# Chemistry

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## Abstract

## Full Text

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# INTERACTION OF FURAN ALCOHOLS AND THEIR DERIVATIVES WITH $\alpha,\beta$-UNSATURATED ALDEHYDES AND KETONES

Furan and its derivatives having a mobile hydrogen atom in the $\alpha$-position of the ring are capable, in the presence of acid catalysts, of adding $\alpha,\beta$-unsaturated compounds by a Michael-type reaction ([1]). The length of the aliphatic radicals both in the furan ring and at the double bond of the $\alpha,\beta$-unsaturated compounds has no substantial effect on the yield of the addition products ([2,3]).

We have shown that the presence of cyclopropyl groups in the furan ring, for example in 1-methyl-2-$\alpha$-furylcyclopropane and 1-cyclopropyl-2-$\alpha$-furylcyclopropane, does not hinder the addition of $\alpha,\beta$-unsaturated aldehydes and ketones ([1]). In the present work it was found that 1,3-dicyclopropylbut-2-en-1-one, cinnamaldehyde, and furfurylideneacetone do not add to silvan under the usual conditions.

It also seemed of interest to study the influence of the nature of functional groups and of their position in the side chain of furan compounds on the course of this reaction. The most readily available furan derivatives were chosen as the objects of study. It turned out that furfural, furfural diacetate, and furfuryl alcohol acetate do not react with acrolein in the presence of acetic acid. This is apparently explained by the influence of the electronegative carbonyl group of the indicated compounds, which diminishes the mobility of hydrogen in the furan ring, since furfuryl alcohol and $\beta$-furfuryloxypropionitrile do enter into this reaction, although in low yield.

$$\mathrm{ROCH_2furan\ ring} + \mathrm{CH_2{=}CHCHO} \xrightarrow{\mathrm{CH_3COOH}} \mathrm{ROCH_2furan\ ringCH_2CH_2CHO}$$

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$$R = \text{a) H;}\quad \text{b) } \mathrm{NCCH_2CH_2}-$$

1-($\alpha$-furyl)butan-3-ol, 1-($\alpha$-furyl)-3-(cyanopropoxy)butane, and acetate of 1-($\alpha$-furyl)butan-3-ol add acrolein with yields as high as 60%.

$$R'OCH(CH_3)CH_2CH_2\text{furan ring}+CH_2{=}CHCHO \xrightarrow{CH_2COOH} R'OCH(CH_3)CH_2CH_2\text{furan ring}CH_2CH_2CHO$$

(III) (IV)

$$R' = \text{a) } H; \quad \text{b) } NCCH_2CH_2-; \quad \text{c) } CH_3C(=O)-$$

Acetate of 1-($\alpha$-furyl)butan-3-ol ($R'-CH_3C(=O)-$) in the presence of sulfuric acid also adds crotonaldehyde and mesityl oxide.

Consequently, an electronegative group in the $\gamma$-position of the side chain, not conjugated with the furan ring, has practically no effect on the mobility of hydrogen in the furan ring.

## Experimental Part

**Furfuryl alcohol (Ia)** was obtained from furfural and a 33% solution of caustic soda in a yield 34% higher than that indicated in the literature [4], by lowering the reaction temperature to −3°.

**$\beta$-Furylacrylonitrile (Ib).** From 169 g of Ia, 140 g of acrylonitrile, and 17 ml of 40% caustic soda, after stirring for 6 h, 208 g (81%) of Ib was obtained, b.p. 98° (3 mm); $n_D^{20}$ 1.4780; $d_4^{20}$ 1.1012. Literature data [5]: b.p. 109–110° (2 mm), $n^{30}$ 1.4742; $d^{30}$ 1.090.

IR spectrum ($\Delta\nu$, $cm^{-1}$): 320(2); 340(2); 383(2) 488(1 sh); 605(1); 633(2); 653(1); 700(1); 753(1); 822(3 sh); 845(0); 896(3); 927(2); 960(1); 1016(2 sh); 1032(2 sh); 1078(3); 1150(2); 1225(3); 1258(1); 1295(1); 1328(2); 1362(1); 1385(5); 1415(1); 1443(2); 1567(10); 1610(3); 2213(2); 2260(10); 2873(3); 2937(6); 2978(3)*.

**1-($\alpha$-Furyl)-3-(cyanopropoxy)butane (IIIb).** To 20 g of IIIa, 60 ml of benzene, and 3.5 ml of 40% caustic soda, 32 g of acrylonitrile was added with stirring and cooling to 4° over 30 min. After stirring for 10 h, 16 g of IIIb (60%) was obtained, b.p. 104° (3 mm); $n_D^{20}$ 1.4675; $d_4^{20}$ 1.0180.

IR spectrum ($\Delta\nu$, $cm^{-1}$): 365(2); 410(1); 887(2); 917(1); 940(1); 1010(2 sh); 1082(2 sh); 1105(2 sh); 1137(2); 1170(1); 1212(3); 1265(0); 1295(0); 1331(1); 1382(2 sh); 1448(2 sh); 1505(10); 1597(2); 2241(5); 2872(4); 2930(6); 2973(5).

**2-(3′-Oxopropyl)-5-(oxymethyl)furan (IIa).** To 100 g of Ia, 50 ml of acetic acid, and 0.2 g of hydroquinone, 56 g of freshly distilled acrolein was added with stirring over 50 min. After stirring for 3 h at 30°, the reaction mixture was diluted with 200 ml of water, extracted with 250 ml of ether, and the ethereal extracts were neutralized with sodium bicarbonate. After washing with 100 ml of water, the ether was distilled off, and the residue was distilled in vacuo. Obtained were 34 g of Ia and 29.5 g (29%) of IIa, b.p. 133° (5 mm); $n_D^{20}$ 1.5210; $d_4^{29}$ 1.1986.

| | | |
|---|---|---|
| Found, %: | C 62.33, 62.44; | H 6.65, 6.66 |
| $C_8H_{10}O_3$. Calculated, %: | C 62.32; | H 6.53 |

**2-(3′-Oxopropyl)-5-(cyanopropoxymethyl)furan (IIb).** To 75 g of Ib, 25 ml of acetic acid, and 0.2 g of hydroquinone, 42 g of acrolein was added with stirring over 15 min. After stirring for 6 h and workup as described above, 50 g of Ib and 14 g of IIb (13.6%) were isolated, b.p. 152° (2.5 mm); $n_D^{20}$ 1.4950; $d_4^{20}$ 1.1328. $MR_D$ found 53.34, calculated $MR_D$ 53.50.

| | | |
|---|---|---|
| Found, %: | C 63.60, 63.69; | H 6.58, 6.66 |
| $C_{11}H_{13}O_3N$. Calculated, %: | C 63.75; | H 6.29 |

**2-(3′-Oxopropyl)-5-(3′-oxybutyl)furan (IVa).** From 40 g of IIIa, 18 ml of acetic acid, 0.2 g of hydroquinone, and 21 g of acrolein, as described above, 9.5 g of IIIa and 28 g (49.7%) of IVa were obtained, b.p. 124° (3 mm); $n_D^{20}$ 1.4975; $d_4^{20}$ 1.1020.

| | | |
|---|---|---|
| Found, %: | C 67.44, 67.38; | H 8.23, 8.25 |
| $C_{11}H_{16}O_3$. Calculated, %: | C 67.32; | H 8.21 |

**2-(3′-Oxopropyl)-5-(3′-cyanopropoxybutyl)furan (IVb).** From 16 g of IIIb, 12 ml of acetic acid, 0.2 g of hydroquinone, and 16 g of acrolein, as described above, 3 g of IIIb and 9 g (44%) of IVb were obtained, b.p. 156° (3 mm); $n_D^{20}$ 1.4845; $d_4^{20}$ 1.0650; $MR_D$ found 67.03; calculated $MR_D$ 67.44.

| | | |
|---|---|---|
| Found, %: | C 67.28, 67.37; | H 7.56, 7.65 |
| $C_{14}H_{19}O_3N$. Calculated, %: | C 67.44; | H 7.68 |

* The IR spectra were recorded by G. K. Gaivoronskaya, for which the authors express their gratitude to her.

**2-(3′-Oxopropyl)-5-(3′-acetoxybutyl)furan (IVb).** From 62 g of IIIb, 40 ml of acetic acid, 0.2 g of hydroquinone, and 43 g of acrolein, as described above, there were obtained 13 g of IIIb with b.p. 65° (3 mm) and 47 g (58%) of IVb with b.p. 124° (4 mm); $n_D^{20}$ 1.4765; $d_4^{20}$ 1.0732; $MR_D$ found 62.58, calculated $MR_D$ 62.97.

Found, %: C 65.55, 65.60; H 7.54, 7.70
$C_{13}H_{18}O_4$. Calculated, %: C 65.52; H 7.61

IR spectrum ($\Delta\nu$, $cm^{-1}$): 298(1); 632(2 w); 799(1 w); 850(3 w); 902(2 w); 955(3 w); 971(5 w); 1017(4 w); 1065(3 w); 1110(0 w); 1168(2 w); 1223(2); 1288(1); 1340(3 w); 1385(4 w); 1440(5 w); 1455(3 w); 1506(2); 1568(10); 1613(1); 1725(2 w); 2846(2 w); 2912(5 w); 2935(10 w).

**2-(1′-Methyl-3′-oxopropyl)-5-(3′-acetoxybutyl)furan (V).** To 18.5 g of IVb, 0.5 ml of 50% sulfuric acid was added with stirring over 15 min. 26 g of crotonaldehyde. After stirring for 4 h and the usual work-up, 8 g of IVb and 11 g (43.7%) of V were obtained with b.p. 115° (3 mm); $n_D^{20}$ 1.4750; $d_4^{20}$ 1.0531; $MR_D$ found 67.45; calculated $MR_D$ 67.62.

Found, %: C 66.35, 66.41; H 7.85, 7.88
$C_{14}H_{20}O_4$. Calculated, %: C 66.64; H 7.99

IR spectrum ($\Delta\nu$, $cm^{-1}$): 636(1); 794(0); 850(0); 895(1); 966(1); 1017(1); 1114(0); 1360(0); 1451(1); 1502(1); 1566(10); 1610(1); 1725(1); 2872(3 w); 2926(3 w); 2965(2).

**2-(1′,1′-Dimethyl-3-oxobutyl)-5-(3′-acetoxybutyl)furan (VI).** To 37 g of IVb, 1.2 ml of 50% sulfuric acid and 0.2 g of hydroquinone were added with stirring and heating to 40° over 30 min. 30 g of mesityl oxide. After stirring for 6 h and the usual work-up, 13 g of IVb and 22 g (38.3%) of VI were obtained with b.p. 120.5° (3 mm); $n_D^{20}$ 1.4720; $d_4^{20}$ 1.0265; $MR_D$ found 76.47; calculated $MR_D$ 76.92.

Found, %: C 68.24, 68.25; H 8.56, 8.62
$C_{16}H_{24}O_4$. Calculated, %: C 68.54; H 8.67

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