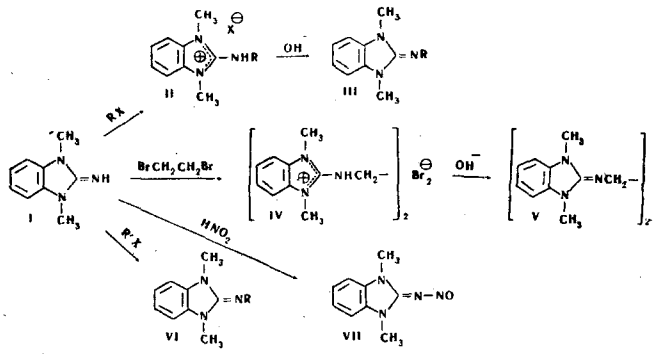
In the arylation and acylation of **I**, as a result of a decrease in the basicity of the system through the introduction of electrophilic radicals into it, N-aryl- and N-acyl-1,3-dimethyl-2-iminobenzimidazolines (**VI**) are formed directly. In order to exclude the binding by the initial imine of the HX formed, in some cases it is desirable to carry out the reaction in the presence of Na_2CO_3. The action of nitrous acid on **I** in a weakly acid medium leads to the N-nitroso derivative (**VII**), which is cleaved by the action of zinc dust in acetic acid (1:1) with the formation of the initial imine (**I**), which confirms its structure as an N-Nitroso compound.



R = alkyl (see table); R′ = acyl or aryl

EXPERIMENTAL

Synthesis of N-substituted 1,3-dimethyl-2-iminobenzimidazolines. A. A mixture of **I** (0.01 mole) and the appropriate alkyl, aryl, or acyl halide* (0.011 mole) was heated in a glycerol bath for 1–3 hr (see table) or until the melt solidified. Exactly 0.01 mole of dibromoethane was used. To obtain **VId–f** (see table), 1 g of sodium carbonate was previously added to the mixture. After cooling, the melt was triturated with a mixture of ethanol and ether (1:5) or with ethanol (**VIa** and **VIb**). When mineral salts were present in the melt, it was treated with hot water. Compound **VIc** was isolated by distilling off the excess of acetic anhydride.

B. With shaking, a solution of 0.015 mole of acyl chloride in 10 ml of benzene was added to a solution of 0.01 mole of **I** and 2 g of sodium bicarbonate in 50 ml of water, and shaking was continued for another 2 hr. The precipitate was filtered off and washed with water, benzene, and a small amount of ethanol.

C. A suspension or aqueous solution of a benzimidazolium salt was treated with an excess of alkali and the precipitate of **V** was filtered off, while **IIIa** and **IIIb** were extracted with ether.

N-Nitroso-1,3-dimethyl-2-iminobenzimidazoline (VII). With stirring at 30–40°C, 1.03 g (15 mM) of dry sodium nitrite was added during 5 min to a solution of 1 g (5 mM) of the hydrochloride of **I** (obtained by adding concentrated HCl to a saturated ethanolic solution of **I**) in 10 ml of water acidified with 3 drops of glacial acetic acid, and stirring was continued for another 30 min. The N-nitroso compound was filtered off and dried at 50–60°C. Yield 0.81 g (85%). Yellow needles (from ethanol) with mp 126°C (with explosive decomposition). Found, %: N 29.15; 29.50. Calculated for $C_9H_{10}N_4O$, %: N 29.45.

2-Amino-1,3-dimethylbenzimidazolium nitrite precipitated when the reaction of **I**·HCl with $NaNO_2$ was carried out without heating or the solution was not acidified with acetic acid. Colorless needles (from ethanol) with mp 194°C (decomp.). The substance gave a reaction for the nitrite ion. Found, %: N 26.79; 26.71. Calculated for $C_9H_{12}N_4O_2$, %: N 26.91.

*Methylation was carried out with methyl benzenesulfonate and acetylation with acetic anhydride (3 moles).

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FORMYLATION OF 1-METHYLBENZIMIDAZOLE

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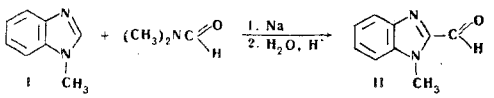
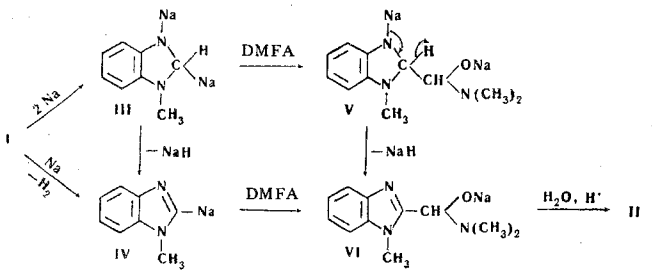
The formylation of 1-methylbenzimidazole in position 2 has been effected by the use of dimethylformamide in the presence of sodium.

Because of the presence in the μ-position of benzimidazole of a positive charge, the direct introduction of an aldehyde group taking place through the stage of the electrophilic replacement of an H atom by a formylating compound is unsuitable for the production of benzimidazole-2-aldehydes. The existing methods for the synthesis of 2-formylbenzimidazoles are based mainly on the oxidation of derivatives of benzimidazole containing a methyl group [1] or a hydroxymethyl group [2] in position 2 and the oxidative degradation of 1,2-dihydroxy-1,2-di(2′-benzimidazolyl)ethane [3] and its N-substituted derivatives [4] and of 2-(d-arabo)-benzimidazole [5]. The production of 2-formylbenzimidazoles from o-arylenediamines and from 1,2-dichloro-1,2-diethoxyethane [6], from the acetal of ethyl glyoxylate [7], and from dichloroacetic acid [8] has been reported.

In the present work it has been established that 1-methylbenzimidazole undergoes formylation in position 2 with dimethylformamide if the reaction is carried out in the presence of metallic sodium.



The formation of II from I may take place by three routes:



The considerable evolution of hydrogen in the absence of dimethylformamide is in favor of the conversion of I into IV; however, the addition of sodium to 1-methylbenzimidazole, as takes place with a number of compounds containing the C=N bond, is also not excluded. Since the hydrogen in position 2 of dihydrobenzimidazoles possesses considerable hydride lability [9], the transition of III into IV and of V into VI is quite possible.

EXPERIMENTAL

2-Formyl-1-methylbenzimidazole (II). A mixture of 4 g of **I**, 2.5 g of dimethylformamide, and 0.8 g of powdered sodium activated with isoamyl alcohol in 45 ml of benzene was stirred in a current of nitrogen for 1.5 hr. At the end of the reaction, 5 ml of acetic acid in 20 ml of water was added in one portion. If aqueous ethanol is used instead of aqueous acetic acid, the II formed rapidly undergoes a Cannizzaro reaction (see following experiment). The mixture was neutralized with saturated sodium carbonate solution, after which the layers were separated. The aqueous layer was extracted with chloroform, the chloroform extract was combined with the benzene solution, and the solvents were distilled off. From the oily residue was isolated 0.75 g of compound **II**, purified via the bisulfite compound. The mp of the II (109°–110° C) and its oxime (215°–216° C) agree with those given in the literature [2, 10].

Copper 1-methylbenzimidazole-2-carboxylate (VII). The synthesis was carried out in a manner similar to the preceding experiment, but the acetic acid solution was replaced by 10 ml of 80% ethanol. When the sodium that had not taken part in the main reaction had reacted, 25 ml of water was added. The aqueous layer was acidified with acetic acid and a 5% solution of copper sulfate was added to it until the separation of the **VII** ceased. Yield 0.42 g. Found, %: C 52.08; 52.49; H 3.34; 3.65. Calculated for $C_{18}H_{14}N_4O_4Cu$, %: C 52.24; H 3.41.

1-Methylbenzimidazole-2-carboxylic acid. This was obtained from **VII** by the method of Tertov and Panchenko [11]. Mp 90°–91° C (decomp.). Literature data [11, 12]: mp 90°–91°, 93° C (decomp.).

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