

A NOVEL RING TRANSFORMATION OF BENZOFUROXANES TO 1-HYDROXY-
2-ARYL-BENZIMIDAZOLE-3-N-OXIDE WITH NITRONES

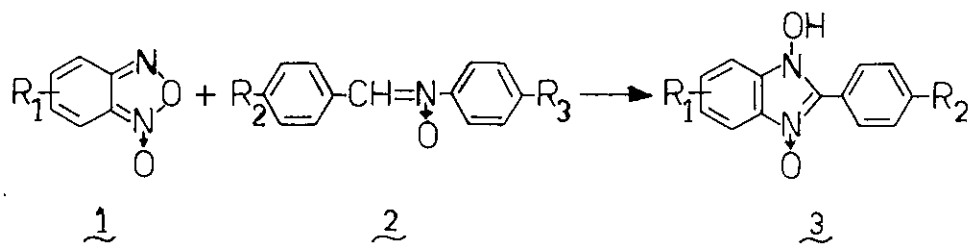
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Abstract - Benzofuroxanes (1) react with nitrones (2) to give
1-hydroxy-2-aryl-benzimidazole-3-N-oxide (3) in good yields.

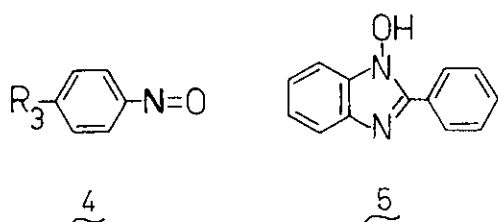
Benzofuroxanes (BFOS) (1) have proved to be excellent synthons in the preparation of a variety of organic N-oxides and enormous developed chemical knowledge has been reviewed¹. In continuation of our studies on BFOS^{2,3}, recently we reported the cycloaddition reaction of diazoacetates as typical 1,3-dipoles⁴ with carbocyclic ring of 1 and leaving heterocyclic ring intact. In the present communication, we describe a novel ring transformation of heterocyclic ring of 1 in the reaction with nitrones (2).

When BFO (1a) was reacted with equimolar quantities of nitrone (2a) in refluxing benzene for 4 h, 1-hydroxy-2-phenyl-benzimidazole-3-N-oxide (3a) was isolated as a solid product. Recrystallization of 3a from DMF afforded light yellow crystals, mp 211-212°C (dec.) in 80% yield. The structure of 3a is fully corroborated by its spectral and microanalytical data ν_{\max} (Nujol) 2950 (broad, -N-OH), 1265 cm^{-1} (s, N→O); δ (CF_3COOH , 100 MHz), 7.52-7.88 (aromatic multiplet) and m/z 226 (11%), 210 (61.5%). Finally the identity of 3a was confirmed by comparison with an authentic sample⁵.

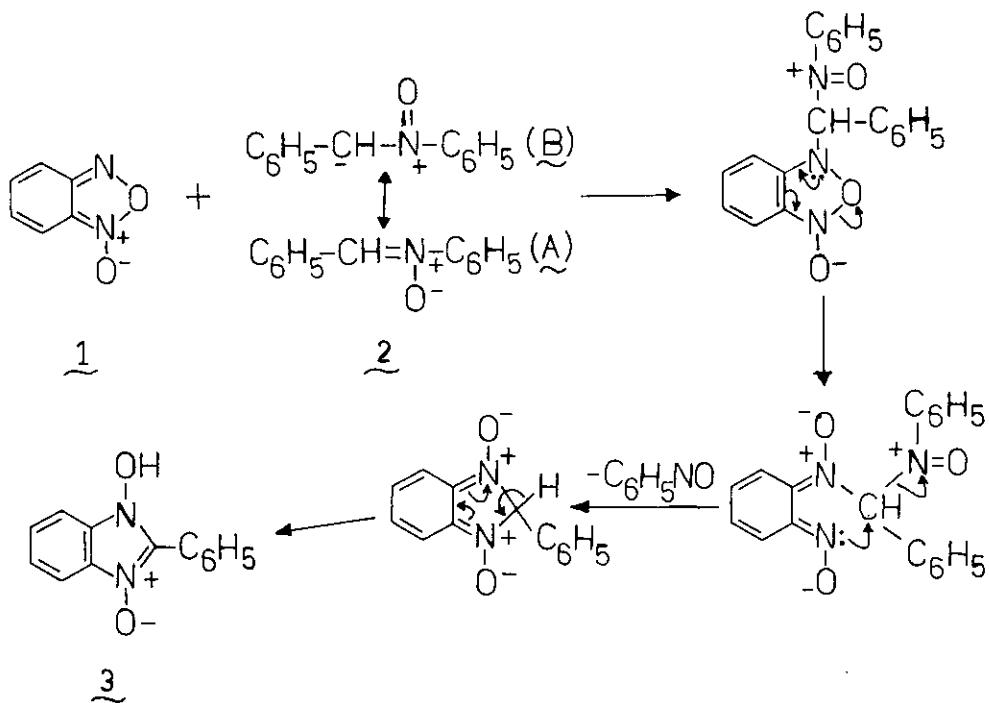
Similarly when benzofuroxane (1a) was reacted with 2b, corresponding 1-hydroxy-2-(p-methoxyphenyl)-benzimidazole-3-N-oxide (3b) was obtained. The reaction of 1a with 2c afforded 3a and the p-nitrosotoluene (4, $R_3 = \text{CH}_3$) was isolated from the mother liquor and identified by comparison with an authentic sample. Reaction of benzofuroxanes (1b-c) with 2a-b under identical conditions afforded 3c-f, respectively⁶. The characteristics of these products are given in Table-1. It is interesting to note that nitrones (2) did not cycloadd onto the carbocyclic ring of 1⁷.



	R ₁	R ₂	R ₃		R ₁	R ₂
a =	H	a = H	H	a =	H	H
b =	5(6)-CH ₃	b = OCH ₃	H	b =	H	OCH ₃
c =	5(6)-Cl	c = H	CH ₃	c =	5(6)-CH ₃	H
				d =	5(6)-Cl	H
				e =	5(6)-CH ₃	OCH ₃
				f =	5(6)-Cl	OCH ₃



Regarding the mechanism of this reaction, a plausible reaction scheme is given below (Scheme 1).



Scheme - 1

The reaction appears to proceed through the initial attack of the carbanion arising from the contribution of the form⁸ (B) of the nitrene (2) on the nitrogen atom of 1, followed by rearrangement and elimination of nitrosobenzene. The isolation of the nitrosobenzene from the reaction mixture lends further support to the proposed reaction sequence.

The negative evidence for the possible formation of benzimidazole-N-oxide (5) from the reaction of 1a with 2a was clearly established through elemental analysis and comparison of spectral data with an authentic sample⁹ (5). When corresponding imines, azoxybenzene and aldehydes were reacted under similar reaction conditions the starting materials were recovered in each case.

Table - 1

Product 3	Mp °C	Yield %	ν_{\max} (KBr)/ cm^{-1}	δ_{H} (100 MHz, CF_3COOH)	MS (M^+) m/e
b	205-207	85	2960, 1270	4.10 (s, 3H), 7.36 (d, 2H, J=9.5 Hz); 7.20-8.00 (m, 4H); 8.28 (d, 2H, J=9.5 Hz).	256
c	217-218	78	2955, 1260	2.66 (s, 3H); 7.62-8.22 (m, 8H).	240
d	221-223	81	2965, 1255	7.65-8.32 (m, 8H).	260
e	210-212	84	2970, 1250	2.66 (s, 3H); 4.80 (s, 3H); 7.32 (dd, 2H, J=10 Hz); 7.58-7.84 (m, 3H); 8.22 (dd, 2H, J=10 Hz).	270
f	209-211	80	2960, 1260	4.05 (s, 3H); 7.25 (d, 2H, J=9.5 Hz); 7.10-7.95 (m, 3H); 8.20 (d, 2H, J=9.5 Hz).	290

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