INFLUENCE OF THE NATURE OF THE ALKALI METAL ON THE CLEAVAGE OF N–N BONDS IN THE REACTIONS OF HETERYLHYDRAZONES WITH ALKOXIDES

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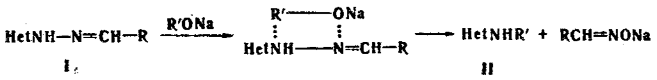
For the reaction we previously found between heterylhydrazones and sodium alkoxides it was postulated [1] that the process proceeds through a four-bond transition state:



With such a mechanism it may be expected that the transition from sodium alkoxides to alkoxides of stronger alkali metals, which would increase the polarity and polarizability of the R'–O bond would greatly facilitate the process. We showed that, in fact, in those cases in which the main direction of the reaction is suppressed [2], the transition to potassium and rubidium alkoxides makes it possible to shift the process significantly in the direction of the N-alkylaminoheterocycles and to lower the reaction temperature.

For example, in the case of I, where Het = pyrazin-2-yl, and R = Ph, with sodium ethoxide, the process began only at 240°C, and the yield of II was 4% (11% 2-aminopyrazine formed in parallel). (The procedures for carrying out the experimental and the analysis of the products by GLC were similar to those described in [1, 2].) In the case of the reaction with potassium ethoxide under the same conditions (240°C, 30 min), amine II was obtained with an 81% yield (18% 2-aminopyrazine formed in parallel). The reaction could also be carried out at 200°C (30 min), and in this case, the yield of II was equal to 39%, that of 2-aminopyrazine was equal to 12%, and that of the original hydrazone I was equal to 48%. In the case of compound I, where Het = pyridazin-3-yl, and R = Ph, with sodium ethoxide, the reaction proceeded at 250°C (60 min) with a 25% yield of amine II (the main direction of the process was the thermal radical splitting of hydrazone I and the formation of the recombination products of the radicals appearing). The use of potassium ethoxide made it possible to lower the temperature to 180°C (3 h) and to obtain amine II with a 32% yield (57% 3-aminopyridazine and up to 11% of a mixture of products of radical reactions formed in parallel). In the reaction with rubidium ethoxide under the same conditions (180°C, 3 h) the yield of amine II increased to 66% (26% 3-aminopyridazine and up to 8% of a mixture of radical-conversion products were also obtained). In the case of I, where Het = 6-ethoxypyrimid-4-yl, and R = Ph, with sodium ethoxide, the original compound was recovered even at temperatures up to 290°C. With potassium ethoxide the process began at 200°C (3 h), and the yield of amine II was 22% (23% 4-amino-6-ethoxypyrimidine formed in parallel, and up to 54% hydrozone I remained). When the temperature was increased to 280°C (30 min), the yield of II increased to 34% (the yield of 4-amino-6-ethoxypyrimidine increased to 58%, and only 8% hydrazone I remained). With rubidium ethoxide at 240°C (30 min) amine II was obtained with a 77% yield (the yield of 4-amino-6-ethoxypyrimidine was 23%).

LITERATURE CITED

1. L. N. Yakhontov and M. F. Marshalkin, Tetrahedron Lett., No. 30, 2807 (1973).
2. M. F. Marshalkin, V. A. Azimov, L. F. Linberg, and L. N. Yakhontov, Khim. Geterotsikl. Soedin., No. 8, 1120 (1978).

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