UDC 547.785.5

2-CYANOBENZIMIDAZOLES

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 3, pp. 472–473, 1966

2-Cyanobenzimidazoles are not described in the literature. As 2-(hydroxyimino) methylbenzimidazoles are readily accessible [1–3], they were suitable starting materials for synthesizing 2-cyanobenzimidazoles. Actually, treatment of the oximes of 2-formylbenzimidazole (I) and 1-methyl-2-formylbenzimidazole (II) with thionyl chloride gave excellent yields of 2-cyanobenzimidazole (III) and 1-methyl-2-cyanobenzimidazole (IV) respectively.

Treatment of the nitrile IV with conc. H_2SO_4 at room temperature converted it quantitatively into 1-methylbenzimidazole-2-carboxamide (V). Heating III, IV, and V with dilute acid or alkali gave the corresponding benzimidazole-2-carboxylic acid.

2.2 g (0.01 mole) II hydrochloride and 5 ml $SOCl_2$ were refluxed together for 30 min, the excess $SOCl_2$ distilled off, the residue treated with water, and the solid filtered off, yield 1.5 g (95%) IV, mp 178–178.5° C (ex benzene). Crystallizes from EtOH, Me_2CO, Et_2O, insoluble in dilute acids and alkalies. In the IR spectrum $\nu_{C\equiv N}$ 2240 cm^{-1}. Found: C 68.91; H 4.54; N 26.72%. Calculated for $C_9H_7N_3$: C 68.77; H 4.48; N 26.73%.

Similarly hydrochloride of I and $SOCl_2$ gave 2-cyanobenzimidazole (III), mp 285°–286° C (ex EtOH), soluble in dilute alkali, insoluble in dilute acid. In the IR spectrum $\nu_{C\equiv N}$ 2240 cm^{-1}. Found: C 66.99; H 3.75; N 29.44%. Calculated for $C_8H_5N_3$: C 67.12; H 3.52; N 29.35%.

1.1 g (0.007 mole) IV was dissolved in 3 ml conc. H_2SO_4, left for 48 hr, then ice added, the mixture neutralized with K_2CO_3, and the amide V filtered off. Yield 1.2 g (98%), mp 201°–202° C (ex Me_2CO). The IR spectra contained bands characteristic of amides: 1696, 3402, 3520 cm^{-1}. Found: C 61.62; H 5.36; N 24.03%. Calculated for $C_9H_9N_3O$: C 61.70; H 5.19; N 23.97%.

0.53 g (0.003 mole) V and 2 ml 10%KOH was refluxed for 20 min, cooled, and the crystals of the ammonium salt of 1-methylbenzimidazole-2-carboxylic acid VI filtered off, yield 0.41 g (70%), mp 343°–345° C (decomp, ex water). Found: N 21.66, 21.69%. Calculated for $C_9H_{11}N_3O_2$: N 21.75%. An aqueous solution of the salt VI after acidifying and heating gave 1-methylbenzimidazole mp 58°–60° C; picrate, 243°–244° C (the literature gives [4]; mp 66° C, picrate mp 246°–247° C.

Nitrile III dissolved in dilute acid on heating. After neutralizing with K_2CO_3, benzimidazole-2-carboxylic acid, mp 169°–170° C, (decomp) was filtered off (the literature gives [3] mp 169°–170° C (decomp).

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2 September 1965

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UDC 547.78 +547.538

DIRECT ARYLATION OF 5-MEMBERED HETEROCYCLIC NITROGEN RINGS

IV. Reaction of Imidazole and Benzimidazole with Benzyne*

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 3, pp. 473–474, 1966

We have found that benzyne can be used as an arylating agent for synthesizing N-phenyl derivatives of imidazole

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*Part I of a series Application of Arynes in the Chemistry of Heterocyclic Rings. For Part III see [1].