

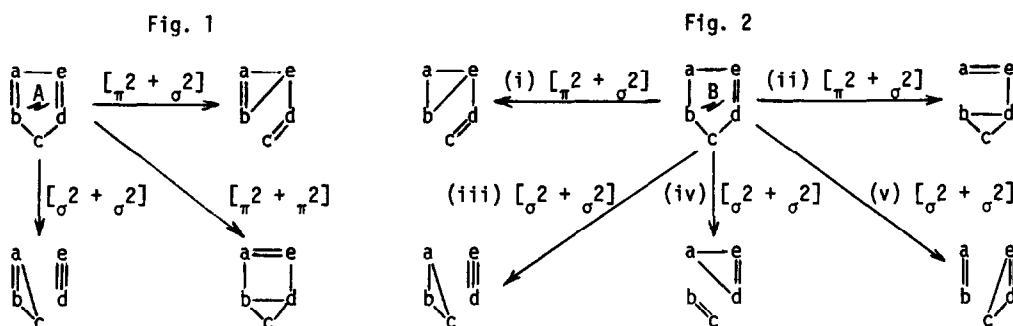
PHOTOINDUCED REACTIONS. LXX. PHOTOCHEMISTRY OF 2-ISOXAZOLINES¹⁾

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Most of photochemical valence tautomerization and fragmentation reactions of five-membered heteroaromatics of type A ($c = 0, S$ or NR)²⁾ can be interpreted by one of three types of reactions occurring at the initial stage (Fig. 1), although other types of bond alternations have been considered in particular cases.³⁾ These three types of reactions may be formally regarded as $[2 + 2]$ reactions. In this respect, photochemical reactions of corresponding dihydroheteroaromatics of type B ($c = 0, S$ or NR) can be classified into five categories (i)-(v) (Fig. 2). Among them, type (i) reaction is known to occur with 4,5-dihydrofurans and 2-thiazolines,⁴⁾ type (iii) with 2-thiazolines and 1,2,3-triazolines^{5,6)} and type (iv) with 3,5-diphenyl-2-isoxazoline.⁷⁾ We now report that types (iii), (iv) and (v) of reactions occur with certain 2-isoxazolines.



Irradiation of a 4.0×10^{-2} M acetonitrile solution of 3,5-diphenyl-2-isoxazoline (1) with a 10W low-pressure mercury lamp (Vycor housing) under nitrogen for 24 hours, followed by the chromatographic separation of products afforded 4,5-diphenyl-3-oxazoline (2) and β -aminochalcone as reported by Schmid et al,⁷⁾ in addition to 2-phenylquinoline (3),⁸⁾ benzonitrile, benzaldehyde, styrene and recovered 1 (24%) and some intractable materials.⁹⁾ Irradiation of 4,5-diphenyl-3-methyl-2-isoxazoline (4), 3,4,5-triphenyl-2-isoxazoline (5) and 3,4-diphenyl-2-isoxazoline (6) in the same manner gave products listed in Table 1, which are analogous to

those from **1**. In order to clarify mechanisms involving, the photoreaction of **1** was examined in some detail.

For the skeletal rearrangement of **1** to **2**, following three pathways may be possible:
 [1] recombination of 2-phenylazirine and benzaldehyde formed by type (iv) fragmentation,⁷⁾
 [2] recombination of benzonitrile and styrene oxide formed by type (iii) fragmentation, and
 [3] type (ii) rearrangement of 3,4-diphenyl-2-isoxazoline (**6**) formed through type (i) valence tautomerization.

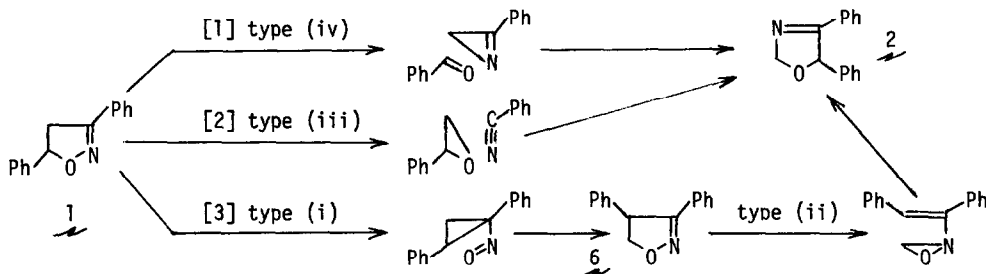


Table 1

	Products from reaction of,		(% yield) ^a	Others
	type (iii)	type (iv)	type (v)	
10a	PhCN (2.0)	2 (19) PhCHO (1.1)	PhCH=CH ₂ (1.6)	3 (15) PhCOCH=C(NH ₂)Ph (3)
10b	—	PhCHO (1.0)	PhCH=CHPh (66) MeC≡N→O (29) ^b	—
10b	PhCN (0.6)	28 ^c PhCHO (0.7)	PhCH=CHPh (39)	—
10b	—	7 ¹³ (6)	—	8 ¹⁴ (86)

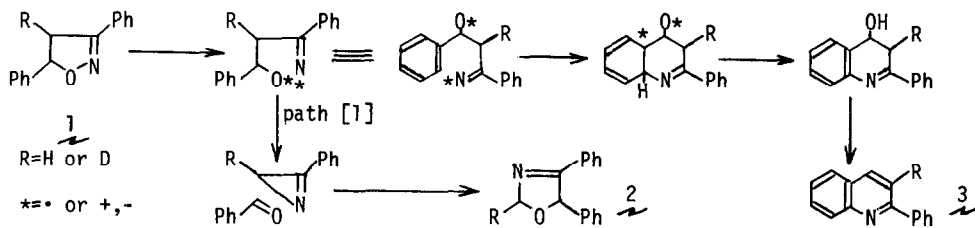
^a Yields were based on the reacted starting material.

^b Trapped as 3-methyl-4,5-trimethylene-2-isoxazoline¹¹⁾ by the irradiation in the presence of cyclopentene in ether. Acetonitrile oxide is regarded as an equivalent of 3-methyl-oxazirine.

^c Cis- and trans-isomers^{7,12)} were isolated in the ratio of 1.6 : 1.

Path [2] was eliminated by the fact that even a trace of 2 could not be detected when a mixture of styrene oxide and benzonitrile was either irradiated under similar conditions or let to stand in the dark. Path [3] was also eliminated, because irradiation of 6 gave 7 and 8 (Table 1) but not 2. Path [1] is strongly supported by the fact that irradiation of an equimolar mixture of 2-phenylazirine and benzaldehyde afforded 2,⁷⁾ which was also confirmed by us. A similar photochemical formation of 3-oxazolines was also recently reported.¹²⁾

The products from type (iii) and (iv) reactions as well as 8 (Table 1) may be attributed to the primary cleavage (homolytic or heterolytic) of the N-O bond of isoxazolines, as seen in the photoreaction of isoxazoles,²⁾ followed by the successive bond cleavage [types (iii) and (iv)] or by intramolecular hydrogen shift in the case of 8. The formation of 3 from 1 can be also attributed to the primary N-O bond cleavage followed by intramolecular attack to the benzene ring. An analogous transformation was observed in the photolysis of 3,5-diphenyl-1,2,4-oxadiazole leading to 2-phenyl-4-quinazoline.¹⁵⁾ This scheme was supported by a deuterium labeled experiment.¹⁶⁾ Thus, irradiation of 1 (R=D)¹⁷⁾ gave 2 (R=D),¹⁶⁾ 3 (R=D),¹⁸⁾ and unlabeled benzaldehyde, and the recovered 1 showed no deuterium scrambling. The result is also consistent with path [1] for the formation of 2.



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