

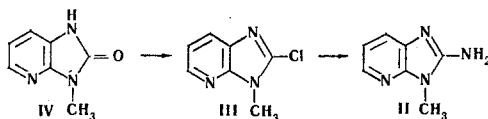
SYNTHESIS OF 2-AMINO-SUBSTITUTED 3-METHYL-
3H-IMIDAZO[4,5-b]PYRIDINES

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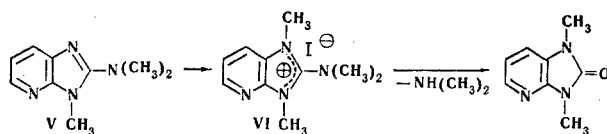
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Attempts have been made to introduce an amino group directly into the molecule of 3-methyl-3H-imidazo[4,5-b]pyridine (I) by the Chichibabin reaction in order to obtain 2-amino-3-methyl-3H-imidazo[4,5-b]pyridine (II), in a similar manner to the amination of N-methylbenzimidazole [1]. When I was heated with sodium amide in dimethylaniline or paraffin oil in the range of temperatures from 115–210°C, it was impossible to obtain an amino derivative (see [2]), and only the starting material was isolated from the reaction mixture (about 80%).

Compound II was synthesized by the action of a 60% aqueous or ethanolic solution of ammonia on 2-chloro-3-methyl-3H-imidazo[4,5-b]pyridine (III) in a sealed tube at 100–110°C for 7 hr. The amine II gives an intense coloration with alkali-metal hypohalites (see [3,5]), which is a convenient method for the qualitative detection of small amounts of II. The 2-chloro derivative III used for the synthesis of II was obtained by heating 3-methyl-2-oxo-1,2-dihydroimidazo[4,5-b]pyridine (IV) [4] with a mixture of POCl₃ and PCl₅ (120°C, 4 hr).



2-Dimethylamino-3-methyl-3H-imidazo[4,5-b]pyridine (V) was obtained in a similar manner to II. On being heated with aqueous alkali, the methiodide of this compound splits out dimethylamine and is converted into 1,3-dimethyl-2-oxo-1,2-dihydroimidazo[4,5-b]pyridine [4] with a yield of 87% (see [5]).



2-Chloro-3-methyl-3H-imidazo[4,5-b]pyridine (III), yield 60%, mp 67–68°C (from n-hexane). Found, %: C 50.37; H 3.39; Cl 21.15. Calculated for C₇H₆N₃Cl, %: C 50.16; H 3.61; Cl 21.15.

2-Amino-3-methyl-3H-imidazo[4,5-b]pyridine (II), yield 70%, mp 182–183°C (from toluene). Found, %: C 56.80; H 5.51. Calculated for C₇H₈N₄, %: C 56.74; H 5.44.

2-Amino-3-methyl-3H-imidazo[4,5-b]pyridine (V), yield 76%, bp 108–110°C (20 mm). Found, %: 31.50. Calculated for C₉H₁₂N₄, %: N 31.79.

N⁺-Methiodide of 2-dimethylamino-3-methyl-3H-imidazo[4,5-b]pyridine (VI), yield 88%, mp 159–160°C (from ethanol). Found, %: N 17.31. Calculated for C₁₀H₁₅N₄I, %, N 17.61.

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