Photochemistry of some Quinoxaline 1,4-Dioxides

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Received August 11, 1977

The photochemical reactions of some 2,3-diarylquinoxaline 1,4-dioxides are described. A mechanistic interpretation of the experimental results is also offered.

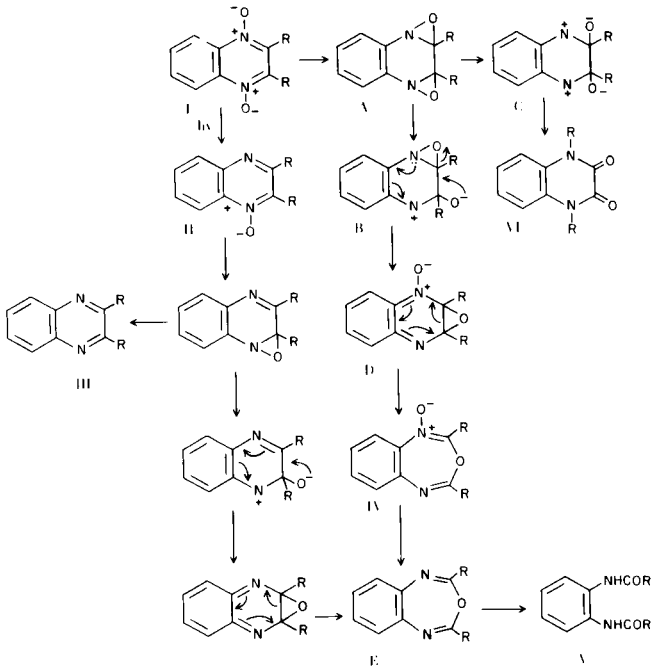
J. Heterocyclic Chem., **15**, 177 (1978)

The photochemical behaviour of quinoxaline 1,4-dioxides was recently the subject of several reports (1). No successful reactions of 2,3-diarylquinoxaline 1,4-dioxides have, however, been described. Apparently the reaction was not fully investigated since 2,3-diphenylquinoxaline 1,4-dioxide (Ia) was reported to give no identifiable products on photolysis in various solvents (1a).

In the present work we describe the photochemical reactions of a number of compounds of this series that are symmetrically substituted by aryl groups at positions 2 and 3 (Ia-Id).

On photolysis in methanol, the title compounds (I) gave the products indicated in Table I (where numbers refer to Scheme I). The unique structure of each substrate clearly influences the outcome of its photolysis, with the result that some of the products are not isolable in certain cases. It is, however, clear that product V is common to all the cited photolyses.

Scheme I



These photolysis results can be partially explained by analogy with explanations offered for the photolysis of quinoline 1-oxides (3) and 3-phenylquinoxaline 1-oxide (4). It is also assumed that: i) Both nitrone functions are excited simultaneously in agreement with previous conclusions in closely related systems (5). ii) Partial or complete deoxygenation takes place either in the substrates themselves or in intermediates formed from them.

One route assumes the formation of the oxaziridine intermediate (A). This undergoes heterolysis (photo-induced or thermal) to zwitterionic intermediates B and C that ultimately lead through D to an oxadiazepine intermediate E, or to a carbostyril-type product VI. Hydrolysis of the oxadiazepine intermediate leads to *N,N'*-diaroyl-*o*-phenylenediamine V.

Another route to V assumes deoxygenation to the monoxide II, which proceeds to E through intermediates analogous to A, B and D. Further deoxygenation of the monoxide leads to III as an isolable product. That the monoxides are intermediates in an alternative route is evidenced by the following: i) 2,3-Diphenylquinoxaline 1-oxide (IIa) under the same conditions of photolysis used for Ia, also gave Va in a reasonable yield. ii) Compound IIa was isolated from the photolysis mixture of Ia. The corresponding monoxide IIc was detected in the photolysis products of Ic (using tlc against an authentic sample prepared by peroxyacid treatment of the corresponding quinoxaline).

Deoxygenation in the first route takes place at a later stage as evidenced by the isolation of the corresponding 2,7-diarylbenz[*d*]-1,3,6-oxadiazepine 3-oxides, IVa and IVc, from the photolysis mixtures of Ia and Ic, respectively.

The isolation of the carbostyril-type product, VI, from

Table I

Reactant	R	Photolysis time (hours)	Products (%) II	III	IV	V	VI
Ia	C_6H_5	4	8	4.5	7	15	
Ib	*p*-$CH_3C_6H_4$	11				15	
Ic	*p*-$CH_3OC_6H_4$	11	traces	10	10	10	18
Id	*m*-$NO_2C_6H_4$	12				12	
IIa	C_6H_5	4				12	

Table II

Compound No.	M.p. °C	Ir, cm^{-1}	Nmr	Analysis Calcd. (Found)
Ia	210-212 (6)			
Ib	212-213	1600, 1480, 1330, 910, 810, 780, 610	s 2.27 (6H), s 7.07 (8H), m 7.76 (2H), m 8.60 (2H),	C, 77.19 (77.01) H, 5.26 (5.50) N, 8.19 (8.15)
Ic	182-184 (6)	1600, 1490, 1330, 1090, 910 820, 660		
Id	219-220 dec.	1610, 1525, 1333, 1090, 945, 880, 760, 715, 640	very limited solubility	C, 59.41 (59.11) H, 2.92 (3.10) N, 13.86 (13.58)
IIa	205-206 (6)			
IIIa	123-125 (6)	1580, 1440, 1395, 1140 980, 800, 770, 700		
IVa	188-190	1660, 1600, 1460, 1300, 1220, 805, 710, 690, 650	m 6.57 (2H), m 7.37 (10H), m 7.88 (1H), m 8.3 (1H)	C, 76.43 (76.39) H, 4.46 (4.61) N, 8.92 (9.00)
IVc	219-220	1650, 1600, 1310, 1180, 840, 810, 755, 655	s 3.80 (3H), s 3.83 (3H), m 7.0 (9H), 6.91 (1H), m 7.87 (1H), d 8.41 (1H)	C, 70.59 (70.37) H, 4.81 (4.89) N, 7.49 (7.36)
Va	301-304 (6)	3260, 1650, 1310, 915, 760, 710, 690, 650		
Vb	233-236	3270, 1645, 1280, 1190, 920, 840, 750, 680, 640	s 2.37 (6H), m 7.51 (12H) m 9.8 (2H)	C, 76.74 (76.95) H, 5.81 (6.02) N, 8.14 (8.12)
Vc	207-209	3260, 1640, 1260, 1180, 1030, 845, 770	s 3.75 (6H), m 7.5 (2H), s 9.9 (2H)	C, 70.21 (69.77) H, 5.32 (5.39) N, 7.45 (7.46)
Vd	236-239	3220, 1640, 1280, 905, 815, 755, 710, 650	m 7.47 (2H), d 7.83 (2H), d 8.28 (2H), m 8.38 (2H), m 8.70 (2H), s 10.27 (2H)	C, 59.11 (59.28) H, 3.45 (3.56) N, 13.79 (13.92)
VIc	275-277 dec.	1690, 1610, 1370, 1300, 1255, 835, 765, 610	s 3.8 (6H), m 6.57 (2H), m 6.9 (2H), m 7.05 (8H)	C, 70.59 (70.47) H, 4.80 (4.86) N, 7.49 (7.37)

the photolysis of Ic is reminiscent of the behaviour noticed in 2-benzylquinoxaline 1,4-dioxide (5).

The two pathways can be thought to proceed simultaneously, and in each of the above cases, lead to compound V, and to some of the other products.

Table II summarizes the melting points, spectral and analytical data for the various compounds involved (nmr and analysis data of compounds reported in literature are not included). They are in accord with the structures indicated in Scheme I.

EXPERIMENTAL

1. Synthesis of the Quinoxaline *N*-Oxides.

Compound Ia was obtained from benzofurazan oxide (BFO) and desoxybenzion using the base sodamide in absolute ether (6). Compounds Ib-d and IIa were obtained by peroxidation of the corresponding quinoxaline using 3-chloroperbenzoic acid, followed by chromatographic separation. The quinoxalines were obtained by condensation of *o*-phenylenediamine with the appropriate 1,2-diketone. The latter were obtained, in high yields by oxidation of the corresponding acyloins with hexacyanoferrate (III) in an alkaline medium (8).

2. Photolysis.

A methanolic solution (1 g. in 400 ml.) of each of the compounds Ia-d and IIa was irradiated with light from a Hanovia 679A36 high pressure lamp with a pyrex filter (photolysis times are shown in Table I). The lamp jacket was water-cooled, and the reaction cell was supplied with a mechanical stirrer and a reflux condensor. The progree of photolysis was followed by tlc to the dissappearance of the starting material. The reaction mixture was then evaporated to about 25 ml. and allowed to crystallize. This treatment led to the isolation of compound V in each of the five cases.

The residue after complete evaporation in the case of Ia and Ic was chromatographed on a silica gel column (Woelm, 0.08-0.2 mm) using the eluents petroleum ether, benzene and ethyl acetate in that order. The fractions collected were identified by tlc.

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