THE REPLACEMENT OF THE HYDRAZINE GROUP BY CHLORINE IN THE BENZIMIDAZOLE SERIES

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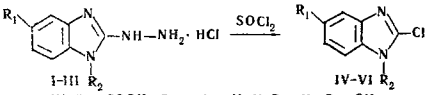
A hydrazine residue in position 2 of benzimidazole can easily and in good yield be replaced by chlorine by boiling the 2-hydrazinobenzimidazole concerned with thionyl chloride.



In order to obtain the corresponding acid chloride, 2-hydrazino-1-methylbenzimidazole-5-carboxylic acid was boiled with an excess of thionyl chloride. The product obtained proved to be the chloride of 2-chloro-1-methylbenzimidazole-5-carboxylic acid. Its structure was shown by the identification of the hydrolysis product in respect of melting point and IR spectra with 5-carboxy-2-chloro-1-methylbenzimidazole of authentic structure (obtained as described by Simonov and Lomakin [1]). 2-Hydrazino-1-methylbenzimidazole and 1-benzyl-2-hydrazino-5-nitrobenzimidazole reacted with thionyl chloride similarly.

The reaction that we have observed is a peculiar case of nucleophilic substitution in the benzimidazole series.

5-Carboxy-2-hydrazino-1-methylbenzimidazole hydrochloride (I). This was obtained from the corresponding thione by its oxidation to the sulfonic acid and the hydrazinolysis of the latter followed by treatment with hydrogen chloride. Needles, mp 309–311° C (from water). Found, %: C 44.66; H 4.84; N 23.56; Cl 14.88. Calculated for $C_9H_{10}N_4O_2 \cdot HCl$, %: C 44.54; H 4.57; N 23.09; Cl 14.6.

2-Chloro-1-methylbenzimidazole-5-carbonyl chloride. A mixture of 1.2 g (0.005 mole) of I and 10 ml of thionyl chloride was boiled for 3 hr, the excess of thionyl chloride was distilled off, and the residue was crystallized from benzene. Mp 197° C (according to the literature [2], 196–197° C). After recrystallization from aqueous dimethylformamide, 2-chloro-1-methylbenzimidazole-5-carboxylic acid was obtained. Mp 210° C (giving no depression with the substance obtained by Simonov and Lomakin's method [1]). Compounds II and III reacted with thionyl chloride under similar conditions. Yields in all cases 80–90%.

REFERENCES

1. A. M. Simonov and A. N. Lomakin, ZhOKh, 32, 2228, 1962.
2. A. N. Lomakin, ZhVKhO [Mendeleev Chemistry Journal], 3, 352, 1968.

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