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Photolysis of Some Quinoxaline-1,4-dioxides. A Method of Structural Assignment

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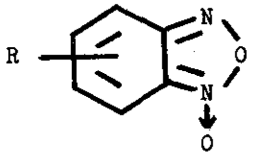
The structures of some 2,3,6(7)-trisubstituted quinoxaline-1,4-dioxides were assigned through their photolytic rearrangement into 1,3,5(6)-trisubstituted benzimidazolones. Photolysis of related quinoxaline-1,4-dioxides demonstrated the generality of the rearrangement.

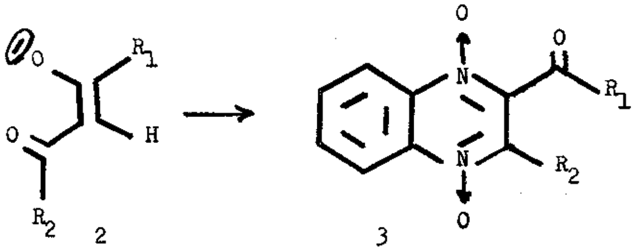
In an earlier study[1] we showed that benzofurazan oxide (1, R=H) reacts with enolate anions derived from symmetrical 1,3-diketones (2, $R_1=R_2$) to give 2,3-disubstituted quinoxaline-1,4-dioxides (3, $R_1=R_2$). In subsequent work[2], we found that the two possible products (4 and 5, R=H) of the reaction of benzofurazan oxide with unsymmetrical 1,3-diketones, such as 2b, may be differentiated by their carbonyl stretching frequencies: 1660 - 1680 cm^{-1} for type 4, and 1700 - 1715 cm^{-1} for type 5.



1

a, $R=CH_3$

b, $R=OCH_3$



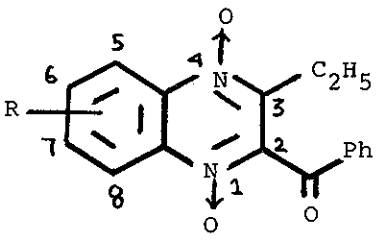
2

3

a, $R_1=CH_3$, $R_2=Ph$

b, $R_1=C_2H_5$, $R_2=Ph$

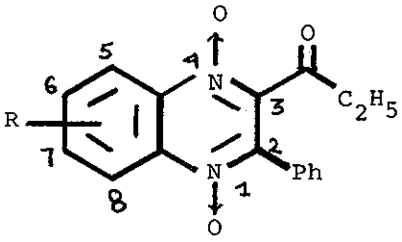
c, $R_1=CH(CH_3)_2$, $R_2=Ph$



4

a, R=CH_3 at C_6

b, R=CH_3 at C_7



5

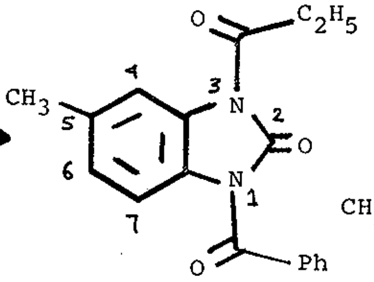
a, R=CH_3 at C_6

b, R=CH_3 at C_7

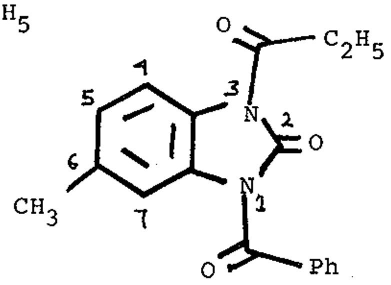
In principle, the reaction of a substituted benzofurazan oxide, such as 1a, with an unsymmetrical diketone, such as 2b, could give rise to as many as four isomeric products (4a, 4b, 5a, and 5b). This report describes a convenient method by which structural assignments can be reliably made.

The reaction of 1a with 2b in diethylamine gave as the major product a single quinoxaline-1,4-dioxide which showed an infrared band at 1715 cm^{-1} and which, therefore, cannot have structure 4 but must be either 5a or 5b. Since, upon photolysis[3], 5a should give by rearrangement the benzimidazolone 6 whereas 5b should give 7, a choice can be made between the two possible quinoxaline-1,4-dioxides on the basis of the structure of the photolytic product.

5a,b $\xrightarrow{h\nu}$



6

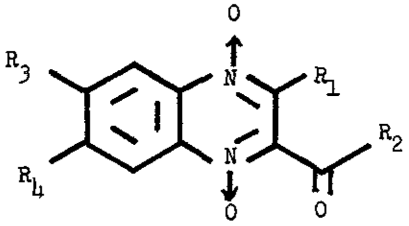


7

It has already been established[4] that the propionyl group in 1-benzoyl-3-propionylbenzimidazolone exists in the endo (Z) conformation[5] and exerts a considerable deshielding effect on the C_4 proton (0.33 τ units downfield from the other aromatic signals), whereas the benzoyl group has a negligible effect on the chemical shift of the C_7 proton. During the present investigation we found that, when the quinoxaline-1,4-dioxide derived from 1a and 2b was photolyzed, the resulting benzimidazolone showed a broad singlet or an incompletely split doublet (1.83 τ, J = 1.5 Hz, 1H) 0.27 τ units downfield from the other aromatic protons. From this, it follows that the benzimidazolone is 6 and not 7 (for which the deshielded hydrogen at C_4 should have given rise to a distinct doublet) and that the precursor quinoxaline-1,4-dioxide must, therefore, be 5a and not 5b.

As expected, photolysis of the quinoxaline-1,4-dioxide 15 (C=O at 1680 cm^{-1}) gives the benzimidazolone 28, which shows a doublet (J = 8.5 Hz) for the deshielded proton at 1.8 τ (Table I). Similarly 16 (1715 cm^{-1}), 17 (1677 cm^{-1}), and 18 (1677 cm^{-1}) yield the benzimidazolones 29 (broad s, 1.83 τ), 30 (d, J = 8.5 Hz, 1.7 τ), and 31 (d, J = 8.5 Hz, 1.65 τ) respectively. Because of the insufficient solubility of the above 1,3-disubstituted benzimidazolones in DMSO-d_6 and their parent benzimidazolones in $CDCl_3$, a study, analogous to that of Monro and Sewell[5], of the solvent effect on the chemical shift of C_4 protons was not possible. The homogeneity of the quinoxaline-1,4-dioxides was established by repeated recrystallization, TLC using different eluents, and consistent sharp melting points.

TABLE I

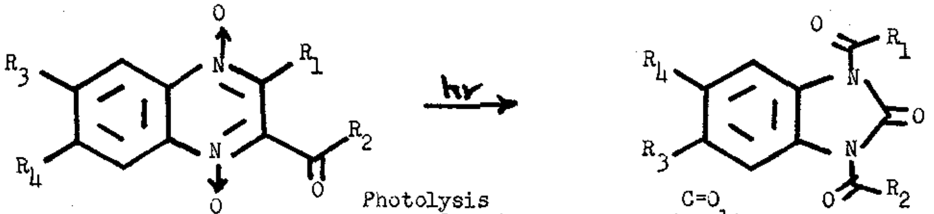


	R_1	R_2	R_3	R_4	% Yield	m.p.	ir (cm^{-1})	Partial nmr (τ)
8	CH_3	Ph	H	H	70	223-4[a]		
9	C_2H_5	Ph	H	H	22	199-0		
10	Ph	$CH(CH_3)_2$	H	H	13	175[a]		
11	Ph	$C(CH_3)_3$	H	H	34	224-5[a]		
12	CH_3	Ph	CH_3	CH_3	48	222	1675,1330	d,1.68(2H),s,7.57(9H)
13	Ph	$CH(CH_3)_2$	CH_3	CH_3	44	190	1710,1330	d,1.6(2H),m,7.2(1H), s,7.45(6H),d,9.1(6H)
14	Ph	$C(CH_3)_3$	CH_3	CH_3	34	237-9	1710,1330	d,1.55(2H),s,7.4(6H) s,9.0(9H)
15	CH_3	Ph	H	CH_3	76	213-4	1680,1330	m,1.2-1.7(2H),s,7.4,7.5(3H each)
5a	Ph	C_2H_5	H	CH_3	22	176-7	1715,1335	m,1.25-1.7(2H), 2.5,7.4(5H), s,6.9(3H)
16	Ph	$CH(CH_3)_2$	H	CH_3	38	185-6	1715,1330	s,1.3(1H),d,1.5(2H),m,7.1(1H), s,7.35(3H),d,8.9(6H)
17[b]	CH_3	Ph	H	CH_3O	36	212-3	1677,1330	d,1.4(1H),s,6(3H),s,7.5(3H)
18	C_2H_5	Ph	H	CH_3O	5	197-8	1677,1330	d,1.45(1H),s,6(3H), q,7.4(2H),t,9(3H)
19	Ph	Ph	CF_3(H)	CF_3(H)	37	217-9	1668,1335	m,0.8-1.3(2H)
20	Ph	Ph	Cl	Cl	36	211-3	1680,1330	d,1.05(2H)

a) Ref. 2.

b) Separated from the major product (R_1 = PhCO; R_2 = CH_3; $R_3(R_4)$ = CH_3O) by recrystallization.

TABLE II



Reactants	Products	R_1	R_2	R_3	R_4	Photolysis time^a hr	%Yield	m.p.	C=O (cm^{-1})	Partial nmr (τ)
8	21	CH_3	Ph	H	H	24	12	166^b	1750,1720	m,1.75(1H)
9	22	C_2H_5	Ph	H	H	24	25	185	1750,1725	m,1.67(1H)
10	23	Ph	$CH(CH_3)_2$	H	H	8	32	158	1740,1725	m,1.72(1H)
11	24	Ph	$C(CH_3)_3$	H	H	2	26	120-1	1765,1695	m,2.1-2.9(9H)
12	25	CH_3	Ph	CH_3	CH_3	6	15	195-7	1760,1710	s,1.93(1H)
13	26	Ph	$CH(CH_3)_2$	CH_3	CH_3	5	34	182	1745,1700	s,1.92(1H)
14	27	Ph	$C(CH_3)_3$	CH_3	CH_3	2	13	149-50	1770,1710	m,2-3(7H)
15	28	CH_3	Ph	H	CH_3	3.5	9	190-2^b	1770^c,1720	d,1.8(1H)
5a	6	Ph	C_2H_5	H	CH_3	6	17	176-7	1750^c,1703	d,1.83(1H)
16	29	Ph	$CH(CH_3)_2$	H	CH_3	6	10	172-4	1750^c,1710	s,1.83(1H)
17	30	CH_3	Ph	H	OCH_3	4	14	166-8	1760^c,1730	d,1.7(1H)
18	31	C_2H_5	Ph	H	OCH_3	4	8	167	1765,1730	d,1.65(1H)
19	32	Ph	Ph	CF_3(H)	(CF_3)H	1.5	13	164-5	1752^c,1700	m,1.7-2.8
20	33	Ph	Ph	Cl	Cl	1.5	10	229-30	1760^c,1700	s,1.9(2H)

a) Photolysis time depends on the lamp used and is best determined by TLC.

b) Y. Ahmad, M.S. Habib, A. Mohammady, B. Bakhtiari, and S.A. Shamsi, J. Org. Chem., 1968, 23, 201.

c) KBr discs.

The photochemical generation of benzimidazolones from appropriately substituted quinoxaline-1,4-dioxides (Table I) in a general reaction, as evidenced by the results summarized in Table II. The photochemical reactions were run on a 0.5-1 g sample in methanol using a Hanovia 679A36 lamp.[6] The quinoxaline-1,4-dioxides used in this study were prepared according to established procedures.[1,2]

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References

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3. M.J. Haddadin, G. Agopian, and C.H. Issidorides, J. Org. Chem., 1971, 36, 514.
4. M.J. Haddadin and A.A. Jarrar, Tetrahedron Lett., 1971, 1651.
5. A.M. Monro and M.J. Sewell, J. Chem. Soc. (B), 1971, 1227.
6. Melting points were determined on a Fisher-Johns melting point apparatus, and are uncorrected. Unless specified otherwise, infrared spectra were taken in nujol mulls on a Perkin-Elmer Grating Infrared Spectrophotometer 257. Nmr (w/v 10%) spectra were run in deuterated chloroform on a Varian A60-D spectrometer. All new compounds gave satisfactory elemental analyses which were performed by F. Pascher, Bonn, Germany.

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