## RESEARCH ON FURAN ACETAL COMPOUNDS

## IX.\* ISOMERIZATION OF 4-ALKYL-2-(5'-X-2'-FURYL)-1,3-DIOXOLANES

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When 4-alkyl-2-(5'-X-2'-furyl)-1,3-dioxolanes are heated in the presence of tert-butyl peroxide the acetal ring is opened at the C=O 3=4 bond to give isomeric esters of 5-substituted furan-2-carboxylic acid. The structure of the product was confirmed by means of the UV and IR spectra, gas-liquid chromatography, and alternative synthesis.

The ability of cyclic acetals, primarily 1,3-dioxanes, to undergo various types of isomeric rearrange ments [2-5], which are observed both in the gas [2, 3] and liquid phases [4, 5], has been previously observed. A radical mechanism has been proposed for the homogeneous-catalytic isomerization of 1,3-dioxanes, during which an increase in their reactivity when substituents are present in the 2 position of the acetal ring was noted [6]. From this point of view, the behavior in this reaction of 2-furyl-1,3-dioxolanes, the isomeric transformations of which would make it possible to obtain derivatives of the furan series that are difficult to obtain by other methods, seemed of interest.

The starting materials for the syntheses were furfural (Ia) and 5-methyl- (Ib) and 5-nitrofurfural (Id) (see the scheme below). 1,3-Dioxolanes (IIa-e, Table 1) are formed in quantitative yields in the condensation of furan aldehydes with 1,2-diols. The latter are converted to the isomeric esters (IVa-e) (Table 2) with high selectivity when they are heated in the presence of an organic peroxide.

To identify the target products we carried out alternative syntheses of them through the corresponding 5-X-furan-2-carboxylic acids (IIIa, b), which also made it possible to compare the two methods for the preparation of esters IV.

In this case, it should be noted that the preparation of 5-nitropyromucic acid esters IVd, e via the method proposed by us is realized in one step – by isomerization of the corresponding dioxolanes IId, e. The previously well-known method [7] assumes the preparation of the desired products in two steps including esterification of free acid IIIa and nitration of esters IVa, c.



I-IV **a** X = H, R = H; II, IV **b** X = H,  $R = CH_3$ ; I-IV **c**  $X = CH_3$ , R = H; I, II, IV **d**  $X = NO_2$ , R = H; II, IV **e**  $X = NO_2$ , R = CH.

A mixture of isomers of acetyl and ester character is formed as a result of a homogeneous-catalytic transformation. To separate the components of the reaction mixture we used highly efficient columns or fractionating columns. Sharp separation of the isomeric esters and dioxolanes was achieved under the conditions of

\*See [1] for communication VIII.

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TABLE 1. 4-Alkyl-2-(5'-X-2'-furyl)-1,3-dioxolanes (IIa-e)

		R	bp <b>, °</b> C (mm)	UV spec	Viold of	
Compound	X			$\lambda_{max}$ , nm	lg ε	
II a II b II c II d II e	H H CH. NO <sub>2</sub> NO <sub>2</sub>	H CH3 H H CH3	$\begin{array}{c} 89 (15) \\ 70 (7) \\ 83 (4) \\ 162 (8) \\ 153 (4) \end{array}$	208 211 219 395 503	3.23 3,91 3.94 3.98 3.92	75 69 76 78 73

\* See [1] for communication VIII.

TABLE 2. 5-X-Furan-2-carboxylic Acid Esters (IVa-e)

Com - pound	х	R	bp, °C (mm)	Empirical formula	Calculated (found), %			UV spectrum		Yield based on
					с	н	N	). <sub>max</sub> , nm	lgε	dioxolane
i∖∵a	11	II	34 89—91	C-11203	60,00 (39,80)	5.71 (5.75)		251	4.08	94
IV P	П	CH	(o) 89 (4)	C <sub>5</sub> H <sub>10</sub> O <sub>3</sub>	62.34	6,49		254	4.14	93
IV c	CH3	H	71 (4)	C <sub>3</sub> H <sub>10</sub> O <sub>3</sub>	62.34 (62.30)	6.49		270	4.14	92
I∖ d	$NO_2$	Н	100*	C <sub>7</sub> H <sub>7</sub> NO <sub>5</sub>	45.71 (45.30)	3.78 (4.20)	7,57	296	4,05	96
IV e	$NO_2$	СHз	87	C <sub>8</sub> H <sub>9</sub> NO <sub>5</sub>	48.24 (48.50)	4.52 (4,64)	7,04 (7,00)	295	4,08	98

\* These are the melting points.

gas-liquid chromatography (GLC); the conversion of the latter, determined by GLC or UV spectroscopy, was 30-40%. The experiments showed that under the conditions of the reaction under consideration here the acetal ring is opened with selective formation of an ester grouping. The introduction of a furan substituent in the 2 position of the dioxane ring evidently increases the lability of the hydrogen atom in this position; the yield of esters ranges from 92 to 98%.

The isolated products were identified by spectral and chromatographic methods. The UV spectra of most of the esters are characterized by a considerable bathochromic shift as compared with the starting dioxolanes; this is associated with enlargement of the conjugation chain due to the carbonyl group of the ester. The IR spectra of model esters and esters obtained by isomerization of the acetals were identical. Absorption bands of a carbonyl group at  $1700 \text{ cm}^{-1}$  are observed, and absorption bands of a nitro group in the furan ring at 1560 and  $1320 \text{ cm}^{-1}$  are observed in the case of IVd-e. The characteristic absorption bands of the starting dioxolanes [8] are absent.

The formation of esters with an alcohol radical that has a normal or iso structure is possible in the isomerization of 4-methyl-substituted acetals (IIb, e), since in this case the C=O 1=5 and 3=4 bonds are nonequivalent. The gas-liquid chromatograms showed that the relative retention times, determined with respect to tetralin, of the isomerization products IVb, e coincide with the corresponding retention times of the model compounds that have an alcohol radical of normal structure. Thus it was established that 4-substituted 1,3dioxolanes undergo ring opening at the C=O 3=4 bond under the conditions of radical rearrangement.

Some of the synthesized esters are of promise as physiologically active preparations; IVd, e display fungicidal activity and suppress the development of plant diseases, for example, phytophthora of tomatoes. It is significant that an increase in the length of the alkyl radical promotes an increase in the activity of the preparation. The examined method of radical isomerization makes it possible to obtain esters with different substituents in the furan ring and in the alcohol radical.

## EXPERIMENTAL

The UV spectra were recorded with an SF-4A spectrophotometer. The IR spectra were recorded with a Specord spectrometer. Analysis by GLC was carried out with an LKhM-7A chromatograph under conditions of linear programming of the column temperature; the stationary phase was Apiezon L on Chromaton.

<u>5-Nitrofurfural (Ic).</u> This compound, with mp  $35^{\circ}$ , was obtained in 60% yield from furfural through the nitrofurfural diacetate by hydrolysis of the latter in an alkaline medium [9].

4-Alkyl-2-(5'-X-2'-furyl)-1,3-dioxolanes (IIa-e). These compounds were obtained by condensation of the corresponding furan aldehydes (Ia, c, d) with ethylene glycol or 1,2-propylene glycol in benzene in the presence of an acid catalyst by the method proposed for 1,3-dioxanes [10]; 0.1-0.2 mole samples of each component were used. Data on dioxolanes IIa-e are presented in Table 1.

Furan-2-carboxylic Acids (IIIa, e). These compounds were obtained by oxidation of the corresponding aldehydes (Ia, c) with potassium hypobromite [11] or by hydrolysis of the ethyl ester [7]. Acid IIIa, with mp 134° was obtained in 90% yield, and acid IIIc, with mp 108-109° was obtained in 50-80% yield.

5-X-Furan-2-carboxylic Acid Esters (IVa-e). 1) Isomerization. A glass ampul was charged with 0.05 mole of dioxolane (IIa-e) and 0.73 g (0.005 mole) of tert-butyl peroxide, after which the ampul was filled with an inert gas, sealed, and thermostatted at 140° for 8-12 h. The resulting esters were isolated by vacuum fractionation with an efficient fractionating column. The physical constants and yields of esters IVa-e are presented in Table 2.

2) Esterification. Esters IVa-e were obtained in 60-70% yields in excess absolute ethanol or n-propyl alcohol by passage of dry HCl [7].

3) Nitration. Esters IVd, e were obtained in 70-80% yields by nitration of esters IVa, c in acetic anhydride [9]. The properties of the esters obtained by methods 2, 3, and 1 were in agreement, and this proves their identical character.

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