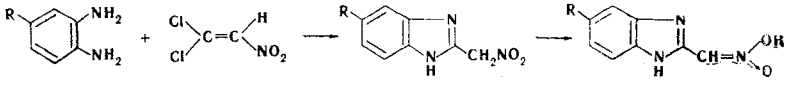
METHOD FOR THE SYNTHESIS OF BENZIMIDAZOLES WITH A NITRO GROUP IN THE SIDE CHAIN

V. V. Rudchenko, V. A. Buevich,
V. S. Grineva, and V. V. Perekalin

UDC 547.785.5

A new method for the construction of a benzimidazole ring by nucleophilic addition of aromatic o-diamines to 1,1-dichloro-2-nitroethylene (III) is proposed in the present paper. The synthesis takes place under mild conditions (in methanol at 10° in 30-40 min with a diamine to III ratio of 2 : 1) and terminates with the formation of 2-nitromethylbenzimidazole derivatives.



I, II Ia, IIa

I R=H; II R=CH_3

The hydrochloride of the diamine precipitated during the reaction. After 30 min, the reaction mixture was heated to room temperature and poured, together with the solid material, into water. The resulting crystalline product was removed by filtration, washed with water, and recrystallized from methanol. Thus 2-nitromethylbenzimidazole (I), with mp 162° (light-yellow crystals), was obtained in 80% yield from o-phenylenediamine, and 5-methyl-2-nitromethylbenzimidazole (II), with mp 170° (light-yellow crystals), was obtained in 70% yield from 4-methyl-1,2-phenylenediamine.

The results of complete elementary analysis of I and II are in good agreement with the calculated values.

The realization of this method makes benzimidazoles with a nitro group in the side chain readily accessible.

The reaction mechanism probably consists of double nucleophilic addition of the amino groups of the o-diamine to the double bond of the halo nitroalkene and is accompanied in each step by splitting out in alkaline medium of hydrogen chloride, which is tied up by excess diamine. Migration of the multiple bond occurs during the cyclization to give an energically more favorable aromatic benzimidazole ring. The strong basicity of benzimidazole makes the existence of the nitro group in the aci form (structures Ia and IIa) possible due to formation of an inner salt; this is confirmed by the presence of the high-intensity maxima in the UV spectrum at 210 and 370 nm (ε 34,000 and 26,000) that are characteristic for salts of a nitro group.

A. I. Gertsen Leningrad State Pedagogical Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, p. 1576, November, 1975. Original article submitted May 27, 1975.