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THE PHOTOCHEMICAL REARRANGEMENT OF 2,5-DIPHENYLOXAZOLE(1)

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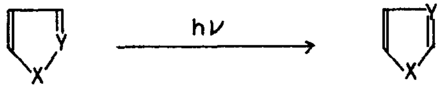
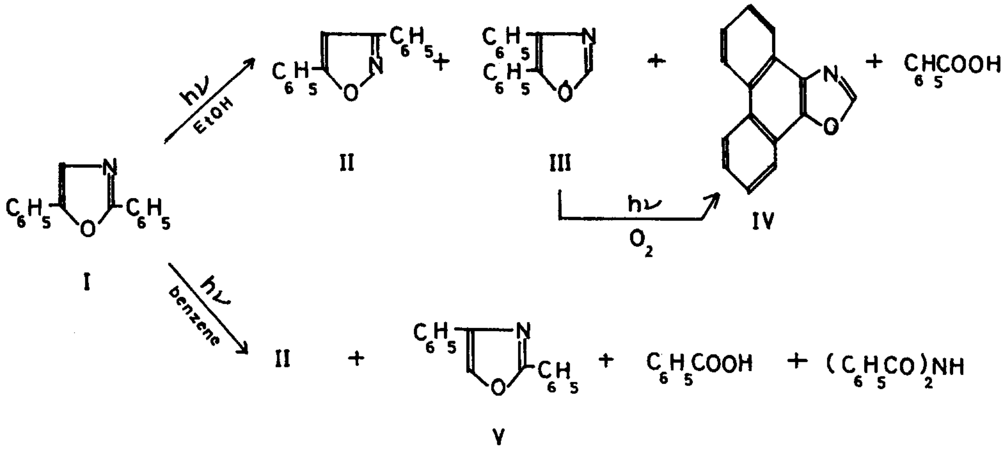
Recently, it has been reported that the five-membered heterocyclic compounds containing two vicinal hetero-atoms interchanged their positions to 1,3-systems as a common mode of reaction when irradiated with ultraviolet light. Examples include the photo-induced rearrangement of indazoles to benzimidazoles(2), pyrazole to imidazole(2), 3,5-diphenylisoxazole to 2,5-diphenyloxazole(3), benzisoxazoles to benzoxazoles(4), and 1,3,5-trimethylpyrazole to 1,2,4-trimethylimidazole(5). On the other hand, there is no record of the rearrangement of 1,3- to 1,2-system.



Here we wish to report the new photo-induced rearrangement of 2,5-diphenyloxazole(I). A 2.3 x 10^{-2} M ethanol solution of I was irradiated for 50 hr. at 80° under a nitrogen atmosphere using 100 w. high pressure mercury-vapour lamp with a Pyrex filter. The reaction was followed by UV spectroscopy. Chromatography on silica gel of the evaporated reaction mixture gave 3,5-diphenylisoxazole(II)(3%), m.p. 141°[authentic sample(6), m.p. 140-141°], 4,5-diphenyloxazole (III)(20%), m.p. 44°[authentic sample(7), m.p. 44°], phenanthr(9,10)oxazole(IV)(1.5%), m.p. 152-153°[authentic sample(8), m.p. 152-153°], and benzoic acid(1%), and approximately 5% of the starting material was recovered. All the isolated compounds were identified in comparison with those of authentic samples by mixed m.p. and I.R. spectra. Irradiation of a 1.4 x 10^{-3} M ethanol solution of III in the presence of air led to the formation of IV(42%). The result showed that IV was not derived directly from I, but the photo-oxidation product of III.

Further, when a 2.3 x 10^{-2} M benzene solution of I was irradiated for 72 hr. under similar conditions, II(7%), benzoic acid(2%), dibenzamide(0.4%), and a new product, 2,4-diphenyloxazole

(V)(4.5%), m.p. 103-104°, identified by direct comparison with authentic sample(9), were isolated together with unchanged I(17%). In benzene solution, I was not converted to III.

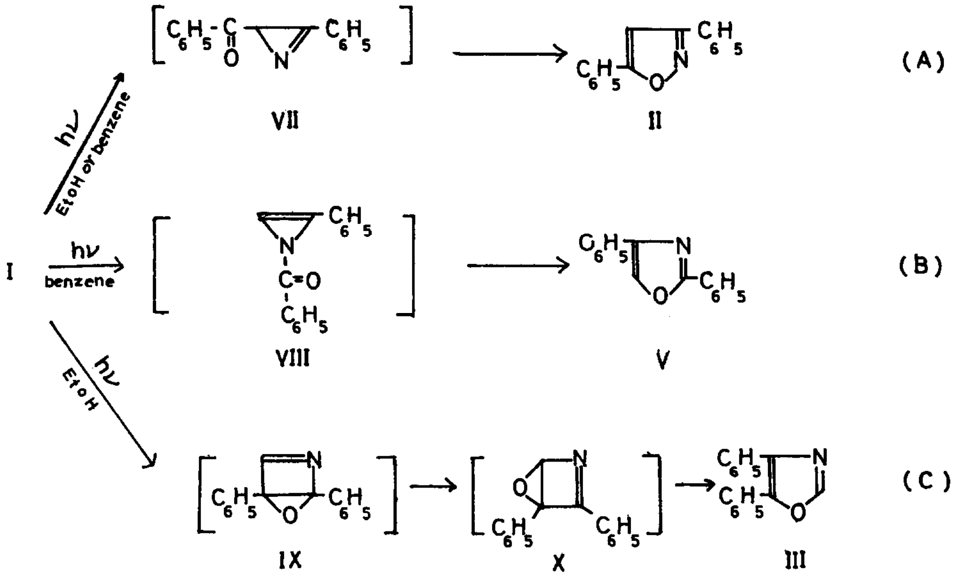


On the basis of the above experiments, the photochemical reactions of I are affected by the protic nature of the medium, and the isomerization between I and II should be photochemically reversible. In the rearrangement of isoxazole(II) to oxazole(I), the azirine derivertive(VII) was isolated as a true intermediate, by Ullman and Singh(3). On the rearrangement of I to II, although efforts to isolate the azirine(VII) from the reaction mixture were unsuccessful, I in ethanol or benzene solutions undergoes O-C_2 bond cleavage upon irradiation with ultraviolet light, and the initial photoproduct should be the azirine(VII), which undergoes a further photo-induced rearrangement to II(eq A).

Similarly, the mechanism of the rearrangement of I in benzene solution to V, involves the breaking of O-C_5 bond, giving a supposed intermediate, 1-benzoyl-2-phenyl-azirine(VIII), which is then transformed to V(eq B).

In a pathway of I in ethanol solution to III, we consider four-membered ring intermediates IX and X, similar to the photo-rearrangement of 1,2,5-trimethylpyrazole to 1,2,4-trimethylimidazole, suggested by P. Beak et al.(5)(eq C).

The investigations on the detailed mechanisms of these reactions are in progress.



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