

SHORT
COMMUNICATIONS

Reaction of Substituted Benzofuroxanes with Styrene*

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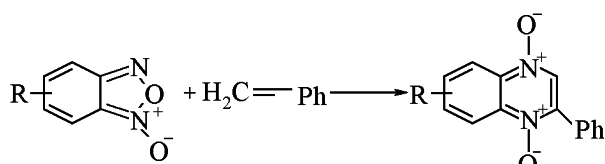
Reactions of benzofuroxanes with nucleophiles (Beirut reaction) is a procedure providing quinoxaline-*N,N'*-dioxides. In this reaction take part imines [1], enamines [2], enolate-anions [3], phenols [4], and also olefins with a less active bond than that in enamines [5]. The least studied are the latter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

We established that 6(7)-*R*-3-phenylquinoxaline-*N,N'*-dioxides **Ia-e** form in 38-65% yields in reac-

tion of 5-substituted benzofuroxanes **Ia-e** with styrene in a boiling 2-propanol.

The duration of the process decreased with growing electron-withdrawing character of the *R* substituent. For instance, 5-methoxybenzofuroxane (**Ia**) was not fully consumed within 7 days whereas the reaction between 5-nitrobenzofuroxane **Ie** 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 dihydroquinoxaline-*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



Ia-e

IIa-e

R = OMe (**a**), Me (**b**), Cl (**c**), COOMe (**d**), NO₂ (**e**).

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
Ia	40	12:88	8.84	7.77	8.44	7.57	7.95, 7.55	3.99
Ib	27	31:69	8.78	8.22	8.38	7.76	7.97, 7.54	2.55
Ic	46	100:0	8.94	8.46	8.54	8.03	7.98, 7.57	-
Id	63	15:85	8.97	8.95	8.65	8.41	8.00, 7.58	3.98
Ie	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
Ia	67.16	4.51	10.44	C ₁₅ H ₁₂ N ₂ O ₃	67.24	4.75	10.47
Ib	71.42	4.79	11.10	C ₁₅ H ₁₂ N ₂ O ₂	71.47	4.90	11.11
Ic	61.66	3.33	10.27	C ₁₄ H ₉ ClN ₂ O ₂	62.01	3.54	10.31
Id	64.86	4.08	9.46	C ₁₆ H ₁₂ N ₂ O ₄	65.12	4.18	9.52
Ie	59.37	3.20	14.84	C ₁₄ H ₉ N ₃ O 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, ^1H 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 $[M-16]^+$ and $[M-32]^+$ corresponding to successive loss of two oxygen atoms as is characteristic for N-oxides of azines [9].

As show the ^1H 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.

^1H 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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