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Corresponding Member of the Academy of Sciences of the USSR N.
I. SHUIKIN, I. F. BEL' SKII,

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Abstract

Full Text

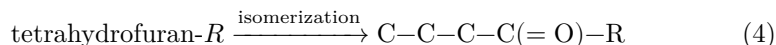
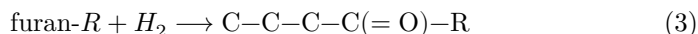
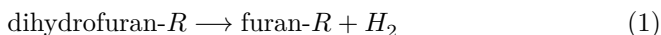
CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR N. I. SHUIKIN,
I. F. BEL' SKII,
R. A. KARAKHANOV

CATALYTIC DEHYDROGENATION OF DI-HYDROFURANS

SYNTHESIS OF 2,4-DIALKYL FURANS

Our studies have established that dihydro- and tetrahydrofuran rings are capable of undergoing dehydrogenation in the vapor phase over catalysts—metals of Group VIII of the periodic system (^{1,2}). This reaction is less characteristic of the tetrahydrofuran ring, since the latter reacts to a considerably greater extent as a cyclic ether, i.e., isomerizes with cleavage of one of the C—O bonds to aliphatic oxo compounds (³). 2,3- and 2,5-dihydrofurans are readily dehydrogenated to the corresponding furans over metallic catalysts (Pt, Pd, Rh, etc.) at relatively low temperatures of the order of 200–300° (reaction 1). Side reactions occur at the same time. The hydrogen evolved hydrogenates dihydrofurans to tetrahydrofurans (reaction 2) or brings about hydrogenolysis of the furans formed (reaction 3). On the other hand, tetrahydrofurans isomerize, especially readily on platinum, to aliphatic ketones (reaction 4). All these transformations are explained by the following scheme:



As a consequence of these side reactions, the catalytic dehydrogenation of 2,3- and 2,5-dihydrofurans gives furans in an average yield of 50%. However, in the case of 3,5-dihydrofurans it is possible to carry out dehydrogenation in the presence of such inert contacts as charcoal or quartz at 470–500°. Under these conditions side reactions 2–4, since they are catalytic, do not occur, and therefore the yields of furans reach 95% (⁴). By this route, however, it is impossible to

dehydrogenate 2,3-dihydrofurans, since under the action of temperature (470–500°) they isomerize to carbonyl compounds of the cyclopropane series (5).

In the present work, the synthesis of 2,4-dialkylfurans was carried out by catalytic dehydrogenation of the corresponding homologs of 2,3-dihydrofuran. To obtain the latter, a modified method was used for the synthesis of tetrahydrofuran homologs from 1-furylalkanols-3 (6). The hydrogenolysis was applied not to the furan alcohols themselves, but to their acetates (I), which made it possible

Table 1

Products of the transformations of dihydrofurans on Pt–C at 300°

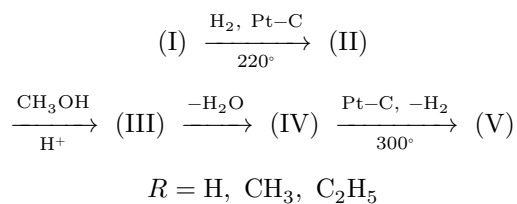
Starting sub- stance	Catalyst com- pou- nd	Yield, B.p.,		m_D^{20}	d_4^{20}	M.p. of semi- car- bazone °C	MR_D , cu- lated	MR_D , cal- culated	Found, %	Found, %	Calculated, %	Calculated, %
		%	°C/mm									
[[structure for- mula: one di- hy- dro- fu- ran ring bear- ing a propyl sub- stituent]]	138	—	142	1.4085	0.8180	131	34.47	34.53	—	—	—	—
	4-	40	—	—	—	—	—	—	—	—	—	—
			143/740			132						

Starting position	Catalyst composition	Yield, %	B.p., °C/mm _D ²⁰	<i>d</i> ₄ ²⁰	M.p. of semi-carbazone, °C	<i>M</i> <i>R</i> _{<i>D</i>} , calculated	<i>M</i> <i>R</i> _{<i>D</i>} , found	%, C	%, H	%, C	%, H
[[structure]] for- mula: di- hy- dro- fu- ran ring a bear- ing sub- a propyl sub- stituent]]	100	114	1.4400	0.8880	—	32.69	33.03	—	—	—	—
[[structure]] for- mula: di- hy- dro- fu- ran ring a bear- ing sub- a propyl sub- stituent]]	36	154	1.4108	0.8125	123	39.16	39.15	—	—	—	—
[[structure]] for- mula: methy- substituted di- hy- dro- fu- ran ring bear- ing a propyl sub- stituent]]	100	156	1.4108	0.8125	124	—	—	—	—	—	—

Starting sub- stance	Catalyst com- po- sition	Yield, %	B.p., °C/mm ²⁰ _D	<i>d</i> ₄ ²⁰	M.p. of semi- car- bazone, °C	<i>M</i> R _D , cu- lated		Found		Calculated	
						<i>M</i> R _D , found	<i>M</i> R _D , cal- culated	%, C	%, H	%, C	%, H
[[[structure]]] for- mula: methyl- substituted di- hy- dro- fu- ran ring bear- ing a propyl sub- stituent]]	total	142	1.4435	0.8832	—	37.31	37.65	77.20	9.88	77.37	9.74
[[[structure]]] for- mula: methyl- substituted di- hy- dro- fu- ran ring bear- ing sub- stituent]]	total	60	1.4212	0.8236	61	43.81	43.77	—	—	—	—
[[[structure]]] for- mula: methyl- substituted di- hy- dro- fu- ran ring bear- ing a propyl sub- stituent]]	5-Methyl- stan-	62/11	—	62	—	—	—	—	—	—	—

Starting substance	Catalyst composition	Yield, %	B.p., °C/mm _D ²⁰	d ₄ ²⁰	M.p. of semi-carbazone, °C	MR _D , found	MR _D , calculated	Found, %		Calculated, %	
								C	H	C	H
[[structure]] for- mula: methyl- substituted di- and hy- propyl- dro- substituted fu- fu- ran ran ring ring]]	50%	48.5	1.446	10.8776	—	42.00	42.27	78.12	10.30	78.21	10.21
for- mula: methyl- substituted di- and hy- propyl- dro- substituted fu- fu- ran ran ring ring]]	—	49.5/11	—	—	—	—	—	—	—	—	—

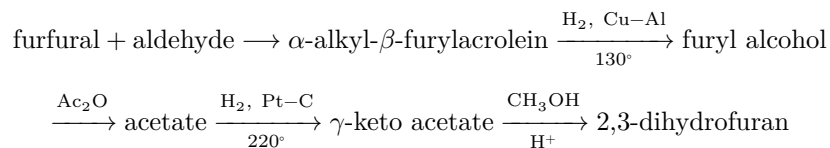
to obtain acetates of γ -keto alcohols (II), and from them the corresponding keto alcohols (III) and dihydrofurans (IV).



Dehydrogenation of the dihydrofurans (IV) to the corresponding furans (V) was carried out over platinized charcoal at 300°. The 2,4-dialkylfurans were obtained in 50% yield. As a result of side reactions (2) and (4), aliphatic ketones (35-40%) and paraffin hydrocarbons were formed (Table 1).

Experimental Part

2,3-Dihydrofurans were obtained according to the following scheme:



The condensation of furfural with aldehydes, the hydrogenation of α -alkyl- β -furylacroleins to furan alcohols, and the acetylation of the latter have been described in (7-9).

The properties of the obtained homologs of 2,3-dihydrofuran are given in Table 2.

Table 2
Properties of 2,3-dihydrofurans

Dihydrofurans	B.p., °C/mm	n_D^{20}	d_4^{20}	MR_D , found	MR_D , calculated
2-propyl- 2,3-dihydrofuran	129- 131/741	1.4345	0.8791	33.26	33.50
2-propyl- 4-methyl- 2,3-dihydrofuran	150- 152/756	1.4380	0.8734	37.91	38.12
2-propyl- 4-ethyl- 2,3-dihydrofuran	61- 62/1178- 80/22	1.4401	0.8713	42.42	42.73

Catalyst—platinized charcoal (10% Pt) was prepared by impregnating activated birch charcoal with a solution of chloroplatinic acid, which was then reduced with formalin in the presence of caustic alkali.

The starting dihydrofurans were passed over the catalyst at a space velocity of 0.1 h^{-1} . The liquid catalyzates, obtained in yields of more than 95%, were distilled on a column. The results of the experiments are presented in Table 1.

Thus, it has been established that by catalytic dehydrogenation in the vapor phase over Pt-C at 300° from homologs of 2,3-dihydrofuran, 2,4-dialkylfurans are obtained in 50% yield.

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

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