The Photochemistry of Santonin: Zwitterionic Intermediates

By MICHAEL H. FISCH
(*Department of Chemistry, University of California, Irvine, California* 92664)

Summary Trapping of intermediates in the low-temperature photolysis of santonin and lumisantonin is described.

THE photochemistry of santonin (**1a**), and lumisantonin (**2a**) has been interpreted on the basis of mesoionic zwitterions (**3a**)[1] and (**4a**)[2] respectively.

Recently, the observation of a dienone–lumiketone rearrangement in the gas phase led to the suggestion that non-zwitterionic pathways probably exist in these systems.[3] This suggestion has excited some comment.[4] I report some new results which support the intermediacy of zwitterions in the condensed-phase photochemistry of santonin and lumisantonin.

Photolysis of α-chloro- and α-bromo-santonin[5] (2537 Å, EtOAc) led to formation of the corresponding chlorolumisantonin, (**2b**), and bromolumisantonin (**2c**) with quantum yield of 0·6—0·7.[6] Thus, the halogeno-substituent affects the efficiency of the reaction, but not its course.[7]

Irradiation of lumisantonin at 77°K in methyltetrahydrofuran–isopentane glass (1 : 1) generated the previously described blue colour.[2] The halogen substituent has essentially no effect upon the absorption spectrum of the trapped intermediate (Figure 1). A trappable species was likewise obtained by irradiation of the santonins under the same conditions; again, with essentially no effect of halogen substitution upon the difference spectrum (Figure 2).

As formulated, the zwitterionic species (**3**) and (**4**) are ethylenic and benzenium carbonium ions in which the negatively-charged oxygen substituent effects a strong bathochromic shift.[8] The observed transition may be of charge-transfer type in which the energy required is lowered due to the reduction of charge separation in the excited state. Precedent for the lumisantonin example is found in the photolysis of the enone epoxide (**5**) which is known to result in an unusually stable red zwitterion, (**6**) (λ_{max} 544 nm.).[9]

We had previously argued[2] that the coloured species could not be uncharged cyclopropanone derivatives such as (**7**) and (**8**) since these would not be expected to absorb in the visible.[10] In agreement with this formulation, low-temperature i.r. examination of these photolysis mixtures† reveals no cyclopropanone formation, or indeed the presence of any carbonyl band other than that of the previously observed keten.[11] The failure of the halogen substituent to shift appreciably the absorption spectrum supports the given formation of the zwitterion rather than forms such as (**9**) derived directly from the cyclopropanone, and thus is in agreement with calculations by Hoffmann[12]

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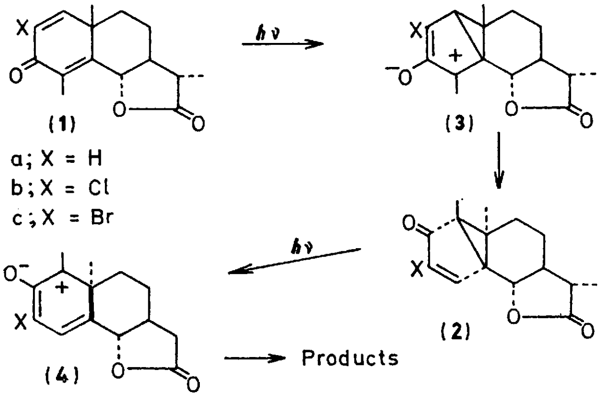
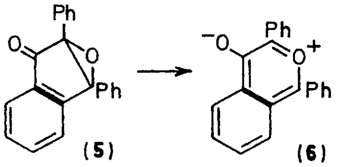
† I thank Professor O. L. Chapman and Mr. L. L. Barber for these data.

on the zwitterionic form to be expected from cyclopropanone.

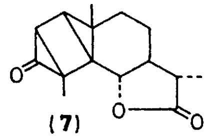


(1) (3) (2) (4)

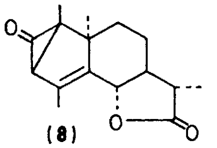
a; X = H
b; X = Cl
c; X = Br



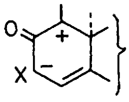
(5) (6)



(7)



(8)



(9)

We originally attributed the stability of the coloured species (**4a**) at 77°K to an effect of solvent viscosity.[2] I have now examined the photolysis of santonin and lumisantonin in polystyrene plastic and find that, although reaction occurs normally, the coloured species are not trapped at room temperature. Consequently, the original explanation based on solvent viscosity must be discarded. The stability of (**3**) and (**4**) at liquid nitrogen temperature presumably derives from an energy barrier to further reaction. Experiments designed to trap the proposed zwitterions in the room temperature photolysis are in progress and will be reported later.[13]

I thank the Research Corporation for support of this work.

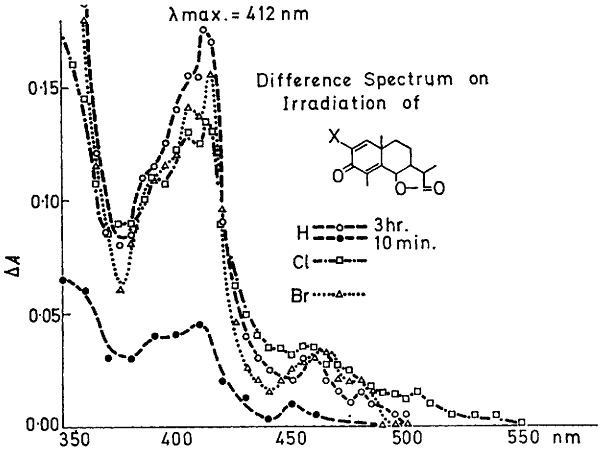


FIGURE 1

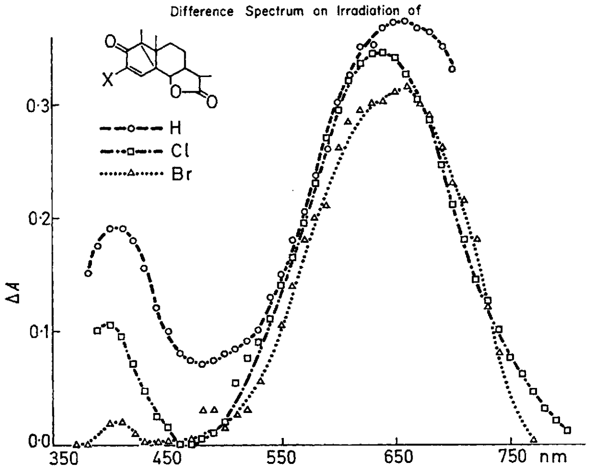


FIGURE 2

(*Received, August 25th,* 1969; *Com.* 1289.)

[1] H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, 1961, **83**, 4486; *ibid.*, 1962, **84**, 4527.

[2] M. H. Fisch and J. H. Richards, *J. Amer. Chem. Soc.*, 1968, **90**, 1547 and references cited therein.

[3] J. S. Swenton, E. Saurborn, R. Srinivasan, and F. I. Sonntag, *J. Amer. Chem. Soc.*, 1968, **90**, 2990.

[4] D. I. Schuster and D. J. Patel, *J. Amer. Chem. Soc.*, 1968, **90**, 5145, footnote 48a.

[5] E. Wedekind and A. Koch, *Ber.*, 1905, **38**, 429; E. Wedekind and K. Tettweiler, *ibid.*, 1931, **64**, 387. Dehydrohalogenation with pyridine was found to be superior to that described.

[6] Loss of bromine is a problem in the photolysis of bromosantonin at room temperature. However, at temperatures of 0° or below, no apparent loss occurs and physical properties of the product obtained agreed with those reported (R. A. Silva in conjunction with D. H. R. Barton, J. T. Pinhey, and R. J. Wells, *J. Chem. Soc.*, 1964, 2518). Satisfactory analyses (C, H, and halogen to 0·3%) were obtained for the four halogenated compounds.

[7] The effect of the halogens reflects the intervention of two triplet states in the photoconversion of santonin into lumisantonin, and will be discussed later. M. Fisch and R. Nonnenmacher, Abstracts, Amer. Chem. Soc., 157th National Meeting, Minneapolis, Minnesota, April 11—15, 1969, Org. no. 88.

[8] G. A. Olah, C. V. Pittman, jun., and M. C. R. Symons, in "Carbonium Ions," vol. 1, eds. G. A. Olah and P. von R. Schleyer, Interscience, New York, 1968, ch. 5.

[9] E. F. Ullman and W. A. Henderson, jun., *J. Amer. Chem. Soc.*, 1966, **88**, 4942.

[10] N. J. Turro and W. B. Hammond, *J. Amer. Chem. Soc.*, 1966, **88**, 3672; W. B. Hammond and N. J. Turro, *ibid.*, p. 2880.

[11] L. Barber, O. L. Chapman, and J. D. Lassila, *ibid.*, *J. Amer. Chem. Soc.*, 1968, **90**, 5933.

[12] R. Hoffmann, *J. Amer. Chem. Soc.*, 1968, **90**, 1475.

[13] For an instance in which a zwitterion generated at 77°K has been trapped, see L. L. Barber, O. L. Chapman, and J. D. Lassila, *J. Amer. Chem. Soc.*, 1969, **91**, 3664. An example of a room-temperature photolysis in which the zwitterionic structure is isolated in one of the products has recently been reported: D. I. Schuster and V. Y. Abraitys, *Chem. Comm.*, 1969, 419.