FURAN ACETAL COMPOUNDS

II.* 2-α'-FURYL-5-ALKYL-5-O-ACYLOXYMETHYL-1,3-DIOXANES

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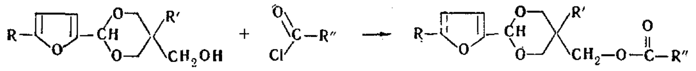
Esters of the furan series were synthesized by the reaction of 2-α'-furyl-5-alkyl-5-methylol-1,3-dioxanes with aliphatic acid chlorides. Their IR, UV, and NMR spectra were studied. The set of bands at 3150, 3132, 1735, 1300-1000, and 960-720 cm^{-1} is proposed to confirm the structures of the compounds obtained.

The furan 5-hydroxymethyl-5-ethyl-1,3-dioxanes, α'-substituted in the 2-position, previously obtained by us [1] have an extremely reactive functional group in the 5-position of the dioxane ring; this made it possible to accomplish a number of further transformations of them.

To ascertain the stability of the furan and dioxane rings during acid catalysis [2], we synthesized 2-α'-furyl-5-alkyl-5-O-acyloxymethyl-1,3-dioxanes via the scheme



R = H, CH_3, Br, NO_2; R' = CH_3, C_2H_5; R″ = CH_3, C_3H_7, C_5H_{11}, C_7H_{15}, $-C_4H_3O$

Since furan derivatives in which the ring is not stabilized by electronegative substituents are extremely sensitive to the action of acidic agents at high temperatures [3, 4], several refinements were introduced into the method used to synthesize them [5]: absolute benzene is used as the solvent, the acid chlorides of the appropriate acids are added gradually during refluxing of the reaction mass and constant bubbling of pure, oxygen-free nitrogen through the mixture, and the reaction time is no more than 45 min. The observance of these conditions resulted in an increase in the yields of the reaction products.

An absorption band with one maximum which, depending on the substituent introduced into the α'-position of the furan ring, is shifted to the long-wave region is observed on examination of the UV spectra of the compounds obtained. The similarity between the UV spectra and the spectra of furan 1,3-dioxanes [1] is an additional confirmation of the acetal structure of the synthesized products.

An important feature of the IR spectra of I-X is their considerable similarity. The investigated compounds are esters which have three characteristic absorption bands due to the presence of C=O and C−O groups. The carbonyl band at 1735 cm^{-1} in this case is shifted to lower values as compared with the starting acid chlorides (1790 cm^{-1} for the caproyl chloride C=O). Increasing the size of the R″ radical from I to V does not affect the frequency of the carbonyl absorption. As would be expected, conjugation of the carbonyl group with the furan double bond in VI leads to a decrease of 20 cm^{-1}. Compounds I and III-X have one $\nu_{C=O}$ absorption maximum; II, for which this band is split into two peaks, is an exception, and this made it possible to assume the presence of different stereoisomeric forms.

The NMR data [6] confirmed the configuration in the preferred conformational forms. The molecules of I are trans isomers and exist in the chair conformation, while samples of II are a mixture of two isomers

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*See [11] for communication I.

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TABLE 1. 2-α'-Furyl-5-alkyl-O-acyloxymethyl-1,3-dioxanes

Compound	R	R′	R″	mp, °C (pressure, mm)	d_4^{20}	n_D^{20}	λ_{max}, nm (lgε)	MR_D		Empirical formula	Found, %		Calc., %		Yield, %
								found	calc.		C	H	C	H	
I	H	C_2H_5	CH_3	59,5—60*	—	—	214 (3,96)	—	—	$C_{13}H_{18}O_5$	61,00	7,32	61,40	7,01	95
II	H	C_2H_5	C_3H_7	180 (5)	1,1150	1,4769	214 (3,95)	72,98	73,48	$C_{15}H_{22}O_5$	63,78	7,96	63,81	7,86	94
III	H	C_2H_5	C_4H_9	195 (1)	1,0870	1,4770	214 (3,96)	77,47	78,14	$C_{16}H_{24}O_5$	64,79	8,38	64,84	8,16	87
IV	H	C_2H_5	C_5H_{11}	210 (1)	1,0577	1,4741	214 (3,97)	82,61	82,79	$C_{17}H_{26}O_5$	66,10	8,61	65,78	8,44	81
V	H	C_2H_5	C_7H_{15}	222 (0,5)	1,0490	1,4775	214 (3,96)	91,98	92,08	$C_{19}H_{30}O_5$	67,41	8,96	67,43	8,93	80
VI	H	C_2H_5	C_4H_3O	200 (10)	—	1,4975	212 (4,1)	—	—	$C_{16}H_{18}O_6$	60,03	5,68	60,37	5,66	49
VII	H	CH_3	C_7H_{15}	200 (1)	—	1,4570	214 (3,94)	—	—	$C_{18}H_{28}O_5$	69,93	9,10	70,07	9,08	82
VIII	CH_3	C_2H_5	C_7H_{15}	245 (10)	—	1,4610	220 (3,9)	—	—	$C_{20}H_{32}O_5$	68,42	9,01	68,10	9,15	78
IX	Br	C_2H_5	C_7H_{15}	92—93*	—	—	222 (4,04)	—	—	$C_{19}H_{29}O_5Br$†	54,86	7,49	54,68	7,00	80
X	NO_2	C_2H_5	C_7H_{15}	38—39*	—	—	310 (3,91)	—	—	$C_{19}H_{29}NO_7$ ‡	58,99	7,91	59,52	7,62	93

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*mp (from benzene–heptane).

† Found %: Br 18.97. Calculated %: Br 19.16.

‡ Found %: N 3.61. Calculated %: N 3.65.

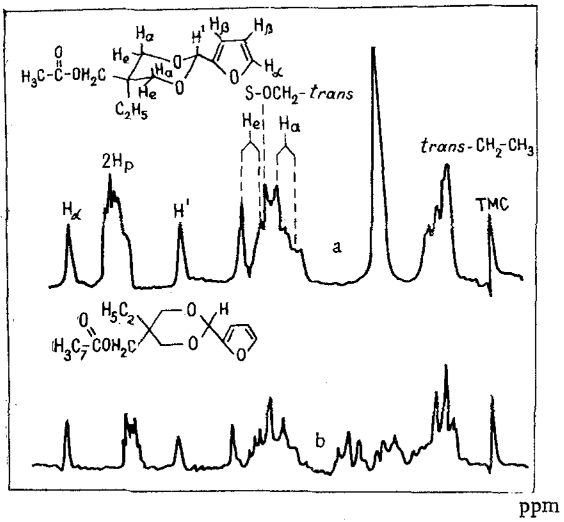

Fig. 1. PMR spectra: a) 2-furyl-5-ethyl-5-O-acetoxymethyl-1,3-dioxane; b) 2-furyl-5-ethyl-5-O-butyryloxymethyl-1,3-dioxane.

which exist in the chair conformation, since the lines of the methylene groups of the dioxane ring indicate great nonequivalency of the axial and equatorial protons* (Fig. 1).

The absorption bands of the C−O valence vibrations are found in the absorption region of both the furan and dioxane rings, but despite this, the presence of bands in this region is so characteristic that they can be accurately assigned. The maxima at 1200 and 1100 cm^{-1} are the valence vibrations of the C−O of the ester grouping. The first should be ascribed to the C−O of the carbonyl group, while the second should be related to the C−O of the alcohol residue [7]; the first band is shifted to lower frequency with increasing R" from I (1195 cm^{-1}) to V (1165 cm^{-1}).

The vibrations of the furan ring are characterized by bands of medium intensity at 1600 and 1500 cm^{-1}. The bands above 3000 cm^{-1} indicate the presence of an unsaturated bond (=CH). Compounds I-VII have two maxima at 3150 and 3130 cm^{-1}, while VIII-X have one. The difference in the intensities and frequencies of these bands for α- and α,α'-substituted furans confirms the statement in [8] regarding the different reactivities of α- and β-bonds of the furan ring. The bands at 1243 and 1060 cm^{-1} pertain to the asymmetrical and symmetrical valence vibrations of the =C−O−C grouping in the furan ring. The region of out-of-plane deformation vibrations of the CH group is used to determine substitution in the furan ring; thus, I-VII correspond to the bands at 920, 880, and 820 cm^{-1}, while VIII-X correspond to the bands at 980 and 800 cm^{-1}.

The bands at 1150 and 1027 cm^{-1}, which characterize, respectively, the asymmetrical and symmetrical valence vibrations of the ring [9], pertain to the ring vibrations of the dioxane ring.

The deformation vibrations of CH in CH_3 and CH_2 absorb at 1370 and 1460 cm^{-1}. The clearly expressed high-intensity band at 1370 cm^{-1} facilitates the identification, since during acetal formation it is often greater than the band at 1480 cm^{-1} and is split [10]. A rather sharp absorption appears on the low-frequency side (at 1350 cm^{-1}). The peak at 1410 cm^{-1} (between those at 1460 and 1370 cm^{-1}) indicates the presence of a $-CH_2CO$ grouping. This peak is very sensitive to a change in frequency under the influence of an intramolecular environment. Thus in VI the frequency decreases by 10 cm^{-1}, while it increases by 20 cm^{-1} in VIII-X.

The intensity of the valence vibrations of the methylene band changes considerably on lengthening the hydrocarbon chain. Thus, the $\nu_{as\,CH_3}$ band in I-IV (2962 cm^{-1}) is more intense than the $\nu_{as\,CH_2}$ band (2926 cm^{-1}), while the opposite is true in V-X.

The peak at 740 cm^{-1} pertains to the pendulum vibrations of the CH_2 groups. A proof of the correctness of this assignment is its split character on changing the aggregate state of the compounds from liquid (for II-VIII) to solid (for I, IX, and X) [7].

The absence of a frequency for the hydroxyl group at 3200-3600 cm^{-1}; the appearance of an ester group absorption at 1735 cm^{-1}, 1200, and 1100 cm^{-1}; and the preservation of bands from the furan and dioxane rings confirm the assumed structures of the synthesized compounds.

EXPERIMENTAL

2-Furyl-5-alkyl-5-O-valeryloxymethyl-1,3-dioxane (III). 2-Furyl-5-methyl-1,3-dioxane [5.33 g (0.025 mole)] (mp 67°) was dissolved in 50 ml of benzene with heating, and 3.0 g (0.025 mole) of valeryl chloride was added in the course of 20 min. The mixture was refluxed for 45 min, cooled, and washed with 200 ml of water. The benzene layer was separated and dried over magnesium sulfate. The benzene was re-

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moved, and the residue was distilled to give 6.3 g (87%) of a light-yellow product (III) with bp 95° (1 mm). Compounds II and IV-VII were similarly obtained. After removal of the benzene, I, IX, and X were crystallized from benzene–heptane (1 : 3) (Table 1).

The UV spectra in ethanol were obtained with an SF-4 spectrophotometer. The IR spectra of thin liquid layers (0.04 mm) or mineral oil suspensions (I, IX, and X) were obtained with an IKS-14 spectrophotometer at 650-1800 and 2600-3700 cm^{-1} with NaCl and LiF prisms. The PMR spectra were obtained at 60 MHz with an NMR RYa-2303 spectrometer constructed by the Special Design Office of Analytical Instrument Making, Academy of Sciences of the USSR.

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