, **16**, 565 (1961).

[2] This work was supported, in part, by Grant No. A-709, U. S. Public Health Service.

[3] D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960).

[4] W. G. Dauben, P. D. Hance, and W. K. Hayes, *J. Am. Chem. Soc.*, **77**, 4609 (1955).

[5] R. B. Turner and D. M. Voitle, *J. Am. Chem. Soc.*, **73**, 1403 (1951).

[6] A. T. Nielsen, *J. Org. Chem.*, **22**, 1539 (1957).

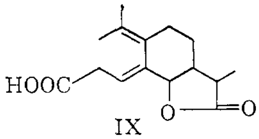
This formation of an α,β-unsaturated lactone from the bromolactone shows that the bromine in the latter material was present on the β-carbon and that a β,γ-olefinic bond was present in the original photoproduct IV.

Evidence with regard to the degree of substitution of the two olefinic linkages was obtained when the photo-product ester was converted into a monoepoxide (VIII) with perbenzoic acid. The epoxide possessed an end absorption at 205 mμ of only 2600, a value which is characteristic of a trisubstituted linkage. In comparison, the bromolactone showed an end absorption at 205 mμ of 5200, showing that a different double bond had reacted and that the remaining double bond (that which epoxidized) was most likely tetrasubstituted.

The NMR spectra of IV, VI, and VII clearly established these general conclusions. The spectrum of IV showed a doublet at 66 and 75 c.p.s.[7] due to the methyl group on the lactone ring fused to the cyclohexene ring. The peak is split by the α-hydrogen on the lactone ring. The two methyl groups on double bonds absorbed at 97 and 106 c.p.s. Between 106 and 151 c.p.s. there was general unidentified absorption which can be attributed to the methylene and methine hydrogens on the cyclohexene ring. A doublet at 168 and 175 c.p.s. was appropriate for the hydrogens on the methylene group between the carboxyl group and the carbon-carbon double bond in the sidechain. The γ-hydrogen on the lactone ring absorbed at 246 c.p.s. A triplet centered at 324 c.p.s. (and equal to the absorption of one hydrogen) was assigned to the sole vinyl hydrogen in the structure, the triplet splitting being due to the adjacent methylene group.

The NMR spectra of VI and VII were practically identical with that of IV. In the bromolactone, the main difference was noted by the loss of the vinyl proton band at 324 c.p.s. and the appearance of a new band at 290 c.p.s. due to the hydrogen on the carbon atom also carrying a bromine atom. In the unsaturated lactone, again the vinyl proton absorption was different, absorption being found at 360 c.p.s. and 458 c.p.s. due to the hydrogen on the α and β carbon atoms of the unsaturated butenolide.

The NMR spectra of IV, VI, and VII were closely related to the spectrum of photosantonic acid (IX),[8] showing the expected close similarity of the structures.



IX

Experimental[9]

Irradiation of Δ^{2,4}-1-Oxosantadiene-8α,12-olide (III).—A solution of 2.0 g. (8.14 mmoles) of III in 700 ml. of ether (previously saturated with water) was irradiated with a G. E. AH-6 mercury lamp for 30 min. The solution was concentrated to a small volume and extracted with 5% sodium bicarbonate. The alkaline extract was acidified, extracted with ether, and the ethereal solution dried. The solvent was evaporated and the oily residue crystallized from ether–petroleum ether, yield 1.0 g. (47%), m.p. 97–98°, $[\alpha]^{25}\text{D}$ +80.6°, ν_{max} 1770 cm.$^{-1}$ (γ-lactone), 1710 cm.$^{-1}$ (carboxyl group), $\epsilon_{205}^{C_2H_5OH}$ 5900, $\epsilon_{210}^{C_2H_5OH}$ 4650.

Anal. Calcd. for $C_{15}H_{20}O_4$ (264.31): C, 68.16; H, 7.63. Found: C, 67.97; H, 7.51.

The methyl ester was prepared by allowing the "photoacid" (IV) to react with an ethereal solution of diazomethane. The product was crystallized from ether-hexane, m.p. 89–90°, ν_{max} 1775 cm.$^{-1}$ (γ-lactone), 1715 cm.$^{-1}$ (ester), $\epsilon_{205}^{C_2H_5OH}$ 6900, $\epsilon_{210}^{C_2H_5OH}$ 5400. The same ester could be prepared by irradiation of III in methanol.

Anal. Calcd. for $C_{16}H_{22}O_4$ (278.34): C, 69.04; H, 7.97. Found: C, 68.79; H, 7.85.

Bromolactone (VI).—To a chilled solution of 93 mg. (0.36 mmole) of IV in 15 ml. of 5% sodium bicarbonate solution, there was added, slowly with stirring, 25 ml. of bromine water (1.5 g. of bromine in 100 ml. of water). The bromolactone precipitated immediately and was filtered, washed with water, and dried in the dark. The crude material (70 mg.) was recrystallized from benzene–petroleum ether, yield, 40 mg. (31%), m.p. 149–150° (dec.), ν_{max} 1775 cm.$^{-1}$ (γ-lactone), $\epsilon_{205}^{C_2H_5OH}$ 5200, $\epsilon_{210}^{C_2H_5OH}$ 330.0

Anal. Calcd. for $C_{15}H_{19}O_4Br$ (343.22): C, 52.49; H, 5.58; Br, 23.39. Found: C, 52.72; H, 5.69; Br, 23.02.

Unsaturated Lactone (VII).—A solution of bromolactone VI (100 mg., 0.29 mmole) in 2 ml. of toluene and 4 ml. of 2,4,6-collidine was heated at 130–135° for 90 min. A precipitate of collidine hydrobromide formed immediately. The reaction mixture was cooled, poured into water, and extracted with chloroform. The chloroform solution was washed with dilute hydrochloric acid, sodium bicarbonate solution, and dried. The solvent was evaporated and the residual oil molecularly distilled at 0.5 mm., yield, 60 mg. (79%), ν_{max} 1775 cm.$^{-1}$ (γ-lactone), 1750 cm.$^{-1}$ (α,β-unsaturated butenolide). The ultraviolet spectrum showed no maximum ($\epsilon_{205}^{C_2H_5OH}$ 14,300, $\epsilon_{210}^{C_2H_5OH}$ 11,300) but when the absorption of the bromolactone VI was subtracted at maximum at 206 mμ (ε 8700) was obtained.

Anal. Calcd. for $C_{15}H_{18}O_4$ (262.29): C, 68.68; H, 6.92. Found: C, 68.60; H, 6.75.

Methyl Ester Epoxide (VIII).—The methyl ester of "photo acid" IV (0.200 g., 0.7 mmole) was allowed to react with an excess of perbenzoic acid in chloroform solution at 0° for 68 hr. One mole equiv. of perbenzoic acid was found to react. The chloroform solution was extracted with 10% potassium carbonate, washed with salt solution, and dried. The solvent was removed and the residual oil chromatographed on silica-gel. The infrared spectrum has bands at 1775 cm.$^{-1}$ (γ-lactone) and 1730 cm.$^{-1}$ (ester). The ultraviolet spectrum showed $\epsilon_{205}^{C_2H_5OH}$ 2600, $\epsilon_{210}^{C_2H_5OH}$ 1600.

Anal. Calcd. for $C_{16}H_{22}O_5$ (294.34): C, 65.29; H, 7.53. Found: C, 64.20; H, 7.35.

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[7] The spectra were taken in $CDCl_3$ and at 60 Mc.; the units are relative to tetramethylsilane.

[8] E. E. Van Tamelen, S. H. Levin, G. Brenner, J. Wolinsky, nd P. E. Aldrich, *J. Am. Chem. Soc.*, **81**, 1666 (1959).

[9] Analyses were performed by the Microanalytical Laboratory. Department of Chemistry, University of California, Berkeley, Calif.