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THE PHOTOLYSIS OF 1,4-DIPHENYLPHTHALAZINE N-OXIDE TO 1,3-DIPHENYLISOBENZOFURAN (1)

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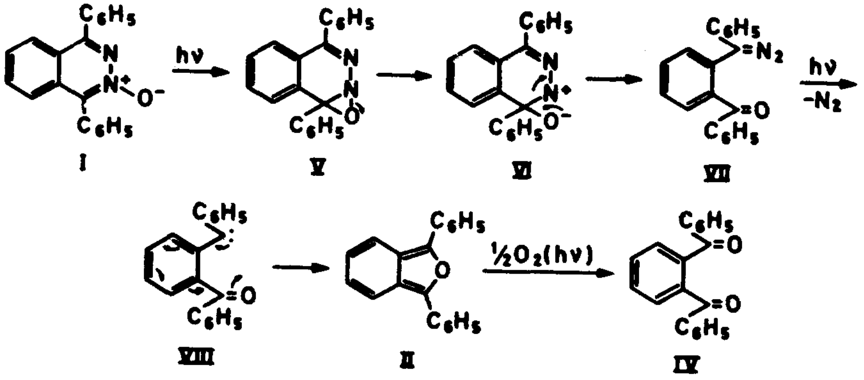
We wish to report a novel photoinduced reaction of an aromatic amine N-oxide.

Photolysis (3) of 1,4-diphenylphthalazine N-oxide (I) in acetone resulted in gas evolution. The gas was shown to be N_2 by mass spectrometry.

When the photolysis of 1,4-diphenylphthalazine N-oxide (I) in acetone flushed with deoxygenated nitrogen was followed by TLC, it was found that one product predominated in the beginning of the reaction. This compound had the same characteristic fluorescence and Rf-value as well as the same short lifetime on the plate after chromatography (4) as a commercial sample of 1,3-diphenylisobenzofuran. When the photolysis was continued several new spots appeared, one of which showed the same Rf-value as 1,4-diphenylphthalazine (III) and another of which corresponded to 1,2-dibenzoylbenzene (IV). By preparative layer chromatography of the mixture obtained from photolyses of I in acetone, with or without deoxygenation, 1,3-diphenylisobenzofuran (II) (~ 5%), 1,2-dibenzoylbenzene (IV) (40-60%) and 1,4-diphenylphthalazine (III) (0-15%) (5) were isolated. Compounds II-IV were all identified by their melting points and by the identity of their IR-spectra with those of authentic samples. Besides compounds II-IV, some as yet unidentified compounds were found, one of which, a red amorphous substance, was formed in yields of 5-15%. The remainder occurred in much smaller amounts.

To account for the above results, a tentative reaction sequence is suggested.



The loss of oxygen from I resulting in the formation of 1,4-diphenylphthalazine parallels the behaviour of other aromatic amine N-oxides (5). The formation of 1,3-diphenylisobenzofuran is believed to involve formation of the unstable oxaziridine (V) and heterolysis to the zwitterionic species VI (2), which in turn is depicted as rearranging to the diazo-compound VII. The photoreactivity of diazo-compounds is well known, and VII may be expected to react as in the formulas, giving 1,3-diphenylisobenzofuran (II) via the carbene-intermediate (VIII). According to the literature, II is easily oxidized in a thermal (7) as well as in a photoinduced reaction (8) to 1,2-dibenzoylbenzene (IV), which explains the high yield of IV relative to II. Control experiments have shown that 1,4-diphenylphthalazine (III) as well as 1,2-dibenzoylbenzene (IV) are stable towards photolysis in acetone under conditions which caused 1,4-diphenylphthalazine N-oxide (I) to react to a high extent (cf. Ref. 9). The photochemistry of the corresponding monocyclic compounds has recently been reported (10). No products corresponding to the loss of nitrogen were observed.

REFERENCES

1. This paper is no. XII in the series "Photochemical Studies". For paper XI see Ref. 2.
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3. The light source was a medium pressure mercury lamp (Q-700, Hanau). All irradiations were performed in Pyrex vessels.
4. On aluminium oxide and silica gel plates, the characteristic fluorescence of IIa disappeared within a min after drying of the plate in air.
5. The formation of appreciable amounts of III occurred only in the absence of flushing with deoxygenated nitrogen during photolysis. This parallels results obtained for other aromatic amine N-oxides (6).
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