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V. G. GLUKHOVTSEV, S. V. ZAKHAROVA,

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Abstract

Full Text

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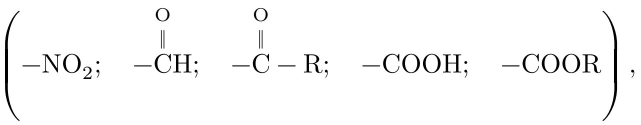
V. G. GLUKHOVTSEV, S. V. ZAKHAROVA,
Corresponding Member of the Academy of Sciences of the USSR A. D. PETROV

SYNTHESIS OF MONO- AND DIACETALS OF FURAN DIALDEHYDES

Furan aldehydes, ketones, acids, and their esters with electron-acceptor groups isolated from the furan ring enter into a substitutional addition reaction with α,β-unsaturated compounds, forming the corresponding difunctional furan derivatives ([1–6]).

Electron-acceptor groups



$$\left(-NO_2;\quad -\overset{\overset{O}{\|}}{C}H;\quad -\overset{\overset{O}{\|}}{C}-R;\quad -COOH;\quad -COOR\right),$$

conjugated with the furan ring, hinder electrophilic addition of α,β-unsaturated aldehydes and ketones to the furan ring. Weak nucleophilic substituents in the furan ring

$$(-C-OH;\quad -COR;\quad >C=C<)$$

impede the course of this reaction ([7,8]).

It seemed of interest to study the possibility of electrophilic addition of α,β-unsaturated aldehydes to furan acetals. It was found that furfural acetal, unlike furfural, reacts with crotonaldehyde in the presence of sulfuric acid according to the scheme:

$$C_4H_3O{-}CH(OCH_3)_2 + CH_3CH{=}CHCHO \xrightarrow{H_2SO_4} OHCCH_2CH(CH_3){-}C_4H_3O{-}CH(OCH_3)_2.$$

In this case, the yield of the reaction product proved to be analogous to the yield of the product from addition of crotonaldehyde to 2-(cyanopropoxymethyl)furan:

$$\mathrm{C_4H_3O{-}CH_2OCH_2CH_2CN + CH_3CH{=}CHCHO \xrightarrow{H_2SO_4} OHCCH_2CH(CH_3){-}C_4H_3O{-}CH_2OCH_2CH_2CN.}$$

At the same time, furfural acetal, unlike 2-(cyanopropoxymethyl)furan (^{7}), does not react with acrolein in the presence of acetic acid. Thus, in its influence on the furan ring, the acetal group occupies an intermediate position between an alkoxyl and a carbonyl group.

In accordance with this, as our experiments have shown, 2-(3 ,3 -dimethoxypropyl)furan, 2-(2 -methyl-3 ,3 -dimethoxypropyl)furan, and 2-(2 -ethyl-3 ,3 -dimethoxypropyl)furan react with acrolein in the presence of acetic acid in higher yield than with 2-(3 -oxopropyl)furan. In this way, monoacetals of furan dialdehydes were obtained, which previously could not be obtained directly from furan dialdehydes (^{9}).

$$\mathrm{C_4H_3O{-}CH_2CH(R)CH(OCH_3)_2 + CH_2{=}CHCHO \xrightarrow{CH_3COOH}}$$
$$\mathrm{OHCCH_2CH_2{-}C_4H_3O{-}CH_2CH(R)CH(OCH_3)_2 \xrightarrow[HCl]{CH_3OH}}$$
$$\mathrm{(CH_3O)_2CHCH_2CH_2{-}C_4H_3O{-}CH_2CH(R)CH(OCH_3)_2;} \quad R = \mathrm{H;\ CH_3;\ C_2H_5.}$$

The structures of the mono- and diacetals obtained were confirmed by data from the spectrum of combinational light scattering, as well as by the independent synthesis of 2,5-bis(3 -oxopropyl)furan and its diacetal according to the following scheme:

$$\mathrm{(furyl)CH_2CH_2CHO \xrightarrow[CH_3OH]{[} HCl](furyl)CH_2CH_2CH(OCH_3)_2}$$
$$\mathrm{(furyl)CH_2CH_2CH(OCH_3)_2 \xrightarrow[CH_2{=}CHCHO]{[} CH_3COOH]OHCCH_2CH_2(furyl)CH_2CH_2CH(OCH_3)_2}$$
$$\mathrm{OHCCH_2CH_2(furyl)CH_2CH_2CHO \xrightleftharpoons[CH_3OH,HCl]{[} H_2O, HCl](CH_3O)_2CHCH_2CH_2(furyl)CH_2CH_2CH(OCH_3)_2}$$

In the case of addition of crotonaldehyde to 2-(3 ,3 -dimethoxypropyl)furan and 2-(2 -methyl-3 ,3 -dimethoxypropyl)furan in the presence of sulfuric acid, along with monoacetals of the furan dialdehydes, furan dialdehydes are formed, judging from the analysis. After treatment of the resulting mixtures with methanol in the presence of hydrochloric acid, the corresponding furan diacetals were isolated in quantitative yield.

$$\text{(furyl)CH}_2\text{CH(R)CH(OCH}_3)_2 \xrightarrow[\text{CH}_3\text{CH=CHCHO}]{[} \text{H}_2\text{SO}_4]$$

$$\text{OHCCH}_2\text{CH(CH}_3\text{)(furyl)CH}_2\text{CH(R)CH(OCH}_3)_2$$
$$+\text{OHCCH}_2\text{CH(CH}_3\text{)(furyl)CH}_2\text{CH(R)CHO} \rightarrow$$

$$\rightarrow \xrightarrow[\text{CH}_3\text{OH}]{[} \text{HCl](CH}_3\text{O)}_2\text{CHCH}_2\text{CH(CH}_3\text{)(furyl)CH}_2\text{CH(R)CH(OCH}_3)_2, \quad \text{R} = \text{H};\ \text{CH}_3$$

Experimental Part

2-(2 -Methyl-3 ,3 -dimethoxypropyl)furan (I). To 95 g of 2-(2 -methyl-3 -oxopropyl)furan and 50 ml of methanol was added 0.4 ml of hydrochloric acid. After stirring for 30 min at 67°, the reaction mixture was neutralized with an aqueous solution of caustic potash, extracted with ether, and the ether was distilled off. From the residue there were obtained 108 g (85%) of I with b.p. 85° (8 mm); n_D^{20} 1.4546; d_4^{20} 1.0167.

Found, %: C 64.60; 64.78; H 8.91; 8.92
$C_{10}H_{16}O_3$. Calculated, %: C 65.19; H 8.76

2-(3 ,3 -Dimethoxypropyl)furan (II). From 40 g of 2-(3 -oxopropyl)furan and 80 ml of methanol in the presence of 0.2 ml of hydrochloric acid, as described above, 52.2 g (95%) of II were obtained, with b.p. 101° (20 mm); n_D^{20} 1.4540; d_4^{20} 1.0259. Literature data [10]: b.p. 109° (30 mm); n_D^{20} 1.4546.

2-(1 ,1 -Dimethoxymethyl)furan (III). From 192 g of furfural and 250 ml of methanol in the presence of 1 ml of hydrochloric acid, as described above, 182 g (64%) of III were obtained, with b.p. 62° (12 mm), n_D^{20} 1.4502; d_4^{20} 1.0678.

Literature data [11]: b.p. 55-56° (11 mm); n_D^{20} 1.4502.

2-(2 -Ethyl-3 ,3 -dimethoxypropyl)furan (IV). From 192 g of 2-(2 -ethyl-3 -oxopropyl)furan and 380 ml of methanol in the presence of 0.6 ml of hydrochloric acid, as described above, 263 g (98%) of IV were obtained, with b.p. 104° (8 mm); n_D^{20} 1.4585; d_4^{20} 0.9965.

Found, %: C 67.14; 67.33; H 9.21; 9.12
$C_{11}H_{18}O_3$. Calculated, %: C 66.63; H 9.15

2-(3 -Oxopropyl)-5-(3 ,3 -dimethoxypropyl)furan (V). To 28 g of (II), 0.2 g of hydroquinone, and 28 g of acetic acid, 15 g of acrolein was added with stirring. After stirring for 4 h, the reaction mixture was diluted with water, extracted with ether, and the ethereal extracts were neutralized with sodium bicarbonate. After removal of the ether, 18.2 g (50%) of V was obtained, b.p. 120° (2.5 mm); n_D^{20} 1.4795; d_4^{20} 1.0831.

Found, %: C 63.63; 63.58; H 8.02; 8.09
$C_{12}H_{18}O_4$. Calculated, %: C 63.74; H 8.01

IR spectrum ($\Delta\nu$, cm^{-1}): 803 (0); 863 (0); 917 (0); 967 (2 sh); 1017 (1); 1055 (1 sh); 1130 (2); 1169 (1); 1238 (1); 1295 (2); 1340 (2); 1374 (2 sh); 1395 (3); 1442 (4); 1467 (2 sh); 1516 (3); 1573 (10); 1613 (5); 1726 (2); 2835 (3); 2908 (3 sh); 2934 (3 sh).

2-(3 -Oxopropyl)-5-(2 -methyl-3 ,3 -dimethoxypropyl)furan (VI). From 20 g of I and 15 g of acrolein in the presence of 0.2 g of hydroquinone and 19 ml of acetic acid, as described above, 11.5 g (44%) of VI was obtained, b.p. 117° (2 mm); n_D^{20} 1.4750; d_4^{20} 1.0599.

Found, %: C 64.85; 64.73; H 8.26; 8.11
$C_{13}H_{20}O_4$. Calculated, %: C 64.97; H 8.38

IR spectrum ($\Delta\nu$, cm^{-1}): 860 (0); 966 (2 sh); 1018 (2); 1048 (v.sh); 1075 (1 sh); 1105 (1 sh); 1178 (v.sh); 1215 (v.sh); 1278 (1 sh); 1340 (1 sh); 1392 (2); 1438 (2); 1467 (2 sh); 1508 (4); 1570 (6); 1614 (1); 1666 (1); 1723 (1); 2832 (1); 2903 (2 sh); 2925 (2 sh).

2-(3 -Oxopropyl)-5-(2 -ethyl-3 ,3 -dimethoxypropyl)furan (VII). From 35 g of IV and 20 g of acrolein in the presence of 0.2 g of hydroquinone and 34 ml of acetic acid, as described above, 17.1 g (38%) of VII was obtained, b.p. 149° (6 mm); n_D^{20} 1.4822; d_4^{20} 1.0585.

Found, %: C 65.92; 65.98; H 8.63; 8.68
$C_{14}H_{22}O_4$. Calculated, %: C 66.11; H 8.71

2,5-Bis-(3,3-dimethoxypropyl)furan (VIII). To 6 g of V and 20 ml of methanol, 0.1 ml of hydrochloric acid was added. After stirring for 1 h at 67° and work-up analogous to I, 6.7 g (93%) of VIII was obtained, b.p. 125° (3 mm); n_D^{20} 1.4618; d_4^{20} 1.0452.

Found, %: C 61.73; 61.92; H 9.01; 8.96
$C_{14}H_{25}O_5$. Calculated, %: C 61.74; H 8.88

IR spectrum ($\Delta\nu$, cm^{-1}): 970 (0); 1018 (1); 1068 (0); 1125 (1 sh); 1280 (1); 1345 (v.sh); 1375 (1 sh); 1430 (4 sh); 1470 (4 sh); 1504 (2); 1570 (8); 1620 (1); 2830 (2p); 2877 (1 sh); 2925 (2 sh); 2950 (2 sh).

2-(3 ,3 -Dimethoxypropyl)-5-(2 -methyl-3 ,3 -dimethoxypropyl)furan (IX). From 4.5 g of VI and 25 ml of methanol in the presence of 0.1 M hydrochloric acid, analogously to VIII, 4.4 g (82%) of IX was obtained, b.p. 129° (3 mm); n_D^{20} 1.4620; d_4^{20} 1.0341.

Found, %: C 62.58; 62.45; H 9.06; 9.21
$C_{15}H_{26}O_5$. Calculated, %: C 62.91; H 9.15

2-(3 ,3 -Dimethoxypropyl)-5-(2 -ethyl-3 ,3 -dimethoxypropyl)furan (X). From 12 g of VII and 35 ml of methanol in the presence of 0.1 ml of hydrochloric acid, as described above, 13.2 g (93%) of X was obtained, b.p. 137° (2.5 mm); n_D^{20} 1.4665; d_4^{20} 1.0285.

Found, %: C 63.85; 63.89; H 9.29; 9.24
$C_{16}H_{28}O_5$. Calculated, %: C 63.97; H 9.39

2-(3 ,3 -Dimethoxypropyl)-5-(1 -methyl-3 ,3 -dimethoxypropyl)furan (XI). To 26 g of (II), 30 g of crotonaldehyde, and 0.2 g of hydroquinone, 0.2 ml of 50% sulfuric acid was added. After stirring for 2 h and work-up analogous to (V), 12 g of a mixture was obtained, b.p. 122° (3.5 mm); n_D^{20} 1.4824; d_4^{20} 1.0725. From 7.5 g of this mixture and 25 ml of methanol in the pres—

in the presence of 0.2 ml of hydrochloric acid, after stirring for one hour at 67° and the usual work-up, 8.8 g of XI was obtained, b.p. 118° (2 mm); n_D^{20} 1.4620; d_4^{20} 1.0353.

Found, %:	C 62.82; 62.87;	H 9.09; 9.04
$C_{16}H_{28}O_5$. Calculated, %:	C 62.91;	H 9.15

2-(1 -Methyl-3 ,3 -dimethoxypropyl)-5-(2 -methyl-3 ,3 -dimethoxypropyl)furan (XII). From 20 g of I and 18 g of crotonaldehyde, in the presence of 0.2 g of hydroquinone and 0.2 ml of 50% sulfuric acid, 7.5 g of a mixture was obtained as described above, b.p. 107° (2 mm); n_D^{20} 1.4765; d_4^{20} 1.0360. From 5 g of this mixture and 25 ml of methanol, in the presence of 0.2 ml of hydrochloric acid, 5.5 g of XII was obtained as described above, b.p. 133° (4 mm); n_D^{20} 1.4594; d_4^{20} 1.0166.

Found, %:	C 63.92; 63.89;	H 9.31; 9.35
$C_{15}H_{28}O_5N$. Calculated, %:	C 63.97;	H 9.39

2-(1 ,1 -Dimethoxymethyl)-5-(1 -methyl-3 -oxopropyl)furan (XIII). From 22 g of III and 20 g of crotonaldehyde, in the presence of 0.2 g of hydroquinone and 0.2 ml of 50% sulfuric acid, 3.8 g (12%) of XIII was obtained as described earlier, b.p. 104° (3 mm); n_D^{20} 1.5052; d_4^{20} 1.0914.

Found, %:	C 62.80; 62.70;	H 7.59; 7.53
$C_{11}H_{16}O_4$. Calculated, %:	C 62.24;	H 7.59

2-(Cyanopropoxymethyl)-5-(1 -methyl-3 -oxopropyl)furan (XIV). From 34 g of 2-(cyanopropoxymethyl)furan and 30 g of crotonaldehyde, in the presence of 0.2 g of hydroquinone and 0.7 ml of 50% sulfuric acid, analogously to XIII, 6 g (12%) of XIV was obtained, b.p. 167° (4 mm); n_D^{20} 1.4891; d_4^{20} 1.1085.

Found, %:	C 65.11; 64.97;	H 6.84; 6.88
$C_{12}H_{15}O_3N$. Calculated, %:	C 65.13;	H 6.83

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

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Note: Figure translations are in progress. See original paper for figures.