# CHEMISTRY OF FURAN AND THIOPHENE COMPOUNDS

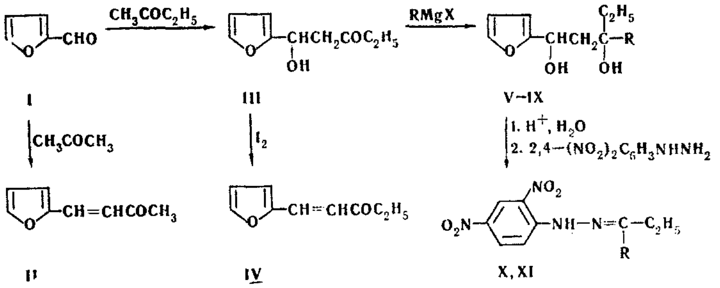
## I. CHARACTERIZATION OF SECONDARY-TERTIARY $\beta$-GLYCOLS WITH $\alpha$-FURYL AND $\alpha$-THIENYL GROUPS

V. I. Esafov, I. F. Utrobina,
N. I. Kiskina, and Yu. B. Tuganov

UDC 547.724:542.957.2

1-($\alpha$-Furyl)pentan-1-ol-3-one and 1-($\alpha$-thienyl)pentan-1-ol-3-one were synthesized by the reaction of furfural and $\alpha$-formylthiophene with methyl ethyl ketone. The products were used to synthesize secondary-tertiary $\beta$-glycols with $\alpha$-furyl and $\alpha$-thienyl groups attached to the secondary carbinol carbon. It was proved that these $\beta$-glycols are capable of undergoing hydrolytic cleavage at the $C_2-C_3$ bond.

The possibility of the application of ketolization to benzaldehyde was demonstrated in [1], and it was therefore of interest to extend this method to the condensation of furfural and $\alpha$-formylthiophene with acetone and methyl ethyl ketone in order to obtain the corresponding $\beta$-ketols and use them to synthesize the previously undescribed secondary-tertiary $\beta$-glycols (the reaction scheme is given for furan derivatives).



V-X $R=C_2H_5$; VI $R=n\text{-}C_3H_7$; VII $R=n\text{-}C_4H_9$; VIII $R=n\text{-}C_5H_{11}$; IX, XI $R=C_6H_5$

Experiments on the condensation of furfural (I) and $\alpha$-formylthiophene (XII) with acetone demonstrated that furfurylideneacetone (II) and $\alpha$-thienylideneacetone (XIII) are obtained instead of $\beta$-ketols. On the other hand, the condensation of I and XII with methyl ethyl ketone proceeded normally to give $\beta$-ketols – 1-($\alpha$-furyl)pentan-1-ol-3-one (III) and 1-($\alpha$-thienyl)pentan-1-ol-3-one (XIV) – in yields of 68 and 50%, respectively.

The structure of III was confirmed by the presence of an absorption band characteristic for the C=O group (1700 $cm^{-1}$) in its IR spectrum, as well as a band due to intramolecular hydrogen bonding (3545 $cm^{-1}$).

1-($\alpha$-Furyl)pent-1-en-3-one (IV) and 1-($\alpha$-thienyl)pent-1-en-3-one (XV) were obtained when III and XIV were vacuum-distilled at 4 mm with traces of iodine. Secondary-tertiary $\beta$-glycols (V-IX and XVI-XX) were synthesized from III and XIV and the appropriate Grignard reagents.

To find out whether these $\beta$-glycols retain the capacity for hydrolytic cleavage [2] that is characteristic for secondary-tertiary $\beta$-glycols, we performed experiments with 1-($\alpha$-furyl)-3-ethylpentane-1,3-diol (V), 1-($\alpha$-furyl)-3-phenylpentane-1,3-diol (IX), 1-($\alpha$-thienyl)-3-methylpentane-1,3-diol (XVI), and 1-($\alpha$-thienyl)-3-phenylpentane-1,3-diol (XX). Hydrazones corresponding to diethyl ketone (X), methyl ethyl ketone (XXI), and propiophenone (XI) were isolated by treatment of the hydrolyzates (obtained after heating weighed

---

A. M. Gor'kii Ural State University, Sverdlovsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 295-297, March, 1972. Original article submitted March 22, 1971.

samples of the β-glycols for 2 h with 0.1 N aqueous $H_2SO_4$ at 100°C with 2,4-dinitrophenylhydrazine. This serves as proof of the secondary-tertiary nature of the synthesized β-glycols.

## EXPERIMENTAL

The IR spectra of 0.001 M $CCl_4$ solutions were recorded with a UR-20 spectrometer. Compounds III, IV, XIV, and XV were identified by thin-layer chromatography on a layer of aluminum oxide–gypsum in a benzene–ethyl acetate system (1 : 1).

1-(α-Furyl)but-1-en-3-one (II). The condensation of I with acetone was carried out as in [2]. A solution of 48 g (0.5 mole) of freshly distilled I in 29 g (0.5 mole) of acetone was added with stirring in the course of 6 h to a cooled (to −2°C) solution of 261 g (4.5 mole) of acetone and 362 ml of 1.4% aqueous sodium hydroxide. At the end of the reaction, water was added to the reaction mixture, and the resulting oily layer was separated. The acetone was removed by distillation at 150 mm, and the residue was recrystallized from pentane to give 90% of II with mp 39-39.5°C. The preparation did not depress the melting point of a sample of furfurylideneacetone obtained by the method in [3].

1-(α-Furyl)pentan-1-ol-3-one (III). A solution of 48 g (0.5 mole) of I in 36 g (0.5 mole) of methyl ethyl ketone was added dropwise with stirring in the course of 6 h to a cooled (−2°C) solution of 324 g (4.5 mole) of methyl ethyl ketone and 400 ml of a 1.4% aqueous sodium hydroxide solution. The mixture was neutralized with a dilute (1 : 8) acetic acid solution, and finely ground table salt (25 g per 100 ml of water used) was added. The methyl ethyl ketone was removed from the salted-out layer by distillation at 150 mm, and the water was removed by distillation at 75 mm. The residue – the product of the condensation of I with methyl ethyl ketone – was vacuum-fractionated at 2 mm to give 68.4% of III with bp 100-101°C (2 mm), $d_4^{20}$ 1.1146, $n_D^{20}$ 1.4950, and $R_f$ 0.67. Found: C 64.12; H 7.08; OH 10.0%; M 167; $MR_D$ 44.00. $C_9H_{12}O_3$. Calculated: C 64.34; H 7.14; OH 10.12%; M 168; $MR_D$ 43.80.

1-(α-Furyl)pent-1-en-3-one (IV). This was obtained by distillation of III with traces of iodine at 4 mm and had bp 100-102°C (4 mm), $d_4^{20}$ 1.0498, $n_D^{20}$ 1.5372, and $R_f$ 0.76. Found: $MR_D$ 44.63, exaltation +2.82. $C_9H_{10}OF_3$. Calculated: $MR_D$ 41.81.

1-(α-Furyl)-3-ethylpentane-1,3-diol (V). An ether solution of 0.25 mole of III was added dropwise to an ether solution of 0.52 mole of ethylmagnesium bromide (cooled to −17°C) in the course of 3 h. The mixture was allowed to stand at room temperature for 12 h. It was then cooled with ice and decomposed, first with water and then with the calculated amount of dilute (1 : 8) acetic acid. The ether layer was separated, and the aqueous layer was extracted three times with ether. The combined ether extracts were washed with sodium bicarbonate solution and water and dried with potassium carbonate. The ether solution was filtered, the ether was removed by distillation, and the residue was vacuum-fractionated at 2 mm. The physicochemical constants and the results of elementary analysis for V are presented in Table 1. Secondary-tertiary β-glycols VI-IX were synthesized from III and the appropriate Grignard reagents under the conditions described above.

TABLE 1. Physicochemical Constants and Results of Elementary Analysis of β-Glycols

$$R-\underset{\displaystyle OH}{CH}-CH_2\overset{\displaystyle R'}{\underset{\displaystyle OH}{C}}C_2H_5$$

| Compound | R | $R_1$ | Bp, °C (pressure, mm) | $d_4^{20}$ | $n_D^{20}$ | $MR_D$ |  | Empirical formula | Found, % |  |  | Calc., % |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | found | calc. |  | C | H | OH | C | H | OH |
| V | Furyl | $C_2H_5$ | 128—130 (2) | 1,0594 | 1,4930 | 54,31 | 54,56 | $C_{11}H_{18}O_3$ | 66,55 | 8,92 | 17,0 | 66,67 | 9,09 | 17,17 |
| VI | Furyl | $C_3H_7$ | 134—136 (2) | 1,0391 | 1,4900 | 58,98 | 59,17 | $C_{12}H_{20}O_3$ | 67,81 | 9,37 | 15,9 | 67,92 | 9,43 | 16,04 |
| VII | Furyl | $C_4H_9$ | 140—142 (2) | 1,0297 | 1,4875 | 63,17 | 63,79 | $C_{13}H_{22}O_3$ | 68,87 | 9,70 | 15,0 | 69,03 | 9,73 | 15,04 |
| VIII | Furyl | $C_5H_{11}$ | 148—150 (2) | 1,0009 | 1,4840 | 68,60 | 68,41 | $C_{14}H_{24}O_3$ | 69,95 | 9,78 | 14,0 | 70,00 | 10,0 | 14,17 |
| IX | Furyl | $C_6H_5$ | 110—110,5* | — | — | — | — | $C_{15}H_{18}O_3$ | 73,18 | 7,22 | 13,7 | 73,17 | 7,32 | 13,82 |
| XVI | Thienyl | $CH_3$ | 128—129* | — | — | — | — | $C_{10}H_{16}O_2S$ | 59,82 | 7,95 | 16,8 | 60,00 | 8,00 | 17,00 |
| XVII | Thienyl | $C_2H_5$ | 141—143 (3) | 1,1066 | 1,5360 | 60,29 | 60,19 | $C_{11}H_{18}O_2S$ | 60,97 | 8,35 | 15,7 | 61,21 | 8,41 | 15,88 |
| XVIII | Thienyl | $C_3H_7$ | 145—146 (2) | 1,0991 | 1,5340 | 64,48 | 64,81 | $C_{12}H_{20}O_2S$ | 62,96 | 8,68 | 14,8 | 63,16 | 8,77 | 14,91 |
| XIX | Thienyl | $C_4H_9$ | 156—157 (2) | 1,0667 | 1,5230 | 69,22 | 69,43 | $C_{13}H_{22}O_2S$ | 64,25 | 8,92 | 13,8 | 64,46 | 9,09 | 14,05 |
| XX | Thienyl | $C_6H_5$ | 167,5—168* | — | — | — | — | $C_{15}H_{18}O_2S$ | 69,32 | 7,07 | 12,9 | 68,74 | 6,87 | 12,98 |

*Mp, °C.

1-(α-Thienyl)but-1-en-3-one (XIII). This was obtained by the reaction of XII [4] with acetone, as in [2], and had mp 32-33°C [5].

1-(α-Thienyl)pentan-1-ol-3-one (XIV). The condensation of XII with methyl ethyl ketone was carried out under the same conditions that were used to obtain III to give 50% of XIV with bp 128-130°C (4 mm), $d_4^{20}$ 1.1595, $n_D^{20}$ 1.5390, and $R_f$ 0.65. Found: C 58.42; H 6.57; S 17.17; OH 9.1%; M 183; $MR_D$ 49.71. $C_9H_{12}O_2S$. Calculated: C 58.69; H 6.52; S 17.39; OH 9.24%; M 184; $MR_D$ 49.42.

1-(α-Thienyl)pent-1-en-3-one (XV). This compound was obtained by distilling XIV with traces of iodine and had bp 78-80°C (2 mm), $d_4^{20}$ 1.0194, $n_D^{20}$ 1.5685, $R_f$ 0.75, and an exaltation of +3.36. Found: $MR_D$ 49.79. $C_9H_{10}OSF_3$. Calculated $MR_D$ 46.43.

1-(α-Thienyl)-3-methylpentane-1,3-diol (XVI). This compound was obtained by a method similar to that used to prepare V.

The secondary-tertiary β-glycols (XVI-XX) with an α-thienyl group were obtained from XIV and the appropriate Grignard reagents by the method indicated for V. The physicochemical constants and results of elementary analysis for XVI-XX are presented in Table 1.

Hydrolytic Cleavage of β-Glycols. Weighed samples of 0.001 mole of V, IX, XVI, or XX were heated for 2 h at 100°C with 50 ml of 0.1 N aqueous $H_2SO_4$ in sealed ampuls. A sulfuric acid solution of 2,4-dinitrophenylhydrazine was added to the resulting hydrolyzates. The precipitated hydrazones were removed by filtration and recrystallized from alcohol. Diethyl ketone hydrazone (X) with mp 154-155°C was obtained from V, methyl ethyl ketone hydrazone with mp 113.5-114.5°C (XXI) was obtained from XVI, and propiophenone hydrazone (XI) with mp 189-190°C was obtained from IX and XX.

## LITERATURE CITED

1. V. I. Esafov and I. F. Utrobina, Izv. Vuzov, Ser. Khim., 13, 1154 (1970).
2. V. I. Esafov and L. P. Zhukova, Zh. Obshch. Khim., 32, 2816 (1962).
3. Organic Syntheses [Russian translation], Vol. 1, Inostr. Lit., Moscow (1949), p. 451.
4. General Laboratory Course in Organic Chemistry [Russian translation], Mir, Moscow (1965).
5. E. Grishkevich-Trakhimovskii and I. Matsurevich, Zh. Russk. Khim. Obshchestva, 44, 570 (1912).