Amino-dioxetans and Chemiluminescent Peroxides

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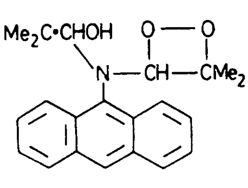
Summary A recent paper reporting the isolation of a stable chemiluminescent amino-dioxetan may be interpreted differently in view of the behaviour of a peroxide derived from tetrahydrocarbazole and the known instability of amino-dioxetans.

A recent report[1] describes what appears to be a stable amino-dioxetan (**1**). Although we have not worked directly on this compound we have some experimental observations and comments which may suggest revision of the conclusions. The accompanying communication[2] describes some Schiff bases which are considerably more chemiluminescent than our first example whose discovery prompted the paper by Omote and his co-workers.[1] We are therefore in no doubt that such compounds are effective chemiluminescent materials. However, we would urge caution in making the often common assumption that light emission implies a dioxetan structure.



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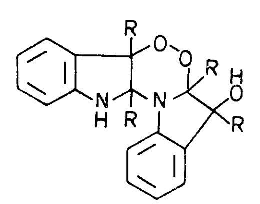

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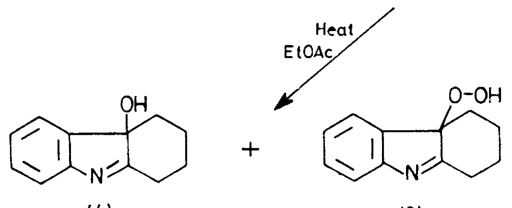
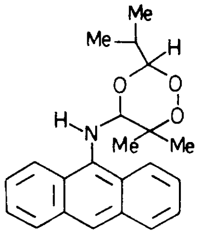


(4) (2)

The tetrahydrocarbazolyl hydroperoxide[2] (**2**) is chemiluminescent on pyrolysis, and on treatment with base in Me$_2$SO. We have previously presented evidence for the involvement of a transient dioxetan in the reaction.[4] However, if the peroxide is prepared by keeping a solution of tetrahydrocarbazole at room temperature for 24 h, the compound first isolated has the structure (**3**, R = cyclohexane ring residues). The stereochemistry is not known but the expected micro-analysis, and mass, i.r., u.v., and n.m.r. spectra have been obtained. The characteristic indoline u.v. spectrum changes to that of an indolenine on refluxing in ethyl acetate, since dissociation to equivalent amounts of the hydroperoxide (**2**) and the alcohol (**4**) occurs. Thus attempted recrystallisation above room temperature gives the crystalline hydroperoxide (**2**) as the least soluble component.



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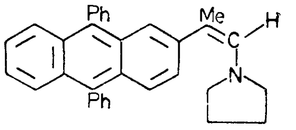

(6)

Although the evidence to hand does not eliminate other isomers, any possible differences are immaterial to the main point. This compound, on pyrolysis and on treatment with base in Me$_2$SO solution, is chemiluminescent to exactly the same degree as is the peroxide (**2**) under the same conditions. We feel that (**5**) which would be expected to behave like (**3**) and which fits all the experimental data is a more likely structure for the compound isolated by Omote *et al.* Its formation by autoxidation of the Schiff base in the presence of excess of aldehyde is also much more reasonable than is the formation of a dioxetan.[5]

It is suggested that steric hindrance is the source of the unique stability of the dioxetan structure, and we also have evidence which bears on this proposal. Photo-oxidation of the enamine (**6**) at −70 °C gives a compound which emits light on decomposition, forming the expected cleavage products. Any dioxetan formed would be about as sterically hindered as is the structure proposed by Omote *et al.*, yet the light emission occurs as the solution is warmed to 0 °C. This is in accord with the fairly extensive evidence available concerning the stability of aminodioxetans.[6] It is also not clear, on the basis of the structure proposed, why treatment with base in Me$_2$SO is required for the room temperature *decomposition* of the presumed dioxetan although a role for the catalyst can be readily assigned in the synthesis of an unstable dioxetan intermediate.

Since many different peroxides are known to emit light[7] during their decomposition, rearrangement to a dioxetan in this and similar cases although feasible is a matter for conjecture at present.

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[1] M. Akutagawa, H. Aoyama, Y. Omote, and H. Yamamoto, *J.C.S. Chem. Comm.*, 1976, 180.

[2] F. McCapra and A. Burford, preceding communication.

[3] R. J. S. Beer, L. McGrath, A. Robertson, and A. B. Woodier, *J. Chem. Soc.*, 1950, 2118, 3283.

[4] F. McCapra, D. G. Richardson, and Y. C. Chang, *Photochem. Photobiol.*, 1965, **4**, 1111, F. McCapra and Y. C. Chang, *Chem. Comm.*, 1966, 522.

[5] For a discussion of related reactions and their interpretation see A. G. Davies, 'Organic Peroxides,'Butterworth, London, 1961; K. H. Pausacker, *J. Chem. Soc.*, 1950, 3478; R. Criegee and G. Lohaus, *Chem. Ber.*, 1951, **84**, 219.

[6] W. Ando, T. Saiki, and T. Migita, *J. Amer. Chem. Soc.*, 1975, **97**, 5028; M. Nakagawa, K. Yoshikawa and T. Hino, *ibid.*, p. 6496; H. H. Wasserman and S. Terao, *Tetrahedron Letters*, 1975, 1735; C. S. Foote and J. W. Lin, *ibid.*, 1968, 3267.

[7] F. McCapra, 'Progress in Organic Chemistry,' eds. W. Carruthers and J. K. Sutherland, Butterworth, London, 1973, p. 231.