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PHOTOCHEMISTRY OF 3,5-DIPHENYL-1,2,4-OXADIAZOLE II. PHOTOLYSIS IN PROTIC MEDIA

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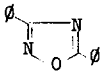
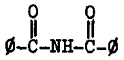
In the preceding communication[1] we discussed the behavior of 3,5-diphenyl-1,2,4-oxadiazole (1) on photolysis in the aprotic solvents ether and acetone. We describe here the photolytic behavior of 1 in the protic solvents methanol and isopropanol.



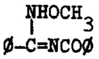
1

The irradiation of a 0.01 M solution of 1 in methanol with a 450 W Hanovia high-pressure mercury arc through a water cooled quartz immersion well for 2 hr. proceeded cleanly to give, after evaporating the methanol, a product mixture from which 30% of starting 1 was recovered by sublimation. Partition chromatography[2] of the residue permitted the isolation of two crystalline products in addition to another 25% of starting 1. The major product, obtained in 40% yield (based on unrecovered starting material), was a colorless, crystalline solid, melting at 150-152° after recrystallization from methanol, and was soluble in 10% aqueous sodium hydroxide but not in aqueous bicarbonate. It analysed for a 1:1 adduct of methanol and 1 (Fd. C, 70.8; H, 5.7; N, 11.0), showed absorption in the infrared at 5.94 μ (strong, single peak) and absorbed in the ultraviolet (MeOH) at 260 mμ infl. (ε 13,300) and 237 mμ (ε 20,200). Its nmr spectrum showed a 10-proton multiplet in the aromatic region between 8.0 and 7.4 δ and a 3-proton sharp singlet at 4.0 δ due to the methoxy methyl protons. Acid hydrolysis of the adduct (dilute aqueous-ethanolic hydrochloric acid, steam bath, 20 min.) gave a product mixture which was separated into starting adduct and benzoylbenzamide (2) by partition chromatography.[2]



$$\phi-\overset{\overset{\displaystyle O}{\|}}{C}-NH-\overset{\overset{\displaystyle O}{\|}}{C}-\phi$$

2

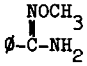


$$\phi-\overset{\overset{\displaystyle NHOCH_3}{|}}{C}=NCO\phi$$

3

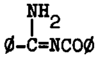
The foregoing data uniquely define the structure of the adduct as 3 (or its tautomer).

It is an interesting aside that, whereas 3 (and of course 2) is soluble in 10% aqueous sodium hydroxide, both phenylamidoxime methyl ether (4) and benzoylbenzamidine (5) are not.



$$\phi-\overset{\overset{\displaystyle NOCH_3}{\|}}{C}-NH_2$$

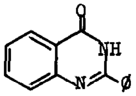
4



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

5

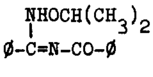
The minor photoproduct, m.p. 235-237° after trituration with ether (obtained in 7.5% yield based on unrecovered starting material) was identified as 6 on the basis of the evidence already presented in the accompanying communication.[1]



6

Photolysis of 1 in isopropanol again gave as the predominant reaction product [17% yield based on unrecovered starting material (52%)] a crystalline solid, m.p. 125-127.5°, after recrystallization from n-hexane, which showed absorption at 5.95 µ (strong, single peak) in the carbonyl region in the infrared and analysed for a 1:1 adduct of isopropanol and 1 (Fd. C, 72.1; H, 6.4; N, 9.6).

The ultraviolet spectrum of the adduct, λ_{max}^{MeOH} 260 infl. (ε 14,000) and 237 mµ (ε 20,000), which is essentially identical with that of 3 and its nmr spectrum, which shows a 10 proton multiplet in the aromatic region between 8.0 and 7.3 δ, a 1-proton signal at 4.45 δ due to the C-2 proton of the isopropoxy moiety[3] and a sharp 6-proton doublet at 1.3 δ (J = 5Hz) due to the methyl groups of the ixopropoxy moiety, are most reasonably compatible only with structure 7 (or tautomer).



$$\phi-\overset{\overset{\displaystyle NHOCH(CH_3)_2}{|}}{C}=N-CO-\phi$$

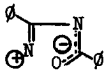
7

Isolated along with 7 in somewhat lower yield (11%, based on unrecovered starting material) was benzoylbenzamidine (5), while thin-layer chromatography also indicated the presence of very small amounts of 6, certainly much less than was formed during the photolysis of 1 in methanol.

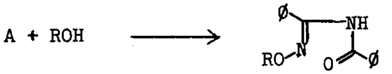
The formation of benzoylbenzamidine (5) in the photolysis of 1 in isopropanol but not in methanol is in accord with the greater ease of hydrogen atom abstraction from the carbinol carbon in the case of the former.[4] In fact, it was with the thought of converting 1 to 5 in high yield, by taking advantage of the reported excellent reducing properties of isopropanol under photolytic conditions,[5] that the photolysis of 1 in that solvent was investigated.

The fact that the photolysis of 1 in isopropanol gives both 5 and 7 appears to indicate the simultaneous operation of a homopolar and heteropolar process. By analogy with other reductions in isopropanol,[5] the formation of 5 presumably involves a homopolar intermediate derived from 1 which abstracts hydrogen radical from the carbinol C-H of isopropanol. The preference for homolysis of this bond rather than the O-H bond in the alcohol would leave unexplained the formation of 7 if only a homopolar photointermediate were involved. The concurrent operation of a heteropolar process in which a photointermediate adds isopropanol *via* heterolytic O-H bond cleavage would, however, accomodate the results. By analogy, the methanol photoadduct 3 is presumed to be similarly formed.

A species such as A could serve as a common precursor for 3 and 7, and 6.[6]

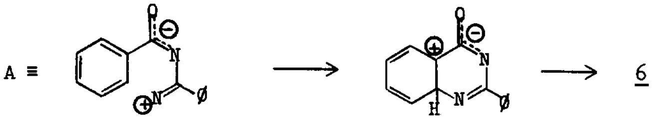


A



3, R = CH_3

7, R = $-CH(CH_3)_2$



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References

1. H. Newman, *Tetrahedron Letters*, 2417 (1968).
2. The partition chromatogram was run on Celite 545 using heptane-methanol as the partitioning system.
3. Only the middle two peaks of the expected quadruplet were clearly discernible. The two side ones were masked by the background noise. The coupling constant of the two visible peaks **was** 5 Hz.
4. While no actual comparison figures could be found for methanol vs. isopropanol, the greater susceptibility of the carbinol C-H bond in the latter to homolytic cleavage would seem to follow from the work of Beckett and Porter[5d] in which ethanol and isopropanol were compared.
5. a) G. Ciamician and P. Silber, *Ber.*, **33**, 2911 (1900); **34**, 1530 (1901); b) S. G. Cohen, D. A. Laufer and W. V. Sherman, *J. Am. Chem. Soc.*, **86**, 3060 (1964); c) M. Fischer, Tetrahedron Letters, 5273 (1966); d) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963); 3) S. G. Cohen and R. J. Baumgarten, *J. Am. Chem. Soc.*, **89**, 3471 (1967).
6. **A**, or its homopolar counterpart must be an intermediate in the formation of **6**.