MECHANISM OF THE NITRATION OF 2-SUBSTITUTED 3-HYDROXYPYRIDINE N-OXIDES

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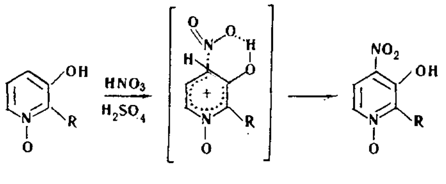
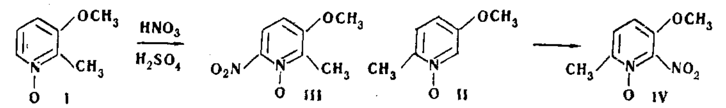
It was recently demonstrated [1] that the 4-position of the pyridine ring is exclusively subjected to substitution in the nitration of 2-methyl-2-chloro-3-hydroxypyridine N-oxides. To explain this orientation, we assumed the effect of the 3-OH group on the direction of the substitution by means of the formation of a "chelate" structure in the transition complex with the participation of the hydroxyl group and the attacking nitronium ion:



In this paper we have studied the direction of the nitration of the N-oxides of 3-methoxy-2-methylpyridine (I) and 3-methoxy-6-methylpyridine (II). It is obvious that the methoxyl group cannot exert the same effect as the hydroxyl group on the orientation during nitration. In fact, the nitration of the indicated compounds leads to N-oxides of 6-nitro-3-methoxy-2-methylpyridine (III) and 2-nitro-3-methoxy-6-methylpyridine (IV), respectively.



Compound I was obtained by the oxidation of 2-methyl-3-methoxypyridine with H_2O_2 in acetic anhydride [2] and had bp 130° (2 mm) and mp 76.5-78.5° (from dioxane). Found %: C 60.2; H 6.5; N 10.1. $C_7H_9NO_2$. Calculated %: C 60.4; H 6.5; N 10.07. The nitration of I was carried out under the conditions described previously in [1]. Compound III had mp 141-143° (from dioxane). Found %: C 45.7; H 4.3; N 15.2. $C_7H_8N_2O_4$. Calculated %: C 45.7; H 4.3; N 15.2. Dioxidation of III by means of $POCl_3$ [3] gave 6-nitro-3-methoxy-2-methylpyridine, which did not depress the melting point of an authentic sample [1].

The possible steric effect of the alkoxy group should be taken into account in examining the regularities of substitution. However, the nitration of 2-methyl- and 3-methoxypyridine N-oxides is directed at the 4-position [3,4], from which it follows that the steric effects are extremely insignificant. This is clearly seen in the case of II, which gives the 2-nitro derivative (IV) rather than the 4-nitro derivative on nitration under similar conditions. The melting point of IV was 148.5-150° (from alcohol). Found %: C 45.5; H 4.2; N 15.2. $C_7H_8N_2O_4$. Calculated %: C 45.7; H 4.3; N 15.2. The spin–spin coupling constant of the two protons in the PMR spectrum of IV lies in the region characteristic for the interaction of the 4-H and 5-H protons (J 9.0 Hz), which confirms the formation of a 2-nitro compound.

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