the related ketones IIIa[4] and IIIb[5] to phenols IVa and IVb. The ketene–carbene mechanism previously suggested to account for the conversion of I to II[2,3] fails to account for the conversion of IIIa and IIIb to the corresponding phenols. The polar state concept[6-8] provides a smooth rationalization of both processes and in addition implicates a potentially isolable intermediate V between I and II.[9] Photochemical conver-

I

II   V

IIIa   IVa
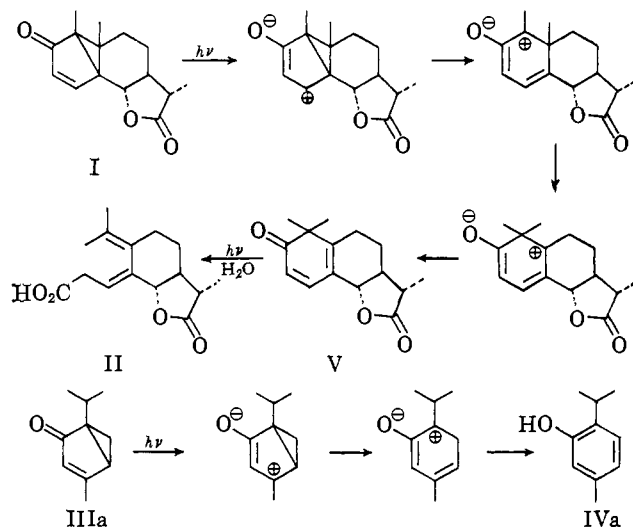
sion of a 2,4-cyclohexadienone such as V to an unsaturated acid such as II is a well documented process.[7,10]

Irradiation[11] of lumisantonin (I) in anhydrous ether leads to formation of an oily product identified as V by the following observations. The intermediate, purified by vapor phase chromatography, shows infrared absorption at 5.62 (lactone carbonyl), 6.03 (conjugated carbonyl), and 6.13 μ (double bonds) and ultraviolet absorption at 308 mμ in accord with expectation. The n.m.r. spectrum of V shows two olefinic protons as a pair of doublets (J_{AX} = 9.9 c.p.s.) at 2.85 and 4.00 τ.[12]

Treatment of V under mild conditions with 2,4-dinitrophenylhydrazine in phosphoric acid gives the 2,4-dinitrophenylhydrazone of V,[13] m.p. 252–254°. Treatment of V with 2,4-dinitrophenylhydrazine in ethanolic sulfuric acid gives an isomeric 2,4-dinitrophenylhydrazone, m.p. 228–230°, identical with the 2,4-dinitrophenylhydrazone of VI prepared previously.[3] It seems reasonable that the more vigorous acid condi-

VI
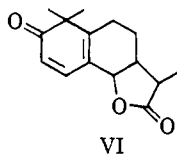
(4) J. W. Wheeler and R. H. Eastman, *J. Am. Chem. Soc.*, **81**, 236 (1959);

(5) H. E. Zimmerman and D. I. Schuster, *ibid.*, **84**, 4527 (1962).

(6) O. L. Chapman and S. L. Smith, *J. Org. Chem.*, **27**, 2291 (1962).

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

(8) C. Ganter, R. Warszawski, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **46**, 320 (1963).

(9) The possibility of an intermediate such as V between I and II has been considered previously. See footnote 53 of ref. 5 and K. Weinberg, E. C. Utzinger, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **43**, 236 (1960).

(10) W. G. Dauben, D. A. Lightner and W. K. Hayes, *J. Org. Chem.*, **27**, 1897 (1962).

(11) A General Electric UA-3 mercury arc lamp was used. Irradiation was carried out in a Pyrex vessel.

(12) This value for the olefinic coupling constant is in accord with expectation for *cis*-vinyl protons in a six-membered ring (O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963); G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963); P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1963). The low field position of the β-olefinic proton is consistent with the deshielding effect of the carbonyl group and the second double bond.

(13) This derivative is identical in melting point and infrared absorption with a sample prepared by Prof. J. Richards and co-workers, *J. Am. Chem. Soc.*, **85**, 3029 (1963).

tions epimerize C-6 giving the more stable fusion of the lactone ring.

The intermediate V is rapidly converted to photosantonic acid in the presence of light and water. The ultraviolet absorption of V is not observed in the conversion of lumisantonin (I) to photosantonic acid (II) in aqueous organic solvents because the rate of destruction of the intermediate is greater than the rate of formation. Irradiation[11] of lumisantonin (II) in anhydrous ether in a Pyrex vessel required 2.5 hr. to achieve the maximum concentration of V. Addition of 2% water and continued irradiation under identical conditions leads to complete disappearance of V in less than 45 min.

The isolation of V as an intermediate in the conversion of I to II emphasizes the dangers inherent in interpretation of photochemical processes without a detailed knowledge of the nature and number of discrete photochemical reactions involved.

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The Mechanism of the Photoconversion of Santonin

Sir:

The photochemistry of santonin has an illustrious history which has dealt, in the main, with the isolation, characterization, and interrelation of the manifold products formed on exposure of santonin to light in various media.[1] The established course of the reaction in certain media is from santonin (I) to lumisantonin (II) and thence to photosantonic acid (IV).[2,3]

I   II

III   IV
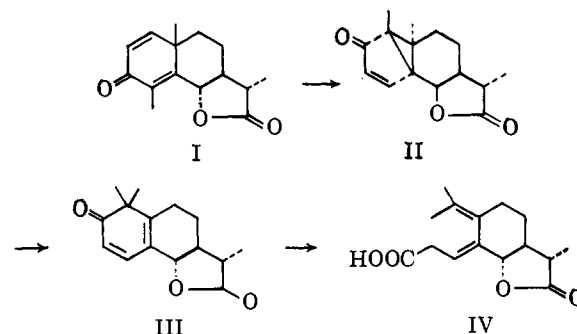
We should like to report evidence that the photoconversions of santonin and lumisantonin involve as intermediates the triplet states of the respective substances and that there exists an important intermediate (III)[4] between lumisantonin and photosantonic acid.

The evidence relative to the first assertion is the demonstration that in appropriate systems there is a transfer of triplet character and energy from photo-

(1) D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger, and L. J. Krebaum, *Helv. Chim Acta*, **40**, 1732 (1957).

(2) D. H. R. Barton, P. de Mayo, and M. Shafiq, *J. Chem. Soc.*, 3314 (1958).

(3) E. E. van Tamelen, S. H. Levin, G. Brenner, J. Wolinsky, and P. Aldrich, *J. Am. Chem. Soc.*, **81**, 1666 (1959).

(4) The presence of III as an intermediate in the photoconversion of lumisantonin to photosantonic acid has been previously suggested. [K. Weinberg, E. C. Utzinger, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **43**, 236 (1960); H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962).]

sensitizers such as benzophenone (E_T = 68.5 kcal.[5]) to santonin resulting in the photoconversion of santonin. The following comparison illustrates this point. One Pyrex tube contained a 1.95 × 10^{-2} M solution of santonin which absorbed 58% of the incident radiation. Another tube contained a solution 4.3 × 10^{-2} M in benzophenone and 1.95 × 10^{-2} M in santonin such that the benzophenone absorbed 91% and the santonin 9% of the incident light. Both tubes were irradiated with the 3660-Å. line of mercury. The conversion of santonin to lumisantonin was 1.7 times as rapid in the tube containing the benzophenone. This indicated also that the photolysis of santonin alone was probably an efficient process, a surmise which was confirmed by the finding that this reaction has a quantum yield of approximately unity. On the other hand, Michler's ketone (E_T = 61.0 kcal.[6]) did not sensitize the photoconversion of santonin but acted only as a filter.

If the photolysis is carried out in piperylene as solvent, the photoconversion is completely quenched. This requires the intermediacy of triplets as the energy of the piperylene singlet (~2300 Å.) lies far higher than that of the incident radiation.[7] However, the photoconversion of santonin does not cause the cis–trans isomerization of dilute solutions (e.g., 0.2 M) of piperylenes or stilbenes.

From these results we conclude that the conversion of santonin to lumisantonin involves the following steps: excitation of santonin to a singlet state which crosses with near unit efficiency to the triplet state which undergoes a very rapid molecular rearrangement to lumisantonin.

In a similar fashion it has been possible to demonstrate the transfer of triplet character and energy from photosensitizers such as Michler's ketone to lumisantonin. The first isolable product of this reaction (and likewise of unsensitized reactions) is a new substance which has been shown to have structure III by physical and chemical methods and is identical with a substance isolated by Chapman and reported in an accompanying communication.[8] This substance is very easily converted by dilute acid to an isomer V with the epimeric configuration at C-6, which is, in fact, the compound synthesized earlier by van Tamelen, et al.[3] Such epimerization is known to be facile under acidic conditions.[9,10] Further irradiation of III in the presence

V
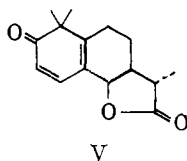
of water yields photosantonic acid (IV).

From these results we conclude that the photochemistry of santonin, lumisantonin, and, by generalization, of other conjugated ketones involves the triplet state as the species which undergoes molecular rearrangements. It has been suggested[11] that the triplet state of similar systems is likely to be more polarizable and also more basic than the ground state. The photo-

chemical rearrangements of these systems can all be easily rationalized by assuming that the rearranging intermediate has negative character localized on the oxygen and positive character distributed through the conjugated system of the carbon skeleton.[12–14] Thus, this demonstration of the intermediacy of triplet states in the photochemistry of santonin leads directly to the suggestion that the photochemical rearrangements of conjugated ketones proceed through triplet states having considerable charge separation which facilitates carbonium ion-type rearrangements of the carbon skeletons. An interesting possibility, which is in accord with the experimental facts just related and results on energies of n → π^*(triplet) and π → π^* (triplet) conversions,[15,16] is that the excitation involved is not of the traditionally assumed n → π^* (triplet) type but rather involves a π → π^* (triplet) conversion which would explain even more convincingly the electron deficiency apparent in the carbon skeleton undergoing molecular rearrangement.

From the observed short lifetime of the santonin triplet, we had not anticipated observing any phosphorescence emission from santonin. However, in a MCIP (5:1 by volume methylcyclohexane:isopentane) glass at 77°K. the purest santonin we have been able to obtain showed a clear, broad phosphorescence emission ($\tau > 5 \times 10^{-4}$ sec.) at 68 ± 1 kcal. This may be interpreted in at least two ways: that the rigidity of the glass imprisoning the santonin prevents the molecular motions necessary for the molecular rearrangement to lumisantonin or that the observed emission comes from some triplet intermediate between santonin and lumisantonin.

(12) D. H. R. Barton and G. Quinkert, J. Chem. Soc., 1 (1960).

(13) O. L. Chapman and S. L. Smith, J. Org. Chem., 27, 2291 (1962).

(14) G. Ganter, R. Warszawski, H. Wehrli, K. Schaffner, and O. Jeger, Helv. Chim. Acta, 46, 320 (1963).

(15) G. S. Hammond and P. A. Leermakers, J. Am. Chem. Soc., 84, 207 (1962).

(16) G. S. Hammond, P. A. Leermakers, N. Turro, J. Saltiel, A. Lamola, et al., unpublished work.

(17) NSF Predoctoral Fellow.

(18) Alfred P. Sloan Research Fellow.

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Diene Studies. I. Relative Stabilities of Dihydrobenzenes and Hexahydronaphthalenes

Sir:

An understanding of the factors governing the relative thermodynamic stabilities of isomeric 1,3- and 1,4-dienes is particularly desirable now that methods for cleanly isomerizing dienes of this type are available.[1]

(5) G. S. Hammond and J. Saltiel, J. Am. Chem. Soc., 84, 4983 (1962).

(6) E. Herkstroeter, unpublished work.

(7) G. S. Hammond, N. J. Turro, and P. A. Leermakers, J. Phys. Chem., 66, 1144 (1962).

(8) O. L. Chapman and L. F. Englert, J. Am. Chem. Soc., 85, 3028 (1963).

(9) H. Ishikawa, J. Pharm. Soc. Japan, 76, 504 (1956).

(10) The configuration at C-6 is assigned on the basis of the n.m.r. spectral comparisons between V and 6-episantonin. Moreover, concomitant epimerization at C-11 is unlikely as the 5% hydrochloric acid in dimethylformamide, which causes epimerization at C-6, is without effect on the configuration at C-11.[9]

(11) J. M. Hirshon, D. M. Gardner, and G. K. Fraenkel, J. Am. Chem. Soc., 75, 4115 (1953).

(1) We found the adaptations described below of the method of N. Turnbull, U. S. Patent 2,316,136 (1943) (Chem. Abstr., 37, 5420 (1943)), to give less than 3% of side reactions (polymerization, disproportionation, etc.). Turnbull describes the conversion of VI to V in up to 71% yield, but does not mention what the remaining material is. For further base-catalyzed diene isomerizations, see: (a) H. Pines, J. A. Vesely, and V. N. Ipatieff, J. Am. Chem. Soc., 77, 347, 6314 (1955); (b) H. Pines and L. Schaap, ibid., 79, 2956 (1957); (c) T. M. O'Grady, R. M. Alm, and M. C. Hoff, Am. Chem. Soc. Div. Petrol. Chem. Preprints, 4, B65 (1959); (d) I. V. Gostunskaya and B. A. Kazanskii, Zhur. Obshch. Khim., 25, 1995 (1955); Chem. Abstr., 50, 8437 (1956); (e) J. H. Mitchell, Jr., H. R. Kraybill, and F. P. Zscheile, Ind. Eng. Chem., Anal. Ed., 15, 1 (1943); (f) J. Davenport, A. J. Birch, and A. J. Ryan, Chem. Ind. (London), 136 (1956); (g) B. Sreenivasan and J. B.