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# CHEMISTRY

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## Abstract

## Full Text

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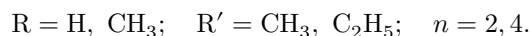
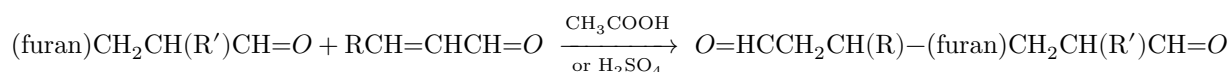
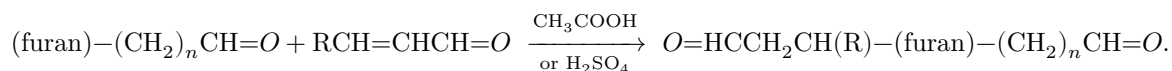
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Corresponding Member of the Academy of Sciences of the USSR A. D. PETROV

# SYNTHESIS OF DIALDEHYDES OF THE FURAN SERIES

Furan alcohols, acids, esters, and difuran ketones react in an acidic medium with  $\alpha, \beta$ -unsaturated aldehydes and ketones according to the Michael reaction type (<sup>1-3</sup>).

It seemed of interest to study furan aldehydes in this reaction with the aim of obtaining little-studied furan dialdehydes. The known methods for the synthesis of furan dialdehydes do not make it possible to obtain dialdehydes of different structures (<sup>4-7</sup>).

It was found that furan aldehydes in which the carbonyl group is conjugated with the furan nucleus do not react in an acidic medium with  $\alpha, \beta$ -unsaturated aldehydes. At the same time, furan aldehydes with a carbonyl group not conjugated with the furan nucleus enter into this reaction, forming symmetrical or unsymmetrical dialdehydes:



Furylacetic aldehyde ( $n = 1$ ) polymerizes readily in the presence of acids, alkalis, atmospheric oxygen, and also when the temperature is raised (<sup>8</sup>).

The furan-series dioxo derivatives synthesized by us, according to data from the Ordzhonikidze All-Union Scientific Research Chemical-Pharmaceutical Institute, possess biological activity against the influenza virus APR-8. From 2,5-bis-(3'-oxopropyl)-furan and isonicotinic acid hydrazide, diisoniazone 2,5-(3'-oxopropyl)-furan was obtained, which, according to available data (<sup>9</sup>), may possess antitubercular activity. It is interesting that when aldehyde and ketone groups are present in the molecule of a furan compound, the aldehyde group reacts first with isonicotinic acid hydrazide.

## Experimental Part

The starting 2-(3'-oxopropen-1'-yl)-furan, 2-(2'-methyl-3'-oxopropen-1'-yl)-furan, and 2-(5'-oxopentaliene-1',3'-yl)-furan were obtained by the described method (<sup>10</sup>). In the synthesis of 2-(2'-ethyl-3'-oxopropen-1'-yl)-furan with b.p. 94° (2 mm);  $n_D^{20}$  1.5948;  $d_4^{20}$  1.0621 (literature data (<sup>11</sup>),  $n_D^{16}$  1.595;  $d_4^{16}$  1.065), a product was also obtained (ratio 6.5 : 1) with b.p. 64° (2 mm);  $n_D^{20}$  1.5638;  $d_4^{20}$  1.0797, apparently 2-(2'-formylbuten-2'-yl)-furan (literature data (<sup>12</sup>),  $n_D^{20}$  1.5668;  $d_4^{20}$  1.061).

Upon hydrogenation of the above-mentioned aldehydes in ethanol over Raney nickel at 20° and a hydrogen pressure of 100 atmospheres, the following furan aldehydes were obtained:

2-(3'-oxopropyl)-furan, b.p. 81° (16 mm);  $n_D^{20}$  1.4760;  $d_4^{20}$  1.0681 (literature data (<sup>6</sup>), b.p. 81° (17 mm);  $n_D^{19}$  1.4772,  $d_4^{19}$  1.0574).

**2-(2'-Methyl-3'-oxopropyl)furan**, b.p. 81° (15 mm);  $n_D^{20}$  1.4711;  $d_4^{20}$  1.0364;  $MR_D$  found 37.26, calculated 37.66.

Found, %: C 69.48, 69.56; H 7.25, 7.31  
C<sub>8</sub>H<sub>10</sub>O<sub>2</sub>. Calculated, %: C 69.54; H 7.29

**2-(5'-Oxopentyl)furan**, b.p. 51° (2 mm);  $n_D^{20}$  1.4720;  $d_4^{20}$  1.0186;  $MR_D$  found 41.83; calculated 42.28.

Found, %: C 70.95, 70.43; H 8.28, 8.23  
C<sub>9</sub>H<sub>12</sub>O<sub>2</sub>. Calculated, %: C 71.02; H 7.94

**2-(2'-Ethyl-3'-oxopropyl)furan**, b.p. 96° (18 mm);  $n_D^{20}$  1.4839;  $d_4^{20}$  1.0323;  $MR_D$  found 42.17; calculated 42.28.

Found, %: C 71.00, 71.09; H 7.93, 8.05  
C<sub>9</sub>H<sub>12</sub>O<sub>2</sub>. Calculated, %: C 71.02; H 7.94

**2,5-Bis-(3'-oxopropyl)furan**. To a mixture of 30 g of 2-(3'-oxopropyl)furan, 3 g of acetic acid, 16 ml of water, and 0.2 g of hydroquinone, 14 g of acrolein was added over 5 minutes. After stirring for 1.5 hours at 55°, the reaction mixture was diluted with water and extracted with ether. The ethereal extracts were neutralized with sodium bicarbonate and the ether was distilled off. There were obtained 9 g of 2-(3'-oxopropyl)furan and 15 g (34.5%) of 2,5-bis-(3'-oxopropyl)furan with b.p. 107° (2 mm); m.p. 41-42°. Literature data (<sup>16</sup>): b.p. 150-153° (10 mm); m.p. 41-42°.

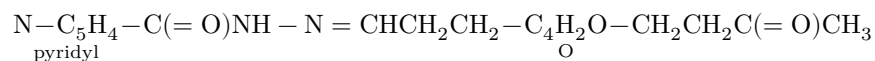
**Diisoniazone of 2,5-bis-(3'-oxopropyl)furan\***, m.p. 184°.

Found, %: C 63.15, 63.25; H 5.17, 5.29  
C<sub>22</sub>H<sub>22</sub>N<sub>6</sub>O<sub>3</sub>. Calculated, %: C 63.14; H 5.30

**Diisoniazone of 2-(3'-oxopropyl)-5-(3'-oxobutyl)furan\***, m.p. 193°.

Found, %: C 63.79, 63.61; H 5.69, 5.32  
 $C_{23}H_{24}N_6O_3$ . Calculated, %: C 68.87; H 5.59

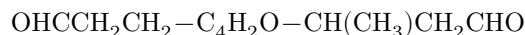
**Isoniazide of 2(3'-oxypropyl)-5-(3'-oxobutyl)furan\***



m.p. 110°.

Found, %: C 65.27, 65.21; H 6.10, 6.12  
 $C_{17}H_{19}N_3O_3$ . Calculated, %: C 65.15; H 6.11

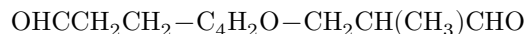
**2-(3'-Oxopropyl)-5-(1'-methyl-3'-oxopropyl)furan**



From 31 g of 2-(3'-oxopropyl)furan and 1.8 g of crotonaldehyde, in the presence of 0.25 ml of sulfuric acid, 18 ml of water, and 0.2 g of hydroquinone, there were obtained, as described above, 3.5 g of crotonaldehyde, 8.5 g of 2-(3'-oxopropyl)furan, and 22.8 g (47%) of 2-(3'-oxopropyl)-5-(1'-methyl-3'-oxopropyl)furan with b.p. 112° (2 mm);  $n_D^{20}$  1.4912;  $d_4^{20}$  1.0871;  $MR_D$  found 51.76; calculated 51.73.

Found, %: C 68.09, 68.14; H 7.30, 7.21  
 $C_{11}H_{14}O_3$ . Calculated, %: C 68.02; H 7.26

**2-(3'-Oxopropyl)-5-(2'-methyl-3'-oxopropyl)furan**



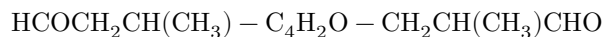
From 19 g of 2-(2'-methyl-3'-oxopropyl)furan and 8 g of acrolein, in the presence of 3 g of acetic acid, 15 ml of water, and 0.2 g of hydroquinone, there were obtained, as described above, 4 g of 2-(2'-methyl-3'-oxopropyl)furan and 9 g (33.7%) of 2-(3'-oxo-

\* Obtained by L. N. Pavlov (Akrikhin plant).

propyl)-5-(2-methyl-3'-oxopropyl)furan with b.p. 117° (3 mm),  $n_D^{20}$  1.4900;  $d_4^{20}$  1.0863;  $MR_D$  found 51.59, calculated 51.73.

Found, %: C 67.56; 67.65; H 7.30; 7.28  
 $C_{11}H_{14}O_3$ . Calculated, %: C 68.02; H 7.27

## 2-(1'-methyl-3'-oxopropyl)-5-(2'-methyl-3'-oxopropyl)furan

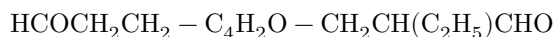


From 28 g of 2-(2'-methyl-3'-oxopropyl)furan, 15.0 g of crotonaldehyde in the presence of 0.2 ml of sulfuric acid, 17 ml of water, and 0.2 g of hydroquinone, there were obtained, as described above, 11 g of 2-(2'-methyl-3'-oxopropyl)furan and 16.5 g (38%) of 2-(1'-methyl-3'-oxopropyl)-5-(2'-methyl-3'-oxopropyl)furan with b.p. 106° (2 mm);  $n_D^{20}$  1.4850;  $d_4^{20}$  1.0577;  $MR_D$  found 56.42, calculated 56.54.

Found, %: C 69.54; 69.53; H 7.96; 7.91  
 $\text{C}_{12}\text{H}_{16}\text{O}_3$ . Calculated, %: C 69.20; H 7.74

Raman spectrum\* ( $\Delta\nu$ ,  $\text{cm}^{-1}$ ): 920 (1); 967 (3); 1018 (4); 1044 (1); 1080 (1); 1105 (0sh); 1170 (0sh); 1218 (0sh); 1245 (0sh); 1276 (1sh); 1315 (3sh); 1340 (4sh); 1378 (3sh); 1395 (4sh); 1427 (2); 1454 (5sh); 1473 (5sh); 1563 (10); 1608 (5); 1628 (3); 1718 (4); 2877 (5sh); 2502 (4sh); 2935 (5sh); 2977 (5).

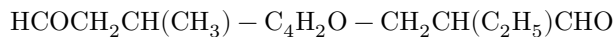
## 2-(3'-oxopropyl)-5-(2'-ethyl-3'-oxopropyl)furan



From 22 g of 2-(2'-ethyl-3'-oxopropyl)furan and 9 g of acrolein in the presence of 3 g of acetic acid, 18 ml of water, and 0.2 g of hydroquinone, there were obtained, as described above, 12 g of 2-(2'-ethyl-3'-oxopropyl)furan and 14.5 g (47%) of 2-(3'-oxopropyl)-5-(2'-ethyl-3'-oxopropyl)furan with b.p. 120° (2.5 mm);  $n_D^{20}$  1.4908;  $d_4^{20}$  1.0726;  $MR_D$  found 56.21, calculated 56.15.

Found, %: C 69.12; 69.14; H 7.89; 7.83  
 $\text{C}_{12}\text{H}_{16}\text{O}_3$ . Calculated, %: C 69.20; H 7.74

## 2-(1'-methyl-3'-oxopropyl)-5-(2'-ethyl-3'-oxopropyl)furan



From 31 g of 2-(2'-ethyl-3'-oxopropyl)furan and 15 g of crotonaldehyde in the presence of 0.2 ml of sulfuric acid, 20 ml of water, and 0.2 g of hydroquinone, there were obtained, as described above, 9 g of 2-(2'-ethyl-3'-oxopropyl)furan and 19 g (41%) of 2-(1'-methyl-3'-oxopropyl)-5-(2'-ethyl-3'-oxopropyl)furan with b.p. 116° (2.5 mm);  $n_D^{20}$  1.4941;  $d_4^{20}$  1.0704;  $MR_D$  found 60.46, calculated 60.76.

Found, %: C 68.40; 68.61; H 8.28; 8.11  
 $\text{C}_{12}\text{H}_{16}\text{O}_3$ . Calculated, %: C 69.20; H 7.74

\* The Raman spectrum was recorded by G. K. Gaivoronskaya, to whom the authors express their gratitude.

## 2-(3'-Oxopropyl)-5-(5'-oxopentyl)furan



From 13.5 g of 2-(5'-oxopentyl)furan, 6 g of acrolein, 2 g of acetic acid, 13 ml of water, and 0.2 g of hydroquinone, as described above, there were obtained 3 g of 2-(5'-oxopentyl)furan and 7 g (38%) of 2-(3'-oxopropyl)-5-(5-oxopentyl)furan with b.p. 108° (2 mm);  $n_D^{20}$  1.4920;  $d_4^{20}$  1.0768;  $MR_D$  found 56.11, calculated 56.14.

Found, %: C 69.50; 69.64; H 7.99; 7.88  
 $\text{C}_{12}\text{H}_{16}\text{O}_3$ . Calculated, %: C 69.20; H 7.74

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

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