Photoreaction of 3,4-Diphenyl-1,2,5-oxadiazole[1]

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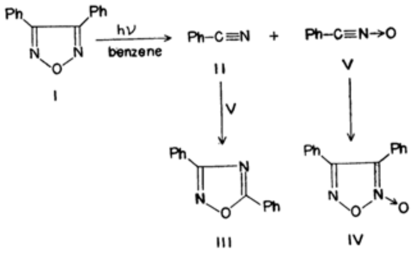
Recent progress in the photochemistry of five-membered heterocycles[2] and our studies of the photochemistry of α-dioximes[3] have led us to investigate the photoreaction of 3,4-diphenyl-1,2,5-oxadiazole (I). Because very recently Cantrell and Haller reported an extensive study of the photochemistry of I and its related compounds[4], we intend to report our results, although our study has not yet been completed.

The irradiation of I in *benzene* (0.17%) in a Pyrex vessel with a high-pressure mercury lamp afforded benzonitrile (II)(50%), 3,5-diphenyl-1,2,4-oxadiazole (III), mp 106—108°C[5] (10%), and diphenylfuroxan (IV), mp 113—115°C, (14%), in addition to I (25%). Although Cantrell and Haller did not observe the formation of III and IV, the formation of all the photoproducts can be explained by the double-fragmentation process proposed by them.[4] That is, III can be derived by the recombination of II and benzonitrile oxide (V),[6] both of which are fragments from I, while IV is formed by the recombination of two moelcules of V.[7] However, the formation of III can also be explained by the ring contraction-expansion process as was first proposed by Ullman and Singh.[2a]

In order to distinguish between these two pathways, the irradiation of I was carried out in the presence of an excess of benzonitrile (5 equiv. to I). The finding that the formation of III increased very much compared to that of IV (III : IV is *ca.* 3.5 : 1) may suggest that the double fragmentation is the correct path for the formation of III.



On electron impact, I exhibits the following peaks (m^+/e): 222 (M^+, 95%), 192 ($M-NO^+$, 85%), 151 (17%), 119 ($Ph-C\equiv N\rightarrow O^+$ and $Ph-N=C=O^+$, 86%), 103 ($PhCN^+$, 10%), 91 (PhN^+, 34%) and 89 (PhC^+, 100%). Thus, it was made clear that the double fragmentation of I was observed not only in photolysis and thermolysis,[8] but also in electron impact.

On the other hand, the irradiation of I in *methanol* (0.17%) gave methyl benzoate (6%), phenacyl alcohol, mp 84—86°C, (3%), 3,5-diphenyl-1,2,4-oxadiazole (3%), and/or benzamide (2%), in addition to benzonitrile (64%). The formation of these minor products will be discussed elsewhere, because our study is still in progress.

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[1] Organic Photochemistry. XI. Preceding paper; T. Oine and T. Mukai, *Tetrahedron Letters*, in press.

[2] a) E. F. Ullman and B. Singh, *J. Am. Chem. Soc.*, **88**, 1844 (1966); **89**, 6911 (1967). b) H. Wynberg, R. M. Kellog, H. van Driel and G. E. Beekhuis, *ibid.*, **89**, 3501 (1967). c) H. Newman, *Tetrahedron Letters*, **1968**, 2417, 2421.

[3] Irradiation of phenanthraquinone-dioxime in methanol afforded phenanthro[9,10-*c*]furazan (30% after 8 hr irr.) or 2,2′-dicyanobiphenyl (8% after 56 hr irr.).

[4] T. S. Cantrell and W. S. Haller, *Chem. Commun.*, **1968**, 977.

[5] All products are reported in the papers. Their structures have no doubt on the basis of reported mp and observed spectral data.

[6] R. Huisgen, W. Mack and E. Anneser, *Tetrahedron Letters*, **1961**, 587.

[7] a) A. Werner and H. Buss, *Ber.*, **27**, 2193 (1894). b) H. Wieland, *ibid.*, **40**, 1667 (1907).

[8] a) K. V. Auwer and V. Meyer, *Ber.*, **21**, 784 (1888). b) F. D. Dodge, *Ann.*, **264**, 178 (1890).