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I. F. Bel’ skii and Corresponding Member of the Academy of Sciences of the USSR N. I. Shuikin

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Abstract

Full Text

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TRANSFORMATION OF AMINES OF THE FURAN SERIES INTO HOMOLOGS OF PYRROLIDINE

Hydrogenolysis of the furan ring generally leads to compounds of the aliphatic series, with the ether oxygen of the ring forming carbonyl or hydroxyl groups. In the case of 2-alkyl- or 2,5-dialkylfurans, the products of hydrogenolysis of the ring, depending on the conditions, are aliphatic alcohols or ketones. New possibilities for the course of the reaction arise in the case of hydrogenation of furan compounds containing, in the side chain in the α-position, functional groups capable, under certain conditions, of intramolecular interaction with the carbonyl or hydroxyl groups formed as a result of hydrogenolysis of the furan ring. Such a functional group is, for example, a hydroxyl group located in position 3 with respect to the furan ring. The hydrogenolysis of furan compounds of this structure, namely 1-furylalkanols-3, was studied by us earlier ([1]). It was shown that under hydrogenation conditions in a flow system over a platinum catalyst, the primary products of hydrogenolysis of the furan ring—alkanediols-1,4—are converted, as a result of intramolecular elimination of water, into tetrahydrofurans

$$\text{(furylalkanol)} \xrightarrow[\text{Pt–C}]{\text{H}_2} [\text{CH}_3\text{CH}_2\text{CH}_2\text{CH(OH)CH}_2\text{CH}_2\text{CH(OH)R}] \longrightarrow \text{(substituted tetrahydrofuran)}+\text{H}_2\text{O}$$

Another analogous case is represented by 2-alkyl-5-acylfurans. Here, however, it is necessary to bear in mind two possible directions of the reaction, connected with the fact that the primary reaction during hydrogenation may be either reduction of the carbonyl group to a CH_2 group ([2]), or hydrogenolysis of the furan ring. Hydrogenolysis of the furan ring before reduction of the carbonyl group can be carried out on a platinum catalyst ([3]). In this latter case, hydrogenolysis of 2-alkyl-5-acylfurans gives as primary products 1,5-diketones and 1,5-diols, which, under vapor-phase hydrogenation conditions, cyclize with elimination of water into six-membered carbocyclic compounds and tetrahydropyrans ([4])

$$\text{R-(furan)-C(=O)R}' \xrightarrow[220^\circ]{\text{H}_2,\ \text{Pt–C}} [\text{R–CH(OH)CH}_2\text{CH}_2\text{CH}_2\text{CH(OH)–R}'] \longrightarrow \text{(substituted tetrahydropyran)}+\text{H}$$

Both of the cases considered contain a common idea, which may be expressed as follows: if the side chain of a furan compound contains functional groups capable of interacting with the hydroxyl or carbonyl group arising during hydrogenolysis of the furan nucleus, and if the bifunctional aliphatic compounds formed as a result of hydrogenolysis of the ring belong to the γ- or δ-series, then hydrogenation of such furan compounds under definite conditions leads to the formation of new five- or six-membered heterocycles.

This general idea immediately predicts the possibility of carrying out new and interesting syntheses. Indeed, a functional group capa-

capable of interaction with hydroxyl or carbonyl may be the amino group; therefore it may be expected that amines of the furan series having an NH_2 group in position 3 relative to the furan nucleus, under hydrogenation conditions, will be converted into five-membered nitrogen-containing heterocyclic compounds—pyrroles or pyrrolidines; i.e., the following reaction will take place:

$$\text{furyl-}CH_2CH_2CH(NH_2)-R \longrightarrow [CH_3CH_2CH_2CH(OH)CH_2CH_2CH(NH_2)-R] \downarrow CH_3CH_2CH_2\text{—pyrrolidine—R} + H_2O$$

The experiments carried out by us fully confirmed our assumptions. We synthesized two amines of the furan series, 1-furyl-3-aminobutane and 1-furyl-3-aminopentane, and subjected them to hydrogenation in a flow system over platinized carbon. As a result of the reaction, 2-methyl-5-*n*-propylpyrrolidine and 2-ethyl-5-*n*-propylpyrrolidine were formed in yields of 70–80%.

Synthesis of 1-furyl-3-aminoalkanes. 1-Furyl-3-aminobutane and 1-furyl-3-aminopentane were obtained by reductive amination of the corresponding furfurylideneketones in the liquid phase over a skeletal Ni–Al catalyst.

$$\text{Fur—CH=CH—C(=O)—R} \xrightarrow[\text{Ni—Al, } 80^\circ]{H_2,\ NH_3} \text{Fur—}CH_2CH_2CH(NH_2)\text{—R}, \qquad R = CH_3 \text{ and } C_2H_5$$

The procedure we used for the reductive amination of furfurylideneketones was analogous to that used in the amination of furfural ([5]). The 1-furyl-3-aminoalkanes obtained in yields of 70–75% were distilled under reduced pressure:

1. 1-Furyl-3-aminobutane, b.p. 94–96° (25); n_D^{20} 1.4760; d_4^{20} 0.9664.

2. 1-Furyl-3-aminopentane, b.p. 98–99° (17); n_D^{20} 1.4786; d_4^{20} 0.9586.

Conversion of 1-furyl-3-aminoalkanes into 2-*n*-propyl-5-alkylpyrrolidines. 1-Furyl-3-aminoalkanes were hydrogenated in a flow-type system over platinum

deposited on carbon, at a space velocity of 0.1 hr^{-1}. The temperature, measured inside the catalyst bed, was maintained in the range 200–210°. The catalyst was prepared as follows: activated carbon was impregnated with a solution of chloroplatinic acid, placed in the reaction tube, after which the chloroplatinic acid was reduced with hydrogen for 13 hours at a temperature gradually raised from 250 to 320°. The resulting catalysts were saturated with caustic potash, separated from water, dried with calcined KOH, and distilled on an efficient column. The isolated pyrrolidines were then redistilled a second time over sodium from a flask with a dephlegmator. After this they had the following properties:

2-Methyl-5-*n*-propylpyrrolidine, b.p. 153–155° (755); n_D^{20} 1.4413; d_4^{20} 0.8329. MR_D found 40.36, $C_8H_{17}N$, MR_D calculated 40.55.

2-Ethyl-5-*n*-propylpyrrolidine, b.p. 175–177° (760); n_D^{20} 1.4463; d_4^{20} 0.8388. MR_D found 44.93, $C_9H_{19}N$. MR_D calculated 45.16.

N. D. Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.