

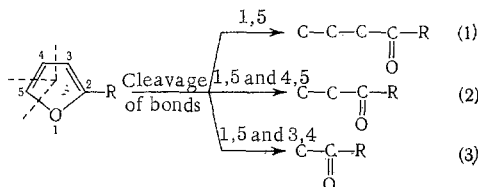
CATALYTIC TRANSFORMATIONS OF FURAN ALCOHOLS  
AND KETONES AND THEIR DERIVATIVES  
COMMUNICATION 2. SOME TRANSFORMATIONS  
OF 3-(2-FURYL)ALKYL ACETATES

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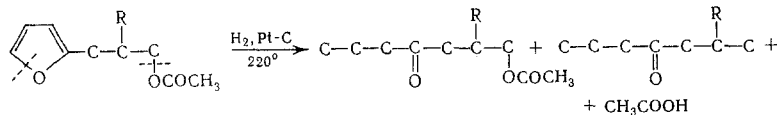
The investigation of the catalytic transformations of furan alcohols presents considerable interest, because it opens up new methods for the synthesis of such difficultly accessible compounds as  $\gamma$ -keto alcohols and their acetates, 2,3-dihydrofuran homologs, and furan itself. The method of synthesizing these compounds is based on the catalytic hydrogenation not of the furan alcohols themselves, but of their acetates, which makes it possible to retain a "protected" hydroxy group in the side chain. The acetates of  $\gamma$ -keto alcohols obtained in this way are readily converted into  $\gamma$ -keto alcohols and mono- and di-substituted 2,3-dihydrofuran homologs [1]. On dehydrogenation over platinized charcoal the latter give good yields of di-substituted furan homologs [2].

The experimental data obtained in the present investigation provide answers to two questions: how does the hydrogenation of 3-(2-furyl)alkyl acetates proceed over a skeletal nickel-aluminum catalyst, and how does the hydrogenolysis of acetates of secondary furan alcohols, such as  $\alpha$ -methyl-2-furanpropanol, proceed over platinized charcoal. It has been shown previously [3] that the furan ring is able to undergo so-called "conjugated" hydrogenolysis in vapor-phase hydrogenation over a skeletal Ni-Al catalyst. In this case the furan ring opens in three directions at bonds 1,5 (1), 1,5 and 4,5 (2), and 1,5 and 3,4 (3), as a result of which butyryl, propionyl, and acetyl groups are formed



in which R = alkyl, hydroxyalkyl, or carboxyalkyl.

By the method of "conjugated" hydrogenolysis a whole series of tetrahydrofuran homologs [4],  $\gamma$ -diketones [5], and  $\gamma$ -keto carboxylic esters [6] have been obtained from various furan compounds. In view of this it was considered to be of interest to investigate the hydrogenation of 3-(2-furyl)alkyl acetates over a skeletal Ni-Al catalyst under "conjugated" hydrogenolysis conditions. We have shown previously [1] that the hydrogenation of 2-alkyl-3-(2-furyl)propyl acetates over Pt-C at 200-220° leads to the formation of two products: the acetate of the corresponding  $\gamma$ -keto alcohol and the aliphatic ketone formed as a result of the side reaction in which the acetoxy group is eliminated as acetic acid.



in which R = H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>

As would be expected, in the hydrogenation of 3-(2-furyl)propyl acetates over a skeletal Ni-Al catalyst acetic esters of  $\gamma$ -keto alcohols and aliphatic ketones are also formed. However, unlike the behavior over platinized charcoal, over the Ni-Al catalyst "conjugated" hydrogenolysis occurs and the elimination of acetoxy groups goes in higher yield than over Pt-C. All this leads to the formation of quite a number of

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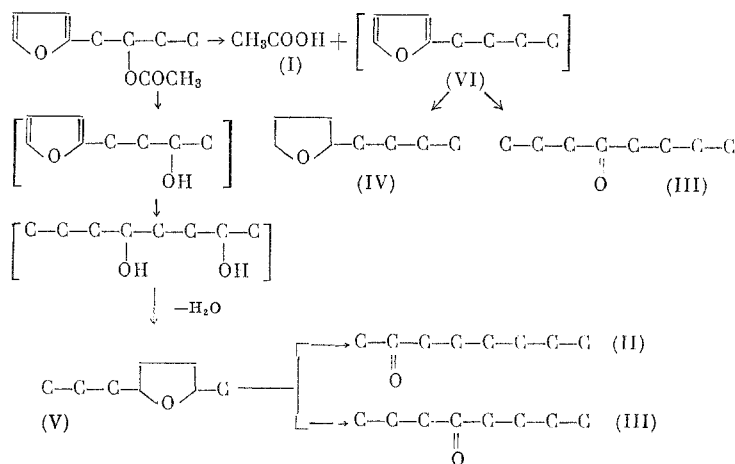
TABLE 1. Properties of Products of the Hydrogenation of 3-(2-Furyl)alkyl Acetates over Pt-C and Skeletal Ni-Al Catalysts at 240-250°

Acetic ester taken	Catalyst	Hydrogenation products	Yield, %	B.P., °C (760 mm)	$n_D^{20}$	$d_4^{20}$	M.p. of semi-carbazone, °C	
3-(2-Furyl)propyl acetate	Ni-Al	2-Pentanone	20	101-102	1,3910	0,8075	110	
		3-Hexanone	15	123-125	1,4013	0,8117	123	
		4-Heptanone	25	140-143	1,4088	0,8175	132	
		5-Hydroxy-2-pentanone acetate	10	107-108(25)	1,4270	1,0171	---	
		6-Hydroxy-3-hexanone acetate	3-4	119-120(25)	1,4293	---	---	
		1-Hydroxy-4-heptanone acetate	15	132-133(25)	1,4310	0,9804	---	
2-Ethyl-3-(2-furyl)propyl acetate	Ni-Al	4-Methyl-2-hexanone	20	137-138	1,4082	0,8139	120	
		5-Methyl-3-heptanone	10	159-161	1,4232	0,8297	107	
		6-Methyl-4-octanone	30	61-62(11)	1,4214	0,8237	61-62	
		4-Ethyl-5-hydroxy-2-pentanone acetate	8	67-69(11)	1,4308	0,9791	---	
		2-Ethyl-1-hydroxy-4-heptanone acetate	20	124-125(11)	1,4383	0,9653	---	
		Acetic acid	12	118-120	1,3623	---	---	
3-(2-Furyl)-1-methylpropyl acetate	Pt-C	Tetrahydro-2-methyl-5-propylfuran	40	141-142	1,4200	0,8381	---	
		2-Butyltetrahydrofuran	10	159-160	1,4281	0,8559	---	
		4-Octanone	30	166-167	1,4136	0,8191	95-96	
		2-Octanone	5	173-174,5	1,4155	0,8197	123	

aliphatic ketones and acetic esters of  $\gamma$ -keto alcohols. The results of the experiments are presented in Table 1.

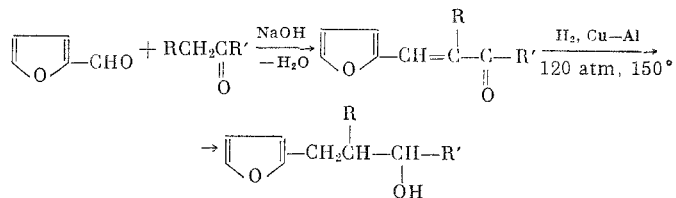
The answer to the second of the questions posed above is given by the investigation of the vapor-phase hydrogenation of 3-(2-furyl)-1-methylpropyl acetate over Pt-C at ordinary pressure and 240-250°. It was found that under these conditions 3-(2-furyl)-1-methylpropyl acetate undergoes complex changes, the final products of which are acetic acid (I), 2-octanone (II), 4-octanone (III), 2-butyltetrahydrofuran (IV), and tetrahydro-2-methyl-5-propylfuran (V). Here again one of the possible courses of reaction is the elimination of the acetoxy group in the form of acetic acid and the formation of an aliphatic ketone (4-octanone) after the hydrogenolysis of the intermediately formed 2-butylfuran (VI), of which a small part is hydrogenated to 2-butyltetrahydrofuran (IV). Another course of reaction appears to be the reduction of the acetic ester taken to  $\alpha$ -methyl-2-furanpropanol (VII), the further hydrogenation of which leads to the formation of tetrahydro-2-methyl-5-propylfuran and the ketones (II) and (III) (see reaction scheme).

#### Reaction Scheme



#### EXPERIMENTAL

2-Furanpropanols were synthesized in accordance with the scheme described by us previously [1,7]:



in which  $R' = \text{H}$ ,  $R = \text{H}$ ,  $\text{C}_2\text{H}_5$ ;  $R' = \text{CH}_3$ ,  $R = \text{H}$ . 3-(2-Furyl) alkyl acetates were prepared by heating the furan alcohols with excess of acetic anhydride and freshly fused sodium acetate taken in an amount of 10% on the weight of the acetic anhydride. The mixture was boiled for 2 h and then

cooled to 40–50°, water (ten times the amount of acetic anhydride taken) was added, and the mixture was left for 3 h. The acetylation product was extracted with ether, dried over fused  $\text{Na}_2\text{SO}_4$ , and vacuum-distilled. We obtained: 1) 3-(2-Furyl)propyl acetate; b.p. 100.7–101.5° (12 mm);  $n_D^{20}$  1.4562;  $d_4^{20}$  1.0449. 2) 2-Ethyl-3-(2-furyl)propyl acetate; b.p. 98–99.5° (8 mm);  $n_D^{20}$  1.4595;  $d_4^{20}$  1.0172. 3) 3-(2-Furyl)-1-methylpropyl acetate; b.p. 110–112° (20 mm);  $n_D^{20}$  1.4578;  $d_4^{20}$  1.0318.

The preparation of the Pt–C and skeletal Ni–Al catalysts and the experimental conditions have been described earlier [1, 6]. The catalyzates were analyzed by means of gas–liquid chromatography. Standard samples were available for most of the compounds. The chromatographic apparatus and the conditions used in the chromatography are described in our previous paper [8]. The experimental results are presented in Table 1.

### CONCLUSIONS

1. A study was made of the conjugated hydrogenolysis of 1-(2-furyl)propyl acetates over a skeletal Ni–Al catalyst at 240–250°. The furan ring undergoes cleavage in three directions, and as a result aliphatic ketones and acetic esters of  $\gamma$ -keto alcohols are formed.

2. The vapor-phase hydrogenolysis of secondary 3-(2-furyl)alkyl acetates was investigated over Pt–C at normal pressure and 240–250°. Under these conditions the final products of the hydrogenation of 3-(2-furyl)alkyl acetates are tetrahydrofuran homologs and aliphatic ketones.

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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 the first issue of this year.

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