Tetrahedron Letters No. 52, pp 4619 - 4622, 1977. Pergamon Press. Printed in Great Britain.

PHOTOCHEMISTRY OF 5,5'-BI-2-ISOXAZOLINE AND ITS RELATED COMPOUNDS.[1] EVIDENCE FOR RADICAL GENERATION IN THE PHOTOCHEMISTRY OF 2-ISOXAZOLES.

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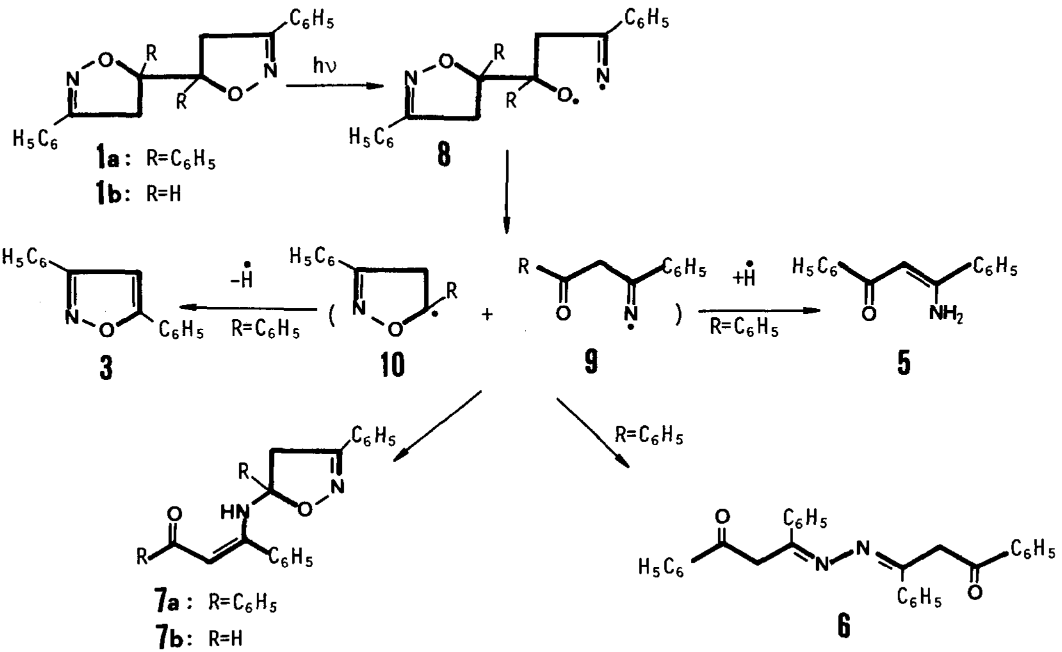
(Received in USA 11 October 1977; received in UK for publication 3 November 1977)

It has been reported that most 2-isoxazoline derivatives, upon irradiation, undergo N-O bond fission as the primary process and afford a variety of products depending on the structure of the starting materials.[2,3,4] The formation of 3-oxazoline,[2,4] β-aminochalcone,[2,4] and 1,3-oxazepines[3] are typical of this N-O bond fission. On the other hand, there are some reactions in which irradiation leads to cleavage of a different bond from the N-O bond, as in the photolysis of 4,5-substituted 3-phenyl-2-isoxazolines.[4,5] Although those photoreactions have been presumed to involve diradicals, neither distinct chemical nor spectroscopic evidence for an intermediate radical species has been obtained. In order to gain insight into the initial stage of the photochemistry of 2-isoxazolines, the photolysis of 3,3',5,5'-tetraphenyl-5,5'-bi-2-isoxazoline (1a), 3,3'-diphenyl-5,5'-bi-2-isoxazoline (1b)[6] and bi-2-isoxazoline fused with cyclopentane ring (2)[7] has been carried out. We wish to report here, chemical and spectroscopic evidence indicating the generation of imino and 2-isoxazolinyl radicals during the photolysis of this series of 2-isoxazoline derivatives.

Irradiation of (1a), mp 275°C (uv max in cyclohexane, 265 nm, ε = 23,000 with end absorption), in benzene through quartz using a high pressure mercury lamp (Toshiba 400W) resulted in the formation of a complex photolysate which, upon separation with tlc (silica gel), afforded five products; 3,5-diphenylisoxazole (3) (7%), 2-benzoyl-3-phenyl-2H-azirine (4) (5%),[8] β-aminochalcone (5) (20%), dibenzoylmethaneazine (6), mp 169°C (20%) and N-(3,5-diphenyl-2-isoxazolin-5-yl)β-aminochalcone (7a), mp 106°C (20%). The structures of hitherto unknown products, (6) and (7a), were unequivocally established on the basis of their spectral properties,[9,10] and by chemical evidence. Acid-catalysed hydrolysis of (6) afforded dibenzoylmethane and 3,5-diphenylpyrazole in 50 and 90% yields, respectively. Similarly, (7a) gave 3,5-diphenylisoxazole and dibenzoylmethane, both in 90% yields.

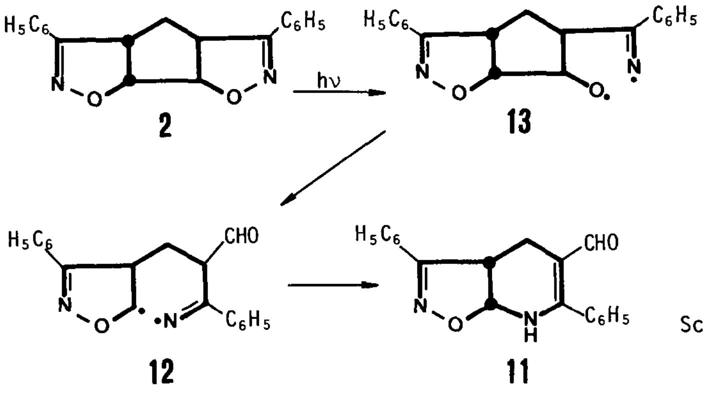


Scheme I

The photolysis of (1b), mp 235°C,[6] (uv max in cyclohexane, 266 nm, ε = 22,000 with end absorption) did not give any clear product under the same conditions as (1a), whereas (7b), mp 174°C, was obtained in 28% yield as the sole product when irradiation was carried out through a filter of aqueous nickel sulfate solution.

To account for the photolyses of (1a) and (1b), we can propose the radical pair mechanism shown in Scheme I. One explanation would be that irradiation of (1) initially involves N-O bond fission to give a radical (8), which in turn collapses to generate a radical pair of imino (9) and isoxazolinyl radical (10). These radicals would also be produced from (1) in the course of the C-C bond fission, followed by N-O bond fission of the resulting radical (10). This radical pair is a key intermediate and undergoes subsequent coupling and disproportionation reactions depending on the stability of the radical within the solvent cage. It is conceivable that the stable radical pair from (1a) affords not only the coupling products (6) and (7a) but also the disproportionation products (3) and (5) in good yields, while the less stable pair from (1b) results in the low yield isolation of only the recombination product (7b).

To investigate the proposed mechanism of Scheme I, irradiation of the bi-isoxazoline fused with cyclopentane (2) was carried out in expectation of the generation of a diradical containing both the imino and isoxazolinyl radical centers. Repeated scanning of the uv spectrum during the photolysis of (2) in a low concentration (3.4×10^{-5}M) exhibited isobestic points at 219, 244 and 282 nm, and the preparative scale photolysis afforded the cyclic enamine aldehyde (11)[11,12] as the sole product in 70% yield (Scheme II). The formation of (11), which corresponds to the structure (7) in Scheme I, can be well explained by an intramolecular recombination of two

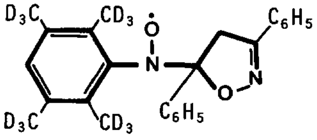


Scheme II

radical sites in the diradical (12) derived, presumably, from the diradical (13).

No esr signal was found in the photolysis of (1a) at temperatures above 77°K, indicating the short lifetimes of the radical intermediates, (8), (9) and (10). A spin trapping technique, however, could clearly prove the intermediacy of the free radicals. Irradiation of (1a) in benzene in the presence of 2,3,5,6-tetrakis(trideuteriomethyl)nitrosobenzene[13] showed a strong esr signal at g = 2.0062 as shown in Fig I. Hyperfine structure of the spectrum with the constants, a_N = 13.6 G (1N) and a_H = 0.8 G (1H), is reasonably explained by the spin adduct with the structure (14). A similar reaction in the presence of 2,4,6-tri-*t*-butylnitrosobenzene[14] exhibited an esr spectrum with the constants, a_N = 10.0 G (1N) and a_H = 1.9 G (2H), at g = 2.0040, which can be interpreted as that of the structure (15) (Fig II). The splitting constants for each product agree well with those of the structural characteristic of the spin trapping agent.[13,14] The above results strongly suggest the intermediacy of the radical pair in Scheme I.

Fig I.



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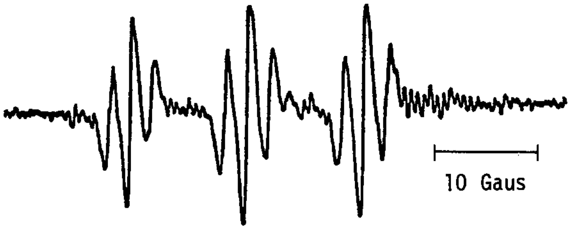
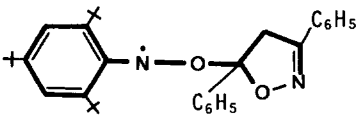


Fig II .



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Acknowledgements. The authors are most grateful to Dr. Shozo Kubota of this institute for the measurement of the esr spectra.

References and Notes

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(7) Compound (5): (3aα, 4aβ, 7aα, 7bβ)tetrahydro-3,5-diphenyl-4H-cyclopenta[1,2-d:4,3-d']-diisoxazole; G. Bario, P. Caramella, G. Cellerino, A. G. Inevernizzi, and P. Grünanger, Gazz. Chim. Ital., 103, 47 (1973).

(8) This compound is the secondary photo-product of (6). See, E. F. Ullman and B. Singh, J. Am. Chem. Soc., 88, 1844 (1966); ibid., 89, 6911 (1969).

(9) Compound (6): mp 164°C; ν_{max}^{KBr}, 1680, 1600, 1570 cm^{-1}; λ_{max}, 244 (22,000), 274 nm (sh); m/e, 444 (M^+), 105 (100%); NMR (δ in $CDCl_3$), 4.7 (s, 4H). Satisfactory elemental analyses were obtained for all the new compounds in this report.

(10) Compound (7): mp 106°C; ν_{max}^{KBr}, 1610, 1585, 1570 cm^{-1}; λ_{max}, 256 (25,000), 340 (19,000) nm; m/e, 444 (M^+), 105 (100%); NMR (δ in $CDCl_3$), 5.9 (s, 1H), 3.9 (d, 1H), 3.5 (d, 1H).

(11) Compound (14): mp 210°C; ν_{max}^{KBr}, 1620, 1595, 1530 cm^{-1}; λ_{max}, 255 (15,000), 203 (10,000) nm; m/e, 304 (M^+), 184 (100%); NMR (δ in $CDCl_3$), 2.16 (dd, 1H), 2.88 (dd, 1H), 3.90 (q, 1H), 5.82 (dd, 1H, converted to doublet in D_2O), 8.42 (d, 1H, disappeared in D_2O), 8.90 (s, 1H).

(12) O. Seshimoto, T. Kumagai, K. Shimizu and T. Mukai, unpublished result.

(13) This reagent was kindly supplied by Dr. R. Konaka, to whom the authors are indebted. See, S. Terabe and R. Konaka, J. Chem. Soc., Perkin II , 369 (1973).

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