QUANTUM-CHEMICAL INTERPRETATION OF RECYCLIZATION REACTIONS.

1,2,5-TRIMETHYLPYRIDINIUM IODIDE*

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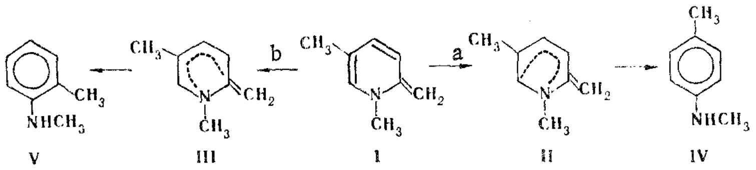
In one of the previous papers [1] of this series, on the basis of our developing approach to the description of the rearrangements of conjugated carbo and hetero systems, we examined the effect of chemical substitution on the recyclization of quaternary pyridinium salts to give anilines; we showed that, in conformity with the experimental results [2], the introduction of electron-acceptor groups such as NO_2 into the 3 and/or 5 positions leads to significant weakening of the 1–6 bond, intensification of the long-range bond orders, and a certain degree of strengthening of the 1–2 bond (see [1]), i.e., it ultimately promotes the occurrence of this reaction.

Using Tables 1 and 2 in [1] it is not difficult to show that the introduction of electron-donor groups into these positions somewhat increases the strength of the 1–6 bond and weakens the 1–2 bond, i.e., in these cases competitive cleavage of the carbon–nitrogen bonds and the formation of isomeric products are possible in the reaction. For example, the introduction of methyl groups into the 1 and 5 positions (compound I) gives $P_{1,2} = 0.3944$ and $P_{1,6} = 0.3610$ (compare with the 5-nitro derivative [1]) and large positive long-range 6–7 bond orders (0.2762 and 0.2126 for intermediates II and III, respectively). These data constitute evidence for the possibility of the recyclization of I via two pathways (see the scheme presented below) and for the preferableness of pathway *a* [since $P_{1,2}$ (I) > $P_{1,6}$ (I), $P_{6,7}$ (II) > $P_{6,7}$ (III), and $P_{1,2}$ (III) = 0.0179 > $P_{1,6}$ (II) = –0.0155].



The present communication is devoted to the experimental verification of this conclusion. In fact, when 1,2,5-trimethylpyridinium iodide was heated in an aqueous solution of methylamine sulfite (pH 10.0) at 150°C in a sealed ampul for 30 h, it was converted to a mixture of isomeric N-methyl-p- and N-methyl-o-toluidines (IV and V, respectively), which were separated and identified in the form of the known N-methyl-p-acetotoluidide (in 42% yield) and N-methyl-o-acetotoluidide (in 17% yield). Starting 2,5-dimethylpyridine was isolated from the reaction mixture in 31% yield.

Quaternary salts of α-picolines that contain other (besides methyl) electron-donor substituents should also undergo similar transformations.

LITERATURE CITED

1. Yu. B. Vysotskii, B. P. Zemskii, T. V. Stupnikova, R. S. Sagitullin, A. N. Kost, and O. P. Shvaika, Khim. Geterotsikl. Soedin., No. 11, 1496 (1979).
2. R. S. Sagitullin and A. N. Kost, Zh. Org. Khim., 16, 658 (1980).

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