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IS THE NITROGEN-OXYGEN BOND FISSION THE PRIMARY PROCESS IN THE PHOTOLYSIS OF BI-2-ISOXAZOLINES ?

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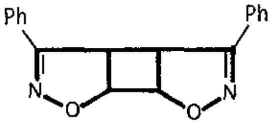
The photochemistry of 3-phenyl-2-isoxazoline derivatives, which are considered to be the simplest heterocycles containing aryl ketoxime chromophore, has been extensively studied. In contrast to a nonconstrained system such as acetophenone oxime ether, most of 2-isoxazoline derivatives, upon irradiation, underwent the N-O bond fission as the primary process and afforded a wide variety of products depending on the structures of the starting materials. The formation of 3-oxazolines, β-aminochalcones and 1,3-oxazepines are typical of the N-O bond fission. On the other hand, there are some reaction in which irradiation cleaved the bond different from the N-O bond, as in the photolyses of 4,5-substituted 3-phenyl-2-isoxazolines. The photolyses of the formally formulated dimers of isoxazole (1 and 2) and the adduct of isoxazole with benzene (3) underwent exclusively the (2 + 2) type cycloreversion to give stable molecules such as isoxazole and benzene. In order to investigate the preference in the bond cleavage between the N-O and the

C-C bonds, the photochemistry of 5,5'-bi-2-isoxazolines (4a and 4b) and bi-isoxazoline fused with cyclopentane ring (5), have been carried out. The chemical and spectroscopic evidence indicating the generation of imino and 2-isoxazolinyl radicals during the photolyses of 2-isoxazoline derivatives will be reported.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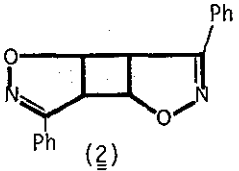
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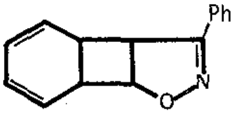
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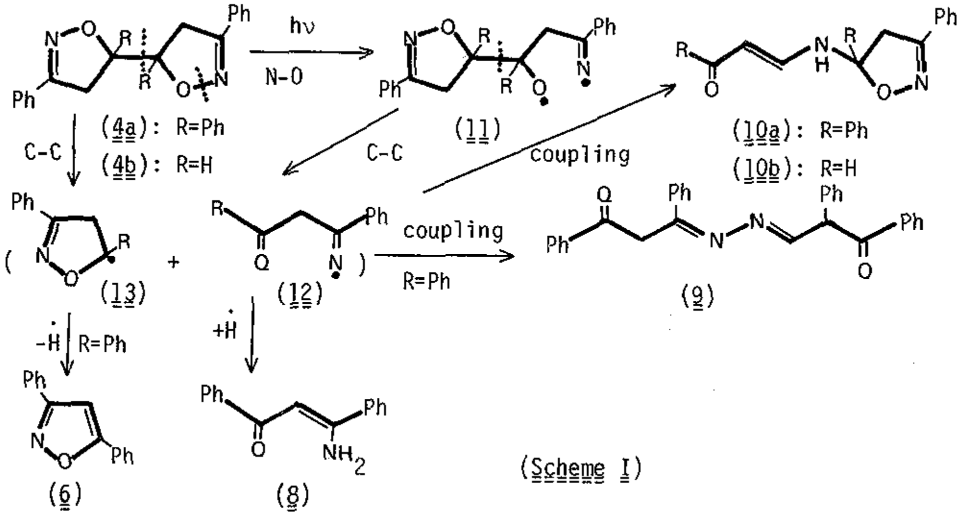
Irradiation of tetraphenyl derivative (4a), mp 275° (uv max in cyclohexane, 265 nm, ε=23,000 with end absorption) in benzene through a quartz using a high pressure mercury lamp (Toshiba H-400P) resulted in the formation of a complex photolysate which, upon seperation with tlc (silica gel), afforded five photoproducts; 3,5-diphenyl-2-isoxazole (6)(7%), 2-benzoyl-3-phenyl-2H-azirine (7) (5%), β-aminochalcone (8)(20%), dibenzoylmethane azine (9), mp 169°, (20%), and (3-phenyl-2-isoxazolin -5-yl)β-aminochalcone (10a), mp 106°, (20%). The structures of hitherto unknown products (9 and 10a) were established by their spectral characteristics and chemical evidence. Acid catalyzed hydrolysis of (9) afforded dibenzoylmethane and 3,5-diphenylpyrazole. Treatment of (10a) with acid gave 3,5-diphenyl-2-isoxazole and dibenzoylmethane.

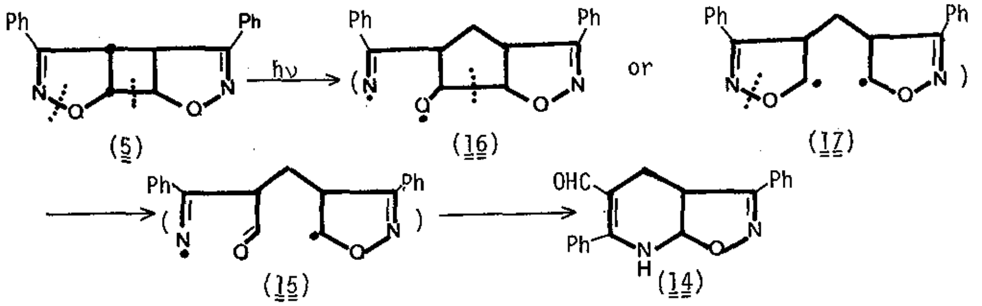
On the other hand, the photolysis of diphenyl derivative (4b), mp 235°, (uv max in cyclohexane, 266 nm, ε=22,000 with end absorption) did not give any clear product under the same conditions as (4a), whereas (10a), mp 174°, was obtained in 28% yield as a sole product when the irradiation was carried out through a filter of aqueous nickel sulphate solution.

To account for the photolyses of (4a) and (4b), we wish to propose a radical pair mechanism shown in Scheme I. One explanation would be that irradiation of (4) initially involves the N-O bond fission to give a diradical (11) which in turn collapses to generate a radical pair of imino (12) and isoxazolinyl radical (13). These radicals would also be derived from (4)by the C-C bond fission, followed by the N-O bond cleavage of the resulting radical (13).



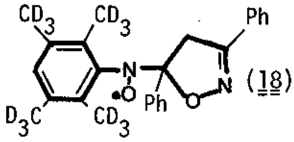
(Scheme I)

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 (4a) affords not only the coupling products (9 and 10a) but also the disproportionation products (6 and 8) in good yields, while the less stable radical pair from (4b) results in the low yield isolation of the recombination product (10b). To confirm the proposed mechanism in Scheme I, irradiation of the bi-isoxazoline fused with cyclopentane (5) was carried out in the 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 (5) in a low concentration (3.4×10^{-5} M) exhibited the isosbestic points at the cyclic enamine aldehyde (14) as a sole product in 70% yield. Thus, the formation of (14) which is the product with the same type as (10) can be well explained by an intramolecular recombination of two radical sites in (15) derived either from the diradical (16) or (17).

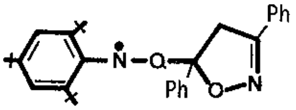


(Scheme II)

No ESR signal was observed in the photolysis of (4a) at temperatures above 77°K, indicating the short life time of the radical intermediates (11, 12 and 13), However, a spin trapping technique could clearly prove the intermediacy of the free radicals. Irradiation of (4a) in benzene in the presence of 2,3,5,6-tetrakis(trideuteriomethyl)nitrosobenzene showed a strong ESR signal at g=2.0062. Hiperfine structure of the spectrum with the constants, a_N=13.6G and a_H=0.8G, is reasonably explained by the spin adduct with the structure (18). The similar reaction in the presence of 2,4,6-tri-*t*-butylnitrosobenzene exhibited the ESR spectrum with the constants, a_N=10.0G and a_H=1.9G at g=2.0040, which can be interpreted as that of the structure (19). The constants for each adduct agree well with those of the adduct characteristic of the spin trapping agent. The above results strongly support the intermediacy of the radical pair in Scheme I. Further investigation on the mechanism, including that to form the radical pair, is in progress.



(18)



(19)