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SHORT COMMUNICATIONS

Reaction of Substituted Benzofuroxanes with Styrene*

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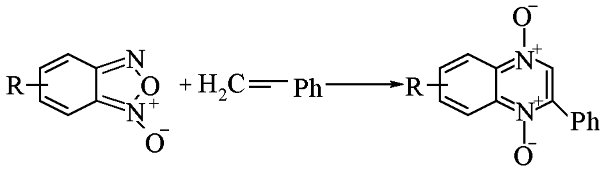
Reactions of benzofuroxanes with nucleophiles (Beirut reaction) is a procedure providing quinoxaline-*N*,*N*'-dioxides. In this reaction take part imines [1], enamines [2], enolate-anions [3], phenols [4], and also olefins with a less active bond than that in enamines [5]. The least studied are the latter reactions. At the same time the availability of olefins is very attractive for preparation of quinoxline-*N*,*N*'-dioxides derivatives.

We established that 6(7)-R-3-phenylquinoxaline-*N*,*N*'-dioxides **IIa–e** form in 38–65% yields in reaction of 5-substituted benzofuroxanes **Ia–e** with styrene in a boiling 2-propanol.



Ia–e **IIa–e**

R = OMe (**a**), Me (**b**), Cl (**c**), COOMe (**d**), NO_2 (**e**).

The duration of the process decreased with growing electron-withdrawing character of the R substituent. For instance, 5-methoxybenzofuroxane (**IIa**) was not fully consumed within 7 days whereas the reaction between 5-nitrobenzofuroxane **IIe** completed in 6–8 h. The yield of 6(7)-R-3-phenylquinoxaline-*N*,*N*'-dioxide also grew with increasing electron-acceptor character of the substituent.

Apparently the reaction involved intermediate formation of dihydoquinoxaline-*N*,*N*'-dioxide **A** as evidenced the red color of the reaction mixture characteristic of these compounds [6]. Intermediate **A** is oxidized by the second benzofuroxane molecule affording aromatic product **II**. Therewith the benzofuroxane was reduced into *o*-benzoquinone dioxime (**III**) that was isolated from the reaction mixture and

Yields and characteristics of compounds synthesized

Compd. no.	Yield, %	Isomers ratio	^{1}H NMR spectrum of the main isomer, δ, ppm					
			H^3, s	$H^{5(8)}$, d	$H^{7(6)}$, d	$H^{8(5)}$, d	Ph, m	R, s
IIa	40	12:88	8.84	7.77	8.44	7.57	7.95, 7.55	3.99
IIb	27	31:69	8.78	8.22	8.38	7.76	7.97, 7.54	2.55
IIc	46	100:0	8.94	8.46	8.54	8.03	7.98, 7.57	–
IId	63	15:85	8.97	8.95	8.65	8.41	8.00, 7.58	3.98
IIe	65	43:57	9.17	9.08	8.71	8.69	8.01, 7.59	–

Compd. no.	Found, %			Formula	Calculated, %		
	C	H	N		C	H	N
IIa	67.16	4.51	10.44	$C_{15}H_{12}N_2O_3$	67.24	4.75	10.47
IIb	71.42	4.79	11.10	$C_{15}H_{12}N_2O_2$	71.47	4.90	11.11
IIc	61.66	3.33	10.27	$C_{14}H_9ClN_2O_2$	62.01	3.54	10.31
IId	64.86	4.08	9.46	$C_{16}H_{12}N_2O_4$	65.12	4.18	9.52
IIe	59.37	3.20	14.84	$C_{14}H_9N_3O_4$	59.78	3.60	14.86

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identified by TLC comparing it with an authentic sample specially prepared by reduction of the corresponding benzofuroxane with hydroxylamine [7]. The capability of benzofuroxanes to reduce the aromatic structure of dihydroazines while converting into ortho-benzoquinone dioximes is well known [8].

The composition and structure of compounds obtained was confirmed by elemental analysis, ^{1}H NMR and mass spectra. In the mass spectra of 6(7)-R-3-phenylquinoxaline-*N,N*'-dioxides the molecular ion peaks are the strongest (100%). Besides in all spectra are observed peaks $[M\text{–}16]^+$ and $[M\text{–}32]^+$ corresponding to successive loss of two oxygen atoms as is characteristic for N-oxides of azines [9].

As show the ^{1}H NMR spectra the obtained 6(7)-R-3-phenylquinoxaline-*N,N*'-dioxides save compound **IIb** (R = Cl) are isomer mixtures. It is not surprising since benzofuroxanes are prone to tautomerism in solutions [10]. However the data available are not sufficient for establishing the structure of the main isomer. The isomer ratio evaluated by integral intensity of signals from protons in *3* position are given in the table.

A solution of 0.01 mol of benzofuroxane **Ia–e** [11] and 0.006 mol of styrene in 40 ml of 2-propanol was heated at reflux till complete consumption of the initial benzofuroxane (TLC monitoring). On cooling the reaction mixture was evaporated to ~10 ml volume and diluted with 20 ml of ether. The separated precipitate was filtered off and recrystallized from 2-propanol. Thus were obtained quinoxaline-*N,N*'-dioxides **IIa–e**. The filtrate was evaporated to dryness, the solid residue was treated with cold 5% solution of NaOH, the solution obtained was filtered again, and the filtrate was acidified with concn. HCl till weakly acidic pH. The precipitated benzoquinone dioxime **III** was filtered off and dried.

^{1}H NMR spectra were recorded on Bruker AC-300 instrument in DMSO-d_6, internal reference DMSO. Mass spectra were measured on mass spectrometer Varian CH-6 (ionizing voltage 70 V). TLC was performed on Silufol UV-254 plates, eluent chloroform.

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