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# PHOTOCHEMICAL REARRANGEMENTS OF CROSS-CONJUGATED CYCLOHEXADIENONES. FORMATION OF SPIRO [4.5] DEC-3-EN-2-ONES.

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IT is well established that 4-methylcyclohexadienones of the santonin type undergo photochemical transformation in aqueous acetic acid to perhydroazulene derivatives of the isophotosantonic lactone type.[1] The photochemical properties of cyclohexadienones which are unsubstituted at $C_4$ have also been studied, but the rearrangement products have not been well characterized.[2] We wish to report that dienones of this type have been found to undergo photochemical transformation in acidic media to spiro [4.5] dec-3-en-2-one derivatives. Irradiation[3] of 4aβ,8α-dimethyl-5,6,7,8-tetrahydro-2(4aH)-naphthalenone (I)[4] in 45% acetic acid at 20° gave the spiro ketone II, m.p. 98-99°, in 16% yield. When

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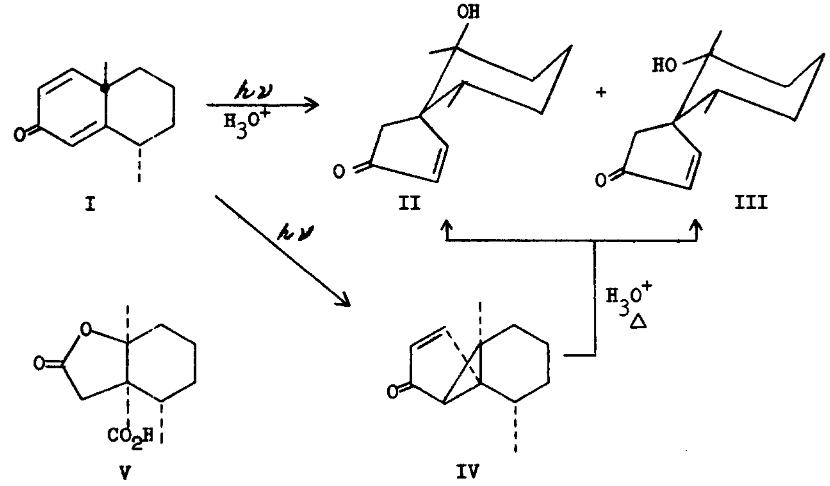
[1] Cf., P. de Mayo and S. T. Reid, Quart. Rev. (London) 15, 393 (1961).

[2] (a) H. Dutler, H. Bosshard, and O. Jeger, Helv. Chim. Acta 40, 494 (1957); (b) L. Ruzicka and O. Jeger, German Patent 1,080,551 (1961) [C.A., 55, 26041 (1961)]; British Patent 866,362 (1961) [C.A., 55, 22388 (1961)].

[3] Irradiations were conducted in Vycor apparatus using a 100- or 200-watt Hanovia high pressure mercury lamp and were continued until all of the starting dienone had just been consumed, as determined by infrared or gas chromatographic examination of aliquots removed periodically. The products were isolated by chromatography on silica gel or alumina. In each irradiation discussed a phenolic product was also isolated in yields of 28-40%. This will be discussed in detail in a future publication. Satisfactory analytical data were obtained for all compounds described in this communication.

[4] S. M. Bloom, J. Amer. Chem. Soc. 80, 6280 (1958); J. Org. Chem. 24, 278 (1959).

the irradiation was conducted under reflux, both II (16% yield) and the epimeric spiro ketone III, m.p. 89.5-90.5°, (5% yield) were obtained. Irradiation in 50% sulfuric acid at 15° also gave the two ketones, in 9% yield each. When irradiation of the dienone in 45% acetic acid or in hexane was interrupted before all of the starting material had been consumed, the cyclopropyl ketone IV (semicarbazone m.p. 205-207°) was obtained in 10-15% yield. Although stable toward aqeuous acetic acid at 20°, the cyclopropyl ketone was cleaved to a 2.5:1 mixture of the spiro ketones II and III under reflux.



The presence of a cyclopentenone unit in the spiro ketones II and III as shown by infrared bands at 5.84, 5.95, and 6.28 μ[5] was confirmed, in the case of II, by conversion to a dihydro derivative (semicarbazone m.p. 200-201°) having only a single band in the carbonyl region at 5.76 μ. The substitution pattern on the cyclopentenone rings of II and III is clearly defined by their n.m.r. spectra. The α- and β-vinylic protons

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[5] P. Yates and L. L. Williams, ibid. **80**, 5896 (1958).

appear as an AB quartet consisting of doublets at 2.46 and 3.77 $\tau$ ($J_{AB}$ = 6 c.p.s.) and the methylene protons appear as a second AB quartet with doublets at 7.29 and 7.91 $\tau$ ($J_{AB}$ = 19 c.p.s.). Coupled with the lack of any secondary splitting of these patterns and the absence of any absorption attributable to an allylic proton, this data can be accommodated only by a cyclopentenone ring which is disubstituted at position 4. In support of the structural assignment II, ozonolysis of the ketone gave an acidic $\gamma$-lactone (assigned the structure V), m.p. 211-212°.

The striking similarity of the infrared, n.m.r., and mass spectra of the ketones II and III emphasizes their simple isomeric relationship, and their concurrent formation from the cyclopropyl ketone IV indicates that they are epimeric only about the hydroxyl-bearing carbon. The stereochemical assignments at this center are based on the presence of intramolecular hydrogen bonding in one isomer (III) which is absent in the other. Molecular models clearly show that only an equatorially oriented hydroxyl group would be capable of hydrogen bonding to the $\pi$-electron system of the cyclopentenone ring.

The assignment of a structure analogous to lumisantonin for the intermediate IV is supported by absorption at 1.677 (tertiary cyclopropyl hydrogen[6]) and 12.00 μ (pentasubstituted cyclopropane ring adjacent to a ketone[7]) and an ABX pattern of quartets (one proton each) at 2.62 and 4.22 $\tau$ ($J_{AB}$ = 5.5, $J_{AX}$ = 0.8, $J_{BX}$ = 1.1 c.p.s.).

Irradiation of $\Delta^1$-dehydrotestosterone acetate[8] in refluxing 45% acetic acid also gave a hydroxy ketone, m.p. 218-219° and $[\alpha]_D^{29°}$ + 29° (c = 0.76) which had infrared, ultraviolet, and n.m.r. spectra exactly

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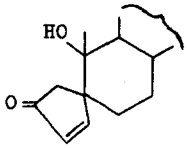
[6] J. Meinwald, A. Lewis, and P. G. Gassman, ibid. 84, 977 (1962).

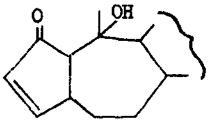
[7] P. Yates and S. Danishefsky, ibid. 84, 879 (1962).

[8] H. H. Inhoffen, G. Zühlsdorff, and Huang-Minlon, Chem. Ber. 73, 451 (1940).

identical in the significant regions with those of II.[9] We therefore propose the structure VI for this compound and suggest that rearrangement to spiro [4.5] decenone derivatives is characteristic of dienones of this type.



VI



VII

It has been proposed[10] that photochemical rearrangements of dienones proceed (via $n \longrightarrow \pi^*$ excitation followed by rebonding between $C_1$ and $C_5$ and subsequent electron demotion) through a charged species of the type VIII, which in turn is in equilibrium with the alternate cyclopropylcarbinyl cation IX. The stability of the cyclopropyl ketone IV to aqueous acetic acid at 20° implies the existence of a direct pathway to the spiro ketone II not involving IV as an intermediate.[11]

It is instructive to note that the intermediate VIII is capable of undergoing nucleophilic attack by water by two pathways, providing either a perhydroazulene (path A) or a spiro [4.5] decenone (path B) derivative. In the case in which R is a methyl substituent (e.g., santonin) the inter-

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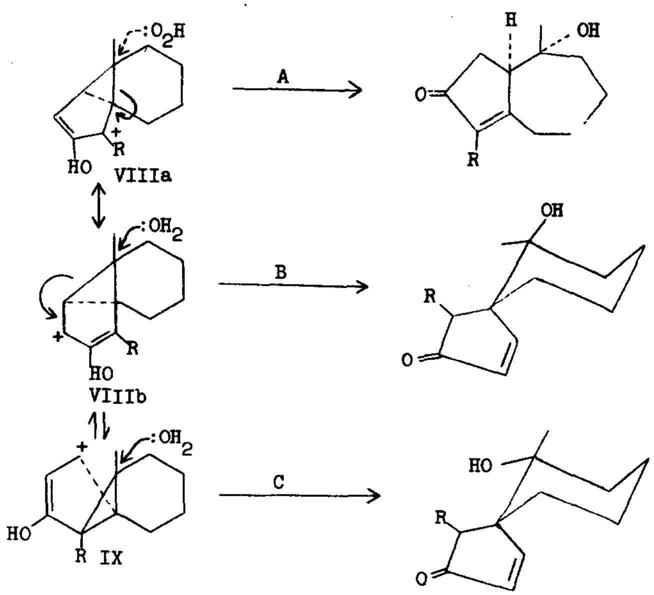
[9] Ruzicka and Jeger[2b] have reported that irradiation of $\Delta^1$-dehydrotestosterone acetate gave a hydroxy ketone, m.p. 208-210° and $[\alpha]_D$ + 21°, for which the structure VII was assigned. The evidence presented above is incompatible with this structural assignment.

[10] H. E. Zimmerman and D. I. Schuster, J. Amer. Chem. Soc. **83**, 4486 (1961).

[11] This is in complete analogy with the santonin-isophotosantonic lactone transformation.[12]

[12] D. H. R. Barton, P. de Mayo, and M. Shafiq, J. Chem. Soc. 140 (1958).



mediate VIII would be expected to more nearly resemble the cannonical form VIIIa, thus favoring rearrangement by path A. In the absence of stabilization of VIIIa by a methyl substituent rearrangement by both pathways would be expected.[13] At higher temperatures the direct pathway is accompanied by thermal cleavage of the cyclopropyl ketone IV to a mixture of the epimeric spiro ketones II and III.[14] Studies directed toward further elucidation of this mechanistic picture are in progress.

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[13] The expected perhydroazulene derivatives were also obtained from the dienone I and $\Delta^1$-dehydrotestosterone acetate. These will be described in our complete paper.

[14] The acid-catalyzed cleavage of the cyclopropyl ketone to spiro ketones has some analogy in the like cleavage of dihydrolumisantonin.[12] However, lumicholestenone, which has no 4-methyl substitutent, undergoes a different rearrangement under the same conditions.[15]

[15] W. W. Kwie, B. A. Shoulders, and P. D. Gardner, J. Amer. Chem. Soc. **84**, 2268 (1962).