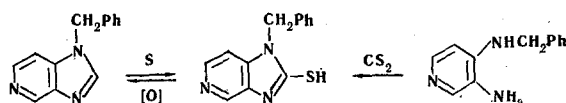


For the first time the direct thiolation of imidazo[4,5-b]- and imidazo[4,5-c]pyridines (I and II, respectively) and their derivatives has been accomplished by heating them with an equimolecular amount of sulfur at 230-260° for 15-60 min. As with purine [1] and benzimidazole [1,2], sulfur is incorporated at the C-H bond in the 2-position to form 2-mercapto derivatives of I and II, since the latter were identical to the products of the reaction of o-diamines with carbon disulfide [3-5]. 2-Mercapto derivatives I and II can



be desulfurated by brief heating with dilute nitric acid at 50-90°. Thus, 1-benzyl derivative II in particular could be obtained in this manner. The 2-mercapto-1-benzylimidazo[4,5-c]pyridine necessary for this was prepared from 4-benzylamino-3-aminopyridine [6] and carbon disulfide.

EXPERIMENTAL

2-Mercaptoimidazo[4,5-b]pyridine. This was obtained in 79% yield and had mp 315-316° (aqueous alcohol) (mp > 300° [4]).

2-Mercaptoimidazo[4,5-c]pyridine. This was obtained in 80% yield and had mp 368-369° (aqueous alcohol) (mp 370° [5]).

2-Mercapto-1-methylimidazo[4,5-c]pyridine. This was obtained in 81% yield and had mp 345-347° (aqueous alcohol) (mp 346-348° [5]).

2-Mercapto-1-benzylimidazo[4,5-c]pyridine. This was obtained in 94% yield by fusion with sulfur and in 99% yield by cyclization of 4-benzylamino-3-aminopyridine with carbon disulfide and had mp 297-298° (aqueous alcohol). Found %: C 64.51; H 4.58; N 17.42; S 13.40. C₁₃H₁₁N₃S. Calculated %: C 64.70; H 4.59; N 17.41; S 13.29 (see Table 1).

TABLE 1. Imidazopyridines Obtained by Oxidation of 2-Mercapto Derivatives

Compound	Reaction cond.		Mp, °C	Yield, %	Mp, °C (literature data)
	temp.	time, h			
I	70-80	3	149-150	82	151 ⁷
1-Methylimidazo[4,5-b]pyridine	60-65	1	94-96	80	95-97 ⁸
3-Methylimidazo[4,5-b]pyridine	60	2	79-80	75	76-78 ⁸
II	75	3	165-167	80	169-170 ⁹
1-Methylimidazo[4,5-c]pyridine	40-45	2	112	80	112.5 ⁸
3-Methylimidazo[4,5-c]pyridine	90	3	101-102	78	101-101.5 ⁸

Donetsk Physical-Organic Chemistry Branch, L. V. Pisarzhevskii Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 3, pp. 428-429, March, 1971. Original article submitted July 21, 1970.

2-Mercapto-3-methylimidazo[4,5-b]pyridine. This was obtained in 75% yield by direct thiolation and in 96% yield by cyclization of the appropriate diamine with carbon disulfide and had mp 264-265° (aqueous alcohol). Found %: C 50.72; H 4.99; N 25.62; S 19.21. $C_7H_7N_3S$. Calculated %: C 50.89; H 4.27; N 25.43; S 19.41.

1-Benzylimidazo[4,5-c]pyridine. This was obtained in 92% yield and had mp 132-133° (carbon tetrachloride). Found %: C 74.51; H 5.26; N 20.37. $C_{13}H_{11}N_3$. Calculated %: C 74.61; H 5.29; N 20.08.

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