## CATALYTIC OXIDATION OF FURAN AND HYDROFURAN COMPOUNDS. 5.\* HYDROXY- AND ETHOXYDIHYDROFURANS AND ETHOXYFURAN — NEW PRODUCTS FROM THE REACTION OF FURAN WITH HYDROGEN PEROXIDE

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It was established for the first time by chromato-mass spectrometry that 2-X-5-Y-2,5-dihydrofurans (X, Y = OH, OEt) and 2-ethoxyfuran are formed during the oxidation of furan by hydrogen peroxide in a mixture of water and ethanol in the presence of  $VOSO_4$ . Stable tautomeric forms of 2-hydroxy- and 2,5-dihydroxyfurans - 2(5H)-furanone and 5-ethoxy-2(5H)-furanone respectively — were isolated from the reaction mixture. A probable scheme for the main reaction paths is proposed.

During the direct synthesis of the difficultly obtainable 2,5-diethoxy-2,5-dihydrofuran by the oxidation of furan with hydrogen peroxide in the presence of  $VOSO_4$  in a mixture of water and ethanol, products of unestablished structure were detected in the reaction mixture [2]. In view of our previous results on the catalytic peroxide oxidation of furan in water and aqueous acetone [3-5] and also the familiar characteristics of the chemical behavior of furan [6] and the mechanism for its reaction with hydrogen peroxide proposed in papers by other authors [7-10], it could be expected that compounds (I-XIX) would be formed in the furan-hydrogen peroxide- $VOSO_4$ -aqueous ethanol reaction system (Scheme 1).

In the present communication we give the results from a detailed investigation of the products from the transformation of furan in the above-mentioned system. The reaction was conducted at 20°C; the molar ratios of furan, hydrogen peroxide, ethanol, and VOSO<sub>4</sub> were 1:2:6:0.02 [2]. After the complete conversion of the hydrogen peroxide, which took 6 h, the composition of the reaction mixture was determined by chromato-mass spectrometry, polarography, GLC, and TLC. Compounds (IV, VII, X) were also obtained preparatively (Table 1).

One of the main products among the compounds formed under the adopted conditions was the stable tautomer of the dihydroxyfuran (I), i.e.,  $cis-\beta$ -formylacrylic acid, which exists as the two equilibrium forms 5-hydroxy-2(5H)-furanone (II) and the acyclic isomer (III). The tautomer (II) accumulates partly in the reaction mixture in the form of the acetal 5-ethoxy-2(5H)-furanone (IV). The yields of compounds (II + III) and (IV), determined by GLC and polarography, were 40 and 12% respectively. After further transformation of the tautomers (II + III) into the acetal (IV) during azeotropic distillation of the water from the reaction mixture in the presence of chloroform [11] the product (IV) was isolated with a yield of 38% by vacuum distillation.

It was established by chromato-mass spectrometry (GLC and ionization by electron impact) that other substances were also formed in the reaction, i.e., 2,5-dihydroxy-2,5-dihydrofuran (V), 2-hydroxy-5-ethoxy-2,5-dihydrofuran (VI), 2,5-diethoxy-2,5-dihydrofuran (VII), 2-ethoxyfuran (IX), and 2(5H)-furanone (X) and also *trans*- $\beta$ -formylacrylic acid (XI), its ethyl ester (XII), and diethyl succinate (XIII).

The mass spectra of compounds (II + III, IV, XI, XII) contain a group of fragment ions with identical m/z values, a scheme for the formation of which from the molecular ions we proposed earlier [11]. Thus, the spectra contain characteristic peaks at m/z 100, corresponding to the [M]<sup>+</sup> ions [for the acids (II + III) and (XI)] and  $[M-C_2H_4]^+$  ions [for the epoxy deri-

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<sup>\*</sup>For Communication 4, see [1].

Scheme 1



vatives (IV) and (XII)] and also fragments at m/2 99 {[M-H]<sup>+</sup> for the products (II + III) and (XI) and [M-C<sub>2</sub>H<sub>5</sub>]<sup>+</sup> for the products (IV) and (XII)}, 84, 83, and 55. The initial fragmentation of the mixture of tautomers (II + III) and the furanone (IV) is accompanied by ejection of the OH, CO, and CO<sub>2</sub> particles (m/z 83, 72, 71, and 56). The IR and PMR spectra of the isolated compounds (II + III) and (IV) and also of the product from their reaction with 2,4-dinitrophenylhydrazine, i.e., 4-(2,4-dinitrophenyl)hydrazono-2-butenoic acid, agree with previously obtained data [4, 11]. Under the conditions of analysis of the reaction mixture the mass spectra of the acid (XI) and its ester (XII) coincide in the set of fragment ions, but the second product, being more volatile, has a shorter emergence time on the chromatogram.

The structure of the unstable 2,5-disubstituted dihydrofurans (V, VI) was established by comparing the results from fragmentation of their molecular ions and the diacetal (VII) isolated from the analogous reaction mixture [2].

The mass spectrum of compound (V) contains a molecular ion  $M^+$  (102), which dissociates according to the main paths indicated in Scheme 2.

Scheme 2



Two substances having an identical fragmentation pattern under electron impact were found in the reaction mixture. The molecular ion was not observed in their mass spectra, but as in the spectra of the isomers of the diacetal (VII), the  $[M-H]^+$  fragment (m/z 129) was present. The obtained data make it possible to identify these products as the *cis* and *trans* isomers of 2-hydroxy-5-ethoxy-2,5-dihydrofuran (VI) and to represent their dissociation in the form of Scheme 3.

Scheme 3



During comparison of the mass spectra of compounds (V-VII) some general features of their fragmentation under electron impact were examined. The main dissociation paths of the molecular ions involve the participation of the OH and  $C_2H_5$ groups and lead finally to a reduction in the size of the heterocycle. During the dissociation of the molecular ions of the hydroxydihydrofurans (V) and (VI), in contrast to the diethoxy derivative (VII), the  $C_2H_3$  fragment and also the CHO [in the case of compound (V)] or  $C_2H_5$  + CO(CHO) [for compound (VI)] fragments are ejected, leading to ions with m/z 73 and 72. The fragmentation of the molecular ion characteristic of the ethoxy compounds (VI, VII) is realized according to the scheme M<sup>+.</sup>  $\rightarrow m/z$  129  $\rightarrow m/z$  99.

The mass spectra of the *cis* and *trans* isomers of the diacetal (VII), obtained during analysis of the reaction mixture by chromato-mass spectrometry, coincide with the spectra of this compound obtained preparatively [2], and in both cases the cis-trans ratio amounts to 2.5:1. It is noteworthy that 2-hydroxy-5-ethoxy-2,5-dihydrofuran (VI) is also formed mainly in the cis form. (The cis-trans ratio in this case amounts to 4.5:1.) For 2,5-dihydroxy-2,5-dihydrofuran (V) only one isomer was detected in the reaction mixture by chromato-mass spectrometry, and in view of the foregoing this probably has the cis configuration.

A substance whose mass spectrum contains the molecular ion  $M^{+1}$  112 was also detected in the reaction mixture. The nature of its dissociation with the formation of fragments at m/z 84  $(M-C_2H_4)^+$ , 83  $(M-C_2H_5)^+$ , 56  $(M-C_2H_2-CO)$ , and 55  $(M-C_2H_5-CO)$  makes it possible to assign it the structure of 2-ethoxyfuran (IX) (Scheme 4).



Product	Method of determination	Yield, %	Mass spectrum, m/z (1, %)
II + III	CMS*, PMR PG†	40	100 (8) [M] <sup>++</sup> , 99 (10) [M-H] <sup>+</sup> , 84 (38), 83 (100) [M-OH] <sup>+</sup> , 71 (3) [M-H—CO] <sup>+</sup> , 69 (3), 56 (9) [M-CO <sub>2</sub> ] <sup>+</sup> , 55 (97), 54 (11), 45 (3)
IV	CMS, PMR, GLC	12	100 (10) $[M-C_2H_4]^+$ , 99 (18) $[M-C_2H_5]^+$ , 84 (39) $[M-C_2H_4-H_2O]^+$ , 83 (100), 55 (98)
v	CMS	—	102 (18) [M] <sup>++</sup> , 75 (9) [M-C <sub>2</sub> H <sub>3</sub> ] <sup>+</sup> , 73 (65) [M-CHO] <sup>+</sup> , 45 (100)
cis -VI	CMS	_	129 (16) $[M-H]^+$ , 101 (22) $[M-C_2H_5]^+$ , 99 (10), 72 (11), 71 (100), 56 (48), 47 (51), 45 (28), 43 (49), 29 (83)
trans-VI	CMS	—	129 (16) $[M-H]^+$ , 128 (9), 103 (9) $[M-C_2H_3]^+$ , 101 (100) $[M-C_2H_4]^+$ , 73 (7), 71 (6), 55 (19), 45 (8), 43 (5), 29 (39)
cis-VII	CMS, PMR <sup>13</sup> C NMR	12	157 (3) $[M-H]^+$ , 129 (2) $[M-C_2H_5]^+$ , 113 (20) $[M-OC_2H_5]^+$ , 99 (2), 86 (7), 85 (100), 84 (11), 83 (40), 73 (4), 68 (2), 57 (17), 56 (2), 55 (46), 54 (2)
trans - VII	CMS, PMR, <sup>13</sup> C NMR	5	157 (4) $[M-H]^{++}$ , 129 (2) $[M-C_2H_5]^{+}$ , 113 (26) $[M-OC_2H_5]^{+}$ , 86 (5), 85 (100), 84 (11), 83 (21), 68 (7), 57 (32), 56 (6), 55 (20)
IX	.CMS	_	112 (4) $[M]^{++}$ , 84 (100) $[M-C_2H_4]^{+}$ , 83 (21) $[M-C_2H_5]^{+}$ , 56 (25) $[M-C_2H_4-CO]^{++}$ , 55 (63) $[M-C_2H_5-CO]^{++}$
x	GLC	2	84 (100) [M] <sup>++</sup> , 83 (21) [M-H] <sup>+</sup> , 56 (41) [M-CO] <sup>++</sup> , 55 (79), 40 (9) [M-CO <sub>2</sub> ] <sup>+</sup>
XI	GLC		100 (10) [M] <sup>+*</sup> , 99 (14) [M-H] <sup>+</sup> , 84 (7), 83(10) [M-OH] <sup>+</sup> , 72 (30) [M-CO] <sup>+*</sup> , 71 (16) [M-H- CO] <sup>+</sup> , 56 (18) [M-CO <sub>2</sub> ] <sup>+*</sup> , 55 (100), 54 (32), 44 (27)
XII	GLC	_	100 (10) $[M-C_2H_4]^+$ , 99 (14) $[M-C_2H_5]^+$ , 84 (6) $[M-C_2H_4-H_2O]^+$ , 83 (9), 72 (29), 71 (15), 55 (100)
XIII	CMS, GLC	i	173 (5) $[M-H]^+$ , 157 (50) $[M-OH]^+$ , 145 (7) $[M-C_2H_5]^+$ , 129 (27) $[M-OC_2H_5]^+$ , 99 (36), 83 (100), 55 (30)
XIV	PG	2	—
xv	PG	Traces	-

TABLE 1. Main Products from the Oxidation of Furan in the Hydrogen Peroxide – Ethanol –  $VOSO_4$  System (molar ratios 1:2:6:0.02, 20°C) and Their Mass Spectra

\*Chromato-mass spectrometry.

<sup>†</sup>Polarography.

It is seen from analysis of the mass spectra of compounds (II-VII, IX) that their fragmentation mainly involves participation of the substituents at the  $C_{(2)}$  and  $C_{(5)}$  atoms of the ring. (Together with the ejection of OH<sup>+</sup>,  $OC_2H_5^+$ ,  $C_2H_5^+$ , or H<sup>+</sup> radicals the elimination of CO, CO<sub>2</sub>, or H<sub>2</sub>O molecules is also observed.) These fragmentation features are also observed in the furanone (X), which is a stable tautomer of 2-hydroxyfuran (VIII) (its spectrum contains fragment ions at m/z 84 [M]<sup>++</sup>, 83 [M-H]<sup>+</sup>, 56 [M-CO]<sup>++</sup>, 55 [M-H-CO]<sup>+</sup>, and 40 [M-CO<sub>2</sub>]<sup>++</sup>) and in the succinic ester (XIII) (its spectrum contains the fragments at m/z 173 [M-H]<sup>+</sup>, 157 [M-OH]<sup>+</sup>, 145 [M-C<sub>2</sub>H<sub>5</sub>]<sup>+</sup>, and 129 [M-OC<sub>2</sub>H<sub>5</sub>]<sup>+</sup>). Compounds (X, XIII) were further identified by GLC in the presence of markers.

In spite of the formation of small amounts of maleic (XIV) and fumaric (XV) acids in the reaction under discussion (total yield about 2%), their ethyl esters (XVI, XVII), like the other products (XVIII, XIX) expected according to scheme 1, could not be detected by chromato-mass spectrometry and GLC. It is not impossible that they are formed in very small amounts that cannot be determined by the employed analytical methods.

To explain the formation of compounds (I-XV) we propose a scheme including the most probable paths for the peroxide oxidation of furan in the presence of  $VOSO_4$  in a water-ethanol medium (Scheme 5).

The preferential formation of the *cis* isomers of the dihydrofurans (V-VII) can be explained by the stereoselective oxidation of the furan ring coordinated with the peroxo form of the catalyst [2]. According to published data and to the experimental data that we obtained it can be supposed that the furan ring in the investigated reaction interacts mainly with two





active particles generated in the hydrogen peroxide – vanadium<sup>IV,V</sup> system in the acidic medium, i.e., the OH· free radical [3, 12] and a peroxo complex of vanadium<sup>V</sup> [13-15]. The addition of the hydroxyl radical to the furan results in the formation of the adduct (XX) [16], which leads to the hydroxyfuran (VIII). In view of the results in [17, 18] it can be expected that the  $\pi$  complex (XXI) will be formed at the first stage in the reaction of the substrate with the peroxo form of the catalyst and will rearrange to the  $\sigma$  complex (XXII) [13, 15]. The latter will dissociate by the alternative paths with the formation of compound (VIII) or the *endo*-peroxide (XXIII), which was described as an intermediate product of the photosensitized oxygenation of furan [19, 20]. The intermediates (VIII, XXIII) are unstable and are quickly transformed: compound (VIII) into the more stable tautomeric forms (X) and (XVIII) [21]; compound (XXIII) into the hydrolysis (alcoholysis) products (XXIV) and (XXV) [20]. In addition, the hydroxyfuran (VIII) is oxidized with the formation of compounds (I) and (XXVI). The products (XXIV) and (XXV) are then converted into the dihydrofurans (V) and (VI), compound (XXVI) into the furanones (II) and (IV), and the hypothetical 2,5-dihydrofuran (I) into the acids (II + IV) and (XIX). The dihydroxydihydrofuran (V) and its hydrolysis product maleic dialdehyde (XXVII) are oxidized to the acids (II + III).

In the light of the published data it can be supposed that the dihydrofurans (V, VI) are mainly formed during the oxidation-reduction dissociation of the hydroperoxides (XXIV) and (XXV), catalyzed by vanadium ions. From the standpoint of the mechanism of the acid-catalyzed transformation of the semiacetals into acetals it is not very likely that the O-alkylation of compounds (V, VI) [to the corresponding products (VI, VII)] would take place to an appreciable degree under our conditions

on account of the presence of a large amount of water in the system and the insufficiently high concentration of protons. However, according to the data from chromato-mass spectrometry, the areas (S) of the chromatographic peaks for the dihydrofurans (V-VII) are related as follows:  $S_V < S_{VI} < S_{VII}$ . This indicates that the equilibrium (V)  $\neq$  (VI)  $\neq$  (VII) in the reaction under discussion is shifted to the right. This fact can be explained by the fact that substitution of the hydroxy group in compounds (V, VI) by ethoxyl is facilitated under the influence of the strong complexing agent (vanadium<sup>V</sup> ions, forming stable complexes with water molecules or HO<sup>-</sup> anions [22]) present in the system. The retention of the stereo structure of the products (VI, VII) formed here may be due to substitution in the coordination sphere of the vanadium catalyst.

The formation of the ethoxyfuran (IX) probably results from attack on the substrate by the ethoxyl radicals formed in the system, but the contribution from this path is small. On the whole, the existing data make it possible to state that the principal stages of the investigated reaction take place with participation of the peroxo complexes of vanadium and not free radicals.

Thus, detailed investigation of the composition of the products from the peroxide oxidation of furan by chromato-mass spectrometry has made it possible for the first time to demonstrate experimentally that the hydroxy- and ethoxydihydrofurans (V-VII) and the ethoxyfuran (IX) are formed under the adopted conditions. These substances represent a special group of heterocyclic compounds, containing an enolic or semiacetal hydroxyl (ethoxyl) group as substituent in the furan ring. The increased interest in these substances is due to the uniqueness of the chemical properties, brought about by the C=C bonds in their molecules together with the endo- and exocyclic C-O-C fragments. Unlike the analogous hydroxy derivatives of the benzene series, compounds (I, V, VII) are extremely unstable. Their intermediate formation has been suggested in various types of peroxide oxidation of furan compounds [7-10], but this has not been established experimentally. In accordance with Scheme 5 and with published data [4, 21, 23] we also regard these compounds as intermediates in the formation of the more stable products (II, IV, VII, X, XVIII).

The presented results, which demonstrate that the hydroxy- and ethoxydihydrofurans, ethoxyfuran, and the tautomeric  $\gamma$ -lactone forms of the hydroxyfurans are formed preferentially in the reaction of furan with hydrogen peroxide and VOSO<sub>4</sub> in aqueous ethanol, supplement our previously obtained data on the mechanism of the peroxide oxidation of furan compounds. They may provide a basis for the development of new procedures for the synthesis of these products.

## EXPERIMENTAL

The conditions for the oxidation of furan and the procedures for analysis of the reaction mixture by chromato-mass chromatography, GLC, and TLC were described in [2]. The total yield of the products (II-IV, XI, XII) and also the yields of the acids (XIV, XV) were determined by polarography [24].

The stable products (IV, VII, X) were isolated by vacuum distillation and were characterized by spectroscopy. 4-(2,4-Dinitrophenyl)hydrazono-2-butenoic acid (XXVIII) and the bis(2,4-dinitrophenyl)dihydrazone of maleic dialdehyde (XXIX) respectively were obtained from compounds (IV, VII). The spectral characteristics of the products (IV, VII) corresponded to the published data [2, 11, 21]. The melting points of the hydrazones (XXVIII) and (XXIV) were 247-250°C (decomp.) and 310°C (decomp.) respectively. Published data: mp > 250°C (decomp.) [25] and 310°C [2] respectively.

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