

Synthesis of Cyclic Derivatives of Carbonyl Compounds of Furan Series

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Abstract—Cyclic acetals of furan aldehydes (furfural, 5-hydroxymethylfuran-2-carbaldehyde and furan-2,5-dicarbaldehyde) and alcohols (ethylene glycol and 2-sulfanylethanol) were synthesized. The effect of the ratio of the starting reagents on the yield of acetals obtained was studied.

Keywords: cyclic acetals, furfural, 5-hydroxymethylfuran-2-carbaldehyde, furan-2,5-dicarbaldehyde, ethylene glycol, 2-sulfanylethanol

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Furfural, 5-hydroxymethylfuran-2-carbaldehyde and their derivatives are formed as the main products of the pentosans processing. They are widely used in small-scale chemistry, fine organic synthesis and for the production of polymeric materials and drugs [1–6]. The synthesis of biodegradable oligoesters and polyesters as well as amides based on 5-hydroxymethylfuran-2-carbaldehyde and furan-2,5-dicarboxylic acid has been described earlier [7]. Furan-2,5-dicarbaldehyde is used to obtain various bisamines and polyamides [8, 9]. The use of 5-hydroxymethylfuran-2-carbaldehyde and furan-2,5-dicarbaldehyde for the alkylation of aromatic hydrocarbons makes it possible to obtain polycyclic compounds important in the synthesis of biologically active preparations [10].

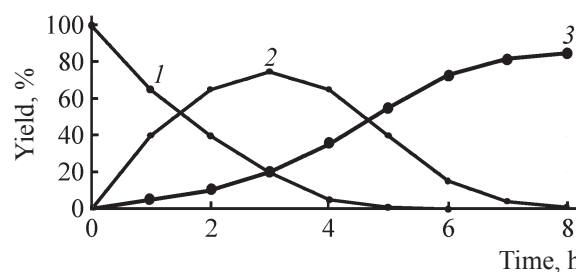
Herein, we reported the synthesis of cyclic acetals of some carbonyl compounds of the furan series. The acid-catalyzed reaction of furfural **1** and 5-hydroxymethylfuran-2-carbaldehyde **2** with an excess of ethylene glycol **4** in non-polar solvents (with water removal by the Dean–Stark method) led to the formation of the corresponding 1,3-dioxolanes **5**, **6** with quantitative yield (Scheme 1).

Furan-2,5-dicarbaldehyde **3** reacted with an equimolar amount of glycol **4** to form mono- (**7**) and diacetal (**8**) in a 6 : 1 ratio. When using a 6-fold excess of diol **4**, compound **8** was isolated as the main condensation product. The Figure shows the kinetic curves of the consumption of the starting dialdehyde **3** and the accumulation of mono- (**7**) and diacetal (**8**). Thus, when using a

6-fold molar excess of glycol **4** (80°C) in the presence of *p*-toluenesulfonic acid, 90% conversion of the starting dialdehyde **3** was achieved in 3.5 h, the maximum yield of monoacetal **7** (75%) was observed after 2 h. For the formation of diacetal **8** with a yield of more than 70%, at least 6 h are required.

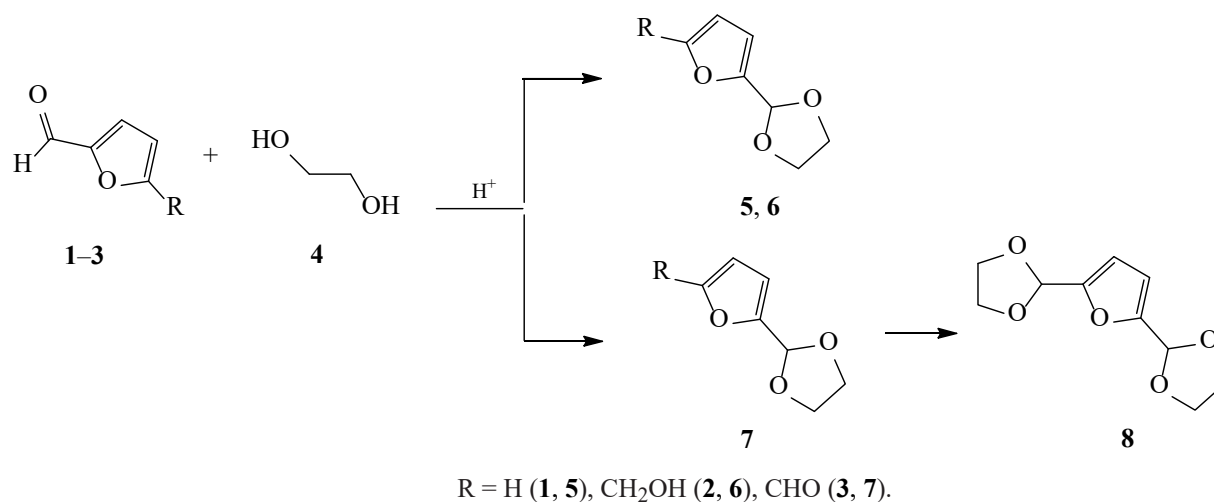
Condensation of dialdehyde **3** with 2-sulfanyl ethanol **9** at an equimolar reagent ratio led to the formation of mono- (**10**) and bicyclic (**11**) reaction products (Scheme 2). The maximum yield (90%) of compound **11** was achieved with a molar ratio of reactants **3** : **9** = 1 : 4 for 5 h.

We compared the activity of glycol **4** and 2-sulfanyl ethanol **9** in the reaction with dialdehyde **3** by the method of competitive reactions. At the initial stages, when mainly mono derivatives **7** and **10** are formed, judging by their yields, ethylene glycol **4** is 1.5 times

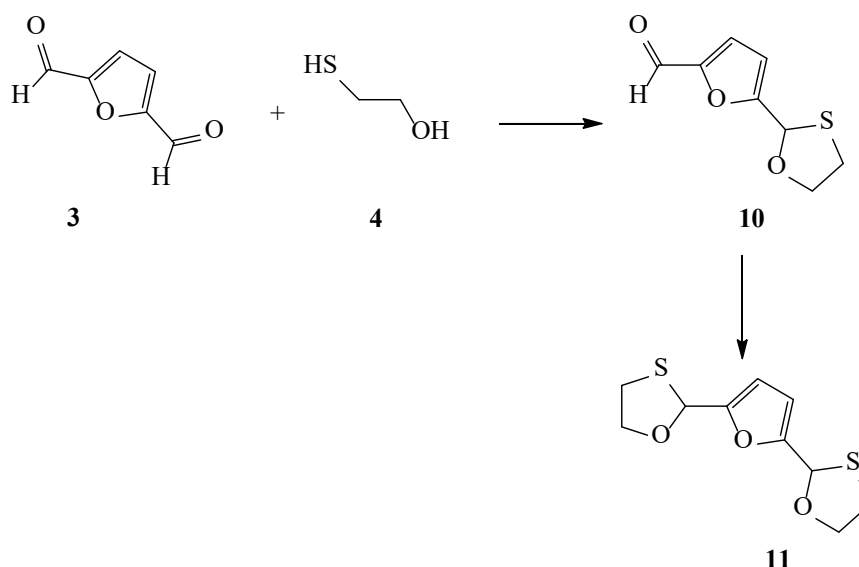


The kinetic curves of the consumption of furan-2,5-dicarbaldehyde **3** (**1**) and the accumulation of mono- **7** (**2**) and diacetal **8** (**3**) in the reaction with glycol **4** (molar ratio **3** : **4** = 1 : 6, 80°C).

Scheme 1.



Scheme 2.



more active than 2-sulfanyl ethanol **9** (initial reagent ratio **3** : **4** : **9** = 0.3 : 1 : 1).

Structure of acetals of ethylene glycol **5–8** and 2-sulfanyl ethanol **10**, **11** was confirmed by NMR spectroscopy and chromatography-mass spectrometry methods.

In conclusion, cyclic acetals of some furanaldehydes and ethylene glycol, and mercaptoethanol were synthesized. The effect of the ratio of the starting reagents on the yield of acetals obtained was revealed. The reaction between 2,5-diformylfuran with an equimolar amount of ethylene glycol resulted in the formation of 5-(1,3-dioxolan-2-yl)-2-furylaldehyde and 2,2-furan-2,5-diyl-1,3-dioxolane in the ratio of 6 : 1. 2,2-Furan-2,5-

diyl-1,3-dioxolane was the main product, when using a 6-fold excess of 1,2-ethanediol with respect to dialdehyde. Ethylene glycol was shown to be 1.5 times more active than mercaptoethanol with respect to 2,5-diformylfuran.

EXPERIMENTAL

NMR spectra were recorded on a Bruker AVANCE-500 spectrometer (500.13 MHz) from $CDCl_3$ solutions relative to internal tetramethylsilane. Chromatographic analysis of the reaction products was performed on a HRGS 5300 Mega Series Carlo Erba chromatograph with a flame ionization detector (carrier gas – helium, flow rate 30 mL/min, column length 25 m, temperature 50–280°C, programmed heating at a rate of 8 deg/min,

detector temperature 250°C, evaporator temperature 300°C). Chromatography-mass spectra were recorded on a Chromatek-Crystal 5000.2 instrument (capillary quartz column 30 m, analysis time 20 min, ion source temperature 260°C, transition line temperature 300°C, scanning range of 30–300 Da, pressure 37–43 mTorr, carrier gas—helium, heating rate of 20 deg/min). To obtain mass spectra of the compounds, the electron impact ionization method was used.

General procedure for the synthesis of acetals of the furan series. A mixture of 0.06 mol (0.12 mol in the case of dialdehyde **3**) of alcohol, 0.02 mol of aldehyde, 0.2 g of *p*-TsOH and 40 mL of benzene (or toluene) was stirred at 80°C for 3–8 h with a Dean–Stark trap until the calculated amount of water was isolated. After the reaction completed, the mixture was dried with calcined calcium chloride, and the filtrate was evaporated. The reaction products were isolated by vacuum distillation.

2-(Fur-2-yl)-1,3-dioxolane (5). Yield 92%, bp 100–101°C (7 mmHg). The physico-chemical characteristics match those reported in [11].

[5-(1,3-Dioxolan-2-yl)furan-2-yl]methanol (6).¹ Yield 90%, bp 150–151°C (3 mmHg), a colorless liquid that gradually crystallizes upon cooling. ¹H NMR spectrum, δ , ppm: 3.88 t (2H, CH₂O, J = 3.1 Hz), 4.03 d (2H, CH₂O, J = 3.1 Hz), 4.50 s (2H, CH₂OH), 5.95 s (1H, CHO), 6.45 d (1H, CH=, J = 3.0 Hz), 6.50 d (1H, CH=, J = 3.0 Hz). ¹³C NMR spectrum, δ_C , ppm: 56.73 (CH₂OH), 65.82 (CH₂O), 95.77 (CH), 113.44 (CH=), 120.98 (CH=), 151.01 (C=), 162.05 (C=). Mass spectrum, m/z (I_{rel} , %): 170 (20), 139 (20), 125 (100), 95 (35), 73 (73).

5-(1,3-Dioxolan-2-yl)furan-2-carbaldehyde (7). Yield 75%, bp 149–150°C (3 mmHg), a colorless liquid that gradually crystallizes upon cooling. ¹H NMR spectrum, δ , ppm: 3.90 t (2H, CH₂O, J = 3.1 Hz), 4.00 d (2H, CH₂O, J = 3.1 Hz), 5.88 s (1H, CH), 6.50 d (1H, CH=, J = 3.0 Hz), 7.10 s (1H, CH=), 9.50 s (1H, CHO). ¹³C NMR spectrum, δ_C , ppm: 65.33 (CH₂O), 97.54 (CH), 128.27 (CH=), 148.84 (C=), 151.83 (C=), 178.01 (CHO). Mass spectrum, m/z (I_{rel} , %): 168 (5), 139 (10), 123 (100), 95 (25), 73 (15).

2,2'-Furan-2,5-diylbis(1,3-dioxolane) (8). Yield 80%, bp 159–161°C (3 mmHg), a colorless liquid that gradually crystallizes upon cooling. ¹H NMR spectrum, δ , ppm: 3.92 t (4H, CH₂O, J = 3.1 Hz), 4.00 t (4H, CH₂O, J =

3.1 Hz), 5.82 s (2H, CH), 6.53 d (1H, CH=, J = 3.0 Hz), 7.10 s (1H, CH=). ¹³C NMR spectrum, δ_C , ppm: 65.33 (CH₂O), 97.54 (CH), 128.27 (CH=), 151.83 (C=). Mass spectrum, m/z (I_{rel} , %): 212 (5), 139 (5), 123 (100), 95 (20), 73 (50).

5-(1,3-Oxathiolan-2-yl)furan-2-carbaldehyde (10). Yield 78%, bp 149–150°C (3 mmHg), a colorless liquid that gradually crystallizes upon cooling. ¹H NMR spectrum, δ , ppm: 3.70 t (2H, CH₂S, J = 6.2 Hz), 4.00 d (2H, CH₂O, J = 6.2 Hz), 5.88 s (1H, CH), 6.50 d (1H, CH=, J = 4.9 Hz), 7.10 s (1H, CH=), 9.50 s (1H, CHO). ¹³C NMR spectrum, δ_C , ppm: 32.77 (CH₂S), 71.55 (CH₂O), 87.54 (CH), 109.54 (CH=), 154.04 (C=), 178.01 (CHO). Mass spectrum, m/z (I_{rel} , %): 184 (22), 183 (70), 155 (8), 95 (25), 89 (100).

2,2'-Furan-2,5-diylbis(1,3-oxathiolane) (11). Yield 80%, bp 159–161°C (2 mmHg), a colorless liquid that gradually crystallizes upon cooling. ¹H NMR spectrum, δ , ppm: 3.90 t (4H, CH₂S, J = 6.1 Hz), 4.10 d (4H, CH₂O, J = 6.1 Hz), 5.82 s (2H, CH), 6.53 d (1H, CH=, J = 4.0 Hz), 7.10 s (1H, CH=). ¹³C NMR spectrum, δ_C , ppm: 33.45 (CH₂S), 72.20 (CH₂O), 87.77 (CH), 110.38 (CH=), 151.05 (C=). Mass spectrum, m/z (I_{rel} , %): 244 (20), 183 (60), 155 (25), 95 (5), 89 (100).

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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¹ Physico-chemical characteristics coincide with those for commercial sample (<https://www.abcr.de/ru/>).

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