RECYCLIZATION OF METHOXY-SUBSTITUTED 1,2-DIMETHYLISOQUNOLINIUM SALTS

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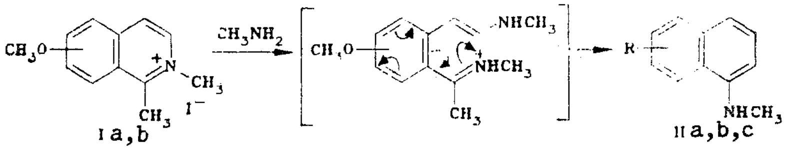
It is known that the introduction of donor substituents into the benzene ring of an isoquinolinium salt decreases the electrophilicity of the pyridine ring and hinders recyclization of the isoquinoline ring to a naphthalene ring. When two methoxy groups are simultaneously introduced into the 6 and 7 positions of the 1-methylisoquinoline molecule, recyclization does not occur [1].

We have shown that the presence of one donor substituent in the 6 or 7 position does not prevent the recyclization of 1,2-dimethylisoquinolinium salts. Thus 1-methylamino-6-methoxynaphthalene (IIa, mp 112-113°C, 4% yield) and 1,6-di(methylamino)naphthalene (IIc, mp 115-116°C, 61% yield) were isolated in the reaction of 1,2-dimethyl-6-methoxyisoquinolinium iodide (Ia) with an alcohol solution of methylamine (sealed ampul, 150°C, 20 h). Naphthalene IIa is the product of the Kost—Sagitullin rearrangement. The formation of diamine IIc is due to the simultaneous replacement of the methoxy group in the 6 position by a methylamino group. This sort of substitution can occur both in starting salt Ia through quaternization of the pyridine ring and in a step involving an acyclic intermediate, when the iminium group formed in the reaction activates substitution of the S_NAr type of the methoxy group in the para position [2].



I a 6-OCH_3, b 7-OCH_3; II a R=6-OCH_3, b R=7-OCH_3, a R=6-$NHCH_3$

Only 1-methylamino-7-methoxynaphthalene (IIb, mp 99-100°C, 72% yield) was isolated from the reaction mixture in the reaction of salt Ib, which contains a methoxy group in the 7 position, with alcoholic methylamine. Replacement of the methoxy group by the methylamino group does not occur in this case, since it is not activated by the imininium substituent in the meta position.

Evidence in favor of the assumption that replacement of the methoxy group occurs in a step involving an acyclic intermediate rather than in the starting salt is provided by the fact that replacement of the methoxy group in both 6- and 7-methoxy-1-methylisoquinoline by the action of alcoholic methylamine in the presence of ammonium chloride at 150°C cannot be accomplished. This sort of substitution takes place only at higher temperatures. Thus at 200°C substitution of the 6- and 7-methoxy groups proceeds with virtually identical yields (~70%). This makes it possible to assume that only the effect of the protonated pyridine ring rather than the activating effect of the iminium group occurs in this case.

A band of stretching vibrations of an NH group at 3445-3455 cm^{-1} is observed in the IR spectra of naphthalenes IIa-c. Signals of protons of 1-NCH_3 (singlets at 3.00 ppm) and NH (broad singlets at 4.10 ppm) groups are characteristic for the PMR spectra ($CDCl_3$) of IIa-c. A signal of the protons of the OCH_3 group of IIa, b is observed at 3.90 ppm, while a signal of the protons of the NCH_3 group of IIc is observed at 2.88 ppm. The results of elementary analysis are in agreement with the calculated values.

LITERATURE CITED

1. V. I. Terenin, L. G. Yudin, R. S. Sagitullin, V. N. Torocheshnikov, V. I. Dulenko, Yu. L. Nikolyukin, and A. N. Kost, *Khim. Geterotsikl. Soedin.*, No. 1, 73 (1983).
2. A. V. Blokhin, Yu. G. Bundel', V. I. Terenin, and A. N. Kurts, *Zh. Org. Khim.*, **23**, 2399 (1987).

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