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PHOTOCHEMISTRY OF 3,5-DIPHENYL-1,2,4-OXADIAZOLE I.
PHOTOLYSIS IN APROTIC MEDIA

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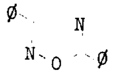
Two recently reported studies prompted our interest in the photolytic behavior of 3,5-diphenyl-1,2,4-oxadiazole (1). The first, was the finding by Ullman and Singh[1] that photolysis

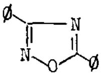


1

of 3,5-diphenylisoxazole (2) in ether at 253.7 mμ resulted in its isomerization to 2,5-diphenyloxazole (3). The second was the report by Cotter et. al.[2] on the mass spectral fragmentation of

2 3

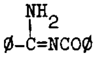
1 in which it was suggested that the principle ion fragments observed ($C_7H_5N^+$ and $C_7H_5NO^+$) arose *via* fragmentation of the bonds indicated in the diagram.



We were interested in seeing a) whether replacing the unsubstituted carbon in 2 with nitrogen affects its photolytic behavior and, if so, how, and b) whether the correspondence between mass spectral fragmentation and photolytic behavior recently found in quite a number of cases[3] also occurs here.

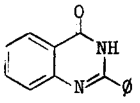
Irradiation of a 0.01 M solution of 1[4] (λ_{max}^{ether} 245 mμ (ε 27,000), 285 mμ infl. (ε 220); λ_{max}^{MeOH} 245 mμ (ε 31,000), strong end absorption) in ether for 2 hr. at 253.7 mμ[5] left it unchanged in contrast to the behavior of 2.

Irradiation of a 0.01 M ethereal solution of 1 with a 450 W. Hanovia high-pressure mercury arc through a quartz water cooled immersion well for 70 min.[6] results in a photolytic transformation.[7] Sublimation of the product mixture returned 64% of starting oxadiazole 1. Partition chromatography[8] of the sublimation residue gave, in addition to another 3% of 1 (total recovery, 67%), four crystalline products. The most abundant of these (31% based on unrecovered starting material) melted at 98.5-100° after recrystallization from n-hexane and gave benzoylbenzamide in good yield on acid hydrolysis (IN HCl) steam bath, 20 min.). Elemental analysis (Fd. C, 74.9; H, 5.4; N, 12.5) suggested the formula $C_{14}H_{12}N_2O$ and its infrared spectrum: λ_{max}^{Nujol} *ca.* 3.0 μ (weak), 6.24 μ (strong) and 6.42 μ (strong), and U.V. spectrum: λ_{max}^{MeOH} 296 (shoulder)(ε 14,000), 282 (ε 17,000) and 249 mμ (ε 11,500), were identical with those of authentic benzoylbenzamidine (4).[9,10] The photoproduct and 4 also showed identical R_f values on thin-layer chromatography and an undepressed mixture melting point.



$\phi-\overset{\overset{NH_2}{|}}{C}=NCO\phi$

4



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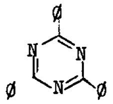


6

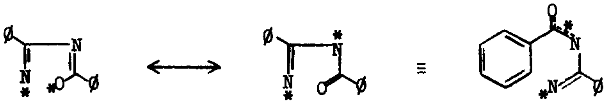
The next most abundant product (obtained in 5% yield based on unrecovered starting material) melted at 235-237° after trituration with ether. It was soluble in dilute aqueous sodium hydroxide (and fairly concentrated hydrochloric acid) but not in aqueous bicarbonate. Its elemental analysis (Fd. C, 75.8; H, 4.6; N, 12.3) and molecular weight [Fd. 235 ($CHCl_3$, thermistor method)] indicated it to be isomeric with starting 1 and its infrared spectrum showed a strong peak in the carbonyl region at 6.0 μ. The foregoing data, together with some mechanistic considerations suggested 2-phenyl-4-quinazolone (5) as a possible structure for this photoproduct and indeed U.V. spectral data [λ_{max}^{MeOH} 317 infl. (ε 8200), 291 (ε 14,300) and 235 mμ (ε 25,000)], melting point, mixed melting point, and thin layer chromatographic comparisons with an authentic sample[11] established the identity.[12]

The two remaining crystalline materials were obtained in extremely small amounts [on the order of 0.5% (yield based on wt/wt ratio with unrecovered starting material)]. One of these was identified as 2,4,6-triphenyl-1,3,5-triazine (6) by melting point, mixed melting point, U.V. spectral and thin-layer chromatographic comparisons with an authentic specimen.[13,14] There was not enough of the other (m.p. 196-199) for identification.

The conversion of 1 to benzoylbenzamidine 4 requires the addition of two hydrogens.

Although relatively rare, there is precedent for ether serving as a hydrogen source under photolytic conditions.[15,16] The nature of the species arising from 1 which is involved in the hydrogen abstraction is open to speculation but is most likely homopolar.[15d]

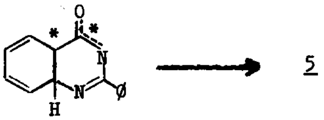
The formation of 5 would appear to implicate an intermediate species such as 7 (homo-



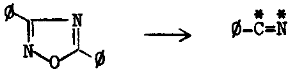
* = . or ±

7

polar or heteropolar) which yields 5 *via* intramolecular attack of the aromatic ring followed by hydrogen transfer.[17]



The isolation of photoproduct 6 might be indicative of a parallel reaction pathway, albeit a *very* minor one, between the photolysis and mass spectral fragmentation of 1, since its formation could involve an excited fragment A, generated from 1. (We have shown that benzonitrile is *not* converted to 6 on photolysis under essentially the conditions employed for 1, but is recovered largely unchanged.)



A

In an attempt to trap a species of type 7, the photolysis of 1 was conducted in acetone (2 hr.) (*cf*. reaction of olefins with ketones to form oxetanes[18]). A photosensitized reaction took place (solution was completely opaque below 323 mμ). Partition chromatography[8] of the product mixture after sublimation to remove starting 1 (51%), permitted the isolation of 4 (15% based on unrecovered starting material), 5 (*ca*. 10% based on unrecovered starting material) and trace amounts of material corresponding in R_f (TLC, silica gel, ØH-EtOAc 4:1) to the unidentified solid, m.p. 196-199°, isolated in trace quantities from the photolysis of 1 in ether, as the only crystalline products. An additional 15% of starting 1 was also isolated, along with considerable amounts of tarry product.[19]

The behavior of 1 in these two aprotic solvents is thus seen to be quite similar. In the accompanying communication we discuss the photolytic behavior of 1 in protic solvents.

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1. E. F. Ullman and B. Singh, J. Am. Chem. Soc., 88, 1844 (1966).
2. J. L. Cotter, G. J. Knight and W. W. Wright, J. Gas Chromat., 5, 86 (1967).
3. See a) C. Djerassi and B. Zeeh, Chem. and Ind., 358 (1967); b) N. J. Turro, D. S. Weiss, W. F. Haddon and F. W. McLafferty, J. Am. Chem. Soc., 89, 3370 (1967); c) M. M. Bursey, L. R. Dusold and A. Padwa, Tetrahedron Letters, 2649 (1967).
4. R. T. Conley and F. A. Mikulski, J. Org. Chem., 24, 97 (1959).
5. Irradiation was conducted in a Rayonet Photochemical Reactor obtained from the Southern New England Ultraviolet Co., 954 Newfield St., Middletown, Connecticut.
6. The rate of the photolytic transformation was concentration dependent, decreasing with increasing concentration.
7. The light output at 253.7 mμ is considerably greater from the Rayonet apparatus (35 watts) than from the Hanovia 450 W high-pressure arc (5.8 watts).
8. On celite 545. The first partitioning was effected using saturated heptane-methanol (lower phase-stationary; upper phase mobile). The uneluted material was then washed off the column with methanol and rechromatographed using the more polar system heptane:EtOAc:H_2O:MeOH, 75:25:15:6. The eluate was monitored at 270 mμ by passage through a flow cell.
9. A. Pinner, Ber., 22, 1600 (1889).
10. a) The lack of any absorption in the carbonyl region below 6.24 μ would appear compatible with the tautomeric form of 4 shown. b) The stability of 4 under the photolytic conditions employed was independently established.
11. Beilstein's Handbuch Der Org. Chem., 24, 208.
12. The analytical, spectral and solubility data were actually determined on a sample of 5 produced during the photolysis of 1 in methanol (see accompanying communication). That this material was identical with photoproduct m.p. 235-237° isolated from the photolysis of 1 in ether was established by infrared spectral and thin-layer chromatographic comparisons.
13. Beilstein's Handbuch Der Org. Chem., 26, 97.
14. 6 had been previously isolated from the photolysis of 3,5-diphenyl-1,2,4-thiadiazole (unpublished results). It was, therefore, readily recognized here.
15. a) G. Ciamician and P. Silber, Ber., 44, 1554 (1911); b) E. Bergmann and J. Fujise, Ann., 483, 65 (1930); c) E. Muller, H. Metzger and D. Fries, Ber., 87, 1449 (1954); d) S. G. Cohen and S. Aktipis, J. Am. Chem. Soc., 88, 3587 (1966).
16. A much less likely source of hydrogen is the aromatic ring protons of 1. See, for example, A. Beckett and G. Porter, Trans. Faraday Soc., 59, 2038 (1963) and P. J. Kropp and H. J. Krauss, J. Am. Chem. Soc., 89, 5199 (1967).
17. It was independently established that 4 was not converted to 5 under the conditions of the photolysis of 1; it was recovered unchanged.
18. See J. S. Bradshaw, J. Org. Chem., 31, 237 (1966) and references cited there.
19. That acetone can serve as a hydrogen source (required for the formation of 4) would not be unexpected on the basis of the reported behavior of ketones on photolysis (see R. O. Kan, "Organic Photochemistry," McGraw Hill Book Company, New York 1966, p. 71).