For $Ph_2CO + h\nu \rightarrow$ In conversions in excess of 50%, the reaction mixture at the end of the dark reaction will contain In, which will ultimately have to react with atmospheric oxygen upon admission of air. Thus, one can easily obtain quantum yields of Ph_2CO disappearance ranging from 1 to 2. The only case in which this quantum yield can be close to 2 is if the original $Ph_2CO + h\nu \rightarrow$ In conversion is less than 50% and if the dark reaction is allowed to go to completion.

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The Mechanism of the Photochemical Rearrangement of Lumisantonin[1,2]

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Abstract: Sensitization studies on the photolysis of lumisantonin together with a reinvestigation of its pyrolysis have yielded results which support a mechanism involving five discreet steps: (1) excitation; (2) intersystem crossing; (3) bond breaking; (4) electron demotion and relaxation to a dipolar state; (5) rearrangement. Photolysis at low temperature in a matrix allowed the trapping of a colored intermediate the lifetime and spectral characteristics of which are consistent with the postulated dipolar state. The possibilities of electron ejection from an excited state or reaction *via* vibrationally excited ground states are discussed and considered to be unlikely in this system.

For several years interest has centered on "ionic" photochemical processes, *i.e.*, those photochemical rearrangements which bear obvious relationships to carbonium ion type reactions. Chapman has formulated this analogy between carbonium ion processes and the photochemical rearrangements of conjugated, unsaturated ketones as the "polar state" hypothesis,[4] in which a positive charge is developed "on the carbon atom β to the carbonyl group in the product controlling state."[4a]

The undeniable utility of the polar state formalism raises a question of the origin of this utility. In carbonyl groups, the lowest excited singlet state is of $n \rightarrow \pi^*$ type and should have less accumulation of charge at any center than does the ground state, *i.e.*, the excited state should be less, not more, polar than the ground state. Indeed in the $n \rightarrow \pi^*$ excited state, the oxygen atom of the carbonyl group is electron deficient relative to the ground state and the anticipated reactions (in particular hydrogen abstraction) are more likely to be those of diradicals. Photochemical behavior of this "radical" type is well known for simple ketones[5] and even for some unsaturated ketones.[6-11] That the excited state responsible for these "radical" type of reactions should be the same one in which "ionic" types of rearrangements occur seems, however, unlikely.

Since this work was undertaken, the range of reactions from a diradical type of excited state has been considerably broadened. For example, migrations of hydrogen atoms[12] or even alkyl groups[13] occur, though these processes are essentially unknown in analogous ground-state systems.[14] These additional data, however, make it even less plausible that ionic-type rearrangements can be explained on the basis of triplet diradical intermediates. For example, alkyl migration in a diradical may be an activated process.[13a] If so, alkyl migration in a diradical-like excited state would be particularly unlikely in the condensed phase (where most processes suggestive of dipolar intermediates have been observed) because of the rapidity with which collisions would dissipate any excess (vibrational) energy. In the same vein, typically ionic rearrangements occur in steroids[15]

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[1] M. H. Fisch and J. H. Richards, *J. Amer. Chem. Soc.*, **85**, 3029 (1963).

[2] Presented in part at the 2nd SECO conference Praz-sur-Arly (Haute-Savoie), France, April 25–May 2, 1965.

[3] NSF Predoctoral Fellow, 1960–1964.

[4] (a) O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963); (b) O. L. Chapman and S. L. Smith, *J. Org. Chem.*, **27**, 2291 (1962).

[5] (a) H. E. Zimmerman, 17th National Organic Symposium, Bloomington, Ind., 1961, Abstracts, p 31 ff; (b) R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1963); (c) H. E. Zimmerman, *Tetrahedron Letters*, 3134 (1964); (d) J. Saltiel, *Surv. Progr. Chem.*, **2**, 239 (1964); (e) G. Quinkert, "Organic Photochemistry," Butterworth and Co., Ltd., London, 1965, p 605; G. Quinkert, *Pure Appl. Chem.*, **9**, 607 (1965); (f) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 137 ff; (g) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 366 ff.

[6] B. Nann, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **46**, 2473 (1963).

[7] D. I. Schuster and D. J. Patel, *J. Amer. Chem. Soc.*, **87**, 2515 (1965).

[8] T. Matsuura, *Bull. Chem. Soc. Japan*, **37**, 564 (1964).

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

[10] R. Warsawski, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **43**, 500 (1960).

[11] D. I. Schuster and C. J. Polowczyk, *J. Amer. Chem. Soc.*, **86**, 4502 (1964).

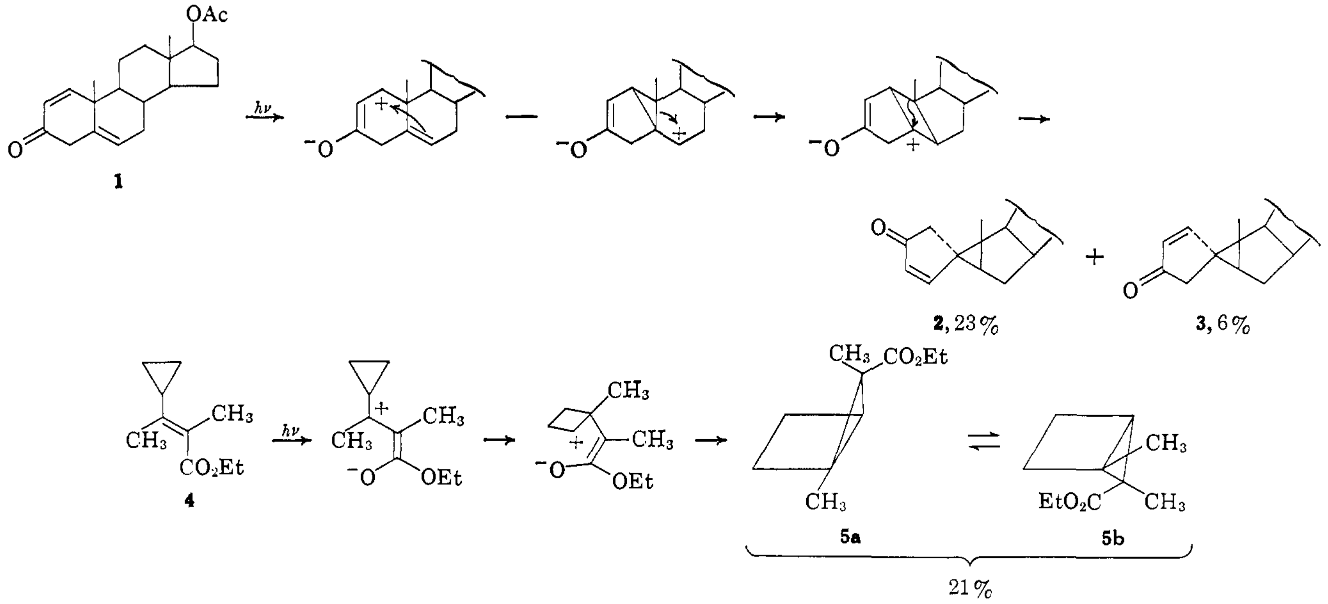
[12] (a) J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964), and references cited therein; (b) D. I. Schuster and I. S. Krull, *J. Amer. Chem. Soc.*, **88**, 3456 (1966).

[13] (a) C. McKnight and F. S. Rowland, *ibid.*, **88**, 3179 (1966); (b) H. Kristinsson and G. W. Griffin, *ibid.*, **88** (1966).

[14] C. Walling in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 416 ff.

[15] H. Dutler, C. Ganter, H. Ryf, E. C. Utzinger, K. Weinberg, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **45**, 2346 (1962).

Scheme I



where the degrees of freedom available to the steroid skeleton provide intramolecular (and consequently extremely rapid) means of dissipating vibrational energy,[16] a factor which will disfavor activated processes in these substances. Furthermore, at least two ionic rearrangements (of 3-oxo-17β-acetoxy-$\Delta^{1,5}$-androstadiene,[6] **1**, and ethyl 2-methyl-3-cyclopropyl-2-butenoate, **4**)[17] formally involve rearrangements of cyclopropylcarbinyl systems *via* cyclobutyl carbonium ions and there is evidence that the cyclopropylcarbinyl radical does not rearrange to the cyclobutyl radical (Scheme I).[18]

Finally the documented cases of alkyl migration in excited diradicals involve hydrocarbon model systems which differ markedly from systems in which a carbonyl group is present, as the difference in electronegativity between carbon and oxygen will stabilize charge separation, and therefore dipolar intermediates, much more effectively in compounds containing a carbonyl group than in analogous hydrocarbon systems. For all these reasons, ketone diradicals, at least insofar as they approximate the classic $n \rightarrow \pi^*$ excited state, seem unlikely species to invoke in accounting for ionic-type photochemical rearrangements. Indeed, the intermediacy of dipolar, ionic intermediates in photochemical rearrangements of ketones is further suggested by the observations that these reactions follow the normal course expected for rearrangements of carbonium ions[19] and that they also show the same substituent effects as those found in carbonium ion rearrangements.[20]

Many explanations have been advanced to rationalize these observations. Zimmerman[21] has suggested that photochemical ionic rearrangements resemble ground-state carbonium ion processes because, before rearrangement, electron demotion from the excited state occurs, yielding a ground-state dipolar species. In this view, though bond making and bond breaking may occur in the electronic excited state, no ionic process takes place before demotion of the electron. Because of the rebonding which does occur in the excited state, the molecule on electron demotion does *not* revert to reactant. The observation[22,23] that some dienones undergo photochemical rearrangements that are *not* characteristic of electron deficiency in the π system of the carbon skeleton does not obviate the Zimmerman hypothesis of electron demotion to a dipolar state which then undergoes ionic rearrangement. In these exceptional cases,[22,23] rearrangement presumably occurs before demotion.

Zimmerman's hypothesis may require modification for certain cases should the recent suggestion be borne out that vibrationally excited ground states (S_0^*) are important in condensed phase photolyses.[24] Photochemical reaction *via* an S_0^* state could be an acceptable explanation for homolytic fissions in substituted ketones[25] and gas phase reactions *via* S_0^* states are well documented.[26] However, results to be discussed subse-

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[16] H. E. Zimmerman and J. W. Wilson, *J. Amer. Chem. Soc.*, **86**, 4036 (1964).

[17] M. J. Jorgenson, *ibid.*, **88**, 3463 (1966).

[18] (a) R. Breslow in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963. (b) It seems plausible that these two reactions involve similar intermediates, although the authors of ref 6 suggested a diradical process. The essential point is that rearrangement occurs from cyclopropylcarbinyl to cyclobutyl species, and that such rearrangements are unusual for ground-state diradical species. On the other hand, the validity of excluding such pathways to excited-state diradicals has not been rigorously tested.

[19] C. Ganter, E. C. Utzinger, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 2403 (1962).

[20] (a) C. Ganter, F. Greuter, D. Kägi, K. Schaffner, and O. Jeger, *ibid.*, **47**, 627 (1964); (b) P. J. Kropp, *J. Amer. Chem. Soc.*, **86**, 4053 (1964), and references cited therein.

[21] (a) H. E. Zimmerman and D. I. Schuster, *ibid.*, **83**, 4486 (1961); (b) H. E. Zimmerman and D. I. Schuster, *ibid.*, **84**, 4527 (1962); (c) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); (d) H. E. Zimmerman, *Tetrahedron Suppl.*, 2, 393 (1963).

[22] H. E. Zimmerman, R. C. Hahn, H. Morrison, and M. C. Wani, *J. Amer. Chem. Soc.*, **87**, 1138 (1965).

[23] D. I. Schuster and D. J. Patel, *ibid.*, **87**, 2515 (1965).

[24] W. G. Dauben and W. T. Wipke, "Organic Photochemistry," Butterworth and Co., Ltd., London, 1965, p 539; W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1965); but see W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltiel, *J. Amer. Chem. Soc.*, **88**, 2742 (1966).

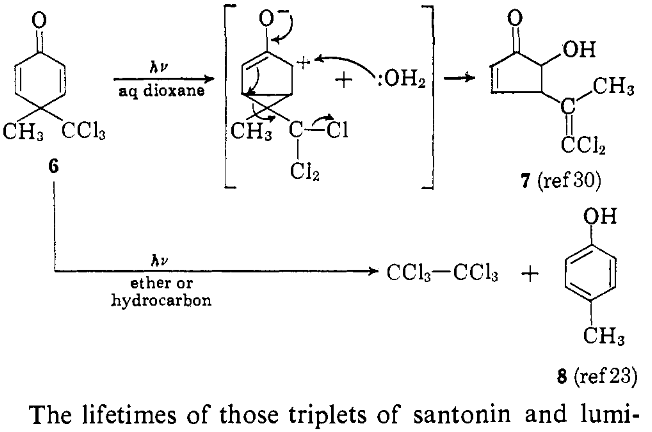
[25] (a) D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960); (b) R. Warsawski, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **43**, 500 (1960); (c) D. I. Schuster and C. J. Polowczyk, *J. Amer. Chem. Soc.*, **86**, 4502 (1964); (d) C. Lehmann, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **45**, 1031 (1962); (e) C. K. Johnson, B. Dominy, and W. Reusch, *J. Amer. Chem. Soc.*, **85**, 3894 (1963); (f) H. E. Zimmerman, B. R. Cowley, C.-Y. Tseng, and J. W. Wilson, *ibid.*, **86** (1964); (g) T. Matsuura, *Bull. Chem. Soc. Japan*, 37, 564 (1964); (h) A. Padwa and D. Crumrine, *Chem. Commun.*, 506 (1965).

[26] (a) I. Haller and R. Srinivasan, *J. Chem. Phys.*, 40, 1992 (1964); (b) R. Srinivasan, *J. Amer. Chem. Soc.*, **84**, 3432 (1962); R. Srinivasan, *J. Chem. Phys.*, **38**, 1039 (1963); (c) R. Srinivasan, *Advan. Photochem.*, **4**, 115 (1966).

quently eliminate this possibility in the case of the photolytic reaction of lumisantonin.

Some years ago, we proposed[1] that, in the case of lumisantonin, ionic rearrangements might involve a π,π^* (triplet) state. We did not intend to suggest that dienones[23,27] or santonin[5c] have π,π^* triplet states. However, a $\pi \rightarrow \pi^*$ triplet state of an unsaturated ketone formed by radiationless deactivation of the first-formed n,π^* singlet state[28] might play a role in some photochemical processes. Since the nature of the lowest triplet may depend on substituent and solvent effects,[28b,29] a shift from a radical to an ionic mechanism might be anticipated when the solvent is changed from aprotic to hydroxylic; such cases have been observed; for example, the photorearrangement of 4-methyl-4-trichloromethylcyclohexadienone, **6** (Scheme II).[23,30]

Scheme II



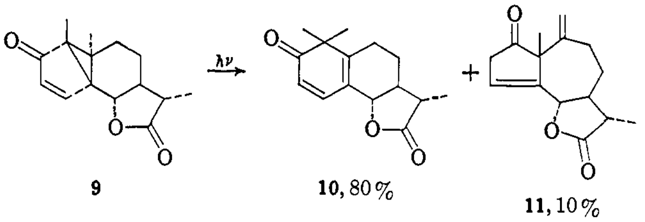
The lifetimes of those triplets of santonin and lumisantonin which react have been shown to be extremely short by the failure of the usual quenching techniques.[1] These results do not, of themselves, require these triplets to be of the n,π^* type. The possibility of a π-π^* triplet as the reactive intermediate would certainly have been eliminated had the *radiative* lifetime of the intermediate been so short.[31] Since the original report of the ineffectiveness of the usual quenchers in the santonin system,[1] similar observations have been reported in other cases.[22,27,32] We shall return to the question of the n,π^* or π,π^* nature of the triplet intermediate subsequently.

Another possibility of ionic photorearrangements has been discussed by Saltiel[5d] and involves an electron ejection from an excited state to give a cation radical which then undergoes rearrangement. Such a process has been observed for some organic molecules[33] and ionic processes analogous to those observed photochemically are well known in mass spectrometry and radiolysis[34] where cation radicals have been shown to play an important role. This possibility in the photolysis of lumisantonin has, however, been eliminated by results to be discussed subsequently.

Results

Irradiation with light from a Hanovia type 5200W source of wavelength longer than 3200 Å of lumisantonin (**9**) in anhydrous benzene yields mazdasantonin[1,35,36] (**10**) in 80% yield, another substance **11** in 10% yield; a variety of minor products the structures of which will form the subject of a subsequent paper account for the remaining 10% (Scheme III). (Yields are based on disappearance of lumisantonin.) For direct irradiation, the quantum yield is 0.26; when benzophenone is used as sensitizer, in such concentration that the benzophenone absorbs practically all the light, the quantum yield is raised to unity. At low conversion both the direct and the sensitized reactions give rise to the same products in the same relative amounts; at high conversion, benzophenone as sensitizer accelerates further reactions of some of the primary photoproducts. These observations provide evidence that the photochemical conversion of lumisantonin to mazdasantonin and other products can proceed *via* the triplet state of lumisantonin. Neither low concentrations of oxygen (10^{-3} *M*) nor of azulene (3×10^{-3} *M*) had any discernible effect on the photolysis. Olefins (isoprene or piperylene) were ineffective as quenchers in the usual sense because they undergo photoreaction with lumisantonin to form adducts.[37]

Scheme III



Discussion

The absence of noticeable quenching by oxygen or azulene suggests a very short lifetime for the triplet ($\tau < 10^{-6}$ sec) which is consonant with the short lifetime seen for the triplet of santonin[1] and other substances discussed previously.[22,27,32] However, the same product distribution is found in the photosensitized reaction (in which case all rearrangement necessarily proceeds through triplet intermediates) and the direct photoreaction (in the absence of sensitizer). Unless a most improbable phenomenon occurs in which the singlet and triplet states both partition identically between the various products, this observation demonstrates that in the direct, as well as in the photosensitized, reaction the triplet state of lumisantonin is an obligatory intermediate.

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(27) H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **86**, 1436 (1964).

(28) (a) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965); (b) M. A. El-Sayed, *ibid.*, 38, 2834 (1963).

(29) G. Porter and P. Suppan, "Organic Photochemistry," Butterworth and Co., Ltd., London, 1965, p 499; G. Porter and P. Suppan, *Pure Appl. Chem.*, **9**, 499 (1965), and references cited therein.

(30) J. King and D. Leaver, *Chem. Commun.*, 539 (1965).

(31) D. R. Kearns and W. A. Case, *J. Amer. Chem. Soc.*, **88**, 5087 (1966), and references cited therein.

(32) (a) A. A. Lamola, P. A. Leermarkers, G. W. Byers, and G. S. Hammond, *ibid.*, **87**, 2322 (1965); (b) G. S. Hammond, H. Gotthardt, L. M. Coyne, M Axelrod, D. R. Rayner, and K. Mislow, *ibid.*, **87**, 4959 (1965).

(33) (a) M. Ottolenghi, *ibid.*, **85**, 3557 (1963); (b) E. W. Schlag and J. J. Sparapany, *ibid.*, **86**, 1875 (1964); (c) J. D. W. van Voorst and G. J. Hoijtink, *J. Chem. Phys.*, **42**, 3995 (1965).

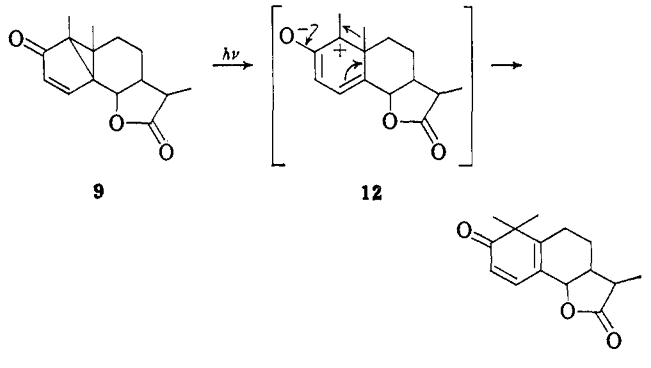
(34) For example, the Norrish reaction. (a) Photochemical: R. G. W. Norrish and M. E. S. Appleyard, *J. Chem. Soc.*, 874 (1938); B. M. Bloch and R. G. W. Borrish, *ibid.*, 1638 (1935); R. G. W. Norrish, *Trans. Faraday Soc.*, 33, 1521 (1937). (b) Mass spectrometric: E. Murad and M. G. Ingraham, *J. Chem. Phys.*, 40, 3263 (1964). (c) Radiolytic: P. Ausloos, *J. Phys. Chem.*, **65**, 1616 (1961); J. Pitts, Jr., and A. B. Osborne, *J. Amer. Chem. Soc.*, **83**, 3011 (1961).

(35) O. L. Chapman and L. F. Englert, *ibid.*, **85**, 3028 (1963).

(36) After Ahura Mazda or Ormuzd, the Zoroastrian god of light.

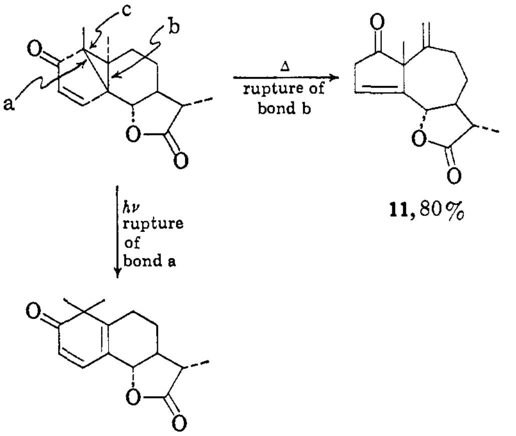
(37) A similar result has been reported in the photolysis of a saturated lumiproduct: O. L. Chapman, J. B. Sieja, and W. L. Welstead, Jr., *J. Amer. Chem. Soc.*, **88**, 161 (1966).

The nature of the skeletal rearrangement between lumisantonin (**9**) and the photoproducts (for example, mazdasantonin (**10**)) gives this reaction the characteristics discussed earlier of an ionic, carbonium ion type of transformation proceeding through a dipolar state such as **12**. This mechanism readily accounts for the methyl migration which occurs in the genesis of mazdasantonin (**10**) and the other products. Thus the rearrangement of lumisantonin to mazdasantonin provides a system which undergoes ionic-type photoinduced rearrangement *via* a triplet state and which might therefore be studied in order to obtain experimental evidence bearing on some of the points discussed previously.



9 **12** **10**

The possibility that a vibrationally excited ground state might be a significant intermediate in the photoreaction[24] will be considered first. Pyrolysis of lumisantonin under vacuum at 200° gave, after purification by chromatography, **11**, in a minimum yield of 80%. Thus pyrolysis of lumisantonin (which populates low-lying levels of the lumisantonin ground state) leads to rupture of bond b at least 80% of the time whereas photolysis on the other hand results in rupture of bond a at least 80% of the time. We therefore suggest that bond breaking in the photolytic reaction does not occur in a vibrationally excited level of the ground state, but rather takes place in an electronically excited state.[38-40a]

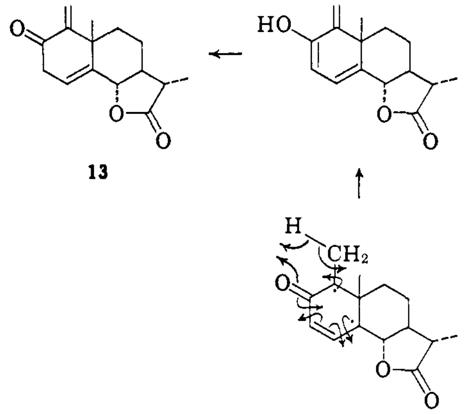


11, 80%

10, 80%

Recently there has been some indication that energy available to a complex organic molecule entering the ground-state vibrational manifold from an electronically excited state may be localized in a few bonds.[40b] However, even if photolytic rupture were to occur in a high vibrational level of the ground state, we would expect that collisional deactivation ($k \geqslant 10^{11}$ sec^{-1}) would occur more rapidly than methyl migration which is relatively slow, at least in the triplet diradical case ($k < 10^8$ sec^{-1}).[13a] In fact, the rarity of methyl migration in ground-state diradicals[14] suggests that the process is generally relatively slow. Examination of models indicates that, in the probable conformation of the diradical formed by rupture of bond a of lumisantonin (ring A in a quasi-chair with overlap between the C-5 radical center and the adjacent double bond), the hydrogen abstraction shown in Scheme IV is geometrically feasible. Since hydrogen abstraction is a commonly observed radical reaction, we would anticipate at least some formation of **13** whereas in fact none was found. The exclusive observation of naphthalenic products derived from methyl migration argues strongly for a dipolar rather than for a diradical precursor.

Scheme IV



13

The question of the n,π* or π,π* nature of the triplet intermediate will be considered next. When the phosphorescence spectrum of lumisantonin was measured in EPA glass[41] at 77°K, a weak structureless emission was observed, the 0–0 band of which falls at 64 ± 1 kcal/mol. Studies with photosensitizers of different triplet energies[42] support this value for the triplet energy for lumisantonin. Attempts to obtain a more precise value by flash spectroscopy were unsuccessful. The value of 64 ± 1 kcal for the triplet energy of lumisantonin lies between the ranges suggested as diagnostic for n,π and π,π* triplets.[43] Solvent shifts were not measurable as no phosphorescence was observed upon irradiation of lumisantonin in hydrocarbon glasses (*e.g.*, MCIP) at low temperatures. Therefore the nature of the triplet involved in the photoconversion of lumisantonin cannot be resolved on the basis of the spectroscopic evidence presently available.

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(38) *Cf.* P. J. Kropp and W. F. Erman, *J. Amer. Chem. Soc.*, **85**, 2456 (1963), footnote 26.

(39) This does not rigorously exclude bond breaking in a high vibrational level of the ground state, *i.e.*, that rupture of the bond occurs before deactivation at the moment the molecule crosses from an electronically excited state into the ground-state manifold. What evidence is available on this point suggests that, for simple molecules, deactivation to the first vibrational level is likely to be the fastest process available to a vibrationally highly excited ground-state species.[16,40a]

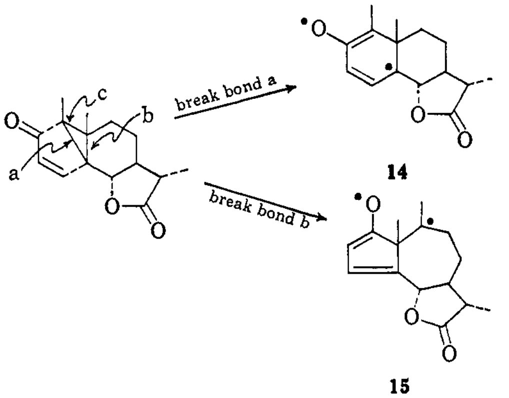
(40) (a) R. G. W. Norrish, *Chem. Brit.*, 289 (1965), and references cited therein; (b) E. F. Ullman and W. A. Henderson, Jr., *J. Amer. Chem. Soc.*, **88**, 4942 (1966).

(41) EPA = ether–pentane–alcohol (5:5:2), MCIP = methylcyclohexane–isopentane (5:1), MTHF–3MP = methyltetrahydrofuran–3-methylpentane.

(42) K. Sandros and H. Bäckström, *Acta Chem. Scand.*, **16**, 958 (1962).

(43) G. S. Hammond and P. A. Leermarkers, *J. Amer. Chem. Soc.*, **84**, 207 (1962); (b) M. Kasha, "Spectroscopy and Photochemistry," Collected Reports from Florida State University, 1960.

Once bond breaking has occurred in the triplet state, two triplet diradicals **14** and **15** are formed, depending on whether scission occurs at bond a or bond b.[44] The manner by which diradical **15** stabilizes itself by hydrogen abstraction to form **11** (a process which is analogous to photoenolization[45,46]) is characteristic of the n,π* [46,47] triplet state. This suggests that the triplet of lumisantonin from which both **15** and **14** are derived may also have n,π* rather than π,π* characteristics.

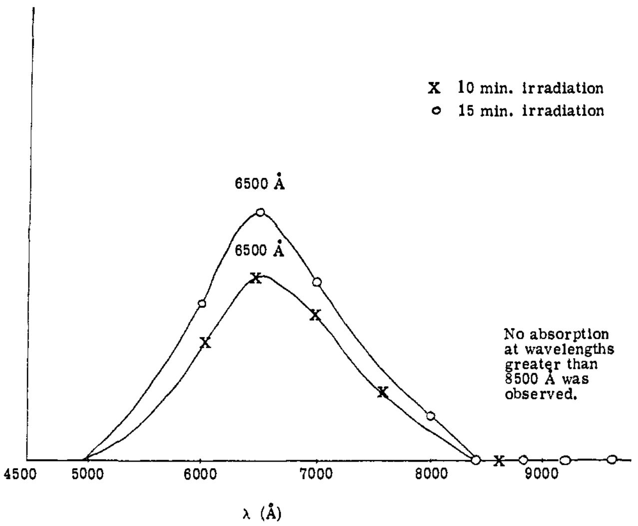


The intermediacy of cation radicals[5c] in the photoreaction of lumisantonin was eliminated by two studies. Nitrous oxide is known[48] to be an efficient electron scavenger by virtue of the reaction

$$N_2O + e^- \longrightarrow N_2 + O^-$$

However, mass spectrometric analysis of the gas phase following irradiation of lumisantonin and nitrous oxide in benzene solution in sealed, evacuated tubes revealed *no* nitrogen. Furthermore, irradiation of lumisantonin in a glass at 77°K in the presence of biphenyl did *not* give rise to the characteristic spectrum of the biphenyl anion radical. Hence, we conclude that, in the case of lumisantonin, the photorearrangement does not involve electron ejection and rearrangement of the resulting cation radical.

The next question to receive attention is whether the methyl migration which gives rise to the carbon skeleton of mazdasantonin occurs in the triplet diradical species **14** or in the dipolar species **12**, formed by electron demotion. Irradiation of lumisantonin in either EPA or MTHF–3MP glass at 77°K generates a blue species, the absorption spectrum of which is shown in Figure 1.[49] At 77°K the blue intermediate has a very long lifetime (samples have been kept without apparent change for up to 36 hr after irradiation has been stopped), but at 100°K the blue color lasts only a few seconds. We suggest that the microscopic rigidity of the EPA glass prevents the geometrical rearrangements necessary to allow migration of the methyl group. When lumisantonin is irradiated at 77°K in MCIP glass (which has a lower setting point than EPA glass), no color is observed, in accord with this hypothesis. Analogous viscosity effects have since been reported by Claridge[50] in optical studies of radicals trapped in matrices.



No absorption at wavelengths greater than 8500 Å was observed.

Figure 1. Difference spectrum of lumisantonin in 50:50 MTHF–3MP.

The low-temperature electron spin resonance spectrum of the blue species was determined to differentiate between the diradical **14** or the dipolar species **12** as the nature of the trapped intermediate.[51-53] At 69°K, a temperature at which the blue color does not fade within the limits of observation, the trapped species is *not paramagnetic* and cannot, therefore, be the diradical **14**. On the basis of this evidence we suggest that the blue intermediate is in fact the dipolar species **12**, which is formed by electron demotion and which undergoes ionic rearrangement to mazdasantonin.

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(44) Scission occurs preferentially at bond a and b rather than c to yield the longer conjugated system. On the other hand, photolysis of a saturated analog is reported to proceed mostly *via* bond c type scission.[37]

(45) E. F. Swicker, L. I. Grossweiner, and N. C. Yang, *J. Amer. Chem. Soc.*, **85**, 2671 (1963).

(46) N. C. Yang and C. Rivas, *ibid.*, **83**, 2213 (1961).

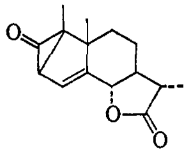
(47) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963).

(48) J. Jortner, M. Ottolenghi, and G. Stein, *J. Phys. Chem.*, **66**, 2037, 2042 (1962).

(49) For reference, the hydrated electron has λ_{max} at 580–600 μ. (a) H. Linschitz, M. G. Berry, and D. Schweitzer, *J. Amer. Chem. Soc.*, **76**, 5833, 5839 (1954); (b) M. R. Ronayne, J. D. Guarino, and W. H. Hamill, *ibid.*, **84**, 4230 (1962); (c) D. Schulte-Frohlinde and K. Eiben, *Z. Naturforsch.*, **179**, 445 (1962); (d) M. J. Blandamer, L. Shields, and M. C. R. Symons, *Nature*, **199**, 902 (1963); (e) J. E. Bennet, B. Milne, and A. Thomas, *ibid.*, **201**, 919 (1964).

(50) (a) R. F. C. Claridge and J. E. Willard, *J. Amer. Chem. Soc.*, **88**, 2404 (1966); Abstracts, 151st Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, N99. (b) Following the completion of this work, Zimmerman and coworkers reported pH dependence and sensitization studies of the photochemistry of 6,6-diphenylbicyclo-[3.1.0]hex-3-en-2-one which strongly suggest an analogous sequence, *viz.*, no phenyl migration to photophenol until after the triplet diradical has been converted into the ground state: H. E. Zimmerman, R. Reese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966). This paper and ref 16 are good leading references to the work of Zimmerman and coworkers.

(51) We did not consider the ground-state, completely bonded isomer **16** for two reasons.



16

(a) The departure from planarity involved in the formation of **16** from **12** or **14**, coupled with the inherent instability of the cyclopropanone moiety[52] and the fact that **16** lacks the conjugative stabilization present in either **12** or **14** made us feel that the equilibrium (**12** or **14**) $\rightleftharpoons$ **16** should lie far to the left.

(b) Cyclopropanone absorbs weakly in the ultraviolet region near 310 mμ[52] and 2,2-dimethylcyclopropanone absorbs near 340 mμ.[53] Consequently, the ultraviolet absorption maximum of **16** would not be expected to be shifted much past 400 mμ, in disagreement with the observed spectrum for the trapped intermediate.

(52) N. J. Turro and W. B. Hammond, *J. Amer. Chem. Soc.*, **88**, 3672 (1966).

(53) W. B. Hammond and N. J. Turro, *ibid.*, **88**, 2880 (1966).

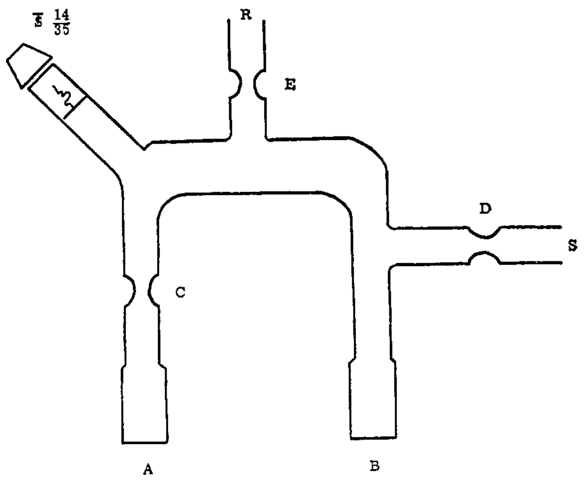


Figure 2.

In a separate experiment, attempts were made to trap the dipolar species by chemical reaction. A sample of lumisantonin in dimethyl acetylenedicarboxylate was cooled to 77°K and irradiated. The same blue color was observed. The matrix was allowed to warm sufficiently to discharge the blue color but the glass was not permitted to thaw. The solid solution was again cooled to 77°K and irradiation resumed. After several such cycles, the reaction products were separated. Only the usual products in the usual proportions were isolated.

Trapping of a dipolar intermediate such as **12** following deactivation of a triplet such as **14** has precedence in the photochemistry of diphenylamine as studied by Linschitz.[54]

Conclusion

On the basis of the foregoing experimental results, the ionic photochemistry of lumisantonin, *i.e.*, that process which results in products derived from methyl migration, can plausibly be resolved into the five discrete steps of the Zimmerman–Schuster mechanism: (1) excitation to a singlet state; (2) intersystem crossing to a very short-lived triplet state, probably of the n,π^* type; (3) bond breaking of the cyclopropane ring to give the triplet diradical **14**; (4) electron demotion and redistribution on the basis of the electronegativities of the atoms involved to give a dipolar state **12**; (5) ionic rearrangement from the dipolar state to mazdasantonin.

In addition to the ionic photochemistry of lumisantonin, a radical type of process occurs, presumably in the excited state, to give **11**. Other cases have been observed in which both ionic and radical pathways have been observed in a single photolysis, but this is the first case in which mass balance in excess of 95% has been obtained and the mechanisms of the two processes were studied in detail.

Experimental Section

Lumisantonin. Santonin (15 g) was dissolved in ethanol (750 ml) and irradiated with the full arc of a Hanovia 200-W lamp (s-654A)for 2hr. The solvent was removed and the residue chromatographed over 200 g of alumina (II). The lumisantonin was collected and chromatographed over 200 g of fresh alumina (II). In addition to recovered santonin (8 g), lumisantonin (3.2 g) was isolated (46% based on reacted santonin). After three crystallizations from acetone–hexane, colorless prisms were obtained, mp 153–155° (lit.[55] mp 153–155°).

Emission spectra were measured at 77°K using a photoelectric spectrophosphorimeter consisting of a Jarrell-Ash Ebert scanning monochromator (*f*/6), an EMI 9558 photomultiplier tube, a "rotating can" phosphoroscope, and appropriate recording electronics. A GE AH4 source was employed along with appropriate Corning glass or interference filters to isolate the group of mercury lines near 3130 or 3660 Å. We wish to thank Professor G. Hammond and Dr. A. Lamola for these spectra.

Actinometry was carried out either by the ferrioxalate method[56] or by use of the benzophenone–benzhydrol actinometer.[57]

For irradiations, a quartz immersion reactor was employed, consisting of an inner well for the light source (Hanovia type S 200W) and sleeve filter with a water cooling system between the inner and outer jackets. The filter was of uranium glass which is essentially opaque below 3200 Å. Solutions of santonin or lumisantonin in benzene were placed in an outer Pyrex vessel protected by a drying tube and equipped with a fritted disk at the bottom, through which nitrogen was bubbled beginning 1 hr prior to the photolysis.

The absorption spectrum of the intermediate **12** was measured on a Cary 14 by use of a dewar with quartz windows. The solution of lumisantonin (~10^{-3} *M*) in 50:50 MTHF-3-MP was cooled and irradiated with an AH6 lamp for the time indicated prior to measurement of the spectrum. Light was passed through a Kasha filter, a Corning No. 9863 filter, and the Pyrex wall of the cell to isolate the region from 3000 to 3200 Å. Consequently, the major line used for irradiation was that at 3130 Å.

Attempted Detection of the Solvated Electron by Spectroscopy. The blue solution prepared as above was scanned in the region 8000–16000 Å, but no absorption was observed. The solvated electron in MTHF is reported to have a monotonically increasing absorption in the range 4000–13000 Å.[58] In a separate experiment, irradiation of lumisantonin in the presence of 0.01 *M* biphenyl did not give rise to the characteristic spectrum of biphenylide anion ($\lambda_{\max}^{\text{MTHF}}$ 3800, 3950, 4100, 6500 Å).[57] Under these conditions, any electrons formed should have been scavenged by biphenyl.[57] We are most grateful to Doctors A. A. Lamola and J. P. Mittal of the Radiation Laboratory, University of Notre Dame, for the low-temperature spectral work.

Attempted nitrous oxide scavenging experiments were carried out in the Pyrex apparatus shown schematically in Figure 2. A 0.1 *M* solution of lumisantonin in benzene (1 ml) was pipetted into bulb A through side arm R. The apparatus was then connected to a vacuum line R, side arm S was connected to a cylinder of nitrous oxide, and both bulbs were cooled in liquid nitrogen. The apparatus was evacuated through R and sealed at E, and a small amount of nitrous oxide was condensed in bulb B. The remaining side arm was sealed at D and the system was allowed to warm to room temperature. In this way significant positive pressure of nitrous oxide was maintained. If no explosion occurred on warming, the lumisantonin solution was irradiated with a high-pressure mercury arc (Hanovia, 200 w) until considerable mazdasantonin had accumulated as shown by its characteristic yellow color. Bulb A was then cooled to liquid nitrogen temperature and sealed at C. No evidence of the presence of nitrogen in the gas in the apparatus was found by mass spectroscopy. We are grateful to Dr. S. Manatt for these determinations.

Flash spectroscopy was attempted on a 1.06×10^{-4} *M* solution of lumisantonin in benzene using a 21-cm Uranyl glass (Pyrex window) cell and a flash photoelectric apparatus after Porter and Wright[59] (~10^{20} quanta/flash; flash duration *ca.* 15 μsec). No transients could be detected in the wavelength range 3650–5000 Å. We are grateful to Dr. W. G. Herkstroeter who performed this experiment.

Pyrolysis of Lumisantonin. Lumisantonin (502 mg) was heated under vacuum in a sealed ampoule at 200° (Wood's metal bath) for 1 hr. Liquid–liquid chromatography at 30.0° (two phases formed by shaking 500 ml of nitromethane, 1 l. of hexane, and 200

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[54] H. Linschitz and K. H. Grellmann, *J. Amer. Chem. Soc.*, **86**, 303 (1964); K. H. Grellmann, G. M. Sherman, and H. Linschitz, *ibid.*, **85**, 1881 (1963).

[55] D. H. R. Barton, P. deMayo, and M. Shafig, *J. Chem. Soc.*, 140 (1958).

[56] (a) J. Saltiel, Ph.D. Thesis, California Institute of Technology, 1964; (b) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 578 (1956).

[57] W. M. Moore and M. Ketchum, *J. Amer. Chem. Soc.*, **84**, 1368 (1962).

[58] M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *J. Amer. Chem. Soc.*, **84**, 4230 (1962).

[59] G. Porter and M. R. Wright, *J. Chim. Phys.*, **55**, 705 (1958).

ml of benzene; all solvents dried and distilled just before use) yielded, in addition to 334 mg of recovered lumisantonin, 172 mg of impure **11**. The identity of **11** with the product of lumisantonin formed in 10% yield by photolysis was established by the superimposability of their infrared, ultraviolet, and nmr spectra.

Graded sensitizer experiments are described in detail in a following paper of the series.

Low-Temperature Electron Spin Resonance Study. A 1-ml sample of lumisantonin in ethanol (approximately 2 × 10^{-2} *M*) was prepared in a quartz epr tube and degassed by three freeze–thaw cycles on a vacuum line. The tube was sealed, cooled to liquid nitrogen temperature, and irradiated with the 3130-Å mercury line in the phosphoroscope dewar apparatus. Within 15–20 min after the irradiation was begun, a rich blue color had been developed at the surface of the sample. The tube was then transferred to the precooled cavity of a Varian X-band spectrometer, Model 4500. The temperature was kept at −190 ± 2° by means of a variable-temperature controller, Model V-4540. A PRD Electronics Frequency meter, Type 535, was used for calibration. The region from 2000 to 4000 G was repeatedly scanned at settings of 6.3 × 100 (modulation amplitude) and 2 × 1000 (gain), but no signal was observed. No observable loss in the intensity of the sample color occurred during this time. Under identical conditions, but with a gain setting of 10, a strong pitch reference gave an easily discernible signal. We are grateful to Mr. Lahmer Lynds for help with this experiment.

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Photoproducts from Irradiation of Lumisantonin in Aprotic Medium

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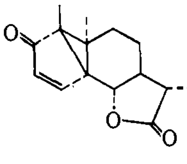
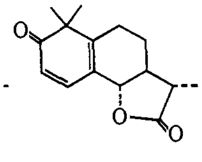
Received July 10, 1967

Abstract: Irradiation of lumisantonin in aprotic medium yields mazdasantonin, II, and double bond isomer of pyrolumisantonin, V. In addition, other monomeric photoproducts are isolated as well as a substance believed to be a dimer of mazdasantonin. Structural possibilities for these are discussed.

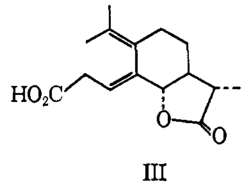
Irradiation of lumisantonin (I) in aprotic solvents such as benzene, with or without benzophenone as photosensitizer, leads to new photoproducts of which the major one is mazdasantonin[3] (structure II) and, together with another substance, probably a dimer of mazdasantonin, to be discussed subsequently, accounts for about 80% of the product mixture. A substance with this structure has previously been invoked as a transitory intermediate in the photoconversion of santonin to santonic acid (III).[4,5] In addition to mazdasantonin, other substances A, B, C, and F in addition to small amounts of photoproducts D and E which arise from B can be isolated from photolysis of lumisantonin in benzene by liquid–liquid partition chromatography.



I



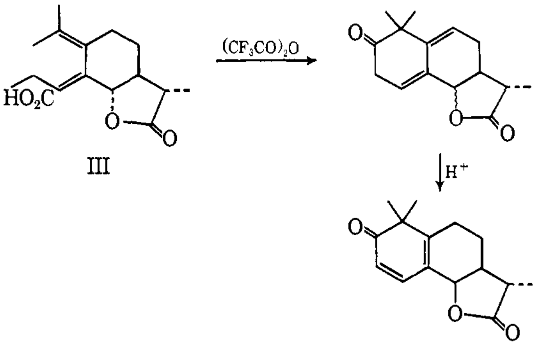
II



III

No phenolic products are, however, formed.

Mazdasantonin ($C_{15}H_{18}O_3$) is isomeric with santonin and shows a single intense peak in the ultraviolet spectrum at 318 mμ (log ε 3.89). The 6-epi isomer of mazdasantonin is chemically accessible by treatment of photosantonic acid with trifluoroacetic anhydride followed by acid-catalyzed rearrangement of the double bonds (III → IV).[6] Chapman also obtained[7] the dinitrophenylhydrazone derivative of 6-epimazdasantonin by treatment of the products of irradiation of lumisantonin with dinitrophenylhydrazine under acidic conditions. In the ultraviolet spectrum, 6-epimazdasantonin has a maximum at 308 mμ which is far from the value of 338 mμ predicted for this system.[8] The hypsochromic shift of 10 mμ when mazdasantonin is isomerized at C-6 (to a *cis*-fused lactone) probably reflects differences in planarity of the dienone chromophore.



III

IV

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(3) Named after Ahura Mazda (also called Ormazd or Ormuzd), the "Good Spirit" and god of light of Zoroastrianism.

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