# THE SYNTHESIS OF 3-BROMOFURAN AND THE PRODUCT OF ITS ACETYLATION

Ya. L. Gol'dfarb, M. A. Marakatkina, and L. I. Belen'kii

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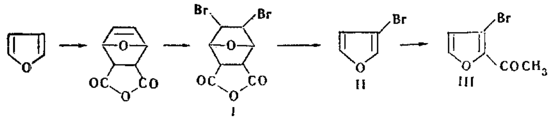
Recently, Z. N. Nazarova et al. [1] published a brief communication devoted to the synthesis and reactions of β-bromo-substituted furans, which may be represented by the following scheme:



In it, with a reference to out paper [2] and to a patent [3] it is shown that "the methods reported in the literature for obtaining them (i.e., β-substituted furans) are cumbersome and give low yields." In relation to our paper [2] this evaluation does not correspond to the true position, since it describes the synthesis not of mono-halogen-substituted furans but of 2-acetyl-4-bromofuran, for the preparation of which the Nazarova et al [1] propose no other method whatever. In addition to this, in evaluating the information from the patent [3] in the way described above, Z. N. Nazarova et al. use essentially the same method, merely replacing the alkali used in the dehydrobromination of I by quinoline which, of course, is more convenient but in principle does not depart from the framework of a purely methodical development of the idea of the patent.

On examining the experimental part of the paper [1], we turned our attention to the fact that the yield of 3-bromofuran (II), according to the authors [1], is 78%. Nevertheless, the amount of quinoline by weight given by the authors amounts to approximately only half of that necessary stoichiometrically for the formation of the hydrobromide, and the yield of II cannot be higher than corresponds to the amount of quinoline taken. In actual fact, on repeating the authors' [1] experiment under the same conditions we obtained not more than traces of II, and only when the amount of quinoline was increased to 2 moles per mole of the dibromide I did the yield of II reach 60%.

However, the most important fact is that the product of acetylation, described by the authors [1] as a liquid with bp 222° C, $n_D^{20}$ 1.5489, $d_4^{20}$ 1.6240, is considered as an individual compound to which the structure III is ascribed. In the first place, it is extremely unlikely that a compound of such structure can be distilled at atmospheric pressure and this not over a range but at a specific temperature. Such a distillation, as we have convinced ourselves, will lead to pronounced darkening of the substance and will even make it impossible to measure its refractive index. More serious, however, is the fact that the authors [1], in ascribing the structure III to the acetylation product, consider that "in accordance with the rules of orientation" there is only one possible direction of substitution. Nevertheless, in the acylation of heterocyclic compounds of this type, just in accordance with the rules of orientation, there is always a considerable probability that the substituent will enter into the second free α position. In actual fact, the product of the acetylation of II that we obtained as described in [1], which is a liquid with bp 107–110° C (15 mm), $n_D^{20}$ 1.5510, crystallizing on cooling, is, as was to be expected, a mixture of 2-acetyl-3- and -4-bromofurans present, according to GLC, in a ratio of ∼4 : 1. By the low-temperature crystallization of this mixture from ether it is possible to isolate a compound which, after recrystallization from heptane, has mp 43.5–44° C and is pure 2-acetyl-3-bromofuran (III). Found, %: C 37.67; H 2.51; Br 42.42. Calculated for $C_6H_5BrO_2$, %: C 38.12; H 2.67; Br 42.28. Semicarbazone, mp 221–222° C (from ethanol). Found, %: N 17.18. Calculated for $C_7H_8BrN_3O_2$, %: N 17.08. The action of sodium hypobromite on the ketone III gave 3-bromofuran-2-carboxylic acid, mp 159.5–160° C from a mixture of heptane and ethyl acetate. Found, %: C 31.63; H 1.64; Br 41.65. Calculated for $C_5H_3BrO_3$, %: C 31.44; H 1.58; Br 41.85. The test of the purity of the acetylation products and an analysis of the mixtures in comparison with authentic samples were carried out on an LKhM-4 chromatograph with a thermal conductivity detector using helium as the carrier gas at a rate of 40 ml/min with a stainless steel column 2 m long and 4 mm in diameter with 0.5% of poly(ethylene glycol succinate) on glass beads, at a temperature of 160° C. The sample of 2-acetyl-4-bromofuran was obtained as described previously [2].

REFERENCES

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2. Ya. L. Gol'dfarb and L. D. Tarasova, DAN, 163, 1393, 1965.
3. US patent no. 2 773 882, 1956; RZhKh, 12760, 1959.

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Zelinskii Institute of Organic Chemistry AS USSR, Moscow