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# Chemistry

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## Abstract

## Full Text

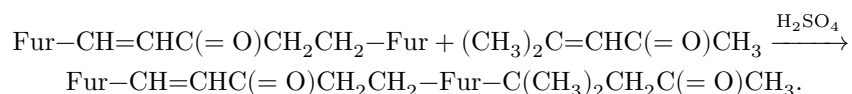
### *Chemistry*

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## SYNTHESIS OF OXO DERIVATIVES OF THE DIFURAN SERIES

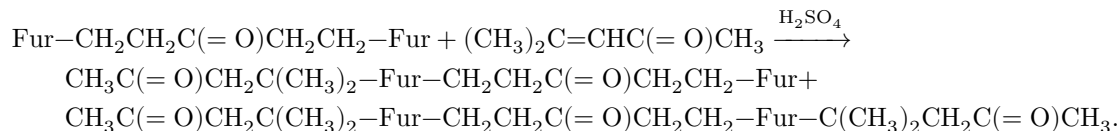
The ability of furan derivatives to react with  $\alpha, \beta$ -unsaturated aldehydes and ketones by the Michael reaction is determined by the nature of the functional groups and by their position in the side chain of the furan compounds (<sup>1,2</sup>). It seemed of interest to study, in this reaction, the behavior of difuran compounds containing furan rings that are both equivalent and nonequivalent with respect to the functional groups. One of the most accessible difuran compounds is 1,5-difurylpentadien-1,4-one-3, in which the furan rings are equivalent. However, it was found that 1,5-difurylpentadien-1,4-one-3 reacts neither with acrolein in the presence of acetic acid nor with mesityl oxide in the presence of sulfuric acid. This is apparently explained by the influence of the electronegative carbonyl group, conjugated through double bonds with the furan rings, which reduces the mobility of the hydrogen atoms in the furan rings. A similar influence is exerted by electronegative groups located in the  $\alpha$ -position of the side chain of a furan compound (<sup>2</sup>).

When a carbonyl group not conjugated with one of the furan rings is present in the side chain of a difuran compound, for example in 1,5-difurylpenten-1-one-3, only one molecule of mesityl oxide is added:

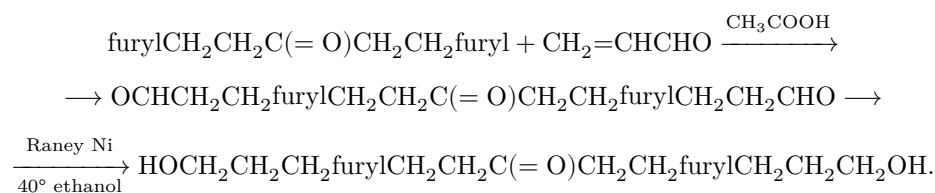


With acrolein in the presence of acetic acid, the reaction of 1,5-difurylpenten-1-one-3 proceeds analogously, but the reaction product cannot be isolated in pure form because of its polymerization during distillation.

In the case of 1,5-difurylpentanone-3, in which both furan rings are not conjugated with the carbonyl group, one or two molecules of mesityl oxide are added, depending on the ratio of the reaction components:



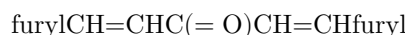
The reaction of 1,5-difurylpentanone-3 with acrolein proceeds similarly; however, only the monoaldehyde can be isolated, since the dialdehyde polymerizes during distillation. With an excess of acrolein only the dialdehyde is formed. The formation of the dialdehyde was proved by hydrogenation of the crude reaction product to the corresponding diol, which distills without polymerization:



The 1,5-difurylpentanone-3 that did not react with acrolein was hydrogenated under these conditions to 1,5-bis(tetrahydrofuryl)-pentanone-3, which previously could not be obtained by direct hydrogenation of 1,5-difurylpentadien-1,4-one-3 over Raney nickel <sup>(5)</sup>.

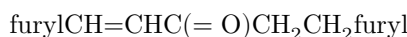
## Experimental Part

### 1,5-Difurylpentadien-1,4-one-3



To a mixture of 240 g of furfural and 70 g of acetone, with stirring and cooling to  $-5^\circ$ , 12.5 ml of 25% sodium hydroxide was added over 15 min. After stirring for 3 h, the reaction mixture was neutralized with dilute sulfuric acid, extracted with ether, and the ether was distilled off. This gave 87 g of 1-furylbuten-1-one-3 (yield 25.5%) with b.p.  $78^\circ$  (6 mm), and 124 g of 1,5-difurylpentadien-1,4-one-3 with b.p.  $192^\circ$  (6 mm); m.p.  $57-57.5^\circ$ ; yield 49%. Literature data <sup>(3)</sup>: m.p.  $60-61^\circ$ .

### 1,5-Difurylpenten-1-one-3



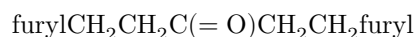
To a mixture of 50 g of 1-furylbutanone-3 and 38 g of furfural, with stirring and cooling to  $5^\circ$ , 10 ml of 20% sodium hydroxide was added. After stirring for 3 h, the reaction mixture was neutralized with acetic acid, extracted with ether,

and the ether was distilled off. This gave 42 g of 1,5-difurylpenten-1-one-3 with b.p. 138° (3 mm);  $n_D^{20}$  1.5730,  $d_4^{20}$  1.1161; yield 53.5%.

$C_{13}H_{12}O_3$ . Found, %: C 72.21; 72.05; H 5.89; 5.61

Calculated, %: C 72.20; H 5.59

### 1,5-Difurylpentanone-3



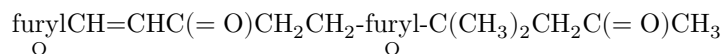
was obtained by hydrogenation in ethanol of 1,5-difurylpentadien-1,4-one-3 over Raney nickel.

at 20° and a hydrogen pressure of 150 atm, b.p. 136.5° (3.5 mm);  $n_D^{20}$  1.5025,  $d_4^{20}$  1.1011. The ketazine of 1,5-difurylpentan-3-one has b.p. 239° (4 mm); m.p. 46.5–47.5°.

Found, %: C 72.08; 71.89; H 5.89; 5.61

$C_{23}H_{28}N_2O_4$ . Calculated, %: C 72.19; H 6.52

Literature data <sup>(4)</sup>, b.p. 148–149° (3 mm). **1-Furyl-5-(1',1'-dimethyl-3'-oxobutylfuryl)-penten-1-one-3**

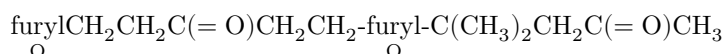


To a mixture of 14.5 g of 1,5-difurylpenten-1-one-3, 12 g of mesityl oxide, and 0.2 g of hydroquinone, 0.5 ml of 50% sulfuric acid was added. After stirring for 6 h, the reaction mixture was diluted with water and extracted with ether. The ether extracts were neutralized with sodium bicarbonate, washed with water, and the ether was distilled off. From the residue there were obtained 4.5 g of mesityl oxide, 5.5 g of 1,5-difurylpenten-1-one-3, and 8 g of 1-furyl-5-(1',1'-dimethyl-3'-oxobutylfuryl)-penten-1-one-3 with b.p. 193° (3 mm);  $n_D^{20}$  1.5608;  $d_4^{20}$  1.1021; yield 38.2%.

Found, %: C 72.50; 72.70; H 6.99; 7.08

$C_{19}H_{22}O_4$ . Calculated, %: C 72.58; H 7.05

### 1-Furyl-5-(1',1'-dimethyl-3'-oxobutylfuryl)-pentanone-3

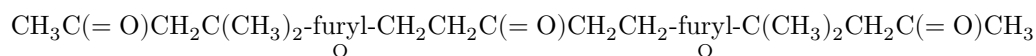


To a mixture of 33 g of 1,5-difurylpentanone-3, 15 g of mesityl oxide, and 0.1 g of hydroquinone, 0.5 ml of 50% sulfuric acid was added. After stirring for 5 h, the

reaction mixture was diluted with water, extracted with ether, and the ether was distilled off. From the residue there were obtained 5 g of mesityl oxide, 16 g of 1,5-difurylpentanone-3, and 17 g of 1-furyl-5-(1',1'-dimethyl-3'-oxobutylfuryl)-pentanone-3 with b.p. 180° (3 mm),  $n_D^{20}$  1.5002;  $d_4^{20}$  1.0747;  $MR_D$  found 86.61, calculated 86.97; yield 35.5%.

Found, %: C 72.12; 72.10; H 7.96; 8.12  
 $C_{19}H_{24}O_4$ . Calculated, %: C 72.12; H 7.64

### 1,5-Bis-(1',1'-dimethyl-3'-oxobutylfuryl)-pentanone-3



To a mixture of 16 g of 1,5-difurylpentanone-3, 15 g of mesityl oxide, and 0.22 g of hydroquinone, 0.5 ml of 50% sulfuric acid was added. After stirring for 6 h and work-up as described above, 7 g of mesityl oxide, 11 g of 1,5-difurylpentanone-3, and 11.5 g of 1,5-bis-(1',1'-dimethyl-3'-oxobutylfuryl)-pentanone-3 with b.p. 215° (2 mm); m.p. 41–42°; yield 38% were isolated.

Found, %: C 72.58; 72.38; H 8.36; 8.29  
 $C_{25}H_{34}O_5$ . Calculated, %: C 72.43; H 8.26

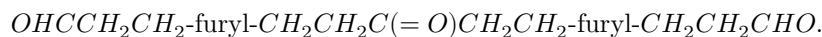
### 1-Furyl-5-(3'-oxopropylfuryl)pentan-3-one



To a mixture of 25 g of 1,5-difurylpentan-3-one, 18 ml of acetic acid, and 0.2 g of hydroquinone, 8 g of acrolein was added with stirring over 30 min. After stirring for 5 h, the reaction mixture was diluted with water and extracted with ether. The ether extracts were neutralized with sodium bicarbonate, washed with water, and the ether was distilled off. From the residue there were obtained 2 g of 1,5-difurylpentan-3-one and 7 g of 1-furyl-5-(3'-oxopropylfuryl)pentan-3-one, b.p. 185° (3 mm);  $n_D^{20}$  1.5060,  $d_4^{20}$  1.1233, which on standing forms crystals, m.p. 47–47.5°.

Found, %: C 70.08, 70.06; H 6.96, 7.02  
 $C_{16}H_{18}O_4$ . Calculated, %: C 70.05; H 6.61

### 1,5-Bis-(3'-oxopropylfuryl)pentan-3-one

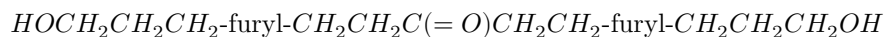


To a mixture of 112 g of 1,5-difurylpentan-3-one, 60 g of acrolein, and 0.2 g of hydroquinone, 30 ml of acetic acid was added with stirring. After stirring for 4 h, the reaction mixture was worked up as described above. The residue after distillation of the ether and acrolein was a light-yellow viscous liquid consisting of unreacted initial 1,5-difurylpentan-3-one and 1,5-bis-(3'-oxopropylfuryl)pentan-3-one. 140 g of the resulting mixture was dissolved in 180 ml of ethanol and hydrogenated in a one-liter autoclave at 40° over 10 g of Raney nickel until 45 atm of hydrogen had been absorbed. After the usual work-up, 36 g of 1,5-bis-(tetrahydrofuryl)pentan-3-one was isolated, b.p. 128° (2 mm),  $n_D^{20}$  1.4785,  $d_4^{20}$  1.0476;  $MR_D$  found 61.20; calculated 61.13.

Found, %: C 69.00, 68.80; H 9.80, 9.82  
 $C_{13}H_{22}O_3$ . Calculated, %: C 68.98; H 9.88

Literature data <sup>(5)</sup>, b.p. 182° (14 mm).

In addition, 39 g of 1,5-bis-(3'-hydroxypropylfuryl)pentan-3-one was isolated,



with b.p. 188° (2 mm),  $n_D^{20}$  1.5015,  $d_4^{20}$  1.0985;  $MR_D$  found 89.75; calculated 90.01.

Found, %: C 68.41, 68.22; H 7.92, 8.20  
 $C_{19}H_{26}O_5$ . Calculated, %: C 68.23; H 7.83

The structures of the compounds synthesized for the first time were confirmed by IR spectral data.

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

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