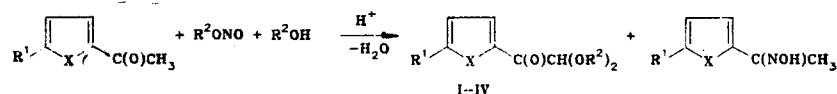


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Reaction of 2-acetyl-substituted thiophenes and furans with alkyl nitrites in the presence of the corresponding aliphatic alcohols and hydrochloric acid leads to the formation of linear acetals of thienyl- and furyl glyoxals, whose structure was established by IR, UV, NMR spectroscopy, and mass spectrometry methods. The main paths of the dissociation of the molecules under electron impact were established.

We have previously shown that alkyl nitrites convert acetone in an acidified alcoholic solution into methylglyoxal acetals [1]. In continuation of the study of the behavior of methyl ketones in this reaction, we found that 2-(2,2-dialkoxyacetyl)thiophenes and furans are obtained from 2-acetylthiophenes and 2-acetyl-5-methylfurans by the action of alkyl nitrites in the medium of the corresponding alcohols. No ring-nitrosation products of the initial ketones were detected.



I R<sup>1</sup>=H, R<sup>2</sup>=C<sub>3</sub>H<sub>7</sub>, X=S; II R<sup>1</sup>=H, R<sup>2</sup>=*i*-C<sub>3</sub>H<sub>7</sub>, X=S; III R<sup>1</sup>=CH<sub>3</sub>, R<sup>2</sup>=C<sub>3</sub>H<sub>7</sub>, X=S;  
IV R<sup>1</sup>=CH<sub>3</sub>, R<sup>2</sup>=C<sub>3</sub>H<sub>7</sub>, X=O

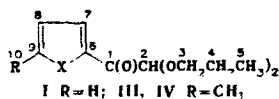
The individual state and the structure of compounds I-IV were confirmed by the data of elemental, chromatographic and spectral analyses. The IR spectra of compounds I-IV are characterized by the presence of an absorption band in the 1660-1680 cm<sup>-1</sup> region corresponding to the stretching vibrations of the C=O bond. An absorption band in the 1420-1450 cm<sup>-1</sup> region corresponds to the vibrations of the C=C bonds in the thiophene ring; analogous bonds in the furan ring absorb in the 1520 cm<sup>-1</sup> region. The absorption band in the 1070-1080 cm<sup>-1</sup> region corresponds to the stretching vibrations of the acetal bond (C-O-C).

The UV spectra of compounds I-IV are practically identical to the spectra of 2-acetylthiophene and 2-acetylfuran [2].

In the PMR spectra of acetals I-IV, the sharp one-proton singlet in the 4.8-4.9 ppm region corresponds to a proton of a methine group adjacent to two oxygen atoms. Compared with linear acetals of aliphatic aldehydes [3-5] and methylglyoxal (4.2-4.4 ppm) [1], the signal of this proton, as the result of the combined influence of the neighboring carbonyl group and the thiophene (furan) ring, is shifted to a still weaker field. A similar shift of the signal is observed also in the <sup>13</sup>C NMR spectra of 2-(2,2-dipropoxyacetyl)thiophenes (I, III) and furans (IV, Table 1), where the doublet at 102.5-103.6 ppm corresponds to the resonance of the carbon atom of a methine group adjacent to two oxygen atoms; signals of similar carbon atoms in the methylene and methine groups of dialkoxymethanes and 1,1-dialkoxyethanes are present in the 90-95 [3, 4] and 100 ppm region [3, 5], respectively, while in the case of the linear benzaldehyde acetals, the signals are at about 100 ppm [5]. The sharp signal in the weak field at 186 ppm (182 ppm for compound IV with a furan substituent) corresponds to the signal of the carbonyl group carbon atom of acetals I-IV; it is present in a weaker field, compared with the signal of the carbon atom in the OC(O)O group of diethyl carbonate (154.4 ppm). The chemical shifts of the carbon atoms contained in the hetero rings, are present in the 109-158 ppm region; their assignment was made on the basis of the multiplicity of signals in the spectra without suppression of the HFI with protons, and also with consideration

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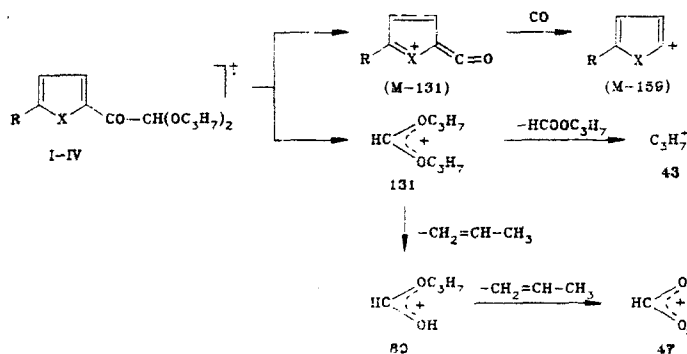
TABLE 1.  $^{13}\text{C}$  NMR Spectra of 2-(2,2-Dipropoxyacetyl)thiophenes (I, III) and Furans (IV) in Deuteriochloroform



| Com-<br>pound | Chemical shifts of carbon atoms, $\delta$ ppm (Hz, Hz) |                         |                         |                         |                         |                         |                         |                         |                    |                          |
|---------------|--|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|--------------------|--------------------------|
|               | C <sub>(1)</sub><br>(s)                                | C <sub>(2)</sub><br>(d) | C <sub>(3)</sub><br>(t) | C <sub>(4)</sub><br>(t) | C <sub>(5)</sub><br>(q) | C <sub>(6)</sub><br>(s) | C <sub>(7)</sub><br>(d) | C <sub>(8)</sub><br>(d) | C <sub>(9)</sub>   | C <sub>(10)</sub><br>(q) |
| I             | 186,2  | 102,5<br>(163,4)        | 68,5<br>(141,8)         | 22,0<br>(122,9)         | 9,4<br>(127,7)          | 139,0                   | 133,6<br>(172,8)        | 133,4<br>(172,8)        | 127,1 d<br>(170,9) | —                        |
| III           | 186,5  | 103,6<br>(161,5)        | 69,3<br>(135,2)         | 23,0<br>(122,0)         | 15,3<br>(136,9)         | 149,9                   | 135,2<br>(169,0)        | 126,9<br>(167,1)        | 138,2 s<br>(112,7) | 10,5                     |
| IV            | 181,7  | 102,5<br>(161,5)        | 69,3<br>(139,9)         | 23,2<br>(123,9)         | 13,5<br>(129,6)         | 158,4                   | 122,7<br>(178,4)        | 109,1<br>(174,4)        | 149,4 s            | 10,5<br>(116,4)          |

of the influence of the substituents on the electron density distribution in the hetero ring.

We were the first to measure the mass spectra of acetals I-IV containing a carbonyl group in the  $\alpha$ -position to the acetal center. In the mass spectra of all the acetals, the peak of the molecular ion ( $M^+$ ) is absent, which indicates its instability. From the analysis of the mass spectra of compounds I-IV (Table 2), it follows that the main fragments are formed from the primary cation-radicals as the result of rupture of bonds binding them with the carbonyl group, of which the greatest contribution is introduced by the splitting of the dipropoxymethyl radical or the corresponding cation:



The dialkoxymethyl cation undergoes  $\beta$ -splitting with the elimination of one or two olefin molecules. A similar splitting is also observed in the case of other  $\alpha$ -alkoxy-substituted cations [6, 7].

The fragmentation process of the primary cation radicals with formation of a ketonic fragment (M-131) and acetal fragment 131 is analogous to the dissociation of ketones [6, 8]. The presence of fragments with  $m/z$  183, 183, 197, and 181, respectively, in the mass spectra of compounds I-IV indicates the existence of cation-radicals, whose dissociation into fragment (with splitting of both olefins and aldehydes) is similar to that previously observed in the case of linear acetals of aliphatic aldehydes [6, 9].

In the mass spectra of all the compounds ( $M\text{-OC}_3\text{H}_7$ )<sup>+</sup> ions are also formed, but their peaks have low intensity.

It can be concluded from our results that a direct gem-dialkoxylation of acetyl-substituted thiophenes and furans in the side-chain acetyl group can be accomplished by the action of nitrosating agents in an alcoholic solution, without affecting the hetero ring. Acetals of thienyl- and furylglyoxals obtained by such a one-step reaction from readily accessible acetyl derivatives, can be used in fine organic synthesis as polyfunctional heterocyclic compounds or for the preparation of free  $\alpha$ -dicarbonyl compounds of the furan (thiophene) series.

#### EXPERIMENTAL

The boiling points of the compounds (Table 3) are given without correction. The PMR spectra of 10% solutions in  $\text{CCl}_4$  were recorded on a Tesla BS-497 spectrometer (100 MHz), using

TABLE 2. Spectral Characteristics of Compounds I-IV

| Compound | IR spectrum, cm <sup>-1</sup> |       |      | UV spectrum, $\lambda_{\max}$ , nm (log $\epsilon$ ) | Mass spectrum, m/z (relative intensity, in % with respect to maximal)*                               |
|----------|-------------------------------|-------|------|--|--|
|          | C=O                           | C-O-C | C-C  |  |  |
| I        | 1670                          | 1080  | 1420 | 267,289 (1,18)                                       | 183 (0,3), 141 (4), 131 (22), 111 (16), 89 (29), 85 (5), 83 (2), 47 (13), 43 (100), 41 (14)          |
| II       | 1670                          | 1075  | 1430 | 270,290 (1,17)                                       | 183 (0,2), 141 (3), 131 (10), 111 (42), 89 (36), 83 (6), 57 (3), 47 (3), 43 (100), 41 (42)           |
| III      | 1660                          | 1070  | 1450 | 273,301 (1,15)                                       | 197 (0,5), 155 (6), 131 (42), 125 (44), 99 (6), 97 (3), 89 (48), 53 (11), 47 (13), 43 (100), 41 (11) |
| IV       | 1680                          | 1080  | 1520 | 225,290 (1,04)                                       | 181 (0,4), 139 (4), 131 (17), 109 (36), 89 (29), 53 (20), 52 (3), 47 (5), 43 (100), 41 (37)          |

\*The ten most intense peaks and the most intense ion peak in the region of high m/z values are given.

TABLE 3. Properties of Compounds Synthesized

| Compound | T <sub>bp</sub> , °C (mm Hg) | d <sub>4</sub> <sup>20</sup> | n <sub>D</sub> <sup>20</sup> | MR <sub>D</sub> |       | Found, % |     |      | Empirical formula                                | Calculated, % |     |      | M      | Yield, % |
|----------|------------------------------|------------------------------|------------------------------|-----------------|-------|----------|-----|------|--|---------------|-----|------|--------|----------|
|          |                              |                              |                              | found           | calc. | C        | H   | S    |  | C             | H   | S    |        |          |
| I        | 145-150 (13)                 | 1,0982                       | 1,5058                       | 65,5            | 64,7  | 59,5     | 7,5 | 13,1 | C <sub>12</sub> H <sub>16</sub> O <sub>3</sub> S | 59,5          | 7,5 | 13,2 | 242,34 | 32       |
| II       | 135-138 (15)                 | 1,0677                       | 1,4950                       | 66,2            | 66,3* | 59,4     | 7,5 | 13,2 | C <sub>12</sub> H <sub>16</sub> O <sub>3</sub> S | 59,5          | 7,5 | 13,2 | 242,34 | 25       |
| III      | 135-140 (3)                  | 1,1023                       | 1,5088                       | 69,4            | 69,4  | 60,8     | 7,8 | 12,5 | C <sub>13</sub> H <sub>20</sub> O <sub>3</sub> S | 60,9          | 7,9 | 12,5 | 256,37 | 29       |
| IV       | 115-120 (13)                 | 1,0409                       | 1,4844                       | 66,1            | 64,8* | 64,9     | 8,4 | —    | C <sub>13</sub> H <sub>20</sub> O <sub>4</sub>   | 65,0          | 8,4 | —    | 240,30 | 45       |

\*According to Vogel.

HMDS as internal standard. The <sup>13</sup>C NMR spectra (Table 1) were measured on a Bruker H-90 spectrometer (22.63 MHz) under conditions with a broad band suppression and without suppression of the spin-spin interaction with protons. The IR spectra were recorded on a Microlab 620 MX apparatus in a thin layer with NaCl plates. The UV spectra were taken on a DU-8 spectrophotometer in alcohol and heptane (Table 2).

The chromato-mass-spectral analysis of acetals I-IV was carried out on a Finnigan 4021 apparatus (a 50,000 × 0.2 mm capillary column with BP-1 from the firm SGE, carrier gas helium, temperature programming from 50 to 200°C at a rate of 5°C/min, evaporator temperature 280°C, ion source temperature 250°C, ionization energy 70 eV). The purity of the compounds was monitored by the GLC method. The TLC was carried out on Silufol plates in a hexane-diethyl ether (3:1) system; developing agent - iodine vapor.

**2-(2,2-Dipropoxyacetyl)thiophene (I).** A 5.1 g portion (0.06 mole) of propyl nitrite is gradually added to a mixture of 6.3 g (0.05 mole) of 2-acetylthiophene, 1.8 g (0.03 mole) of propyl alcohol, and 0.3 g of hydrochloric acid, while the temperature is maintained not higher than 50°C. After cooling, the reaction mixture is kept for 1.5 h at 70°C, then cooled, neutralized with a 20% solution of NaOH, washed with water, and dried over anhydrous magnesium sulfate. Distillation at reduced pressure gives 1 g (32%, based on ketone entering the reaction) of compound I. If necessary, the reaction product can be additionally purified by chromatography on Al<sub>2</sub>O<sub>3</sub> using a mixture of hexane and ether (3:1) as eluent. PMR spectrum (CCl<sub>4</sub>): 0.88 (6H, J = 7.0 Hz, CH<sub>3</sub>); 1.58 (4H, m, J = 7.0 Hz, CH<sub>2</sub>CH<sub>2</sub>); 3.46 and 3.56 (4H, t and t, J = 7.0 Hz, OCH<sub>2</sub>); 4.86 (1H, s, OCHO); 6.98 (1H, d. d, J<sub>3,4</sub> = 4.0, J<sub>4,5</sub> = 5.0 Hz, 4-H); 7.50 (1H, d, J<sub>4,5</sub> = 5.0 Hz, 5-H); 7.90 ppm (1H, d, J<sub>3,4</sub> = 4.0 Hz, 3-H).

**2-(2,2-Diisopropoxyacetyl)thiophene (II).** This was obtained in a similar way using isopropanol and isopropyl nitrite. PMR spectrum (CCl<sub>4</sub>): 1.34 (12H, d, J = 7.0 Hz, CH<sub>3</sub>); 3.8 [2H, m, CH(CH<sub>3</sub>)<sub>2</sub>]; 4.87 (1H, s, OCHO); 6.98 (1H, d. d, J<sub>3,4</sub> = 4.0, J<sub>4,5</sub> = 5.0 Hz, 4-H), 7.50 (1H, d, J<sub>4,5</sub> = 5.0 Hz, 5H); 7.90 ppm (1H, d, J<sub>3,4</sub> = 4.0 Hz, 3-H).

Compounds III and IV were obtained in a similar way from 2-acetyl-5-methylthiophene and 2-acetyl-5-methylfuran, respectively.

2-(2,2-Dipropoxyacetyl)-5-methylthiophene (III). PMR spectrum (CCl<sub>4</sub>): 0.88 (6H, t, J = 7.0 Hz, CH<sub>3</sub>CH<sub>2</sub>); 1.58 (4H, m, J = 6.6 Hz, CH<sub>3</sub>CH<sub>2</sub>); 2.40 (3H, s, CH<sub>3</sub>); 3.42 and 3.52 (4H, t and t, J = 6.0 Hz, OCH<sub>2</sub>); 4.80 (1H, s, OCHO); 6.68 (1H, d, J<sub>3,4</sub> = 3.5 Hz, 4-H); 7.47 ppm (1H, d, J<sub>4,3</sub> = 3.5 Hz, 3-H).

2-(2,2-Dipropoxyacetyl)-5-methylfuran (IV). PMR spectrum (CCl<sub>4</sub>): 0.88 (6H, t, J = 7.0 Hz, CH<sub>3</sub>CH<sub>2</sub>); 1.56 (4H, m, J = 7 Hz, CH<sub>3</sub>CH<sub>2</sub>); 2.30 (3H, s, CH<sub>3</sub>); 3.48 and 3.54 (4H, t and t, J = 6 Hz, OCH<sub>2</sub>); 4.90 (1H, s, OCHO); 6.08 (1H, d, J<sub>3,4</sub> = 3.3 Hz, 4-H); 7.24 ppm (1H, d. d., J<sub>4,3</sub> = 3.3 Hz, 3-H).

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#### MASS-SPECTROMETRIC BEHAVIOR OF N-SUBSTITUTED 2-METHYL-3-ACETYL PYRROLES

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In the dissociation of N-substituted derivatives of 2-methyl-3-acetylpyrroles by the action of electron impact, the methyl group splits off from the acetyl substituent, and then the exocyclic N-C bond is ruptured due to the preferential localization of the charge on the C<sub>(2)</sub>-C<sub>(3)</sub> bond in the pyrrole ring.

It is known that under electron impact, 1-alkylpyrroles preferentially eliminate the alkyl group in the form of an olefin or that, as the result of splitting of the C-C β-bond in the aliphatic radical, stable 1-methylenepyrrolyl cations are formed [1, 2]. However, in the case of acylhetarenes, especially 2-acetylpyrrole, stable acylium ions are formed [3, 4]. It was therefore of interest to study the character of the dissociative ionization processes of pyrrole derivatives simultaneously containing an alkyl (aryl) substituent at the nitrogen atom and an acetyl group at the β-position of the heterocyclic ring. We obtained compounds I-IX by the reaction of 2-methyl-5-ethoxy-3-acetyl-4,5-dihydrofuran with primary amines. Their mass spectra are given in Table 1.

Table 1 shows that the stability of the molecular ions (M<sup>+</sup>) is of an order of magnitude of 10-14%, and decreases uniformly with increase in the length of the aliphatic radical, but in the case of N-aryl derivatives practically does not change in the presence of electron-dono

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