Thus in the present research we were able to detect the presence of the corresponding aldehydes in the reaction mixtures from the chlorophenylation of 2-acetyl- and 2-propionylfuran.

EXPERIMENTAL

The polarograms were recorded with a PO-4 Radiometer polarograph (Denmark). Polarography was carried out in a thermostated cell (25 ± 0.1 deg). The oxygen was removed from the solution with a stream of purified nitrogen. A capillary with a spatula for forced detachment of a drop with the following characteristics for $H = 45$ cm in a 0.1 M solution of potassium chloride was used: $m = 1.06$ mg, $t = 0.305$ sec, and $m^{2/3}t^{1/6} = 0.85$. An external saturated calomel electrode was used as the anode.

The Meerwein arylation of 2-acylfurans was carried out as previously described in [1,2] with p-chlorobenzenediazonium chloride; 0.5 g (4.5 mmole) of 2-acetylfuran and 0.554 g (4.46 mmole) of 2-propionylfuran were used for the reactions.

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NITRATION OF FURAN DERIVATIVES WITH ACETYL NITRATE. INVESTIGATION OF THE PRODUCTS OF NITRATION OF FURFURAL AND FURFURAL DIACETATE

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542.958

It was established that 5-nitro-2-acetoxy-2,5-dihydro-, 5-nitro-4-acetoxy-4,5-dihydro-, and 5-nitrofurfural diacetates and 5-nitrofurfural are formed in the nitration of furfural and furfural diacetate in acetic anhydride. 2,5-Diacetoxy-2,5-dihydro- and 4,5-diacetoxy-4,5-dihydrofurfural diacetate are present in small amounts in the nitration products. 5-Nitrofurfural and 5-nitrofurfural diacetate are formed as a result of direct electrophilic substitution of hydrogen by a nitro group.

A crystalline "intermediate" nitration product, which was found to be 5-nitro-2-acetoxy-2,5-dihydrofurfural diacetate (II) [2-5], was isolated [1] in the nitration of furfural diacetate (Ib). A molecule of acetic acid is split out by treatment of II with weakly alkaline reagents (pyridine, sodium acetate, etc.), and 5-nitrofurfural diacetate (III) is

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formed in almost quantitative yield. Compound II is also formed in the nitration of furfural (Ia) [2,3]. In addition to it, another oily yellow substance [6], the composition of which was not established, was detected in the products of nitration of aldehyde Ia.

In the present research we studied the products formed in the nitration of furfural (Ia) and furfural diacetate (Ib) in acetic anhydride. The nitration was carried out at −5 to −10° by the method in [7]. The nitration products were isolated as in [8] and investigated by thin-layer chromatography (TLC) on silica gel (Table 1).

Four products, which were separated by preparative layer chromatography, were detected after nitration of Ia (or Ib).* It was proved by comparison of the spectroscopic and chromatographic characteristics with the corresponding features of model substances that one of the products is 5-nitrofurfural (IV), the second is II, and the third is 5-nitrofurfural diacetate (III); in addition, a previously unknown adduct (V) of acetyl nitrate with furfural diacetate was isolated, and it was found that, like II, it is readily converted to III under the influence of sodium acetate.† Malic acid (VI) was detected in the products of acid hydrolysis of V. The 5-nitro-4-acetoxy-4,5 dihydrofurfural diacetate structure was assigned to V on the basis of its chemical properties. Its structure is also confirmed by its UV, IR, and PMR spectra. Similarly 4,5-addition of acetyl nitrate to the furan ring was previously observed in the nitration of methyl furan-2-carboxylate [8], but, in contrast to this instance, the PMR spectra of II and V (Table 2) display the presence of only one of the hypothetical cis or trans products of addition of acetyl nitrate.

*The compositions of the products of the nitration of Ia and Ib were identical

†Conversion of this compound to III is observed on some sorts of silica gel (for example, H Ferak) during chromatography; and this was proved by means of two-dimensional chromatography. Similar deacetoxylation and the formation of III are also observed during chromatography of II. Splitting out of a molecule of acetic acid from V and II does not occur on acidic silica gel (for example, on KSK silica gel).

TABLE 1. Thin-Layer Chromatography of the Products of Nitration of Ia and Ib

	Brand of silica gel	Solvent*	R_f values of the products of nitration of Ia and Ib					
			IV	V	II	III	Ia	Ib
Chromatography	KSK	1	0,44	0,44	0,52	0,57	—	—
	H Merck†	1	0,35	0,35	0,43	0,48	0,57	0,66
	DC Woelm†	1	0,18	0,18	0,29	0,37	—	—
	H Ferak†	2	0,44	0,07	0,13	0,32	—	—
	H Ferak†	3	0,30	0,22	0,30	0,39	—	—
	Silufol UV_{254}	1	0,42	0,35	0,40	0,51	—	—
Detection‡	Exposure to NH_3 vapors		yb	yb	yb	yb	—	—
	Sprinkling with 0.1 N $KMnO_4$ solution (color on a violet background)		yb	yb	b	b	b	b
	UV light		d	—	—	d	d	d
	Sprinkling with a 1% solution of 2,4-DNPH in $CH_3OH-HCl$		y	y	y	y	o	o
	Sprinkling with aniline phthalate [15]		yb	yb	yb	yb	c	c

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*Systems: 1) ether−heptane (4:1); 2) dibutyl ether; 3) cyclohexane−benzene−CCl_4−dioxane(5:1:1:1.5:1.5).

†Deacetoxylation of II and V to III is observed on this adsorbent. To avoid deacetoxylation, the plates with the adsorbent were treated with 1% acetic acid in ether prior to the experiments and air dried for 1 h.

‡Spot colors: y is yellow, b is blue, yb is yellow-brown c is crimson, o is orange, and d is dark.

TABLE 2. PMR Spectra of the Products of Nitration of Ia and Ib

Compound	Solvent	Chemical shifts, δ, ppm						SSCC, Hz		
		ring protons			substituent protons					
						$CH(OCOCH_3)_2$				
		H-3	H-4	H-5	$OCOCH_3$	CH_3	CH	$J_{3,4}$	$J_{4,5}$	$J_{5,3}$
II*	$(CD_3)_2CO$	6,56	6,73	6,62	2.08	2,03	7,26	5,9	1,2	1,2
V	$CDCl_3$	6,58	6,71†	6,71†	2,05	2,09	7,40	—	—	—
VII	$(CD_3)_2CO$	6,60	6,39	6,78	2,09 2,03	1,98 1,97	7,14	5,9	1,1	1,1
VIII	$(CD_3)_2CO$	6,37†	6,37†	6,93	2,05 2,03	2,07	7,36	—	—	—

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*The PMR spectrum of II was described [6]. The structure of II is also confirmed by the ^{13}C NMR spectrum [20% solution in $(CD_3)_2CO$; tetramethylsilane as the internal standard, δ, ppm]: C_2 112.8, C_3 131.0, C_4 130.8, C_5 111.7; CH 86.0; C=O and CH_3 at 168.1 and 169.7; 19.8 and 20.9 (with an intensity ratio of 2:1, respectively).

†The previously noted [9] coincidence of the signals in the ring-proton region is observed, and the spin–spin coupling constants (SSCC) were therefore not determined.

We also studied the possibility of interconversion of the products of nitration of Ia and Ib under the experimental conditions.

When the nitration is carried out at −50 to −55°, Ia and Ib are also present along with the previously mentioned products II-V, regardless of the starting compound used. It was observed by TLC that the equilibrium Ia $\rightleftarrows$ Ib is established in acetic anhydride in the presence of mineral acids, and their mixture is subjected to the action of acetyl nitrate in each case. A similar equilibrium is observed in the case of 5-nitrofurfural (IV) and 5-nitrofurfural diacetate (III), but in this case it is shifted almost completely to favor the formation of the diol acetate.

5-Nitrofurfural diacetate (III) is present (∼15% according to the UV spectra) in the nitration products. Its formation may be due either to direct electrophilic substitution of the hydrogen atom in the 5 position of the furan ring by a nitro group or partial deacetoxylation of II and V. It was shown by TLC that III and IV are present in the nitration products even before decomposition of the reaction mixture with water, i.e., prior to the possible deacetoxylation step. In addition, our experiments showed that deacetoxylation of the nitration "intermediate" (II) does not occur either in the nitration step or when the nitration products are diluted with water, and II is isolated almost quantitatively in unchanged form.

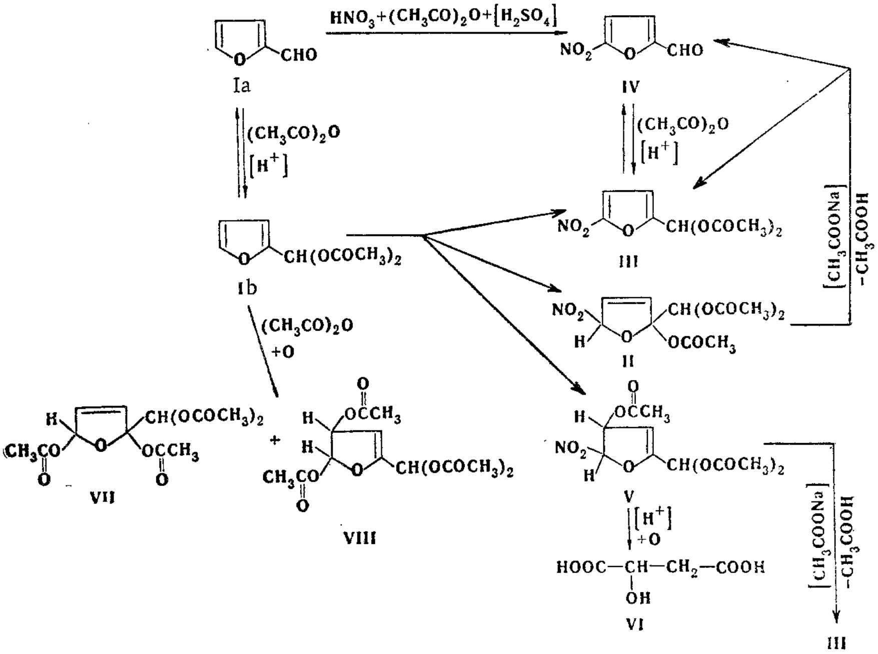
Consequently, in the nitration of Ia and Ib with acetyl nitrate one observes partial direct substitution of the hydrogen atom of the furan ring by a nitro group to give III and IV. Moreover, part of the II may be formed from aldehyde IV as a result of its reaction with acetic anhydride.

An investigation of the deacetoxylation of II with sodium acetate by TLC showed that the reaction products, in addition to III, also contain IV, i.e., hydrolysis of the diol acetate group occurs simultaneously with splitting out of a molecule of acetic acid from the dihydrofuran ring.

In addition to II-V, the products of nitration of Ia and Ib also contain small amounts of a compound with the composition $C_{13}H_{16}O_9$. We isolated this substance from the mother liquors formed in the synthesis of III. Its UV spectra do not contain the absorption of conjugated multiple bonds. Absorption at 1760-1780 cm^{-1} ($\nu_{C=O}$) is observed in its IR spectrum. The PMR spectra (Table 2) showed that this product is a mixture of two isomers with 2,5-diacetoxy-2,5-dihydrofurfural diacetate (VII) and 4,5-diacetoxy-acetoxylation of Ib. They do not undergo any change on treatment with weakly alkaline reagents (sodium acetate).

The preparation of VII by the action of bromine in acetic acid on Ib was described in [10,11], but its detailed characteristics are not available. Our verification showed that a mixture of VII and VIII is also formed in this reaction. We were able to isolate pure isomer VIII from the mixture.

By correlating the data obtained in this study, one can represent the nitration of Ia and Ib by the following scheme:



EXPERIMENTAL

The NMR spectra were recorded with Perkin—Elmer R-12A (60 MHz) and Bruker HX-90 (90 MHz) spectrometers with tetramethylsilane as the internal standard. The IR spectra of mineral oil and hexachlorobutadiene suspensions of the compounds were recorded with a UR-20 spectrometer. The UV spectra were recorded with an SF-4A spectrophotometer. Compound Ia was purified by washing of the commercial preparation with 5% $NaHCO_3$ and water, drying over $MgSO_4$, and vacuum distillation. The purified product had bp 54° (12 mm). Compounds Ib [12], II, III, and IV [2] were prepared by known methods. Purified II had mp 105-107° (from benzene) (mp 106-107° [2].

Products of Nitration of Furfural (Ia) and Furfural Diacetate (Ib). The nitration of Ia and Ib was carried out by the method in [7]. The nitration temperature ranged from —5 to —10°. The molar ratio of Ia (or Ib*), nitric acid, and acetic anhydride was 1:1.4:7 (the catalyst was 3.6 g of concentrated H_2SO_4 per mole of Ia or Ib). After dilution of the reaction mixture with ice water, the nitration products were isolated by the method in [8]. The results of chromatography of the products of nitration of Ia and Ib and the methods used to detect the spots are presented in Table 1. The following fractions were isolated from the mixture of products of nitration of Ia and Ib by preparative chromatography in a layer [with KSK silica gel as the adsorbent and elution with cyclohexane—benzene—CCl_4—ether—dioxane (5:1:1:1.5:1.5)]: V, a mixture of II and IV, and III.

Compound V was obtained as white crystals with mp 97.5-98°. Found: C 43.4; H 4.4; N 4.7%. $C_{11}H_{13}NO_9$. Calculated: C 43.6; H 4.3; N 4.6%. UV spectrum: λ_{max} 284 nm (log ε 2.01) (in glacial acetic acid). IR spectrum: $\nu_{NO_2}{}^{s}$ 1376, $\nu_{NO_2}{}^{as}$ 1572, $\nu_{C-O-C}{}^{s}$ 1025, $\nu_{C=O}$ 1770, $\nu_{C=C}$ 1625 cm^{-1}. The PMR spectrum is presented in Table 2.

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*A total of 8 ml of acetic anhydride was used to dissolve 5 g (0.25 mole) of Ib.

Compound IV was isolated from the mixture of II and IV by repeated chromatography on Merck H silica gel/elution with ether—heptane (4:1)/. Compound II (R_f 0.43) was deacetoxylated on this adsorbent and converted to III (R_f 0.48). Chromatography was carried out II was completely converted to III and IV was isolated in individual form with mp 35-36°.

Treatment of II-IV with a Mixture of Nitric Acid and Acetic Anhydride. This treatment was carried out by the method in [1]. The molar ratio of II (III or IV), nitric acid, and acetic anhydride was 1:1.34:10.3 (with H_2SO_4 as the catalyst). Treatment of II with acetyl nitrate resulted in 92% recovery of the starting material. The formation of other reaction products was not observed. Treatment of III with acetyl nitrate resulted in 90% recovery. The formation of IV was not observed prior to dilution of the reaction mixture with ice water. A small amount of IV together with III was present in the mother liquor after separation of the crystals of III.

The formation of III was established in the reaction mixture by TLC after treatment of IV with acetyl nitrate. A small amount of IV remained unchanged. Compound III was isolated in 89% yield.

Quantitative Determination of III in the Products of Nitration of Ia and Ib. This determination was carried out by the method in [1]. The products of nitration of Ia (or Ib) contained ∿15% III.

Treatment of Ia and Ib with Acetic Anhydride in the Presence of Concentration H_2SO_4. A 0.05-mole sample of Ia or Ib was dissolved in 27 g (0.26 mole) of acetic anhydride, the solution was cooled to —15°, and a solution of 0.18 g (1.8 mmole) of concentrated H_2SO_4 in 8.6 g (0.08 mole) of acetic anhydride was added with stirring. The molar ratio on Ia (or Ib), acetic anhydride, and sulfuric acid was 1:7:0.036. The reaction mixture was investigated by TLC. A mixture of Ia (R_f 0.38) and Ib (R_f 0.52) was detected on the chromatogram [on Silufol UV-254 plates with elution by benzene—ether (9:1)], regardless of the starting compound. In addition, the presence of two substances with R_f 0.12 and 0.16 (light-gray spots in ammonia vapors), the structures of which were not investigated, was observed in the reaction products.

Deacetoxylation of II. A solution of 0.3 g (2.2 mmole) of sodium acetate in 5 ml of water was added at room temperature to a solution of 0.3 g (1 mmole) of II in 6 ml of ethanol, and the mixture was allowed to stand at 20° for 24 h. The organic solvent was removed in vacuo, and the precipitated crystals were removed by filtration and air dried. The yield of III, with mp 90-91°, was 0.18 g (75%). The mother liquor was extracted with three 5-ml portions of ether, and the extract analyzed by TLC. Compounds III and IV were detected in the ether solution.

Deacetoxylation of V. A 1-ml sample of a $3.42 \cdot 10^{-3}$ M solution of V in glacial acetic acid was heated at 55° for 1 h with 4 ml of a 1% sodium acetate solution, after which the mixture was cooled and diluted to 25 ml with ethanol, and the UV spectrum was recorded: λ_{max} 298 nm (ε 9850) (85% conversion of V to III).

Acid Hydrolysis of V. A 10-mg sample of W was dissolved in 1 ml of acetone, 1 ml of water and three drops of concentrated HCl were added, and the mixture was heated at 100° for 30 min. It was then cooled and extracted with two 2-ml portions of ether, and the extract was dried over $MgSO_4$. It was then filtered, and the organic solvent was removed from the filtrate. The residue was heated with 1 ml of concentrated H_2SO_4 and β- naphthol (a freshly prepared solution of 0.0025 g of β-naphtol in 100 ml of concentrated H_2SO_4). The blue fluorescence in UV light provided evidence for the presence of malic acid [13] in the hydrolysis products. Compounds I-IV did not give a positive qualitative test for malic acid.

Compounds VII and VIII. The mother liquor obtained from the synthesis of III [7] was extracted with ether, washed with cold water, dried over $MgSO_4$, and chromatographed preparatively in a layer of KSK silica gel [10] [elution with benzene—ether (9:1)]. A mixture of VII and VIII was eluted from the adsorbent with a small amount of ether. The solvent was removed, and the residue was cooled with dry ice and treated with ether. The resulting crystals of a mixture of VII and VIII were removed by filtration and air dried to give a product with mp 65-85°. Found: C 49.8; H 5.3%. $C_{13}H_{16}O_9$. Calculated: C 49.4; H 5.1%. The PMR spectrum of the mixture of VII and VIII is presented in Table 2. The R_f values were 0.14

[benzene—ether (9:1)] and 0.23 [heptane—ether (3:7)] (Silufol UV-254). Detection: gray-violet spot in NH_3 vapors; yellow spot on a violet background after sprinkling with 0.1 N $KMnO_4$ solutions; brown-violet spot with a 0.2% solution of 2,4-dinitrophenylhydrazine in 2 N HCl.

Oxidative Acetoxylation of Ib. This was accomplished by the method in [11] in acetic acid—acetic anhydride (2:1). A portion of the ether solution of the reaction products was chromatographed by the method used for used for the mixture of VII-VIII in the preceding experiment. According to the PMR and TLC data, the product obtained in this way was a mixture of VII and VIII. Evaporation of the ether solution of the crude reaction product yielded a mixture of crystals and an oil, which was cooled and treated with ether. The crystalline substance was removed by filtration, washed with ether, and air dried to give VIII with mp 89-91°. Found: C 49.3; H 5.0%. $C_{13}H_{16}O_9$. Calculated: C 49.4; H 5.1%. Absorption was not detected in the UV spectrum. IR spectrum: 1760-1780 cm^{-1} ($\nu_{C=O}$). According to the PMR data, the product was VIII. PMR spectrum (δ, ppm, in $CDCl_3$): 7.00 s (H-5) and 6.26 s (H-3 and H-4); 7.09 s (CH of the diol acetate group); 2.09, 2.07, and 2.00, three s (protons of the methyl group in $OCOCH_3$).

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