

degradation. A strong infrared absorption band at 2820 cm.⁻¹ which is shifted on deuteration to 2105 cm.⁻¹ and an n.m.r. peak at 14.4 p.p.m. from TMS suggest the presence of a strong intramolecular N···H—O hydrogen bond.⁵ Substitution of a hydroperoxide for hydrogen peroxide in the reaction with lophyl radical produces a mixed peroxide. Cumyl hydroperoxide is converted to Ib, m.p. 132–134° (*Anal.* Found: C, 80.9; H, 5.18; N, 6.2), and *t*-butyl hydroperoxide yields Ic, a liquid (*Anal.* Found: C, 78.3; H, 6.5; N, 7.5). The infrared spectra of Ia–c are very similar to that of 2,4,4,5-tetraphenyl-4H-isoimidazole (Id)⁶ between 2000 and 650 cm.⁻¹.⁷ This similarity of spectra and the formation of N,N'-dibenzoylbenzamidine III from the chemiluminescent reaction (see below) in 70% yield and from thermal degradation of Ia suggest the peroxidic group is on the C-4 position of the imidazole ring.

The hydroperoxide Ia exhibits several novel properties. It is thermochemiluminescent above 110° and is chemiluminescent on treatment with base. No additional oxidizing agent is required. The hydroperoxide Ia thus could be an intermediate in the known chemiluminescence of lophine. The action spectra from thermochemiluminescence and chemiluminescence of Ia have been found to be essentially identical with that of the chemiluminescence of lophine with the maximum occurring at approximately 530 mμ. For Ia, the quantum efficiency for thermochemiluminescence (*ca.* 3 × 10⁻⁷) has been found to be about a factor of five smaller than that for chemiluminescence. The similarity of products, action spectra, and quantum yields suggests the possibility of a common emitting species from both thermal and base-induced chemiluminescence.

The chemiluminescence may arise from a triplet-to-singlet transition in the anion of lophine. Investigation of the spectral properties of the reaction products⁸ has shown that at -196° lophine phosphoresces strongly at 523 mμ in alcoholic potassium hydroxide and weakly in absolute alcohol. It therefore seems possible that the excited anion of lophine is formed from the decomposition of the anion of Ia and is the light emitter in the chemiluminescence reaction.^{9,10} In the

(5) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2900 (1961).

(6) D. M. White and J. Sonnenberg, *J. Org. Chem.*, **29**, 1926 (1964).

(7) Compounds Ia–d have characteristic absorptions of the same relative intensities near 1600, 1570, 1540, 1490, 1450, 1320, 1270, 1090, 1060, 1025, 940, 760, 720, and 690 cm.⁻¹ but they differ from 2,2,4,5-tetraphenyl-2H-isoimidazole (no corresponding 1570, 1320, 1060, and 720 cm.⁻¹ absorptions) and from *N*-substituted triarylimidazoles (no characteristic imidazolyl 1502 cm.⁻¹ absorption).⁶

(8) The principal products from Ia after base or heat treatment are III, lophine, and oxygen.

(9) Compounds in liquid solution do not ordinarily appear to phosphoresce at room temperature because competing processes successfully quench the phosphorescence. At low temperature or in viscous solutions competing processes are minimized and phosphorescence can sometimes be observed. Using a sufficiently high energy source, such as those used in flash photolysis, it is possible to produce a high concentration of active species at one time to enable phosphorescence to be observed at room temperature. It is expected that a rapid chemical reaction can also generate a similar high concentration.

case of the weaker thermochemiluminescence either free lophine or its anion in smaller concentration may be the emitter.

Since phosphorescence is inefficient at room temperature and oxygen is a quenching agent, it appears reasonable that the decomposition of Ia which produces oxygen should give rise to a low quantum efficiency. The possibility that the chemiluminescence of lophine may arise from singlet-to-singlet transition is difficult to rule out unequivocally. There may be some trace reaction products which have not been examined as possible emitters and the low level of light emission requires large slit widths in the spectrophotometer which results in relatively poor resolution (*ca.* 5 mμ).

(10) For the chemiluminescence of 2-(*p*-dimethylaminophenyl)-4,5-diphenylimidazole (see M. J. C. Harding and E. H. White, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1964, p. 34S), the light emission is attributed to a singlet-to-singlet transition in *N,N*-dibenzoyl-*p*-dimethylaminobenzamidine. For lophine chemiluminescence the analogous amidine (compound III) fluoresces very weakly in basic media at 508 mμ and seems unlikely as the emitting species.

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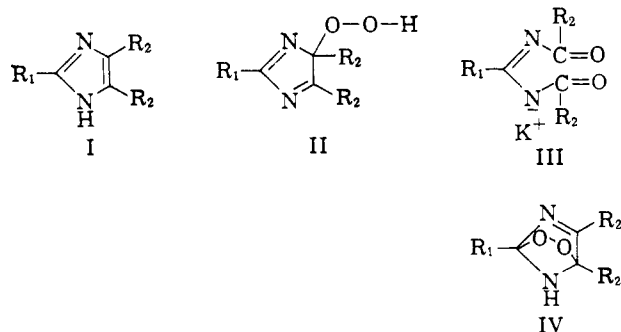
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The Chemiluminescence of Lophine and Its Derivatives¹

Sir:

The chemiluminescence of lophine (2,4,5-triphenylimidazole, Ia) was discovered in 1877 by Radziszewski who stated that, in the presence of air and a strong base, lophine yielded ammonia, benzoic acid, and enough light to illuminate the surroundings.² Kautsky and Kaiser later reported that a radical was formed in the oxidation of lophine and that the radical yielded light on reaction with a base.³ Recently, however, Hayashi and Maeda showed that oxygen was required for the luminescence, and they suggested that peroxides were involved.⁴ We found independently that peroxides could be made from the radical and its dimers,⁵ and, furthermore, that an active peroxide could be made by the irradiation of lophine in the presence of oxygen. This peroxide had, in fact, been prepared earlier,⁶ but its chemiluminescence had apparently not been noticed.

We have synthesized a number of substituted imidazoles (I) and from these, at low temperatures, the peroxides (II). The n.m.r. spectra (*sharp* singlet for



- a, R₁ = R₂ = C₆H₅
 b, R₁ = *p*-CH₃OC₆H₄, R₂ = C₆H₅
 c, R₁ = R₂ = *p*-CH₃OC₆H₄
 d, R₁ = *p*-(CH₃)₂NC₆H₄, R₂ = C₆H₅
 e, R₁ = *p*-(CH₃)₂NC₆H₄, R₂ = *p*-CH₃OC₆H₄

(1) Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1964; Abstracts, p. 34S.

(2) Br. Radziszewski, *Ber.*, **10**, 70 (1877).

(3) H. Kautsky and K. H. Kaiser, *Naturwiss.*, **31**, 505 (1943).

(4) T. Hayashi and K. Maeda, *Bull. Chem. Soc. Japan*, **35**, 2057 (1962).

(5) We thank Dr. J. H. M. Hill for samples of various substituted lophine dimers.

(6) C. Dufraisse, A. Etienne, and J. Martel, *Compt. rend.*, 970 (1957).

the OH at 12.4 p.p.m. in deuterioacetone), the infrared spectra which show a hydrogen-bonded OH band at 3.5μ (not found for the lophines I), and the ultraviolet spectra show that these compounds are hydroperoxides (II) and not endoperoxides (IV) as claimed by Dufrasse.⁶ The ultraviolet spectra of compounds IIa and b (283 and 307 $m\mu$, respectively, in alcohol) are especially instructive in that they are not identical (as required if structure IV were correct or if the peroxides contained a 2-hydroperoxy group), and the absorptions are at considerably longer wave lengths than those of simple imine models for compound IV ($C_6H_5-CH=NCH_2C_6H_5$ at 249 $m\mu$, and $p-CH_3OC_6H_4CH=NCH_2C_6H_4OCH_3$ at 271 $m\mu$).⁷ Independent and conclusive evidence for the hydroperoxide structure of the peroxide of lophine itself has been obtained by Sonnenberg and White.⁸

The derivatives of lophine (Ib-e) are more efficient than lophine itself; electron-releasing substituents have the same effect here as in the chemiluminescence of the phthalic hydrazides.⁹⁻¹¹ All of the imidazoles (I) yielded light on reaction with a base and oxygen, and all of the peroxides (II) yielded light on reaction with base alone. Furthermore, the imidazoles and the corresponding peroxides yielded light of the same wave length (Table I), indicating that for each pair a common

TABLE I
EMISSION WAVE LENGTHS^a

Compound	Wave length, $m\mu^b$	Chemiluminescence (C) or fluorescence (F)
I, IIa	530	C
I, IIb	528	C
I, IIc	525	C
I, IId	489	C
I, IIe	485	C
I, IId	487	F
I, IIe	485	F

^a In ethanol. ^b $\pm 1 m\mu$.

light emitter is involved. The anion of the hydroperoxide (II) is probably a common intermediate in the two reactions.

We found further that salts of diarylarylamidines (III) are products of both reactions and that in the two most efficient cases the fluorescence emissions of the amidine salts match the chemiluminescence emissions of the corresponding lophines¹² (Table I). This suggests that these amidine salts are the light emitters in the chemiluminescence.

The following reaction scheme is a logical possibility for the lophine chemiluminescence; hydrogen bonding by the solvent should facilitate the addition leading to the four-membered ring.

(7) R. Juday and H. Adkins, *J. Am. Chem. Soc.*, **77**, 4559 (1955).

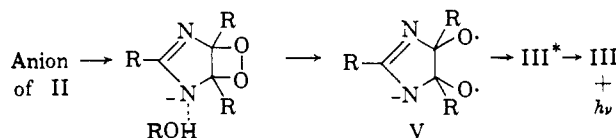
(8) J. Sonnenberg and D. M. White, *ibid.*, **86**, 5685 (1964).

(9) E. H. White and M. M. Bursey, *ibid.*, **86**, 941 (1964); E. H. White, O. Zafrion, H. M. Kagi, and J. H. M. Hill, *ibid.*, **86**, 940 (1964).

(10) The effect of substituents on the chemiluminescence of lophine has been put on a quantitative basis recently by G. E. Philbrook and M. A. Maxwell [*Tetrahedron Letters*, No. 19, 1111 (1964)].

(11) Measured against luminol, which has a quantum yield in chemiluminescence of 0.05; the quantum yield of compound 1e is ca. 10^{-3} .

(12) The amidine derivatives 111a-c are weakly fluorescent and we have not been able to make accurate measurements; preliminary evidence indicates that they emit at wave lengths shorter than the chemiluminescence values. Emission from the triplet states of I, III, etc., should be considered, but in the rare instances where this process has been observed in the liquid phase at room temperature, it is completely quenched by oxygen (H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958)).



Light emission occurs from the excited singlet state of compound III and possibly the singlet state is formed directly; on the other hand, the triplet states of V and III may be intermediates as suggested for the chemiluminescence of the phthalic hydrazides.^{9,13}

We reported earlier that oxygen was a reactant in most if not in all chemiluminescent reactions in solution.^{9,14} As shown for the lophine reaction, the oxygen need not be involved directly in the step giving the excited state of the emitter, but it could yield a peroxide, the decomposition of which would lead to chemiluminescence. Such a peroxide may be involved in the bioluminescence of the bacterium *Achromobacter fischeri* in which a reaction product of oxygen and the enzyme luciferase is formed; this species then yields light under anaerobic conditions on the addition of an aldehyde.¹⁵ Similar peroxides may be involved in the bioluminescence of the jellyfish *Aequorea*, which is triggered under anaerobic conditions by calcium ion¹⁶ and in systems where hydrogen peroxide is a requirement.¹⁷ The need for oxygen is not universal, however, since neither oxygen nor peroxides are apparently involved in some chemiluminescent reactions of radical anions.^{18,19}

Acknowledgment.—We thank the National Institutes of Health for its support of this work (Grant GM 10849).

(13) Efforts to intercept and quench the triplet states with carotene have not been successful.

(14) E. H. White in "Light and Life," W. D. McElroy and B. Glass, Ed., The Johns Hopkins Press, Baltimore, Md., 1961.

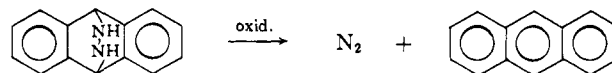
(15) J. W. Hastings and Q. H. Gibson, *J. Biol. Chem.*, **238**, 2537 (1963).

(16) O. Shimomura, F. H. Johnson, and Y. Saiga, *J. Cellular Comp. Physiol.*, **62**, 1 (1963).

(17) L. S. Dure and M. J. Cormier, *J. Biol. Chem.*, **238**, 790 (1963).

(18) "Chemiluminescent Materials," Technical Report No. 4, American Cyanamid Company, 1964; E. A. Chandross and F. I. Sonntag, *J. Am. Chem. Soc.*, **86**, 3179 (1964); D. M. Hercules, *Science*, **145**, 808 (1964).

(19) It is interesting in this connection that an exothermic reaction such as



in which a fluorescent product is formed is not chemiluminescent.

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Photosensitized Coloration of Photochromic Spiropyran

Sir:

Photoisomerization reactions sensitized by ketones and in particular aromatic ketones have been reported to proceed with high yields.^{1,2} The present communication describes similar benzophenone-sensitized photo-coloration of some photochromic spiropyran, whose

(1) G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963), and references cited therein.

(2) (a) S. Malkin and E. Fischer, *J. Phys. Chem.*, **66**, 2482 (1962); (b) *ibid.*, **68**, 1153 (1964).