

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).

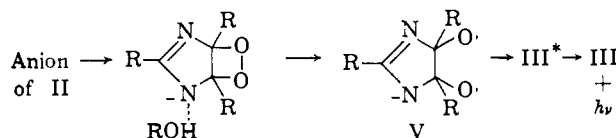
(8) J. Sonnenberg and D. M. White, *ibid.*, **86**, 5685 (1964).

(9) E. H. White and M. M. Bursey, *ibid.*, **86**, 941 (1964); E. H. White, O. Zafrionu, 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 Ie is ca. 10^{-3} .

(12) The amidine derivatives IIIa-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.

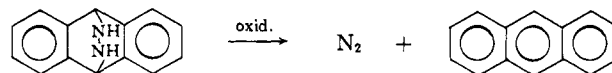
(15) J. W. Hastings and Q. H. Gibson, *J. Biol. Chem.*, **238**, 2537 (1963).

(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:

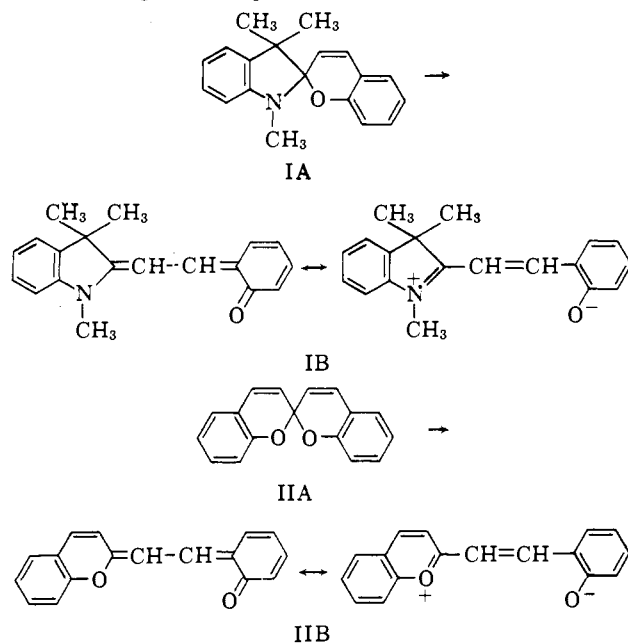
Photoisomerization reactions sensitized by ketones and in particular aromatic ketones have been reported to proceed with high yields.^{1,2} The present communication describes similar benzophenone-sensitized photo-coloration of some photochromic spiropyran, whose

(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).

direct photocoloration and photoerasure have been investigated extensively in this laboratory.³

Color formation in these compounds is usually assumed to be due to transformation of the spiropyran to the corresponding merocyanine, as exemplified by the following two compounds.



In solutions of both compounds the thermal back reaction $B \rightarrow A$ is fast at room temperature, and photoisomerization experiments (other than flash experiments⁴) therefore have to be performed at tempera-

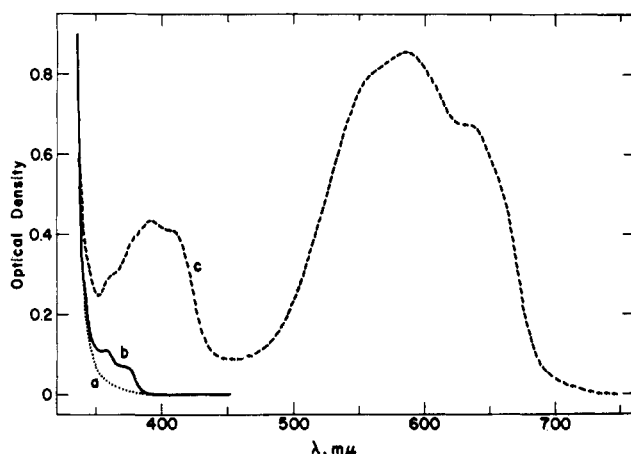


Fig. 1.—Spectra of (a) compound I, 0.02 *M*; (b) I, 0.02 *M* + benzophenone, 0.005 *M*; (c) solution b after irradiation for 5 min. at 365 *mμ* (spectra were measured at 173°K. in a 1-mm. cell).

tures below about -90° . Under such conditions direct photoisomerization $A \rightarrow B$ with light at 313 *mμ* proceeds⁴ with a yield of about 0.10.

The above two compounds are particularly suitable for an investigation of sensitized photoisomerization of spiroyrans since both do not absorb at 365 *mμ*, where benzophenone triplet formation is highly efficient¹ (Fig. 1). Moreover, the product of the photo-reaction, the merocyanine, has a very high extinction coefficient (10^4 – 10^5) in the visible region where neither

the reactant nor the sensitizer absorb. The system spiropyran (*hν*, benzophenone) \rightarrow merocyanine is therefore extremely sensitive, and the kinetics of the reaction $A \rightarrow B$ can be followed easily even if the extent of the over-all conversion amounts to only 1:1000. Thus the yields during the initial phases of the photo-conversion, or else very low yields, such as may be expected in rigid media at low temperatures, can be determined.

Most experiments were carried out in 1-mm. cells, using the low-temperature technique described.^{2a,3c} In a typical experiment (Fig. 1), a mixture of I (0.02 *M*) and benzophenone (0.005 *M*) in methylcyclohexane–2-methylpentane (2:1) was irradiated at 173°K. with light at 365 *mμ*, hitting the surface of the cell at a rate of 3×10^{-7} einstein/min. Under these conditions the optical density at 540 *mμ* after about 6 min. of irradiation is 1.00. In the absence of benzophenone no coloration is detectable after 60 min. of similar irradiation.

In calculating the quantum yield, *i.e.*, the number of moles of merocyanine formed per einstein absorbed by benzophenone, one has to take into account the absorption of light at 365 *mμ* by the merocyanine. However, the photosensitized back reaction $B \rightarrow A$, even if it exists, can safely be ignored since the highest concentration of B is only 2% of that of A. The direct photoconversion $B \rightarrow A$ has a yield of $<10^{-3}$ under those conditions. The resulting yields at the highest spiropyran concentration used (0.02 *M*) and -100° are approximately 1.0, subject to the uncertainty in the determination of the merocyanine concentration.^{3c} These yields are probably close to the limiting ones which should be attained at infinitely high spiran concentrations, when every triplet benzophenone molecule will encounter a spiran molecule during the former's lifetime.

It is to be expected that the diffusion-controlled energy-transfer process⁵ from benzophenone to spiran will be strongly slowed down at temperatures at which the medium is "rigid." Preliminary experiments with the above solution at -169° showed that the rate of merocyanine formation under otherwise identical conditions was indeed reduced to about 3×10^{-2} of its value at -100° . These experiments also proved that the merocyanine isomer formed at such a low temperature, just like the one formed during *direct* photocoloration with light at shorter wave lengths, under similar conditions, is predominantly the "X" isomer^{3e,4} which on warming up is converted into an equilibrium mixture of the various isomers.

Irradiation with 365 *mμ* at -184° did not result in any coloration. It should be noted that *direct* photoisomerization with light at shorter wave lengths proceeds under these conditions with almost the same yield^{3e} as at -100° . This is to be expected for an intramolecular process, as distinct from the bimolecular process of sensitized photocoloration.

As in the case of stilbene,^{2b} no effect of deaeration on the yield of photosensitized isomerization was found.

(5) G. Porter and F. Wilkinson, *Proc. Roy. Soc. (London)*, **A264**, 1 (1961).

(3) (a) Y. Hirshberg and E. Fischer, *J. Chem. Soc.*, 297 (1954); (b) *ibid.*, 3129 (1954); (c) R. Heiligman, Y. Hirshberg, and E. Fischer, *ibid.*, 156 (1961); (d) *J. Phys. Chem.*, **66**, 2465 (1962); (e) *ibid.*, **66**, 2470 (1962).

(4) T. Bercovici and E. Fischer, to be published.