

REVISED STRUCTURE FOR "A NOVEL PEROXIDE, 4,5-DIPHENYL-1,2-DIOXA-3,6-DIAZINE"

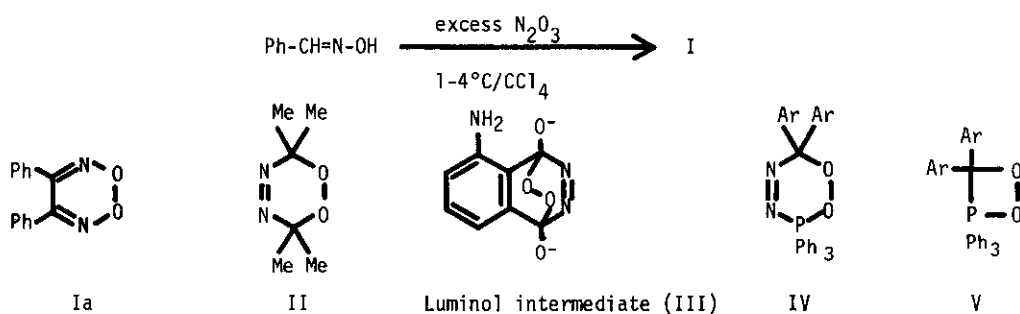
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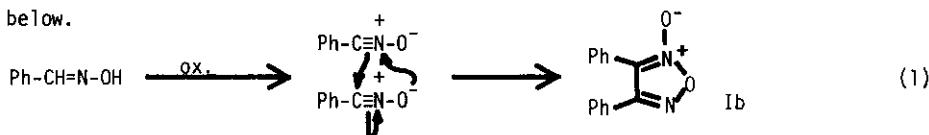
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Benzaldoxime does not give 4,5-diphenyl-1,2-dioxa-3,6-diazine (Ia) on oxidation with N_2O_3 , but gives a furoxane (Ib) in spite of Beckmann's report.

In 1879, Beckmann reported a preparation of 4,5-diphenyl-1,2-dioxa-3,6-diazine (Ia) from the oxidation of benzaldoxime with dinitrogen trioxide (N_2O_3) and some other oxidants.¹ The compound I was assigned as Ia, whose structure is of particular interest from the view of peroxide synthesis, related to the 1,2-dioxa-4,5-diazine (II)² which has been supposed as a derivative of intermediate (III) of luminol chemiluminescence,³ and also to IV which chemiluminesces provably through the corresponding phospho-1,2-dioxetane (V).⁴

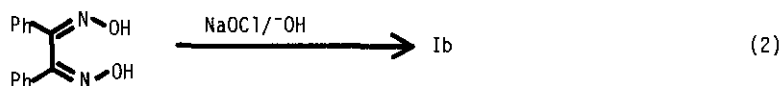


From the data described in the paper,¹ an alternative structure, diphenylfuroxane (Ib), cannot be eliminated and is most probable from the reaction scheme analogous to the literatures⁵ shown below.



In this paper we propose that Ib is indeed the correct structure for I. Compound I [colorless needles, mp 114-115°C (lit.¹ mp 114-115°C)] was prepared according to the Beckmann's method.^{1,6} The compound I shows a negative KI-starch test,⁷ which suggest that I may not be a peroxide. Mass spectrum of I does not show molecular peak of Ia but only M^+-16 , which is characteristic for furoxanes.⁸ C-Nmr of I shows seven signals which could not be explained by the symmetrical peroxide

structure Ia (five or less signals should be appeared) but might be explained by the asymmetric furoxane structure Ib. Moreover, authentic Ib synthesized by an alternative route (2)⁹ shows identical ir, mp, and mixed mp with I.



Thus, we found that oxidation of benzaldoxime with N_2O_3 does not give 4,5-diphenyl-1,2-dioxo-3,6-diazine (Ia), but gives a known furoxane (Ib)¹⁰ in spite of Beckmann's report.¹ The structure of Ia, however, has been referred in even current literatures.^{2b,11} Hence, we propose that the structure Ia from this reaction should be deleted from the literature.

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REFERENCES AND FOOTNOTES

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- 2) (a) G. Rio and J. Berthelot, Bull. Soc. Chim. Fr., 1970, 1509; (b) P. Lechtken, Z. Naturforsch., 1976, 31b, 1436.
- 3) For examples: E. H. White, E. G. Nash, D. R. Roberts, and O. C. Zafiriou, J. Am. Chem. Soc., 1968, 90, 5932.
- 4) N. Suzuki, S. Wakatsuki, and Y. Izawa, Tetrahedron Lett., 1980, 21, 2313.
- 5) (a) G. Tricks and H. Meier, Angew. Chem. Int. Ed. Engl., 1977, 16, 555; (b) A. R. Katritzky and J. M. Lagowski, "Chemistry of the Heterocyclic N-Oxides", Academic, New York, 1971, p. 113.
- 6) I: $\nu_{\text{max}}(\text{KBr})$: 3050w, 1585s, 1565s, and 1415 cm^{-1} . C-Nmr ($\delta_{\text{ppm}}^{\text{TMS}}$)(CDCl_3) 126.9, 127.1, 127.4, 128.7, 128.9, 131.0, and 132.5.
- 7) "Organic Peroxides", vol. 2, ed. by D. Swern, Wiley, New York, 1971, p. 579.
- 8) Ref. 5, p. 17.
- 9) J. H. Boyer, R. F. Reinisch, M. J. Danig, G. A. Stoner, and F. Sahhar, J. Am. Chem. Soc., 1955, 77, 5688.
- 10) Ib: Colorless needles (EtOH), mp 115-117°C (lit.⁹ mp 118°C). Ir spectrum was superimposable with that of I. Mixed samples of I and Ib did not show depressed mps.
- 11) "Shin Jikken Kagaku Koza (New Series of Experimental Chemistry), vol. 15, Oxidation and Reduction, [I-2]", ed. by The Chem. Soc. Japan, Maruzen, Tokyo, 1976, p. 785.

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