diradical generated by spontaneous loss of nitrogen,[9] (4) the source, *via* hydrolysis, of diimide which reacts with VI to yield excited VII,[10] and (5) a species which reacts with hydroperoxide ion, eventually yielding light.[2b,11]

Our experiments with pure I render proposals 1–4, as applied to hydrazide II, untenable. Path 1 is incompatible with the ultraviolet spectrum and nonfluorescence of I, (2) predicts that I is nonchemiluminescent, (3) requires that the diazaquinone lose nitrogen very rapidly, and (4) predicts that I should chemiluminesce in the absence of hydroperoxide ion.[10b] We infer that luminol and other hydrazides which react under similar conditions to yield the excited state of the corresponding dicarboxylate ion[2] also do not chemiluminesce by pathways 1–4.

Since I yields chemiluminescence and since its cyclopentadiene adduct III can be isolated[11] from the chemiluminescent reaction of II with hydrogen peroxide and hemin (or hypochlorite ion), and also from the persulfate oxidation[12,13] of II, compound I must be responsible for some of the light emission from the hydrazide II. It seems probable that diazaquinones are intermediates in the major light-producing pathway of other cyclic hydrazides as well.[14] Kinetic studies[12] of the persulfate oxidation of VII support this hypothesis.

Species corresponding to VIII may originate from the reaction of diazaquinones with hydroperoxide ion, or alternatively from reaction of diazasemiquinones (generated *via* one-electron processes) with hydroperoxy radicals. Closure of VIII to an *endo*-peroxide might then yield the immediate precursor of the excited dicarboxylate ion, although evidence concerning these points is lacking.

Acknowledgment. This investigation was supported by Public Health Service Research Grant No. NB 07868 of the National Institute of Neurological Diseases and Blindness.

[9] J. R. Totter, W. Stevenson, and G. E. Philbrook, *J. Phys. Chem.*, **68**, 752 (1964).

[10] (a) H. O. Albrecht, *Z. Physik. Chem.*, **A136**, 321 (1928); (b) H. Kautsky and K. H. Kaiser, *Z. Naturforsch.*, **5b**, 353 (1950); (c) W. S. Metcalf and T. J. Quickenden, *Nature*, **206**, 507 (1965).

[11] The trapping of an adduct from luminol has recently been claimed: Y. Omote, T. Miyake, and N. Sugiyama, *Bull. Chem. Soc. Jap.*, **40**, 2446 (1967).

[12] M. M. Rauhut, A. M. Semsel, and B. G. Roberts, *J. Org. Chem.*, **31**, 2431 (1966).

[13] The initial oxidation of luminol by persulfate ion does not require hydrogen peroxide.[12]

[14] Our previous report[2b] that phthalazine-1,4-dione is essentially nonchemiluminescent is correct (phthalate ion is *non*fluorescent). The corresponding hydrazide does chemiluminesce weakly, however, but the reaction pathway is different from that found for the other hydrazides (work in progress).

Emil H. White, E. Gary Nash
David R. Roberts, Oliver C. Zafiriou
Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218

Received July 8, 1968

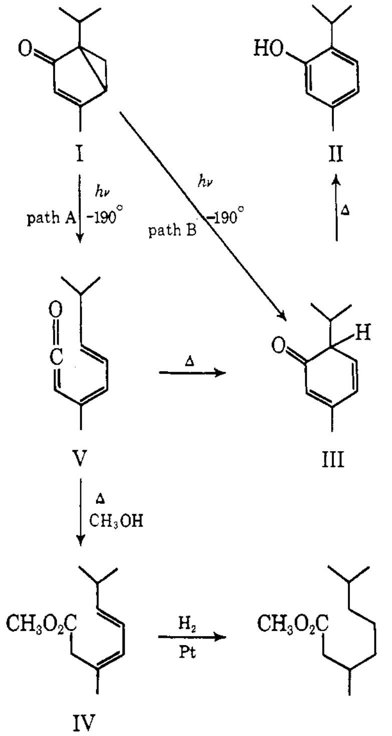
Low-Temperature Photochemistry of Umbellulone and Lumisantonin[1]

Sir:

Wheeler and Eastman reported in 1959 that irradiation of neat umbellulone (I) at room temperature gave quantitatively thymol (II).[2] We have studied the photochemistry of umbellulone (I) at −190°. Our results define two mechanistic paths leading from I to II under these conditions.

Irradiation (Pyrex filter) of neat umbellulone in a liquid nitrogen cooled infrared cell leads to formation of two primary photoproducts, a ketene derivative ($\nu_{C=O}$ 2113 cm^{-1}) and a product with absorption at 1670 and 1630 cm^{-1}. Thymol is not a primary photoproduct under these conditions. During warm-up, the product with absorption bands at 1670 and 1630 cm^{-1} goes rapidly to thymol at about −90° and the ketene goes to thymol[3] above −70°. The absorption bands at 1670 and 1630 cm^{-1} and the conversion to thymol permit tentative identification of this product as the dienone (III) (Scheme I).

Scheme I



Irradiation of umbellulone in methanol at room temperature gives only thymol, but the ketene derivative can be trapped by irradiating unbellulone in an ether–methanol (4:1) glass at −190°, then warming. The structure of the methyl ester (IV) thus obtained follows from its empirical formula, spectral properties,[4] and hydrogenation to methyl 3,7-dimethyloctanoate (identified by comparison with an authentic sample). The structure of the ketene then is V. The 3,4 double bond

[1] Photochemical Transformations. XXVII.

[2] J. W. Wheeler and R. H. Eastman, *J. Amer. Chem. Soc.*, **81**, 236 (1959).

[3] The glass is warmed until the 1670- and 1630-cm^{-1} bands have disappeared (~−80°) and then cooled to −190°. During the warming, the disappearance of the 1670- and 1630-cm^{-1} bands and the appearance of thymol bands can be followed. The spectrum of the glass after the initial warm-up and recooling to −190° shows the absorption bands of thymol and shows no change in the intensity of the ketene band. A second warm-up is then carried out. The ketene band is monitored and ketene begins to disappear above −70°. The disappearance of the ketene absorption correlates with an increase in the intensity of the thymol absorption bands.

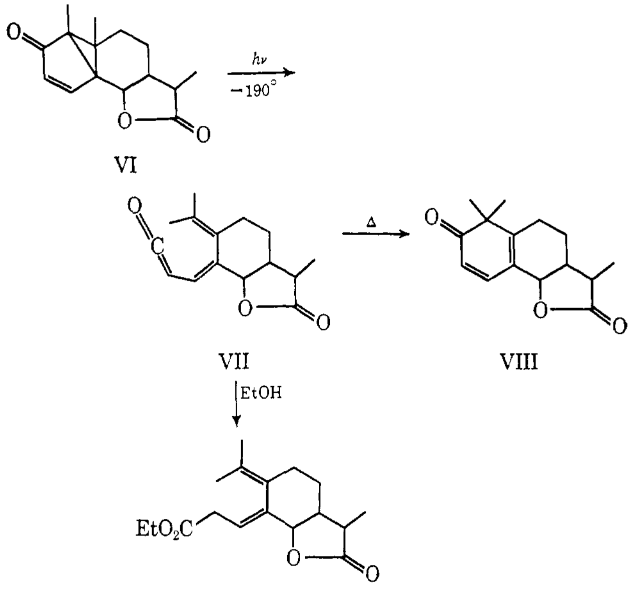
[4] Molecular weight 182 (mass spectrum); ν_{max}^{film} 1739 cm^{-1}; 3 olefinic H (δ 4.9–6.3, m), OCH$_3$ (δ 3.63, s), CH$_2$ (δ 3.08, s), isopropyl methine H (δ 2.2–3.0, m), olefinic methyl H (δ 1.87), isopropyl methyl H (δ 1.0, d, J = 6.5 Hz).

must be *cis*, and the 5,6 double bond is tentatively considered to be *trans* on the basis that this stereochemistry is most consistent with the facile cyclization of the diene ketene.[5] Thermal cyclizations of diene ketenes to 2,4-cyclohexadienones have been observed in other systems.[6–8]

There are two routes from umbellulone to thymol at low temperature, both involving ground-state intermediates. In the methanol-trapping experiments at −190° comparable yields of ester and thymol are obtained. This result suggests that path A accounts for at least half of the thymol produced under these conditions. The fact that irradiation of umbellulone in methanol at room temperature gives no ester could mean either that diene ketene (V) cyclization to III is too fast at this temperature for nucleophilic attack by methanol to compete or that only path B is operative.

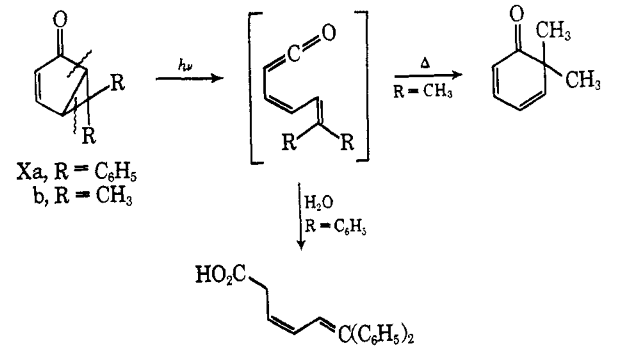
Irradiation of lumisantonin (VI) at room temperature gives a variety of products including VIII.[9–11] Irradiation of lumisantonin (VI) (crystalline or in an EPA glass) at −190° gives a ketene (VII) as a primary photoproduct (Scheme II). It is possible that a trace of dienone VIII is produced as a primary product. We have observed also the blue species reported by Fisch and Richards,[10] but we have not been able to show conclusively that it goes thermally to dienone VIII. The ketene is assigned structure VII because on warming to room temperature it cyclizes to the dienone VIII. When lumisantonin (VI) is irradiated in an EPA glass at −190° then warmed above −160° the ketene absorption (2113 cm^{-1}) disappears with concurrent appearance of an absorption at 1738 cm^{-1} assigned to the carbonyl group of the ester IX. The sequence VI (*hν*) → VII (Δ) → VIII is an important but probably not unique path from VI to VIII.

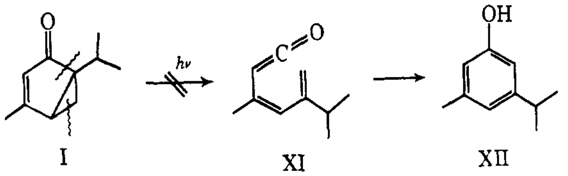
Scheme II



Cyclization of ketenes V and VII is analogous to that reported in related systems.[6–8] The opening of the cyclopropane rings in I and VI, however, follows a different course from that observed in Xa[12] and Xb[7] (Scheme III). Cleavage of umbellulone in this fashion would produce a diene ketene (XI) which should cyclize to *sym*-thymol (XII). *sym*-Thymol is not formed at room temperature[2] and could not be detected in any of our spectra.

Scheme III





The difference in the nature of the ring-opening process in I and VI as opposed to Xa,b may be due to differences in the position of substituents. Formation of ketenes V and VII from umbellulone and lumisantonin may involve a ketene–carbene mechanism as suggested by van Tamelen and coworkers.[13]

Acknowledgment. This investigation was supported by Public Health Service Grant GM 14305 from the National Institute of General Medical Sciences. A generous sample of umbellulone was provided by Professor James Wheeler.

---

(5) It is assumed that the stereochemistry of the double bonds is maintained in the addition of methanol. This has been shown to be true for related diene ketenes (P. M. Collins and H. Hart, *J. Chem. Soc. C*, 1197 (1967)).

(6) J. Griffiths and H. Hart, *J. Amer. Chem. Soc.*, **90**, 3297 (1968).

(7) J. S. Swenton, E. Saurborn, R. Srinivasan, and F. I. Sonntag, *ibid.*, **90**, 2990 (1968).

(8) J. D. Hobson, M. M. A. Holly, and J. R. Malpass, *Chem. Commun.*, 764 (1968).

(9) For a review of the photochemistry of santonin and related compounds see P. J. Kropp in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 1.

(10) M. H. Fisch and J. H. Richards, *J. Amer. Chem. Soc.*, **90**, 1547, 1553 (1968); **85**, 3029 (1963).

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

(12) H. E. Zimmerman, R. Keese, J. Masielski, and J. S. Swenton, *ibid.*, **88**, 4895 (1966); H. E. Zimmerman and D. I. Schuster, *ibid.*, **84**, 4527 (1962).

(13) E. E. van Tamelen, S. H. Levin, G. Brenner, J. Wolinsky, and P. Aldrich, *ibid.*, **80**, 501 (1958); **81**, 1666 (1959).

(14) NASA Trainee, 1965–1968.

Loren Barber,[14] O. L. Chapman, Jean D. Lassila
Department of Chemistry, Iowa State University
Ames, Iowa 50010

Received July 1, 1968

Steric Effects in the Ozonolysis of 1,2,3,4-Tetraphenylcyclobutenes

Sir:

The renewed interest in the mechanism of olefin ozonolysis has demonstrated that steric requirements of the olefinic substituents play an important role in determining product stereospecificity.[1,2] This has led to