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PHOTOCHEMICAL REACTIONS OF 3-PHENYL-2-ISOXAZOLINES FUSED WITH CYCLOALKANE RING[1]

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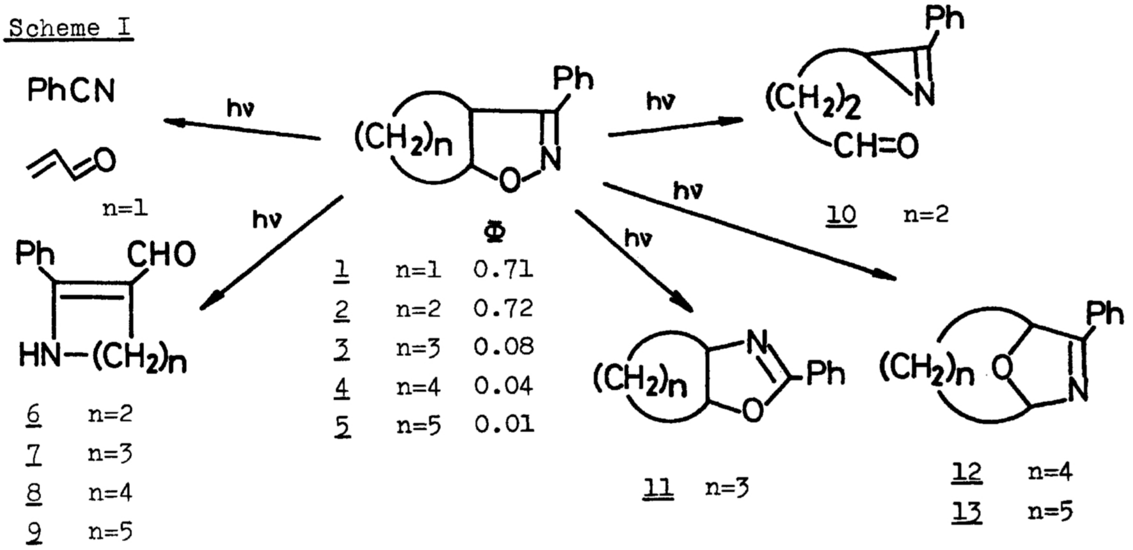
In order to clarify the initial stage of the photoexcitation of the rigid Ph-C=N-O system, the photochemistry of several 2-isoxazolines possessing fused cycloalkane ring has been investigated. Several photoproducts such as 2H-azirine, cyclic enamine aldehydes, bicyclic oxazolines were isolated, and a generalized pattern of the photoreaction which is initiated by the N-O bond fission is proposed.

In contrast to the non-constrained Ph-C=N-O system such as O-methyl ether of acetophenone oxime,2) 3-phenyl-2-isoxazolines, which are considerd to be the simplest cyclic compounds containing the same chromophore, upon irradiation, undergo readily photolyses.3,4) Nevertheless,the photoreactions are usually complex, and there still remain some ambiguities concerning the reaction paths. The main purpose of this study is to gain insight into the chemical behavior of the photoprimary process by means of incorporation of methylene linkage with different length into the C_4-C_5 positions of the isoxazoline ring. Chosen compounds are bicyclo-2-isoxazolines possessing fused cyclopropane (1), cyclobutane (2), cyclopentane (3), cyclohexane (4) and cycloheptane ring (5). Thus, we succeeded in the isolation of 2H-azirine intermediate, which is the first example in the photoreactions of 2-isoxazolines. In addition, we wish to propose here a generalized photolysis pattern which can accomodate the formation of all photo-products.

Photoreaction of the benzene solution (ca 100 times by volume) was carried out in a quartz vessel by external irradiation with a high pressure Hg lamp (Toshiba 400 W). The obtained photoproducts are shown in Scheme I. The quantum yields for depletion of the materials which were determined in cyclohexane using potassium ferrioxalate as an actinometer are listed in Scheme I. Photolysis of 1 was an unique reaction where benzonitrile and acrolein were obtained in 89 and 60 % yields respectively. In the case of 2, 3, 4, and 5, benzonitrile was formed as a common minor product (less than 9 % yields), but major products could be classified into two groups :

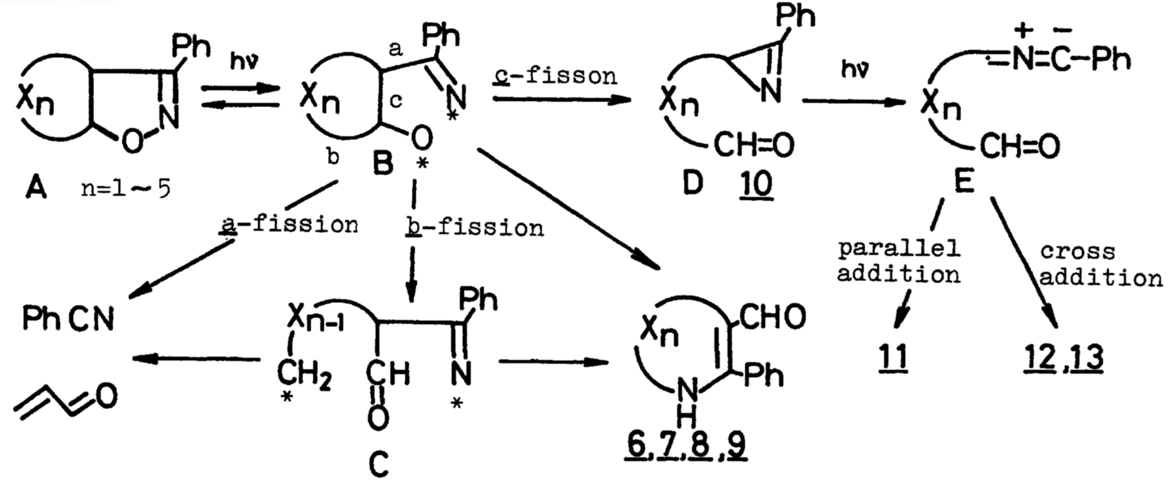
Scheme I



cyclic enamine aldehydes5) (6, mp 154°, 7, mp 150°, 8, mp 129.5°, and 9, mp 105°, in 26, 13, 9, and 41 % yields, respectively), and 2H-azirinyl alkanal and bicyclic oxazolines (10, 11, 12, and 13 in 37, 32, 27, and 22 % yields, respectively). Schmid et al have already reported on the phototransformation of 3 into 11.6) The structural assignments of these products are based on their spectral properties.7,8,9) The following chemical evidences confirmed the structures of 6 and 10 unequivocally. Dehydrogenation of 6 with DDQ gave 2-phenyl-3-formylpyrrole. Heating of a benzene solution of 10 (150°, sealed tube) resulted in the formation of 2-phenylpyridine.10)

Thus, a generalized reaction mechanism is proposed in Scheme II. The starting materials (A) undergo the nitrogen-oxygen bond fission to afford biradicals (B), from which in turn several paths diverge depending on which bonds a, b, and/or c are broken. The bond a fission produces benzonitrile, but no counterpart was detected except for acrolein. The formation of cyclic enamine aldehydes (6-9) is rationally explained by recombination in biradicals (C), which are derived from (B) by bond b fission. If n (No of CH$_2$) is 1 in (C), the recombination may be impossible due to the severe strain, and benzonitrile and acrolein are formed instead.

Scheme II



A one-step path from (B) cannot be ruled out for the formation of the cyclic enamine aldehydes, especially when n is larger than 4. Bond c fission followed by recombination in thereby formed biradicals gives 2H-azirinyl alkanals (D). When n is 2, 3-phenyl-2H-azirinylpropanal 10 was obtained. Such double cleavage reaction giving 2H-azirines is one of the known reactions of 2-isoxazolines, but to our knowledge this is the first example of isolation of the azirine aldehyde as an intermediate. The isolation of 10 from 2 must be ascribed to the fact that the two-methylene linkage in (D) is not long enough to lead to the internal 1,3-dipolar addition. Contrary to the fact that nitrile ylides4) which are derived by irradiation of 2H-azirines add to carbonyl compounds with high regiospecificity to give only 3-oxazoline derivatives,11) we found the different type of intramolecular addition in the transient nitrile ylide-aldehydes (E).1) This is the parallel addition leading to 11. Products, 12 and 13, can be derived by the normal cross addition. Very recently, independently from us, Padwa and Kamigata reported the same example of the intramolecular 1,3-dipolar cycloaddition with the inversion of regiospecificity which is forced by geometrical factor, and discussed this problem from the view point of frontier orbital theory.12)

The quantum yields in Scheme I should be argued on the basis of the proposed mechanism. The large values for 1 and 2 reflect the ring strain effect after the initial nitrogen-oxygen bond cleavage. The quantum yields for 3, 4 and 5 are not so large, because the five, six and seven membered ring have no strain energy and keep two photochemically induced radical centers adequately close, and thus make the recombination for the starting material easy. These quantum yields may be compared with that of 3-phenyl-2-isoxazoline (Φ=0,61), in which the radical sites are separated from each other by rotation around the C_4-C_5 bond.[1)]

We are continuing our studies to clarify the electronic state of the constrained aryl ketoxime chromophores.[1,13)]

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5) Wrong structures were proposed for these compounds at IUPAC VI Symposium on photochemistry (Aix-en-Provence, July 1976). Cf. ref. 1.

6) P. Claus, P. Gilgen, H.-J. Hansen, H. Heimgartner, B. Jackson, and H. Schmid Helv. Chim. Acta, 57, 2173 (1974).

7) Spectral properties of 7, 8, and 9 are similar to those of 6 which exhibits the following spectra : ir (KBr), 3160 and 1589 cm^{-1}; uv (ethanol), 238.5 nm (log ε 4.05), and 331 (4.19); nmr ($CDCl_3$, δ), 2.92 (2H, t, J=10 Hz), 3.74 (2H, t, J=10 Hz), 5.9 (NH), 7.38 (arom, 5H), and 9.05 (CHO).

8) Spectral data of 10 : ir (neat), 1729 cm^{-1} ; uv (ethanol), 244.5 nm (log ε 4.10), 278 (3.29), and 288 (3.11) ; nmr (CCl_4, δ), 1.6~2.6 (5H, m), 7.9~7.4 (arom, 5H), and 9.74 (CHO).

9) Spectral data of 12 : ir (neat), 1627 cm^{-1} ; uv (cyclohexane), 242 nm (log ε 4.07) ; nmr ($CDCl_3$, δ), 1.1~2.2 (8H, m), 5.32 (1H, d, J=6.8 Hz), 6.08 (1H, t, J=3.2), 7.2~7.9 (arom, 5H) ; picrate, mp 170°.

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