SYNTHESIS OF 2-NITROMETHYLBENZIMIDAZOLES

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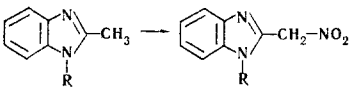
The usual methods for the synthesis of nitro compounds proved to be unsuitable for obtaining 2-benzimidazolylnitromethanes. Only 2-nitromethyl-1-acetylbenzimidazole, obtained by the reaction of o-phenylenediamine with nitroacetic acid imido ester, has been described [1]. According to [2], heterylnitromethanes can be obtained by the nitration of heterocyclic compounds that contain methyl groups that are strongly activated by the heterocyclic ring by means of alkyl nitrates in the presence of sodium amide. We were able to apply this reaction to the benzimidazole series, although the activity of a methyl group in the 2 position of the benzimidazole ring is extremely low, according to the data in [3]. The action of propyl nitrate on N-substituted 2-methylbenzimidazoles in liquid ammonia in the presence of sodium amide gives 2-benzimidazolylnitromethanes. The structures of the compounds obtained were established on the basis of elementary analysis and their conversion to the corresponding nitrolic acids. According to IR spectroscopy, they exist in the acid form.



I, II III, IV

I, III R=C_6H_5; II, IV R=CH_3

EXPERIMENTAL

2-Nitromethyl-1-phenylbenzimidazole (III). A 0.025-mole sample of I was introduced into a suspension of 0.065 mole of sodium amide in 100 ml of liquid ammonia; the mixture was stirred for 30 min, and 0.08 mole of propyl nitrate was added dropwise. After 30 min, 100 ml of absolute ether was added, and the ammonia was evaporated. The sodium salt was removed by filtration and decomposed with water in acetic acid to give 34% of pale-yellow prisms (from alcohol) with mp 127° (dec.). Found: C 66.1; H 4.4%. $C_{14}H_{11}N_3O_2$. Calculated: C 66.4; H 4.4%. IR spectrum (mineral oil), cm^{-1}: 1160, 1060 ($C=NO_2^-$); 3310 (OH).

2-Nitromethyl-1-methylbenzimidazole (IV). This compound was obtained in 33% yield as pale-yellow prisms (from alcohol) with mp 147° (dec.). Found: C 56.1; H 4.8%. $C_9H_9N_3O_2$. Calculated: C 56.5; H 4.7%. IR spectrum, cm^{-1}: 1010, 1160 ($C=NO_2^-$); 3225 (OH).

1-Phenyl-2-benzimidazolylmethylnitrolic Acid. Sodium nitrite was added to a solution of III in dilute hydrochloric acid, and 72% of the nitrolic acid with mp 115° (dec.) precipitated. Found: C 58.8; H 3.4%. $C_{14}H_{10}N_4O_3$. Calculated: C 59.6; H 3.6%. IR spectrum, cm^{-1}: 1080, 1110 ($C=NO_2^-$); broad band at 2240-2260 (H^+); 1600 (C = N).

1-Methyl-2-benzimidazolylmethylnitrolic Acid. This compound was obtained in 70% yield and had mp 108° (dec.). Found: C 49.6; H 4.3%. $C_9H_8N_4O_3$. Calculated: C 49.1; H 3.6%. The IR spectrum was identical to the spectrum of the compound obtained in [4].

LITERATURE CITED

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