By saturating **II** with hydrogen bromide in an atmosphere of nitrogen first in the cold and then at 100° C we obtained 1-bromo-2-(β-bromopropyl)cyclohexane (**III**), the structure of which was confirmed by its IR spectrum. Bp 99–100° C (2 mm), n_D^{20} 1.5280, d_D^{20} 1.5251. Found, %: C 38.19; H 5.70; Br 56.34; MR_D 57.09. Calculated for $C_9H_{16}Br_2$, %: C 38.03; H 5.63; Br 56.23; MR_D 57.03. Yield 86.3%.

The reaction of **III** with a threefold excess of anhydrous Na_2S in dimethylformamide at 125° C gave a 54.5% yield of **I** in the form of a mixture of cis- and trans-isomers. Bp 89°–90° C (20 mm), n_D^{20} 1.5090, d_4^{20} 0.9783. Found, %: C 57.24; H 10.35; MR_D 47.61. Calculated for $C_9H_{16}S$, %: C 57.22; H 10.25; MR_D 47.43. The structure of I was confirmed by its IR spectrum.

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NITRATION OF 3-METHYL-3H-IMIDAZO[4, 5-b]PYRIDINE

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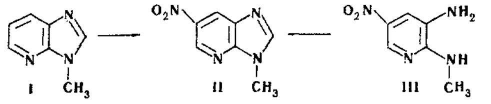
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 5, p. 953, 1968

UDC 547.785.5+547.822.7+542.958.1

We have effected the direct introduction of a nitro group into the molecule of an imidazo[4,5-b]pyridine for the first time. In contrast to benzimidazole, the nitration of which takes place readily even in the cold [1], 3-methyl-3H-imidazo[4,5-b]pyridine (**I**) undergoes nitration with a mixture of nitric and sulfuric acids only at 140–160° C. The reaction product [yield 50%, mp 220–221° C (ethanol). Found, %: C 46.92; H 3.34; N 31.34. Calculated for $C_7H_6N_4O_2$, %: C 47.19; H 3.39; N 31.45] proved to be identical with the compound obtained from 3-amino-2-methylamino-5-nitropyridine (**III**) and formic acid, which shows its structure to be 3-methyl-6-nitroimidazo[4,5-b]-pyridine (**II**).



No other nitro derivatives apart from **II** were detected. Compound **III** was obtained by the reduction with ammonium sulfide of the product of the interaction of 2-chloro-3,5-dinitropyridine with methylamine [2]. Mp 199–200° C (water). Found, %: C 42.94; H 4.83. Calculated for $C_6H_8N_4O_2$, %: C 42.86; H 4.79.

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8 January 1968

Donetsk Branch of IREA [All-Union Scientific-Research Institute for Chemical Reagents and Particularly Pure Chemical Substances]

QUATERNIZATION OF 3-METHYL-3H-IMIDAZO[4,5-b]PYRIDINE

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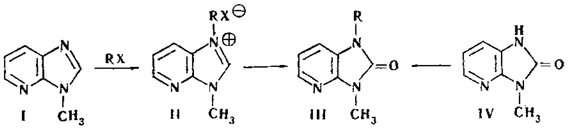
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 5, p. 954, 1968

UDC 547.785.5

3-Methyl-3H-imidazo[4,5-b]pyridine (**I**), which has two basic centers [1], reacts with alkylating agents at the N^1 atom with the formation of monoquaternary salts. The structure of such compounds as N^1-alkyl(aryl, aralkyl)-N^3-methylimidazolium salts (**II**) has been shown by the oxidation of some of them ($R = CH_3, X = I$; $R = CH_2C_6H_5$, $X = Cl$) with potassium ferrocyanide in alkali at a temperature not exceeding 10° C to N^1,N^3-disubstituted imidazo[4,5-b]pyridin-2-ones (**III**) ($R = CH_3, CH_2C_6H_5$). The same substances have been obtained by the methylation with dimethyl sulfate and the benzylation with dimethylphenylbenzylammonium hydroxide of 3-methylimidazo[4,5-6]pyridin-2-ones (**IV**) in an alkaline medium. Compound **IV** was synthesized by fusing 3-amino-2-methylaminopyridine with urea at 170° C.



All the quaternary salts II synthesized have similar UV absorption spectra [λ_{max}, nm (log ε): 245 (3.80), 275 (4.05)].

1,3-Dimethyl-3H-imidazo[4,5-b]pyridinium iodide (II, R = CH_3, X = I). Yield 84%, mp 219° C (isopropanol). Found, %: C 35.12; H 3.82; I 46.00. Calculated for $C_8H_{10}IN_3$, %: C 34.93; H 3.66; I 46.13.

1-Benzyl-3-methyl-3H-imidazo[4,5-b]pyridinium chloride (II, R = $CH_2C_6H_5$, X = Cl). Yield 85%, mp 214–215° C (mixture of chloroform and carbon tetrachloride). Found, %: C 64.43; H 5.39; Cl 13.67. Calculated for $C_{14}H_{14}ClN_3$, %: C 64.35; H 5.43; Cl 13.65.

3-Methyl-1-(β-hydroxyethyl)-3H-imidazo[4,5-b]pyridinium chloride (II, R = CH_2CH_2OH, X = Cl). Yield 86%, mp 199–200° C (mixture of ethanol and ether). Found, %: C 50.42; H 5.51; Cl 16.37. Calculated for $C_9H_{12}ClN_3O$, %: C 50.59; H 5.66; Cl 16.59.

1,3-Dimethylimidazo[4,5-b]pyridin-2-one (III, R = CH_3). Yield 65% by the oxidation of II and 55% by the methylation of IV. Mp 73° C (hexane). Found, %: N 25.74. Calculated for $C_8H_9N_3O$, %: N 25.75.

1-Benzyl-3-methylimidazo[4,5-b]pyridin-2-one (III, R = $CH_2C_6H_5$). Yield 40% by the oxidation of II and 75% by the benzylation of IV. Mp 96° C (heptane). Found, %: C 70.47; H 5.57. Calculated for $C_{14}H_{13}N_3O$, %: C 70.28; H 5.47.

3-Methylimidazo[4,5-b]pyridin-2-one (IV). Yield 75%. Mp 235° C (ethanol). Found, %: N 27.99. Calculated for $C_7H_7N_3O$, %: 28.17.

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8 January 1968

Donetsk Branch of IREA [All-Union Scientific Research Institute for Chemical Reagents and Particularly Pure Chemical Substances]

CONVERSION OF 1-ARYL-5-BROMODIHYDROURACILS INTO 1-ARYLURACILS

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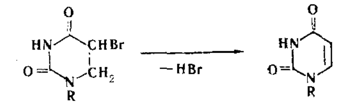
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 5, pp. 954-955, 1968

UDC 547.853

It is known [1-3] that when 5-bromo-1-methyldihydrouracil is heated at 155-160° C or when 1-aryl-5-bromodihydrouracils are heated with lithium chloride in dimethylformamide, hydrogen bromide is split out and 1-alkyl- or 1-aryluracils are formed.

We have found that the action on 1-aryl-5-bromodihydrouracils (**Ia–c**) of potassium cyanide, ammonia, or p-aminobenzoic acid, like that of lithium chloride in dimethylformamide, forms 1-aryluracils (**IIa–c**).



I a—c II a—c

a R=p-$CH_3C_6H_4$; b R=p-$CH_3OC_6H_4$; c R=p-$C_2H_5OC_6H_4$.

Preparation of 1-aryluracils. a) A mixture of 0.016 mole of Ia–c, 0.02 mole of potassium cyanide, and 15 ml of quinoline was boiled for 45 min, and the **IIa–c** were extracted from the reaction mixture with benzene or chloroform. b) A mixture of 0.009 mole of **Ia–c** and 40 ml of a 9% solution of ammonia in methanol was heated in a tube at 150-155° C for 8 hr. On the addition of water IIa–c separated out. c) A mixture of 0.0075 mole of **Ia–c**, 0.008 mole of p-amino-benzoic acid, and 15 ml of ethanol was heated in a tube at 175-180° C for 5 hr 30 min. On the addition of water, **IIa–c** separated out. d) The reaction was carried out as described previously [3] with 0.0085 mole of **Ia–c**, 0.02 mole of lithium chloride, and 25 ml of dimethylformamide.

1-Aryluracils

Compound	Mp, °C (solvent)	Empirical formula	N, %		Yield, %			
			found	calculated	a	b	c	d
IIa	226.5—228 (dioxane)	$C_{11}H_{10}N_2O_2$	13.81	13.85	17	26	24	86
IIb	230.5—231.5 (dioxane)	$C_{11}H_{10}N_2O_3$	12.88	12.85	32	24	28	92
IIc	229—231 (ethanol)	$C_{12}H_{12}N_2O_3$	12.20	12.18	24	37	23	80

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4 April 1968

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