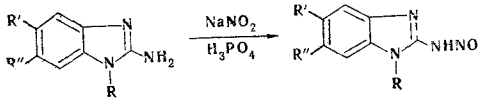
DIRECT NITROSATION OF 2-AMINO-1-ALKYL-(ARALKYL)BENZIMIDAZOLES

S. N. Kolodyazhnaya, A. M. Simonov, and L. N. Podladchikova

UDC 547.785.5+542.958.3

Primary nitrosamines are the most stable form of diazo compounds in the azole series [1]. However, nitrosamines could not be obtained for imidazole and benzimidazole. We have found that 2-(N-nitrosamino)-benzimidazoles (II) are formed by the action of sodium nitrite on 2-amino-1-alkyl(aralkyl)benzimidazoles (I) in 60% phosphoric acid at −5°. Under these conditions, 5-alkyl- and 5-alkoxy-substituted I undergo intermolecular diazo coupling at the 6 position, whereas 1-aryl-2-aminobenzimidazoles undergo intramolecular coupling to give dibenz[a,g]imidazo[2,1-c]-1,2,4-triazines [2].



I II

a R=CH_3, R′=H, R″=Br; b R=CH_3, R′=R″=Br; c R=CH_3, R′=NO_2, R″=H; d R=CH_3, R′=R″=H; R=$C_6H_5CH_2$, R′=R″=H

Nitrosamines II are also resistant to the action of dilute acids on storage, but compounds with electronegative substituents (IIa,b) undergo denitrosation on heating in alcohol solutions.

TABLE 1. 2-(N-Nitrosamino)benzimidazoles

Compound	Dec. point, °C	Empirical formula	Found, %			Calc., %			IR spectrum,* cm^{-1}	Yield, %
			C	H	N	C	H	N		
IIa	163	$C_8H_7BrN_4O$ †	38,0	2,5	22,0	37,7	2,8	22,0	3060	62
IIb	138	$C_8H_6Br_2N_4O$ ‡	28,6	1,7	16,9	28,8	1,8	16,8	3200—3000	59
IIc	169	$C_8H_7N_5O_3$	43,1	3,1	32,0	43,4	3,2	31,7	3100	51
IId	162	$C_8H_8N_4O$	54,5	4,5	32,2	54.5	4,6	31,8	3260	74
IIe	187	$C_{14}H_{12}N_4O$	66,8	4,3	22,4	66,7	4,8	22,2	3260—3160	60

*The spectra of suspensions of the compounds in hexafluorobutadiene were recorded with a UR-20 spectrometer.

† Found, %: Br 31.2. Calculated, %: Br 31.3.

‡ Found, %: Br 47.7. Calculated, %: Br 47.9.

LITERATURE CITED

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Rostov State University, Rostov-on-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1573-1574, November, 1974. Original article submitted December 10, 1973.