CATALYTIC TRANSFORMATION OF FURAN AMINES INTO PYRROLE AND PYRROLIDINE HOMOLOGS

I. F. Bel'skii

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

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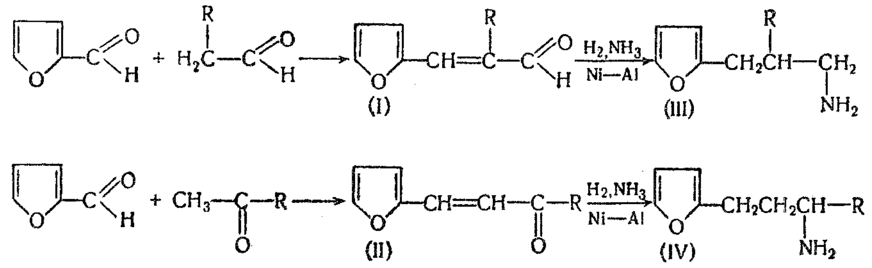
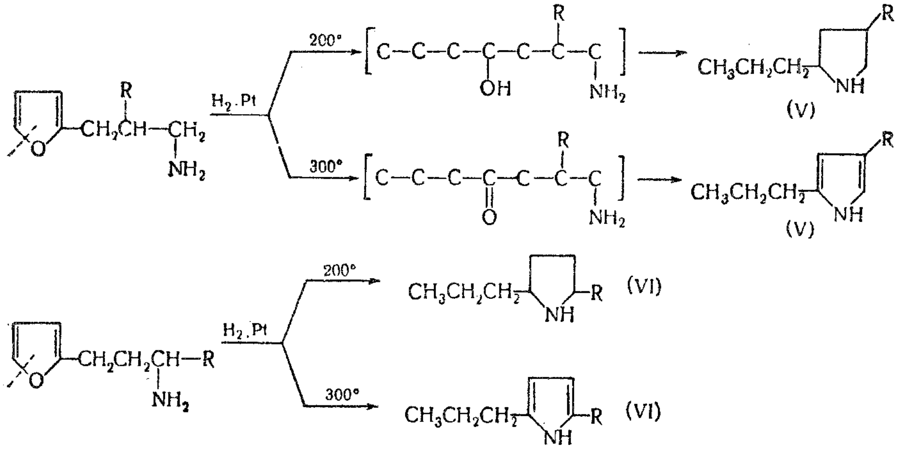
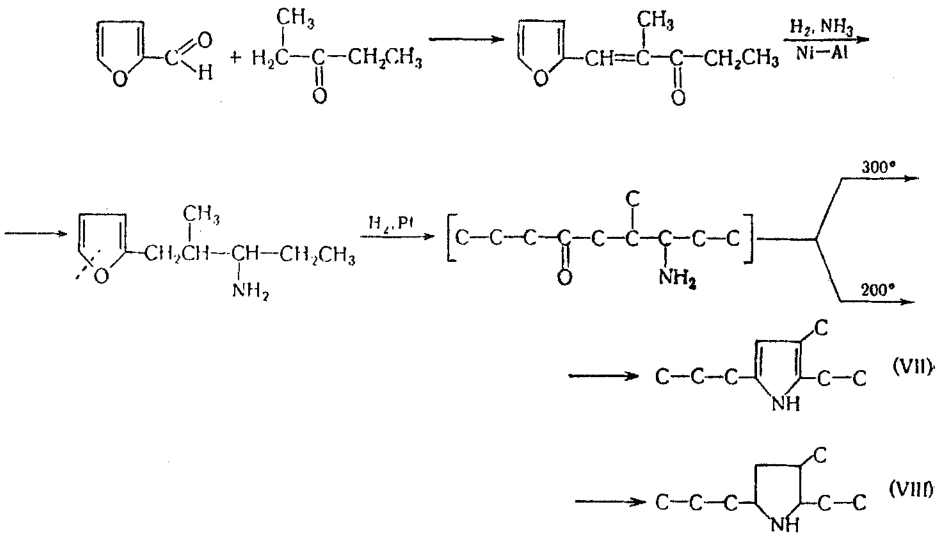
Furan amines containing the amino group in position 3 with respect to the furan nucleus have recently acquired importance because of their ability to be converted into pyrrole and pyrrolidine homologs as a result of vapor-phase hydrogenation over a platinum catalyst [1]. Furan amines of such a structure are obtained by the reductive amination of 2-furanacroleins (I) and 2-(2-furyl)vinyl ketones (II); in the first case β-alkyl-2-furanpropylamines (III) and in the second case α-alkyl-2-furanpropylamines (IV) are formed.



It is easily seen that the furan amines (III) and (IV) will give dialkylpyrroles and the corresponding dialkylpyrrolidines of two series: 2,4-dialkyl homologs (V) from (III) and 2,5-dialkyl homologs (VI) from (IV).

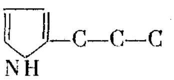
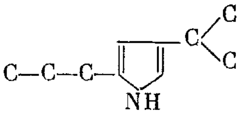
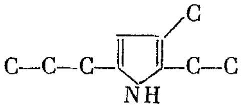
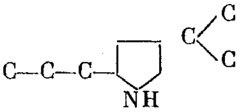
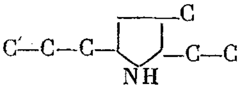


Since at lower temperatures (about 200°) pyrroles are hydrogenated into pyrrolidines and at higher temperatures (about 300°) the reverse reaction occurs [2], it is clear that these conditions will determine the temperature limits for the conversion of furan amines into pyrroles or pyrrolidines. As will be seen from the schemes given above, the structures of the pyrrole homologs depend essentially on the structures of the furan and the aliphatic carbonyl compounds. By using 2-furaldehyde as the furan carbonyl compound and ketones of the type RCH_2COCH_2R as the aliphatic carbonyl compound we may obtain tri-substitued pyrrole and pyrrolidine homologs. In the present work we prepared 2-ethyl-3-methyl-5-propylpyrrole (VII) and the corresponding pyrrolidine (VIII) starting from 2-furaldehyde and 3-pentanone:



Also, by the catalytic-hydrogenation method we synthesized 2-propylpyrrole from 2-furanpropylamine, 2,5-dipropylpyrrole and 2,5-dipropylpyrrolidine from α-propyl-2-furanpropylamine, and 4-isopropyl-2-propylpyrrole and the corresponding pyrrolidine from β-isopropyl-2-furanpropylamine. The furan amines were converted into pyrrole and pyrrolidine homologs by vapor-phase hydrogenation over a platinum catalyst at temperatures of 300° and 210°, respectively. The yields of pyrroles and pyrrolidines were 85-95%.

Properties of Pyrrole and Pyrrolidine Homologs

Pyrrole or pyrrolidine homolog	B.p., °C	n_D^{20}	d_4^{20}	MR	
				found	calc.
	66—68 (8)	1,4878	0,9127	34,45	34,99
	78—79 (4)	1,4891	0,8925	48,92	48,85
	74—76 (3)	1,4842	0,8876	48,77	48,85
	88—90 (9)	1,4889	0,8973	48,64	48,85
	55—56 (5)	1,4468	0,8379	49,49	49,48
	67—69 (7)	1,4495	0,8473	49,20	49,48
	55—57 (6)	1,4447	0,8379	49,29	49,48

EXPERIMENTAL

2-Furanacroleins and 2-(2-furyl)vinyl ketones were synthesized by the method described in [3] from 2-furaldehyde and aliphatic aldehydes and ketones; they were isolated from the reaction products by fractionation at reduced pressure: α-isopropyl-2-furanacrolein, b.p. 89-91° (5 mm), 1-(2-furyl)-1-hexen-3-one, b.p. 112-113° (6 mm), and 1-(2-furyl)-2-methyl-1-penten-3-one, b.p. 98-101° (2 mm). The conversion of 2-furanacroleins and 2-(2-furyl)-

vinyl ketones into furan amines was effected by reductive amination in presence of a skeletal Ni–Al catalyst [4]. The furan amines, obtained in yields of 50-70%, had the following properties: 1) 2-furanpropylamine; b.p. 71-73° (8 mm); n_D^{20} 1.4831; d_4^{20} 0.9979; 2) β-isopropyl-2-furanpropylamine; b.p. 115-116° (14 mm); n_D^{20} 1.4934; d_4^{20} 0.9667; 3) α-propyl-2-furanpropylamine; b.p. 68-69° (3 mm); n_D^{20} 1.4771; d_4^{20} 0.9483; 4) α-ethyl-β-methyl-2-furanpropylamine; b.p. 71-72° (4 mm); n_D^{20} 1.4770, d_4^{20} 0.9569.

For the reductive amination of 2-furanacroleins and 2-(2-furyl)vinyl ketones we used a skeletal Ni–Al catalyst, which was prepared by treating pieces of an Ni–Al alloy with dilute sodium hydroxide solution under ice cooling. The catalyst was washed free from alkali (neutral to phenolphthalein) and preserved under a layer of methanol.

Furan amines were converted into pyrrole and pyrrolidine homologs as a result of hydrogenation over a platinum catalyst prepared by the deposition of finely dispersed platinum on asbestos. The asbestos was first treated with alkali and with nitric acid, and was then washed with water, dried, and impregnated with chloroplatinic acid solution. The asbestos was then placed in the reaction tube, and the catalyst was reduced with hydrogen at 250-320° for 15 hours. It contained about 10% of metallic platinum.

Conversion of Furan Amines into Pyrrole and Pyrrolidine Homologs. The furan amines were converted into pyrrole and pyrrolidine homologs by hydrogenating them in the vapor phase over platinized asbestos. Hydrogenation at 200-220° gave pyrrolidines, and hydrogenation at 300° gave pyrroles. Catalyzates containing pyrrolidines were saturated with caustic alkali, separated from water, dried with calcined potassium hydroxide, and distilled under reduced pressure. Catalyst containing pyrroles were separated from water, dried with calcium chloride, and vacuum-distilled. Fractions corresponding with pyrroles were treated with dilute hydrochloric acid, washed with dilute sodium carbonate solution, dried with calcium chloride, and distilled under reduced pressure. After distillation the pyrroles and pyrrolidines were colorless liquids. After some time the pyrroles acquired a yellow color. The physical properties of the pyrroles acquired a yellow color. The physical properties of the pyrroles and pyrrolidines obtained are given in the table.

SUMMARY

1. On hydrogenation in the vapor phase over a platinum catalyst, furan amines containing an amino group in position 3 with respect to the furan nucleus are converted, depending on the temperature, into pyrrole or pyrrolidine homologs in yields of 85-95%.

2. The following pyrrole and pyrrolidine homologs were synthesized by the catalytic-hydrogenation method: 2-propylpyrrole, 2,5-dipropylpyrrole and 2,5-dipropylpyrrolidine, 4-isopropyl-2-propylpyrrole and 4-isopropyl-2-propylpyrrolidine, 2-ethyl-3-methyl-5-propylpyrrole and the corresponding pyrrolidine.

LITERATURE CITED

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3. A. Hinz, G. Meyer, G. Schücking, Ber. 76, 676 (1943).
4. C. F. Winans, J. Amer. Chem. Soc. 61, 4, 3566 (1939).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.