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Abstract

Full Text

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SYNTHESIS OF ALDEHYDE AND KETO ALCOHOLS OF THE FURAN SERIES

It is known that furan derivatives having electron-donor substituents in the ring and an α-hydrogen atom react, in the presence of acidic catalysts, with α,β-unsaturated aldehydes and ketones according to a substitution-addition scheme ([1–12]). It was shown in this connection that the presence of carbocyclic, as well as alkyl substituents, in the furan ring does not hinder this reaction. On the contrary, carbocyclic substituents at the carbon atoms connected by the double bond in α,β-unsaturated compounds hinder it ([3]), while alkyl substituents make the reaction more difficult ([8]). In the latter case, harsher conditions are required for carrying out the reaction ([8, 9]), for example, the use of sulfuric acid as catalyst instead of acetic acid, etc. It should be noted, however, that the use of sulfuric acid as a catalyst is not always possible, since it causes complete resinification, for example, of acrolein ([1]) and furfuryl alcohol ([3]). It could be expected that furan alcohols with a hydroxyl group in the γ- and ε-positions relative to the furan ring would prove more resistant to the action of sulfuric acid ([3]) than furfuryl alcohol.

It seemed of interest to investigate the possibility of adding α,β-unsaturated aldehydes and ketones to the above-mentioned alcohols. For this purpose, both primary and secondary furan alcohols with a straight or branched side chain were introduced into the reaction. As our experiments showed, γ- and ε-furylalkanols, in contrast to α-furylalkanol, in the presence of sulfuric acid add α,β-unsaturated aldehydes and ketones having alkyl substituents at the double bond:

$$R^1{-}CH(OH){-}CH(R){-}CH_2{-}C_4H_3O{+}R^2R^3C{=}CHCR^4O \rightarrow R^1{-}CH(OH){-}CH(R){-}CH_2{-}C_4H_2O{-}C(R^2)(R^3)$$

$$CH_3CH(OH)(CH_2)_4{-}C_4H_3O{+}R^1CH_3C{=}CHCR^2O \rightarrow CH_3CH(OH)(CH_2)_4{-}C_4H_2O{-}C(R^1)(CH_3){-}CH_2CR^2C$$

$$R = H,\ CH_3,\ C_2H_5, \quad R^1,\ R^2,\ R^3,\ R^4 = H \text{ or } CH_3.$$

Experimental Part

2-(3′-Oxopropyl)-5-(3′-oxypropyl)furan (I)

$$O{=}HCCH_2CH_2{-}C_4H_2O{-}CH_2CH_2CH_2OH.$$

To 14 g of acrolein, 22 g of acetic acid, and 0.2 g of hydroquinone, 24 g of 2-(3′-oxypropyl)furan (II) was added with stirring. After stirring for 5 hours, the reaction mixture was diluted with water, extracted with ether, and the ether extracts were neutralized with sodium bicarbonate.

After distillation of the ether, 24.1 g (56%) of I was obtained, b.p. 126° (3 mm), n_D^{20} 1.5180; d_4^{20} 1.1524.

Found, %:	C 66.42, 66.41;	H 7.53, 7.64
$C_{10}H_{14}O_3$. Calculated, %:	C 65.91;	H 7.74

2-(1′,1′-Dimethyl-3′-oxobutyl)-5-(3′-hydroxypropyl)furan (III)

$$CH_3C(=O)CH_2C(CH_3)_2{-}C_4H_2O{-}CH_2CH_2CH_2OH$$

To 18 g of II, 15 g of mesityl oxide and 0.2 g of hydroquinone, 0.7 ml of 50% sulfuric acid was added with stirring over 30 min. After stirring for 4 h, there were obtained, as described above, 10 g of mesityl oxide, 4.5 g of II, and 18.5 g (58%) of III, b.p. 124° (2 mm), n_D^{20} 1.4890; d_4^{20} 1.0408.

Found, %:	C 69.67, 69.43;	H 8.95, 8.74
$C_{13}H_{20}O_3$. Calculated, %:	C 69.61;	H 8.98

2-(1′-Methyl-3′-oxopropyl)-5-(3′-hydroxypropyl)furan (IV)

$$HC(=O)CH_2CH(CH_3){-}C_4H_2O{-}CH_2CH_2CH_2OH$$

To 21 g of II, 21 g of crotonaldehyde and 0.2 g of hydroquinone, 0.5 ml of 33% sulfuric acid was added with stirring. After stirring for 2.5 h and ordinary work-up, 18.3 g (56%) of IV was obtained, b.p. 130° (3 mm); n_D^{20} 1.5070; d_4^{20} 1.1105.

Found, %:	C 67.07, 67.32;	H 7.99, 7.97
$C_{11}H_{16}O_3$. Calculated, %:	C 67.32;	H 8.21

2-(1′-Methyl-3′-oxopropyl)-5-(3′-hydroxybutyl)furan (V)

$$HC(=O)CH_2CH(CH_3){-}C_4H_2O{-}CH_2CH_2CH(OH)CH_3$$

From 19 g of 2-(3′-hydroxybutyl)furan (VI), 14 g of crotonaldehyde, 0.1 g of hydroquinone, and 0.5 ml of 33% sulfuric acid, by the method described above, 13.5 g (48%) of V was obtained, b.p. 125° (3 mm), n_D^{20} 1.4880; d_4^{20} 1.0604.

Found, %:	C 68.38, 68.23;	H 8.24, 8.05
$C_{12}H_{18}O_3$. Calculated, %:	C 68.54;	H 8.62

2-(1′,1′-Dimethyl-3′-oxobutyl)-5-(3′-hydroxybutyl)furan (VII)

$$CH_3C(=O)CH_2C(CH_3)_2{-}C_4H_2O{-}CH_2CH_2CH(OH)CH_3$$

From 20 g of VI and 19 g of mesityl oxide in the presence of 0.2 g of hydroquinone and 0.7 ml of 50% sulfuric acid, as described above, 18 g (53%) of VII was obtained, b.p. 129° (3 mm), n_D^{20} 1.4830; d_4^{20} 1.0302.

Found, %:	C 70.43, 70.59;	H 9.07, 9.20
$C_{14}H_{22}O_3$. Calculated, %:	C 70.55;	H 9.30

2-(1′-Methyl-3′-oxopropyl)-5-(2′-methyl-3′-hydroxypropyl)furan (VIII)

$$HC(=O)CH_2CH(CH_3){-}C_4H_2O{-}CH_2CH(CH_3)CH_2OH$$

From 11 g of 2-(2′-methyl-3′-hydroxypropyl)furan (IX) and 10 g of crotonaldehyde in the presence of 0.1 g of hydroquinone and 0.3 ml of 33% sulfuric acid, as described above, 8.4 g (51%) of VIII was obtained, b.p. 133° (3 mm); n_D^{20} 1.5057; d_4^{20} 1.0964.

Found, %:	C 68.55, 68.23;	H 8.46, 8.58
$C_{12}H_{18}O_3$. Calculated, %:	C 68.54;	H 8.62

2-(1′,1′-Dimethyl-3′-oxobutyl)-5-(2′-methyl-3′-hydroxypropyl)furan (X)

$$CH_3C(=O)CH_2C(CH_3)_2 - \underset{O}{\text{furan ring}} - CH_2CH(CH_3)CH_2OH$$

From 13 g of IX and 11 g of mesityl oxide in the presence of 0.2 g of hydroquinone and 0.7 ml of 50% sulfuric acid, as described above, 13.2 g (60%) of X was obtained, b.p. 135° (3 mm); n_D^{20} 1.4848; d_4^{20} 1.0232.

Found, %:	C 70.22, 70.40;	H 9.40, 9.43
$C_{14}H_{22}O_3$. Calculated, %:	C 70.55;	H 9.30

2-(1′,1′-Dimethyl-3′-oxobutyl)-5-(2′-ethyl-3′-hydroxypropyl)furan (XI)

$$CH_3C(=O)CH_2C(CH_3)_2 - \underset{O}{\text{furan ring}} - CH_2CH(C_2H_5)CH_2OH$$

From 15 g of 2-(2′-ethyl-3′-hydroxypropyl)furan (XII) and 13 g of mesityl oxide in the presence of 0.2 g of hydroquinone and 1 ml of 50% sulfuric acid, as described above, 13.3 g (54%) of XI was obtained, b.p. 130° (2 mm); n_D^{20} 1.4858; d_4^{20} 1.0149.

Found, %:	C 71.26, 71.18; H 9.64, 9.43
$C_{15}H_{24}O_3$. Calculated, %:	C 71.39; H 9.58

2-(1′-Methyl-3′-oxopropyl)-5-(2′-ethyl-3′-hydroxypropyl)furan (XIII)

$$HC(=O)CH_2CH(CH_3) - \underset{O}{\text{furan ring}} - CH_2CH(C_2H_5)CH_2OH$$

From 8 g of XII and 10 g of crotonaldehyde in the presence of 0.2 g of hydroquinone and 0.3 ml of 33% sulfuric acid, as described above, 6.7 g (55%) of XIII was obtained, b.p. 136° (3 mm); n_D^{20} 1.5055, d_4^{20} 1.0796.

Found, %:	C 69.46, 69.69; H 8.86, 9.21
$C_{13}H_{20}O_3$. Calculated, %:	C 69.61; H 8.98

2-(1′,1′-Dimethyl-3′-oxobutyl)-5-(5′-hydroxyhexyl)furan (XIV)

$$CH_3C(=O)CH_2C(CH_3)_2 - \underset{O}{\text{furan ring}} - (CH_2)_4CH(OH)CH_3$$

From 15 g of 2-(5′-hydroxyhexyl)furan with b.p. 93° (3 mm), n_D^{20} 1.4760, d_4^{20} 0.9902, and 15 g of mesityl oxide in the presence of 0.2 g of hydroquinone and 1.2 ml

From 50% sulfuric acid, as described above, 5 g (22%) of XIV was obtained, b.p. 142° (3 mm); n_D^{20} 1.4870; d_4^{20} 1.0150.

Found, %: C 71.78, 71.96; H 9.54, 9.73
$C_{16}H_{26}O_3$. Calculated, %: C 72.14; H 9.83

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

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