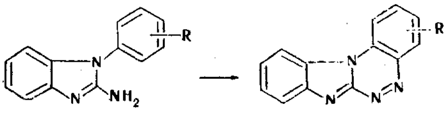
INTRAMOLECULAR AZO COUPLING IN A NUMBER OF 1-SUBSTITUTED 2-AMINOBENZIMIDAZOLES

S. N. Kolodyazhnaya, A. M. Simonov,
N. N. Zheltikova, and A. F. Pozharskii

UDC 547.785.5.556.3

Benzimidazole-2-diazonium salts formed by the action of nitrosylsulfuric acid on 2-aminobenzimidazoles have extremely high activity and can enter into azo coupling at the 5 and 6 positions of the starting amine [1]. We have found that in the case of 1-aryl-2-aminobenzimidazoles (I), one observes, in addition to intermolecular azo coupling, intramolecular azo coupling, which proceeds at the ortho position of the N-aryl radical and leads to the formation of dibenz[a,g]imidazo[2,1-c][1,2,4]triazines (II-V). The cyclization proceeds smoothly in concentrated H_3PO_4; the presence of concentrated H_2SO_4 promotes the formation of 5- and 6-azobenzimidazoles. A methyl group in the meta position of the N-aryl radical appreciably facilitates cyclization; in this case, two isomers (Va,b), which could be separated on plates with a thin layer of aluminum oxide in benzene–chloroform (1:2), are formed. The reaction is carried out by mixing (in the cold) 2 mmole of I [2], 5-7 ml of concentrated H_3PO_4, and 0.5 g (4 mmole) of solid nitrosylsulfuric acid [3]. The mixture is held at 20-25°C for 6 h and worked up as described in [1]. The triazines are isolated with a column filled with aluminum oxide; the bright-yellow fraction is washed out with chloroform. The structures of II-V were confirmed by the results of elementary analysis, IR spectroscopy, determination of the molecular weights by the Rast method, and by the observed analogy in the properties of II-V and benz[a]imidazo[2,1-c][1,2,4]triazines obtained from N-(o-aminophenyl)imidazoles [4]. Consequently, the concept of the structure of the previously obtained II as being a diazoamino compound [1] must be considered to be erroneous.



I II-V

This method was used to obtain dibenz[a,g]imidazo[2,1-c][1,2,4]triazine (II, in 64% yield, mp 312-313°; $C_{13}H_8N_4$) and its 3-methyl (III, in 67% yield, mp 289-290°; $C_{14}H_{10}N_4$), 3-methoxy (IV, in 70% yield, mp 255-256°; $C_{14}H_{10}N_4O$), 2(or 4)-methyl (Va, mp 308-309°; $C_{14}H_{10}N_4$), and 4(or 2)-methyl (Vb, mp 288-289°; overall yield of Va and Vb 91%; $C_{14}H_{10}N_4$) derivatives.

LITERATURE CITED

1. A. M. Simonov and S. N. Kolodyazhnaya, Khim. Geterotsikl. Soedin., 543 (1969).
2. A. F. Pozharskii and A. M. Simonov, Chichibabin Amination of Heterocycles [in Russian], Izd. RGU, Rostov-on-Don (1971), p. 97.
3. M. R. Piercey and E. Ward, J. Chem. Soc., 3843 (1962).
4. A. F. Pozharskii, A. M. Simonov, and L. M. Sitkina, Khim. Geterotsikl. Soedin., 916 (1969).

Rostov State University, Rostov-on-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 714-715, May, 1973. Original article submitted October 20, 1972.