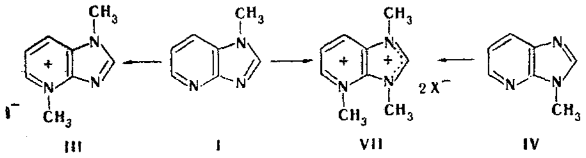
DIRECTION OF QUATERNIZATION OF 1-METHYL-1H-IMIDAZO[4,5-b]PYRIDINE

R. M. Bystrova and Yu. M. Yutilov

UDC 547.781'821

Heating of 1-methyl-1H-imidazo[4,5-b]pyridine (I) with methyl iodide gives a quaternary salt that differs from 3-methyl-3H-imidazo[4,5-b]pyridine N^1-methiodide (II), and this provides a basis for assigning the 1,4-dimethyl-1H-imidazo[4,5-b]pyridinium iodide structure (III) to it. One's attention is directed to the specificity of this reaction, since II cannot be detected in the reaction mixture. Thus, in contrast to 3-methyl-3H-imidazo[4,5-b]pyridine (IV) [1], isomeric I adds methyl iodide at the N-atom of the pyridine ring. Bases I and IV react similarly with methyl chloride. The resulting 1,4-dimethyl-1H-imidazo[4,5-b]pyridinium (V) and 1,3-dimethylimidazolio[4,5-b]pyridine (VI) chlorides can be converted to the corresponding iodides (III and II) by replacement of the anion.

For the first time, we have obtained the diquaternary salt of I by fusing it with excess methyl o-nitrobenzenesulfonic acid at 160-180° for 2.5 h. The structure of this salt as 1,3,4-trimethylimidazolio[4,5-b]pyridinium di(o-nitrobenzenesulfonate) (VII) is confirmed by the formation of it also from IV.



$X = o\text{-}NO_2C_6H_4SO_3$

EXPERIMENTAL

1,4-Dimethyl-1H-imidazo[4,5-b]pyridinium Iodide (III). Base I was heated with excess methyl iodide at 40-50° for 30 min to give 98% of III with mp 202-203° (from isopropyl alcohol). The melting point of a mixture of this product with salt II was 179-185°; λ_{max}, nm (log ε): 295 (4.21) (in alcohol). Found: C 34.7; H 3.4; I 46.3%. $C_8H_{10}IN_3$. Calculated: C 34.9; H 3.7; I 46.13%.

1,4-Dimethyl-1H-imidazo[4,5-b]pyridinium Chloride (V). Base I was heated with excess methyl chloride at 90-95° for 30 min to give 97% V with mp 238-239° (from alcohol–ether) and R_f 0.52 [Al_2O_3, chloroform–alcohol (1:3)]; λ_{max}, nm (log ε): 292 (4.11) (in alcohol). Found: N 22.7%. $C_8H_{10}ClN_3$. Calculated N 22.9%.

1,3-Dimethylimidazolio[4,5-b]pyridine Chloride (VI). This compound was obtained in 98% yield from IV and excess methyl chloride at 120° (2 h) and had mp 227-228° (from alcohol) (the melting point of a mixture with salt V was 196-200°) and R_f 0.35 [Al_2O_3, chloroform–alcohol (1:3)]; λ_{max}, nm (log ε): 242 (3.61), 274 (3.95), 282 (3.89) (in alcohol). Found: C 52.3; H 5.4; Cl 19.2%. $C_8H_{10}ClN_3$. Calculated: C 52.3; H 5.5; Cl 19.3%.

1,3,4-Trimethylimidazolio[4,5-b]pyridinium Di(o-nitrobenzenesulfonate) (VII). This compound was obtained in 95% yield as prisms with mp 234-235° (from isopropyl alcohol). No melting-point depression was observed for a mixture of salts obtained from bases I and IV. Found: N 12.4%. $C_{21}H_{21}N_5O_{10}S_2$. Calculated: N 12.3%.

Donetsk Branch, L. V. Pisarzhevskii Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR, Donetsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 570-571, April, 1973. Original article submitted October 23, 1972.

LITERATURE CITED

1. Yu. M. Yutilov and R. M. Bystrova, Khim. Geterotsikl. Soedin., 954 (1968).