Tetrahedron Letters No.49, pp. 6097-6102, 1966. Pergamon Press Ltd.
Printed in Great Britain.

THE PHOTO-CANNIZZARO REACTION OF ORTHO-PHTHALALDEHYDE

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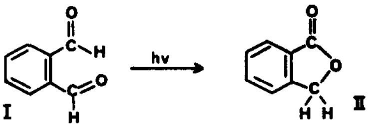
(Received 27 August 1966; in revised form 1 October 1966)

Following earlier reports (1) of its instability in sunlight, Schönberg and Mustafa (2) investigated the photochemistry of ortho-phthaladehyde (I) and described that, in benzene solution, it was almost quantitatively converted to the photodimer III, m.p. 185°. Phthalide (II), which was not isolated, was postulated to be an intermediate in the reaction and to add to the unreacted starting material.

We now wish to describe our preliminary results concerning the photochemistry of I, which suggest that both the structure of the photodimer and the mechanism of its formation were incorrect.

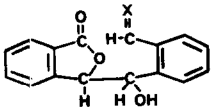
Irradiation of I in carbon tetrachloride or chloroform solution resulted in a very efficient intramolecular reaction and yielded phthalide (II).



In a typical experiment, a solution of I (200 mg) in CCl_4 (50 ml) under nitrogen was irradiated (3) for one hour. The solvent was evaporated under vacuum and the product was shown by NMR to be substantially pure II. A 75-80% yield of crystalline phthalide, melting at 70° and identical in all respects with an authentic sample, was obtained by distillation of the reaction product at 100° under high vacuum in a sublimation tube.

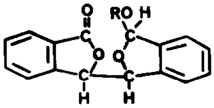
Identical results were observed when the irradiation was performed at 2537 or 3500°A. Furthermore, the presence of air (4) or the concentration of the solution appeared to have little effect on the course of the reaction.

When the irradiation was performed in heptane in a similar manner (0.727 g in 250 ml solvent, under nitrogen at 3500°A for 1 hour), a crystalline precipitate was formed. After recrystallization from $CHCl_3$, a dimer, m.p. 185-186°, was obtained in 67% yield. The mother liquor was shown by NMR to be a mixture of I, II, and IV.



III $X=O$

VI $X=N-NHC_6H_5$



IV $R=H$

V $R=Si(CH_3)_3$

We wish to propose the structure IV for the photodimer, based on the following evidence:

1) Mass spectral analysis did not show a parent peak at m/e 268, but rather one at m/e 250 corresponding to the loss of water, a process frequently encountered in secondary alcohols.

2) NMR analysis of V in CCl_4 at 60 Mc indicated the presence of two protons on adjacent carbon atoms (doublets, J = 7 cps, at 4.94 and 5.36 ppm downfield from TMS), one isolated proton (singlet at 6.46 ppm), and eight aromatic protons (complex signal between 7.2 and 8.0 ppm). The chemical shifts observed for the nonaromatic protons suggested that they were attached to carbon atoms bearing one oxygen substituent in the case of the doublets and two in the case of the singlet. That one of these functions was a hydroxyl group was proved by measuring the spectrum of IV in dimethylsulfoxide (5) or in dimethylformamide. The low field singlet appeared as a doublet under these conditions, coupling (J = 7cps) with the hydroxyl proton which gave a signal at about 18 cps downfield from it. The latter signal and the coupling disappeared upon dilution with D_2O. No aldehyde proton was found.

3) The I.R. spectrum of the photodimer in $CHCl_3$ showed a carbonyl absorption at 5.68 μ in nujol).

4) The photodimer readily gave a phenylhydrazone, m.p. 220° which confirmed the hemiacetal function masking the aldehyde. The NMR spectrum of this derivative in DMSO was consistent with the structure VI and showed the secondary amine proton (singlet

at 10.30 ppm), the aldehydic proton (singlet at 8.21 ppm), the secondary alcohol proton (doublet at 6.0 ppm, J = 4 cps), the two aliphatic protons on oxygen-bearing carbon atoms (one singlet and one doublet with J =4 cps, both at 5.77 ppm), and 13 aromatic protons (complex signal between 6.6 and 8.0 ppm). Upon exchange with D_2O, the hydroxyl and the amine signals disappeared. That the 5-membered ring lactone was retained in VI was indicated by a carbonyl absorption at 5.72 μ in nujol.

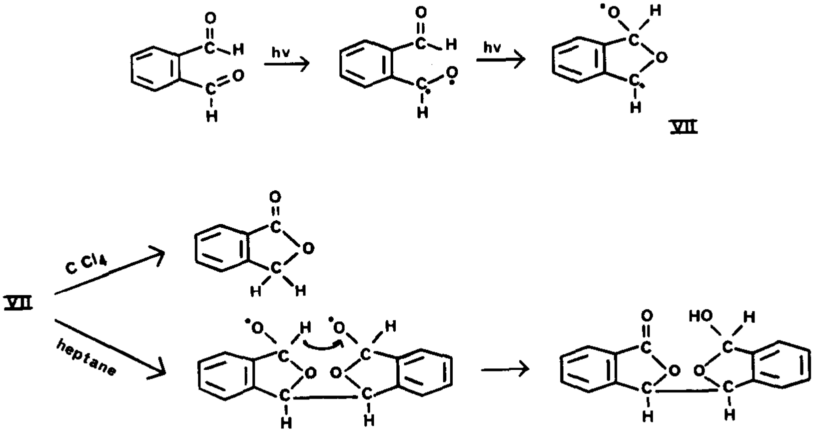
When crystalline I was irradiated without solvent at 3500°A under nitrogen, a mixture of the photodimer and phthalide was formed. For instance, after 3 hours irradiation the slightly sticky solid consisted of 30% I, 15% II, and 55% IV.

When a solution of 0.172 g of I in 50 ml of benzene was irradiated for 70 minutes at 3500 A under nitrogen, there was obtained 4% I, 45% II and 51% IV.

We believe that the photodimer reported by the previous workers (2) was in fact the same as IV (their melting points for the compound and its phenylhydrazone were the same as ours) and that impure samples were probably used for the I.R. spectrum and the thermal decomposition reaction. The isolation of II upon sublimation of their sample of photodimer was one of the arguments used by Schönberg and Mustafa in the structural assignment. In our hands however, IV sublimed at 150° under high vacuum without formation of II, and the previously published results can be interpreted simply in terms of a mixture similar in composition to that obtained in our experiment.

In order to determine if II was an intermediate in the formation of the photodimer, as suggested by Schönberg and Mustafa, an equimolar mixture of I and II was irradiated in benzene solution under nitrogen at 3500 A. No increase in the yield of IV was observed over that found when II was initially absent.

A possible mechanism accounting for the formation of IV is indicated below:



The lack of dimer formation in the chlorinated solvents may be due to efficient quenching of the dimerization step by chlorine radicals from the solvents. The results of experiments designed to understand the solvent effect and the nature of the excited state leading to products will be reported later.

The photochemical oxidation and the photochemical reduction of aldehydes are processes which are well known independently, but their concurrence in a Cannizzaro reaction has not been previously substantiated. However, an intramolecular reaction similar to the conversion of I to II, namely the photochemical conversion of o-nitrobenzaldehydes to o-nitrosobenzoic acids, is well documented (6).

Acknowledgements

Financial support was received from the Graduate Research Board of the University of Illinois. For the part of this work performed at the University of Texas, we are grateful to Drs. R. E. Alston and T. J. Mabry and collaborators for their hospitality. We also thank Dr. M. Yusem for useful discussions.

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2) A. Schönberg and A. Mustafa J. Am. Chem. Soc., 77 5755 (1955).

3) A. Rayonet photochemical reactor from the Southern N. E. Ultraviolet Co was used in this work.

4) The reaction was conveniently followed by NMR when the irradiation was performed in quartz sample tubes, available through NMR Specialties Inc., New Kensington, Pa.

5) O. L. Chapman and R. W. King, J. Am. Chem. Soc., 86, 1256 (1964).

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