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Sulfides, Sulfones, and Sulfoxides of the Furan-2(5*H*)-one Series. Synthesis and Structure

L. Z. Latypova[a], E. Sh. Saigitbatalova[a], D. R. Chulakova[a], O. A. Lodochnikova[b], A. R. Kurbangalieva[a], E. A. Berdnikov[a], and G. A. Chmutova[a]

[a] *Butlerov Institute of Chemistry, Kazan (Volga Region) Federal University, ul. Lobachevskogo 1/29, Kazan, 420008 Tatarstan, Russia*

[b] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, ul. Arbuzova 8, Kazan, 420088 Tatarstan, Russia*
e-mail: Almira.Kurbangalieva@ksu.ru

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Abstract—A number of 4- and 5-R-sulfanylfuran-2(5*H*)-one derivatives were synthesized, and their oxidation with various reagents was studied. The corresponding sulfones were obtained using hydrogen peroxide in acetic acid. 4-R-sulfanyl derivatives were selectively oxidized to sulfoxides with *m*-chloroperoxybenzoic acid. The molecular and crystal structures of some new sulfones and sulfoxides were determined by X-ray analysis.

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The chemistry of organosulfur compounds, namely sulfides, sulfoxides, and sulfones, attracts increased attention due to importance of these compounds from the practical viewpoint, their biological activity, and broad synthetic potential [1–6]. Sulfur-containing fragments are present in many natural compounds involved in a number of biologically important processes, as well as in synthetic medicinal agents exhibiting diverse physiological activity [1, 4–6]. Sulfoxides and sulfones are widely used in fundamental studies and preparative organic chemistry for building up C−C bonds via cycloaddition and Michael addition reactions and in various stereocontrolled transformations of functional groups. Insofar as sulfonyl and sulfinyl groups are capable of stabilizing carbanionic centers, sulfones and sulfoxides readily react with various electrophiles [1–3, 5–7].

Being ambident nucleophiles, sulfoxides form complexes with transition and non-transition metal cations and therefore attract interest as extractants for salts derived from metals and acids [3, 7, 8]. Chiral sulfoxides ensure efficient asymmetric induction and are widely used in numerous practically important asymmetric reactions and syntheses of biologically active molecules [1, 6, 7]. Sulfonyl group inhibits various enzymatic processes, and many compounds containing a sulfonyl group are used in medicine, engineering, and agriculture; they are also useful as dyes, plasticizers, detergents, etc. [1, 4, 5, 9].

Sulfoxides and sulfones of the furan-2(5*H*)-one series are potential biologically active compounds. The presence in their molecules of a sulfonyl or sulfinyl group in combination with the pharmacophoric unsaturated γ-lactone fragment [10, 11] is expected to extend the scope of application of such heterofunctional compounds and endow them with new kinds of biological activity. Published data on sulfonyl and sulfinyl derivatives of furan-2(5*H*)-one are fairly few in number [12–17]. Their synthesis via oxidation of the corresponding sulfides with *m*-chloroperoxybenzoic acid-based systems and Oxone (potassium peroxymonosulfate) has been reported. The anti-inflammatory drug Vioxx acting as highly selective cyclooxygenase-2 inhibitor is one of the most shining examples of compounds comprising a furan-2(5*H*)-one fragment and a sulfonyl group [12, 13].

We previously developed methods for selective introduction of sulfur-containing substituents into positions *3*, *4*, and *5* of furan-2(5*H*)-one derivatives. Reactions of 3,4-dichloro-5-hydroxyfuran-2(5*H*)-one (**I**, mucochloric acid) with a number of aromatic thiols [18] and 2-sulfanylacetic acid [19] under base or acid catalysis afforded various sulfides of the furanone series, whereas analogous reactions with 2-sulfanyl-

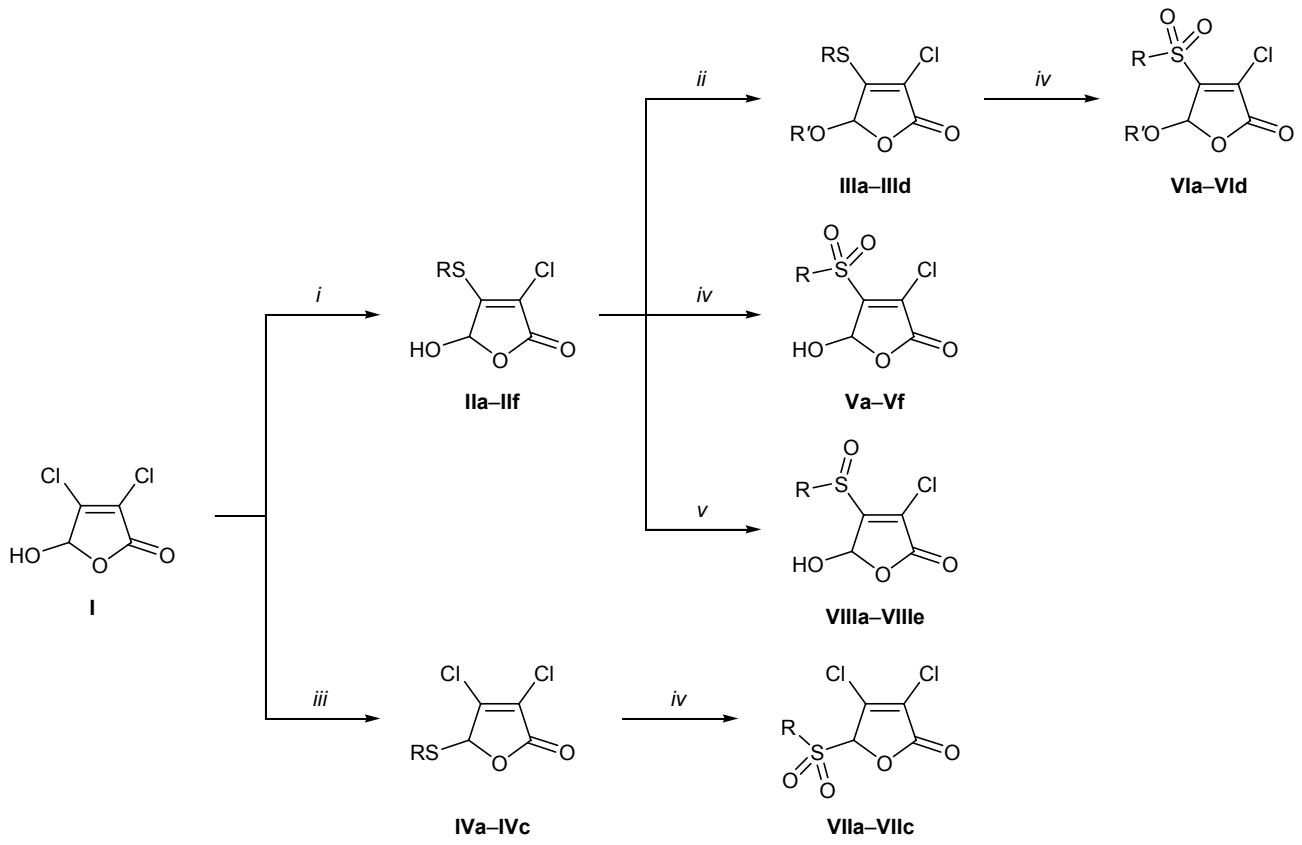
ethanol [20] and ethane-1,2-dithiol [21], apart from the corresponding sulfides and bis-sulfides, produced various sulfur-containing bicyclic compounds. The products of these reactions are very attractive as stable and accessible substrates for their subsequent transformation into sulfinyl and sulfonyl derivatives. In this work we examined oxidation of various 4- and 5-R-sulfanyl-substituted furan-2(5*H*)-ones with a view to develop preparative procedures for the synthesis of new sulfones and sulfoxides and study their structure and properties.

The initial sulfides were prepared from mucochloric acid (**I**) according to the procedures described previously in the presence of acids or bases [18]. By reactions of **I** with aromatic thiols and phenylmethanethiol in the presence of triethylamine we obtained 4-R-sulfanyl derivatives **IIa**–**IIf** (Scheme 1), some of which were converted into 5-alkoxy derivatives **IIIa**–**IIId** by heating in boiling ethanol or propan-2-ol in the presence of a catalytic amount of concentrated sulfuric acid. Reactions of acid **I** with benzenethiols in benzene under acidic conditions produced 5-arylsulfanylfuranones **IVa**–**IVc**. All sulfides **II**–**IV** are stable solids; compounds **IId**, **IIe**, and **IIIa**–**IIId** were not described previously.

Oxidation of R-sulfanyl-substituted furan-2(5*H*)-ones to sulfones. In order to obtain the corresponding sulfones from 4- and 5-R-sulfanylfuran-2(5*H*)-ones, the latter were subjected to oxidation with a classical oxidizing system, a solution of hydrogen peroxide in acetic acid. It is well known that this oxidant, in addition to its accessibility and efficiency and simplicity of the experimental procedure, offers such advantages as the possibility for carrying out the reactions at room temperature and the absence of inorganic by-products (except for water) [1–3, 22–24].

Treatment of compounds **IIa**–**IIf**, **IIIa**–**IIId**, and **IVa**–**IVc** with excess 33% hydrogen peroxide in acetic

Scheme 1.



II, **V**, R = 4-MeC_6H_4 (**a**), 4-ClC_6H_4 (**b**), 4-BrC_6H_4 (**c**), 3,5-(*t*-Bu)$_2$-4-HO-C_6H_2 (**d**), $PhCH_2$ (**e**), 1-naphthyl (**f**); **III**, **VI**: R′ = Et, R = 4-MeC_6H_4 (**a**), 4-BrC_6H_4 (**b**), $PhCH_2$ (**c**); R = 4-MeC_6H_4, R′ = *i*-Pr (**d**); **IV**, **VII**, R = 4-MeC_6H_4 (**a**), 4-ClC_6H_4 (**b**), 4-BrC_6H_4 (**c**); **VIII**, R = 4-MeC_6H_4 (**a**), 4-ClC_6H_4 (**b**), 4-BrC_6H_4 (**c**), 3,5-(*t*-Bu)$_2$-4-HO-C_6H_2 (**d**), $PhCH_2$ (**e**). Reagents and conditions: *i*: RSH, Et_3N, Et_2O, 20°C; *ii*: excess ROH, concd. H_2SO_4, reflux; *iii*: RSH, concd. H_2SO_4, PhH, 80°C [18]; *iv*: excess 33% H_2O_2, AcOH, 20°C; *v*: 3-$ClC_6H_4CO_3H$, Et_2O, –12°C.

acid at room temperature led to the formation of the corresponding sulfonyl derivatives **Va**–**Vf**, **VIa**–**VId**, and **VIIa**–**VIIc** (Scheme 1). The products were isolated from the reaction mixtures as colorless crystalline substances (yield 60–80%) by precipitation with water, followed by recrystallization.

The oxidation of 5-R-sulfanyl-substituted furanones **IVa**–**IVc** was accompanied by a side process, cleavage of the C^5–S bond, with formation of a small amount of mucochloric acid (**I**). The ^{1}H NMR spectrum of the reaction mixture obtained in the oxidation of **IVa** with 3 equiv of H_2O_2 contained signals belonging to sulfone **VIIa**, mucochloric acid **I**, and *p*-toluenesulfonic acid, whose ratio was estimated at 10:1:1. In another experiment, sulfide **IVa** was stirred for 6 days in glacial acetic acid at room temperature without addition of H_2O_2, and no hydrolysis of the initial compound was observed (only signals of **IVa** were present in the ^{1}H NMR spectrum of the mixture).

Mucochloric acid (**I**) was also isolated previously in preparative electrochemical oxidation of sulfide **IVa** in $MeCN/Bu_4NBF_4$ [25]. Furthermore, the results of quantum chemical calculations showed that dissociation of the C^5–S bond with formation of arenesulfanyl radical and 3,4-dichloro-5-oxofuran-2-yl cation is energetically favorable; the subsequent reaction of the cation with water gives acid **I** [25]. Hydrolysis was also observed when the reaction mixture obtained from a solution of 5-ethoxy derivative **IIIb** in acetic acid and excess 33% aqueous hydrogen peroxide was kept for a long time (3 months). According to the ^{1}H NMR data, the reaction mixture contained sulfones **VIb** and **Vc** at a ratio of 4:1.

The structure of new sulfonyl derivatives **Va**–**Vf**, **VIa**–**VId**, and **VIIa**–**VIIc** was proved by IR spectroscopy and NMR. These compounds displayed in the IR spectra strong narrow peaks corresponding to stretching vibrations of the sulfonyl group at 1310–1357 (antisymmetric vibrations) and 1140–1165 cm^{-1} (symmetric vibrations) [26]. The number of signals in the ^{1}H and ^{13}C NMR spectra of oxidation products **V**–**VII** was the same as in the spectra of initial sulfides **II**–**IV**. In the spectra of 4-R-sulfonyl derivatives, all signals in the ^{1}H and ^{13}C NMR spectra were displaced downfield. Analogous pattern was observed in the spectra of 5-R-sulfonyl derivatives **VIIa**–**VIIc**; an exception was the 5-H signal which appeared in a stronger field ($\Delta\delta$ ~0.05 ppm in acetone-d_6 and ~0.33 ppm in $CDCl_3$).

The ^{1}H NMR spectra of 5-ethoxyfuranones **IIIa**–**IIIc** and **VIa**–**VIc** characteristically showed an ABX_3 pattern from the OCH_2CH_3 group, a triplet at δ 0.9–1.4 ppm from the methyl protons and a multiplet at δ 3.1–4.1 ppm from the diastereotopic methylene protons (Fig. 1). We calculated the chemical shifts and coupling constants for protons of the 5-ethoxy group in **IIIa**–**IIIc** and **VIa**–**VIc**. The smallest nonequivalence of the diastereotopic protons was found for compound **VIb** having a *p*-bromophenylsulfonyl group on C^4 ($\Delta\delta_{AB}$ = 0.004 ppm; cf. $\Delta\delta_{AB}$ = 0.35 ppm for initial sulfide **IIIb** in acetone-d_6).

The molecular and crystal structures of some newly synthesized sulfones were determined by X-ray analysis. We recently performed a detailed study of the crystallization of 4-arylsulfonylfuran-2(5*H*)-ones **Va**–**Vc**. It was found that crystallization of sulfone **Va** from chloroform solution is accompanied by spontaneous resolution of enantiomers and that compounds **Vb** and **Vc** crystallized as racemates [27]. The conformations of molecules **Va**–**Vc** in crystal are almost identical. The five-membered furan ring is planar, and the hydroxy group and aromatic ring appear at one side with respect to the heterocycle plane. The substituents on C^4 and S^1 are arranged so that their configuration with respect to the C^4–S^1 bond is staggered, i.e., the aromatic and furan rings are almost orthogonal. Such conformation favors conjugation of the S=O bonds with both π-electron system of the aromatic ring and C^3=C^4 bond in the heteroring. This assumption is supported by almost equal lengths of the C^4–S^1 and S^1–C^6 bonds [for example, 1.748(6) Å in molecule **Va**] [27].

5-Alkoxyfuryl sulfones **VIa** and **VId** crystallized in a conformation similar to sulfones **Va**–**Vc**: staggered conformation along the C^4–S^1 bond, dihedral angle between the furan and benzene ring planes ~94° in both structures (Fig. 2). The alkoxy group and *p*-tolyl fragment reside at the same side of the heterocycle plane. Compound **VIa** in crystal featured disordering of the ethyl group by two positions with a population ratio of 40:60, whereas no disordering was observed for the isopropyl group in sulfone **VId**. Both sulfones **VIa** and **VId** crystallized as racemates (centrosymmetric space group $P2_1/c$ for **VIa** and $P2_1/n$ for **VId**).

5-Arylsulfonyl derivatives **VIIa**–**VIIc** crystallized as racemates in monoclinic crystal system, and conformations of their molecules in crystal differed from those observed for compounds **Va**–**Vc**: the conformation along the C^5–S^1 bond is *gauche*, and the dihedral angle between the furan and benzene ring planes is ~30° (Fig. 3a). Presumably, different conformations of 4- and 5-sulfones **V** and **VII** are related to the lack of

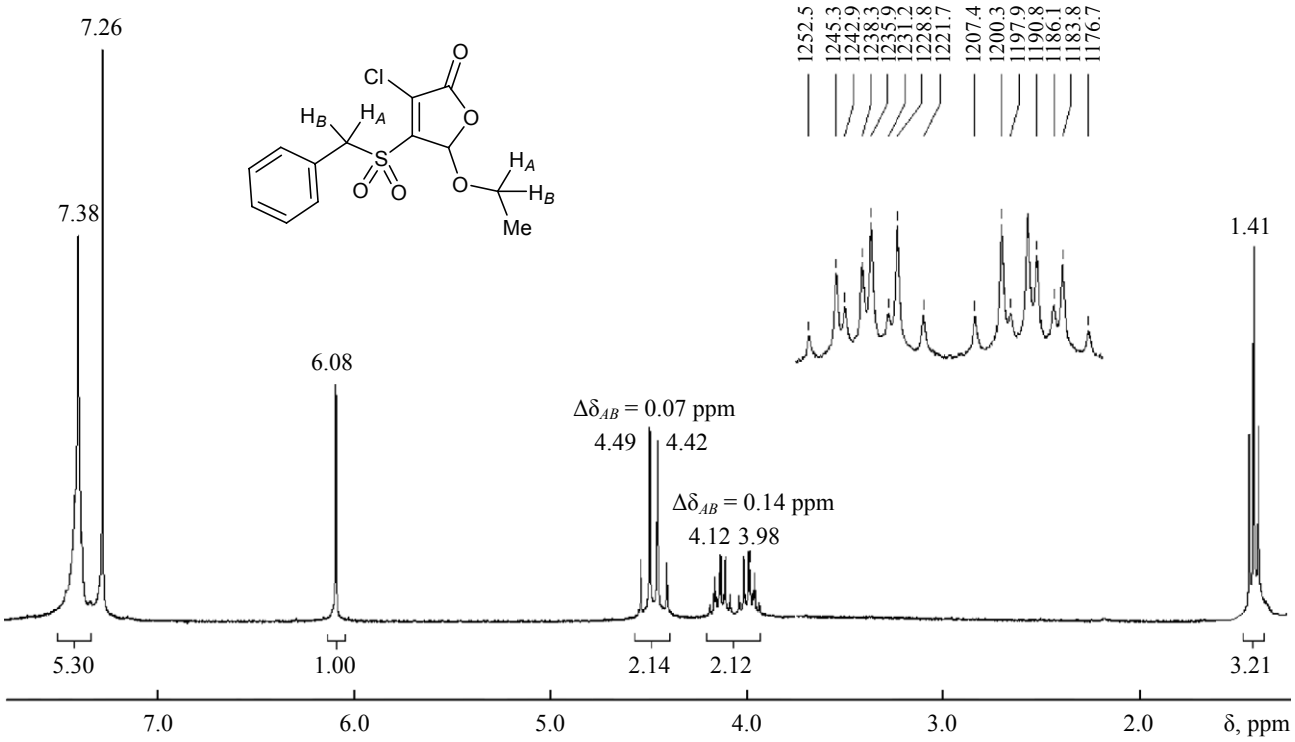


Fig. 1. ^{1}H NMR spectrum of 4-benzylsulfonyl-3-chloro-5-ethoxyfuran-2(5*H*)-one (**VIc**) in $CDCl_3$.

conjugation between the S=O bond and endocyclic C^3=C^4 bond in the latter. Correspondingly, the C^5–S^1 bond in **VIIa**–**VIIc** is considerably longer than the S^1–C^6 and S^1–C^4 bonds in **Va**–**Vc**.

The crystal packing of 5-arylsulfonylfuranones **VIIa**–**VIIc** is characterized by intermolecular interactions C–H···O involving the sulfonyl oxygen atoms and aromatic hydrogen atoms (Fig. 3b). These interactions give rise to infinite parallel chains of molecules with the same chirality. Neighboring chains formed by molecules with opposite chiralities are also linked to each other through analogous C_{arom}–H···O=S contacts.

Oxidation of R-sulfanyl-substituted furan-2(5*H*)-ones to sulfoxides. Unlike oxidation to sulfones, which is achieved fairly readily, selective oxidation of sulfides to sulfoxides is much more difficult to accomplish. Although several tens of various oxidants were successfully used in the synthesis of sulfoxides [1–3,

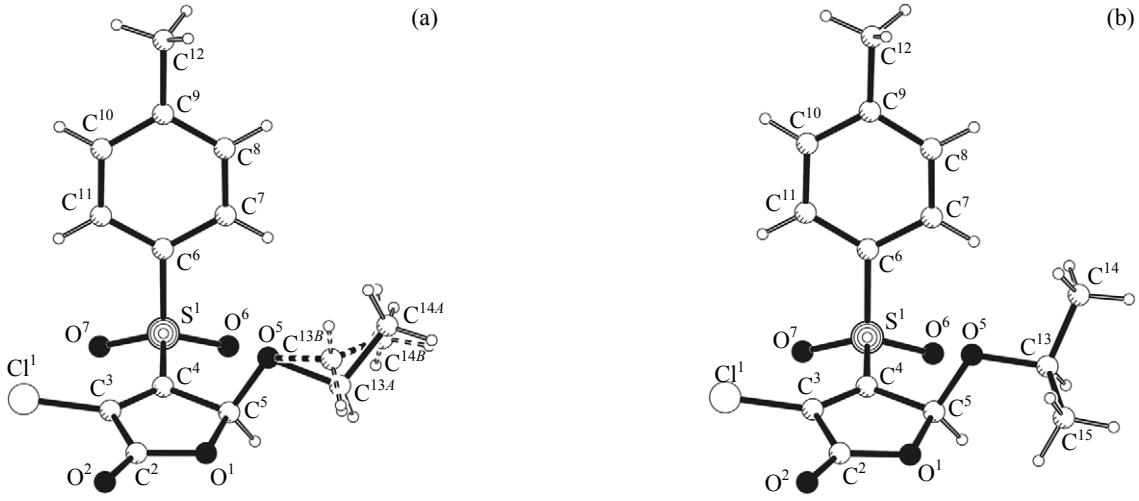


Fig. 2. Structure of the molecules of (a) 3-chloro-5-ethoxy-4-(4-methylphenylsulfonyl)furan-2(5*H*)-one (**VIa**) and (b) 3-chloro-5-isopropoxy-4-(4-methylphenylsulfonyl)furan-2(5*H*)-one (**VId**) in crystal.

6, 22–24], there is no general procedure ensuring formation of sulfoxides without overoxidation to sulfone and undesirable side reactions. Analysis of different available procedures showed that selective synthesis of sulfoxides from sulfides requires thorough selection of reaction conditions in each particular case and strict adherence to these conditions, including the nature of oxidant and solvent, reactant ratio, temperature, reaction time, addition of other compounds, etc. Furthermore, the substrate structure is very important. This was demonstrated by us in the oxidation of sulfides containing RS substituent in position *4* or *5* of the furan ring.

With a view to develop a selective method for the synthesis of R-sulfinyl-substituted furan-2(5*H*)-one derivatives, we studied oxidation of sulfides **IIa** and **IVa** with different oxidants, namely with hydrogen peroxide, *m*-chloroperoxybenzoic acid, Oxone, sodium periodate, and *tert*-butyl hydroperoxide. The oxidation of **IIa** with an equimolar amount of 33% hydrogen peroxide in acetic acid gave a mixture of sulfone **Va** and sulfoxide **VIIIa**. The use of such oxidants as sodium periodate in aqueous alcohol and Oxone in aqueous acetone in the oxidation of sulfides **IIa**–**IIf** is limited due to poor solubility of the substrates in aqueous–organic media at reduced or room temperature. The solubility problem can be solved by raising the temperature, but in this case a mixture of **IIa**, **Va**, and **VIIIa** was obtained.

Experiments with *m*-chloroperoxybenzoic acid showed that the best results (with respect to the yield of sulfoxide **VIIIa** and side formation of sulfone **Va**) were achieved by stirring a mixture of sulfide **IIa** and *m*-chloroperoxybenzoic acid (1.2 equiv) in diethyl ether at –12°C (3 h). Increase of the reaction time and temperature led to overoxidation to sulfone **Va**. Electrochemical oxidation of compound **IIa** afforded only 16% of sulfoxide **VIIIa**.

Using *m*-chloroperoxybenzoic acid as oxidant, sulfides **IIa**–**IIe** were converted into the corresponding sulfoxides **VIIIa**–**VIIIe** (Scheme 1). According to the ^{1}H NMR spectra of the reaction mixtures, sulfoxides **VIIIa**–**VIIIe** were formed as two diastereoisomers at a ratio of 1:1. By recrystallization and (in some cases) by column chromatography we succeeded in obtaining samples slightly enriched in one stereoisomer. Some signals in the ^{1}H and ^{13}C NMR spectra of **VIIIa**–**VIIIe** were doubled due to the presence of diastereoisomers, and their ratio was determined from the intensities of two singlets due to 5-H in the region δ 6.38–6.64 ppm.

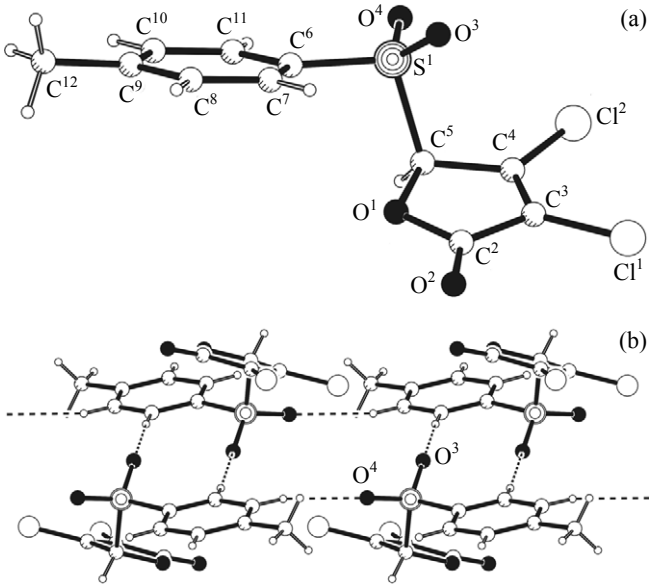


Fig. 3. (a) Molecular structure and (b) a fragment of crystal packing of sulfone **VIIa**. Analogous patterns were observed for sulfones **VIIb** and **VIIc**.

In the ^{1}H NMR spectra of **VIIIa**–**VIIId** in acetone-d_6, the positions of 5-H signals from different diastereoisomers were very similar (Δδ = 0.01–0.04 ppm), while the difference in the chemical shifts of 5-H in sulfoxide **VIIIe** was appreciably larger (Δδ = 0.26 ppm). Diastereotopic methylene protons of one diastereoisomer of benzylsulfinyl derivative **VIIIe** resonated in the ^{1}H NMR spectrum as an *AB* quadruplet ($\Delta\delta_{AB}$ = 0.09 ppm), while those of the second diastereoisomer gave rise to a singlet ($\Delta\delta_{AB}$ = 0.0 ppm).

The IR spectra of **VIIIa**–**VIIIe** contained absorption bands due to stretching vibrations of the endocyclic C=C bond and hydroxy and carbonyl groups, and a strong narrow peak at 1043–1052 cm^{-1}, which is typical of stretching vibrations of sulfinyl group [26]. The OH stretching vibration band in the spectra of **VIII** was located at lower frequencies as compared to the corresponding band in the spectra of sulfones **V** (3146–3260 and 3363–3473 cm^{-1}, respectively). This difference may be attributed to the formation of a stronger intermolecular hydrogen bond between the OH hydrogen atom and oxygen atom of the sulfinyl group, which was confirmed by the X-ray diffraction data for compounds **VIIIa** and **VIIIc**.

Crystals of sulfoxides **VIIIa** and **VIIIc** have similar structures. The conformation of their molecules (Fig. 4a) is analogous to the conformation of structurally related sulfones **Va**–**Vc** [27]. Sulfoxides **VIIIa** and **VIIIc** crystallize in $P2_1$ chiral space group but are

Table 1. Parameters of hydrogen bonds in the crystal structure of sulfoxides **VIIIa** and **VIIIc**

Compound no.	Hydrogen bond	O^5–H^5, Å	$H^5\cdots O^{6'}$, Å	$O^5\cdots O^{6'}$, Å	$\angle O^5H^5O^{6'}$, deg
VIIIa	O^{5A}–$H^{5A}\cdots O^{6B}$	0.84(3)	1.89(4)	2.673(7)	155(3)
	O^{5B}–$H^{5B}\cdots O^{6A}$	0.9(1)	2.1(1)	2.697(7)	130(11)
VIIIc	O^{5A}–$H^{5A}\cdots O^{6B}$	0.8(1)	1.9(2)	2.65(2)	148(13)
	O^{5B}–$H^{5B}\cdots O^{6A}$	0.9(1)	1.9(1)	2.67(2)	152(8)

represented by two independent molecules **A** and **B** that constitute an enantiomer pair (molecules **A** and **B** have opposite configurations of both chiral centers); therefore, spontaneous resolution of enantiomers does not occur. Enantiomeric molecules of sulfoxides **VIIIa** and **VIIIc** are linked in pairs to form H-bonded dimers (Fig. 4b); the parameters of the $S^1{=}O^6\cdots H^5{-}O^5$ hydrogen bonds indicate stability of the dimers (Table 1). The dimers are linked through so-called halogen bonds C=O···Cl to produce infinite zigzag chains along the *b* axis. Here, molecule **B** with the *R*-configured sulfur atom donates the carbonyl oxygen atom (lone electron pair donor), and molecule **A** (*S* configuration of the sulfur atom) provides the chlorine atom (electron pair acceptor).

We also performed a series of experiments on oxidation of 5-(*p*-tolylsulfanyl) derivative **IVa** with different oxidants, the reaction conditions being varied over a wide range. The oxidation of **IVa** with an equimolar amount of hydrogen peroxide in acetic acid or acetone resulted in the formation of a complex mixture of products (Scheme 2) among which we identified by ^{1}H NMR and GC/MS unreacted initial compound **IVa**, sulfoxide **IX**, and sulfone **VIIa**. In addition, mucochloric acid (**I**), disulfide **X**, and *p*-toluenesulfonic acid (**XI**) were detected, which were formed via cleavage of the C^5–S bond in **IVa**. When *m*-chloroperoxybenzoic acid was used as oxidant, the major components were compounds **IVa** and **VIIa**, whereas only traces of sulfoxide **IX** and furanone **I** were present. The oxidation with silica-supported *tert*-butyl hydroperoxide was almost inefficient. As with 4-R-sulfanyl derivatives, sodium periodate in MeCN–H_2O or MeOH–H_2O cannot be used as oxidant because of poor solubility of sulfide **IVa** in aqueous–organic media.

The oxidation of **IVa** with an equimolar amount of another inorganic oxidant, Oxone, in aqueous acetone gave sulfoxide **IX** in the largest amount, as compared to other experiments, but the reaction mixture also contained furanones **IVa** and **I** and traces of sulfone

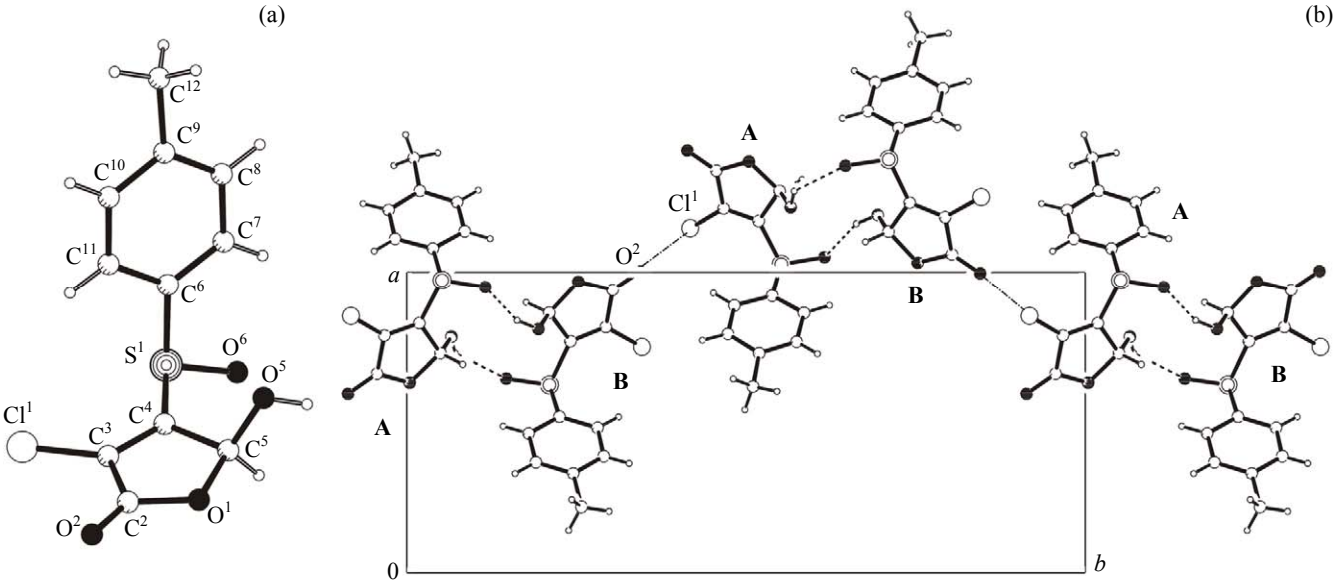
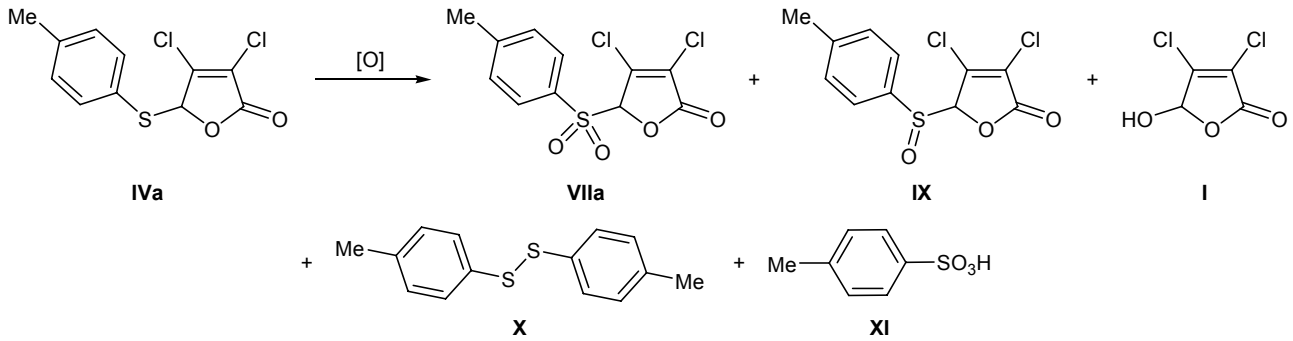


Fig. 4. (a) Structure of the molecule of 3-chloro-5-hydroxy-4-(4-methylphenylsulfinyl)furan-2(5*H*)-one (**VIIIa**) in crystal according to the X-ray diffraction data and (b) zigzag chains formed by hydrogen-bonded dimers of sulfoxide **VIIIa** via halogen bonds along the *b* axis. Hydrogen bonds are shown with dashed lines, and C=O···Cl interactions are shown with dash–dotted lines. Analogous pattern was observed for sulfoxide **VIIIc**.

Scheme 2.



VIIa. In all cases, work-up of the reaction mixture was complicated due to similar solubilities of oxidation products **VIIa** and **IX** in many organic solvents and very close R_f values of compounds **I**, **IX**, and **XI** in different eluent systems, so that we failed to isolate target sulfoxide **IX** as pure substance by recrystallization or column chromatography.

Preliminary tests of chlorine- and sulfur-containing furan-2(5*H*)-ones for antibacterial activity showed that some compounds at a concentration of 1 μg/mL considerably inhibited the growth of Gram-positive bacteria [28]. Search for new antimicrobial agents and inhibitors of bacterial biofilm formation among the synthesized sulfides, sulfones, and sulfoxides of the furan-2(5*H*)-one series will be continued.

EXPERIMENTAL

Commercial 3,4-dichloro-5-hydroxyfuran-2(5*H*)-one (**I**) was recrystallized from water, mp 127°C [29]. 4-Arylsulfanyl-3-chloro-5-hydroxyfuran-2(5*H*)-ones **IIa**–**IIc**, **IIf**, and **IVa**–**IVc** were synthesized according to the procedures described in [18].

The IR spectra of solid compounds were recorded on a Bruker Tensor-27 spectrometer from samples dispersed in Nujol and placed between KBr plates. The ^{1}H and ^{13}C NMR spectra were measured on Varian Unity-300 (299.94 MHz for ^{1}H) and Bruker Avance III 400 spectrometers (400.17 MHz for ^{1}H and 100.62 MHz for ^{13}C) at 25°C; the chemical shifts were determined relative to the residual proton signals of the deuterated solvent. Silufol UV-254 plates were used for thin-layer chromatography (eluent acetone–benzene or acetone–toluene). Column chromatography was performed on Silicagel 60 (Fluka, 70–230 mesh, 0.063–0.200 mm). The melting points were measured on an OptiMelt Stanford Research Systems MPA100 automated melting point apparatus and were not corrected. Gas chromatographic/mass spectrometric analyses were carried out on a Shimadzu GCMS-QP2010 Ultra instrument (HP-1 MS column; carrier gas helium, flow rate 5 mL/min, split ratio 100; injector temperature 250°C, oven temperature programming from 80 to 300°C; electron impact, 70 eV). The X-ray diffraction data were obtained on a Bruker SMART Apex II diffractometer (λMoK_α 0.71073 Å, graphite monochromator, ω-scanning) at 293 K. The crystallographic data and structure refinement parameters are collected in Table 2. Absorption by the crystals was taken into account semiempirically using SADABS program [30]. The structures were solved by the direct method using SHELXS program, and the positions of non-hydrogen atoms were refined first in isotropic and then in anisotropic approximation using SHELXL-97 [31]. Single crystals of **VIIIa** and **VIIIc** were very small needles; the crystal structure of **VIIIa** was refined as a twin crystal with the twinning matrix (1 0 0 0 –1 0 0 0 –1 n = 2); the structure of **VIIIc** was refined as a combined (general and racemic) twin with analogous matrix (n = –4), which enabled acceptable results to be obtained. Hydrogen atoms attached to carbons were placed into calculated positions which were refined according to the riding model. Hydrogen atoms in the hydroxy groups were localized from the difference Fourier map, and their positions were refined in isotropic approximation at the final step. All calculations were carried out using WinGX [32] and APEX2 [33]. The molecular structures were plotted with the aid of PLATON [34]. The X-ray diffraction data were deposited to the Cambridge Crystallographic Data Centre; the corresponding entry numbers are given in Table 2.

3-Chloro-4-(3,5-di-*tert*-butyl-4-hydroxyphenylsulfanyl)-5-hydroxyfuran-2(5*H*)-one (IId). A solution of 4.24 g (17.8 mmol) of 2,6-di-*tert*-butyl-4-sulfanylphenol in 15 mL of diethyl ether was added dropwise under vigorous stirring to a solution of 3 g (17.8 mmol) of mucochloric acid (**I**) in 25 mL of di-

Table 2. Crystallographic data and parameters of X-ray diffraction experiments for compounds **VIa**, **VId**, **VIIa–VIIc**, **VIIIa**, and **VIIIc**

Parameter	VIa	VId	VIIa	VIIb	VIIc	VIIIa	VIIIc
Formula	$C_{13}H_{13}ClO_5S$	$C_{14}H_{15}ClO_5S$	$C_{11}H_8Cl_2O_4S$	$C_{10}H_5Cl_3O_4S$	$C_{10}H_5BrCl_2O_4S$	$C_{11}H_9ClO_4S$	$C_{10}H_6BrClO_4S$
Molecular weight	316.74	330.77	307.13	327.55	372.01	272.69	337.57
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1$	$P2_1$
a, Å	8.919(2)	10.281(3)	10.447(3)	7.894(1)	7.8645(9)	4.964(2)	4.902(4)
b, Å	11.167(2)	8.275(2)	8.095(3)	15.477(3)	15.851(2)	23.23(1)	22.74(2)
c, Å	15.379(3)	18.644(5)	15.660(5)	10.344(2)	10.425(1)	10.277(5)	10.603(8)
β, deg	105.167(2)	94.522(4)	107.03(3)	91.406(2)	91.618(1)	90.248(5)	90.130(10)
V, Å^3	1478.5(5)	1581.2(8)	1266.3(7)	1263.4(4)	1299.0(3)	1184.8(9)	1182(2)
Z (Z')	4 (1)	4 (1)	4 (1)	4 (1)	4 (1)	4 (2)	4 (2)
d_{calc}, g/cm^3	1.423	1.389	1.611	1.722	1.902	1.529	1.897
μ, cm^{-1}	4.14	3.90	6.79	8.91	37.37	4.97	38.79
Scan range (θ, deg)	2.28–27.99	2.19–26.00	2.72–26.28	2.37–27.00	2.34–25.99	1.98–26.00	2.12–25.99
Total number of reflections measured (R_{int})	16451 (0.023)	11465 (0.04)	2638 (0.016)	10019 (0.036)	9689 (0.023)	8633 (0.077)	11167 (0.17)
Number of reflections with $I \geq 2\sigma(I)$	2498	2050	1693	2192	2066	2945	2663
Number of variables	203	193	163	164	163	318	316
R_1 [$I \geq 2\sigma(I)$]	0.0466	0.0497	0.047	0.034	0.031	0.0609	0.1149
wR_2 (all reflections)	0.1343	0.1328	0.179	0.092	0.084	0.1450	0.1920
CCDC entry no.	968537	968539	968542	968543	968544	968540	968541

ethyl ether, and a solution of 2.48 mL (17.8 mmol) of triethylamine in 15 mL of diethyl ether was then added. The mixture slightly warmed up, and triethylamine hydrochloride separated as white solid. The mixture was stirred for 1 h at room temperature, the precipitate was filtered off and washed with diethyl ether, the filtrate was evaporated under reduced pressure to dryness, and the yellow oily residue was recrystallized from benzene. Yield 4.75 g (72%), colorless powder, mp 180–187°C (decomp.), R_f 0.38 (acetone–toluene, 1:6). IR spectrum, ν, cm^{-1}: 3615 (4′-OH), 3445 (5-OH), 1750 (C=O), 1589 (C=C$_{arom}$). ^{1}H NMR spectrum (acetone-d_6, 300 MHz), δ, ppm: 1.44 s (18H, CH$_3$), 5.93 d (1H, 5-H, $^3J_{HH}$ = 8.5 Hz), 6.60 s (1H, 4′-OH), 7.00 d (1H, 5-OH, $^3J_{HH}$ = 8.5 Hz), 7.49 s (2H, H$_{arom}$). Found, %: C 58.01; H 6.16; Cl 9.72; S 8.79. $C_{18}H_{23}ClO_4S$. Calculated, %: C 58.29; H 6.25; Cl 9.56; S 8.65.

4-Benzylsulfanyl-3-chloro-5-hydroxyfuran-2(5*H*)-one (IIe) was synthesized in a similar way from 4.00 g (23.7 mmol) of mucochloric acid (**I**) and 2.78 mL (23.7 mmol) of phenylmethanethiol using 3.30 mL (23.7 mmol) of triethylamine. Yield 4.20 g (69%), colorless crystals, mp 122°C (from benzene), R_f 0.46 (acetone–toluene, 1:6). IR spectrum, ν, cm^{-1}: 3150–3500 br (OH), 1753 (C=O), 1582, 1493 (C=C$_{arom}$). ^{1}H NMR spectrum (300 MHz), δ, ppm: in CDCl$_3$: 4.40 m and 4.47 m (1H each, SCH$_2$, *AB* quartet, $^2J_{AB}$ = 13.2 Hz), 6.02 s (1H, 5-H), 7.29–7.43 m (5H, H$_{arom}$); in acetone-d_6: 4.57 m and 4.59 m (1H each, SCH$_2$, *AB* quartet, $^2J_{AB}$ = 12.7 Hz), 6.38 d (1H, 5-H, $^3J_{HH}$ = 7.0 Hz), 7.26–7.53 m (5H, H$_{arom}$). Found, %: C 51.35; H 3.48; Cl 13.97; S 12.72. $C_{11}H_9ClO_3S$. Calculated, %: C 51.47; H 3.53; Cl 13.81; S 12.49.

3-Chloro-5-ethoxy-4-(4-methylphenylsulfanyl)-furan-2(5*H*)-one (IIIa). Concentrated sulfuric acid, 0.025 mL (0.46 mmol), was added to a solution of 1.18 g (4.6 mmol) of sulfide **IIa** and 27 mL (0.46 mol) of ethanol in 30 mL of benzene, and the mixture was heated under reflux until initial sulfide **IIa** disappeared completely (70 h, TLC). The mixture was cooled and evaporated under reduced pressure to dryness, and the

yellow oily residue was treated with 20 mL of hexane and kept at –7°C for crystallization. Yield 0.93 g (71%), colorless crystals, mp 43–44°C, R_f 0.65 (acetone–benzene, 1:6). IR spectrum, ν, cm^{-1}: 1767 (C=O), 1596, 1493 (C=C$_{arom}$). ^{1}H NMR spectrum (CDCl$_3$, 300 MHz), δ, ppm: 1.04 t (3H, CH$_3$, *X* part of *ABX*$_3$, $^3J_{AX}$ = $^3J_{BX}$ = 7.1 Hz), 2.40 s (3H, 4′-CH$_3$), 3.16 m (1H, OCH$_2$, *A* part of *ABX*$_3$, $^2J_{AB}$ = –9.2, $^3J_{AX}$ = 7.1 Hz), 3.63 m (1H, OCH$_2$, *B* part of *ABX*$_3$, $^2J_{AB}$ = –9.2, $^3J_{BX}$ = 7.1 Hz), 5.46 s (1H, 5-H), 7.23 m and 7.48 m (4H, H$_{arom}$, *AA′BB′*, $^3J_{AB}$ + $^5J_{AB'}$ = 8.0 Hz). Found, %: C 54.72; H 4.63; Cl 12.45; S 11.22. C$_{13}$H$_{13}$ClO$_3$S. Calculated, %: C 54.83; H 4.60; Cl 12.45; S 11.26.

Compounds **IIIb**–**IIId** were synthesized in a similar way.

4-(4-Bromophenylsulfanyl)-3-chloro-5-ethoxyfuran-2(5*H*)-one (IIIb) was synthesized from 4.0 g (12.4 mmol) of furanone **IIc** and 20 mL (0.34 mol) of ethanol using 0.066 mL (1.24 mmol) of concentrated sulfuric acid. Yield 3.62 g (83%), colorless crystals, mp 63–65°C (from petroleum ether), R_f 0.65 (acetone–toluene, 1:6). IR spectrum, ν, cm^{-1}: 1765 (C=O), 1587 (C=C$_{arom}$), 1567 (C^3=C^4). ^{1}H NMR spectrum (acetone-d_6, 300 MHz), δ, ppm: 1.00 t (3H, CH$_3$, *X* part of *ABX*$_3$, $^3J_{AX}$ = $^3J_{BX}$ = 7.1 Hz), 3.28 m (1H, OCH$_2$, *A* part of *ABX*$_3$, $^2J_{AB}$ = –9.4, $^3J_{AX}$ = 7.1 Hz), 3.63 m (1H, OCH$_2$, *B* part of *ABX*$_3$, $^2J_{AB}$ = –9.4, $^3J_{BX}$ = 7.1 Hz), 5.89 s (1H, 5-H), 7.69 m and 7.73 m (4H, H$_{arom}$, *AA′BB′*, $^3J_{AB}$ = $^3J_{A'B'}$ = 7.8, $^4J_{AA'}$ = $^4J_{BB'}$ = 2.1, $^5J_{AB'}$ = $^5J_{A'B}$ = 1.0 Hz). ^{13}C–{^{1}H} NMR spectrum (acetone-d_6, 100 MHz), δ$_C$, ppm: 15.87 (CH$_3$), 67.24 (OCH$_2$), 102.51 (C^5), 118.73 (C^3); 126.52, 126.54, 134.48, 138.87 (C$_{arom}$); 156.42 (C^4), 165.37 (C^2). ^{13}C NMR spectrum (acetone-d_6, 100 MHz), δ$_C$, ppm: 15.86 q.t (CH$_3$, $^1J_{CH}$ = 126.81, $^2J_{CH}$ = 2.4 Hz), 67.24 d.d.q (CH$_2$, $^1J_{CH}$ = 144.3, $^2J_{CH}$ = $^3J_{CH}$ = 4.6 Hz), 102.50 d.t (C^5, $^1J_{CH}$ = 179.4, $^3J_{CH}$ = 2.9 Hz), 118.69 d (C^3, $^3J_{CH}$ = 1.9 Hz), 126.52 t (C^i, C^p, $^3J_{CH}$ = 8.9 Hz), 134.47 d.d (C$_{arom}$, $^1J_{CH}$ = 169.8, $^3J_{CH}$ = 5.2 Hz), 138.87 d.d (C$_{arom}$, $^1J_{CH}$ = 168.2, $^3J_{CH}$ = 5.8 Hz), 156.43 s (C^4), 165.37 d (C^2, $^3J_{CH}$ = 2.9 Hz). Found, %: C 41.49; H 2.89; Br 23.01; Cl 10.43; S 9.38. C$_{12}$H$_{10}$BrClO$_3$S. Calculated, %: C 41.22; H 2.88; Br 22.85; Cl 10.14; S 9.17.

4-Benzylsulfanyl-3-chloro-5-ethoxyfuran-2(5*H*)-one (IIIc) was synthesized from 0.72 g (2.8 mmol) of sulfide **IIe** and 20 mL (0.34 mol) of ethanol using 0.015 mL (0.28 mmol) of concd. H$_2$SO$_4$. The solid residue was recrystallized from hexane–benzene (3:1). Yield 0.57 g (71%), colorless crystals, mp 81–83°C, R_f 0.55 (acetone–toluene, 1:6). IR spectrum, ν, cm^{-1}: 1782, 1769 (C=O), 1595 (C=C$_{arom}$). ^{1}H NMR spectrum (300 MHz), δ, ppm: in (CDCl$_3$: 1.32 t (3H, CH$_3$, *X* part of *ABX*$_3$, $^3J_{AX}$ = $^3J_{BX}$ = 7.1 Hz), 3.70 m (1H, OCH$_2$, *B* part of *ABX*$_3$, $^2J_{AB}$ = –9.2, $^3J_{BX}$ = 7.1 Hz), 3.88 m (1H, OCH$_2$, *A* part of *ABX*$_3$, $^2J_{AB}$ = –9.2, $^3J_{AX}$ = 7.1 Hz), 4.36 m and 4.40 m (1H each, CH$_2$S, *AB* quartet, $^2J_{AB}$ = 13.2 Hz), 5.77 s (1H, 5-H), 7.29–7.45 m (5H, H$_{arom}$); in acetone-d_6: 1.30 t (3H, CH$_3$, *X* part of *ABX*$_3$, $^3J_{AX}$ = $^3J_{BX}$ = 7.1 Hz), 3.87 m (1H, OCH$_2$, *B* part of *ABX*$_3$, $^2J_{AB}$ = –9.5, $^3J_{BX}$ = 7.1 Hz), 3.92 m (1H, OCH$_2$, *A* part of *ABX*$_3$, $^2J_{AB}$ = –9.5, $^3J_{AX}$ = 7.1 Hz), 4.55 m and 4.57 m (1H each, CH$_2$S, *AB* quartet, $^2J_{AB}$ = 12.5 Hz), 6.27 s (1H, 5-H), 7.22–7.57 m (5H, H$_{arom}$); in benzene-d_6: 0.84 t (3H, CH$_3$, *X* part of *ABX*$_3$, $^3J_{AX}$ = $^3J_{BX}$ = 7.1 Hz), 3.06 m (1H, OCH$_2$, *B* part of *ABX*$_3$, $^2J_{AB}$ = –9.3, $^3J_{BX}$ = 7.1 Hz), 3.28 m (1H, OCH$_2$, *A* part of *ABX*$_3$, $^2J_{AB}$ = –9.3, $^3J_{AX}$ = 7.1 Hz), 3.77 s (2H, SCH$_2$), 5.14 s (1H, 5-H), 6.94–7.12 m (5H, H$_{arom}$). ^{13}C–{^{1}H} NMR spectrum (CDCl$_3$, 100 MHz), δ$_C$, ppm: 15.00 (CH$_3$), 34.67 (SCH$_2$), 64.76 (OCH$_2$), 100.27 (C^5), 117.56 (C^3); 128.31, 128.69, 129.08, 134.99 (C$_{arom}$); 154.81 (C^4), 164.36 (C^2). Found, %: C 54.65; H 4.58; Cl 12.57; S 11.02. C$_{13}$H$_{13}$ClO$_3$S. Calculated, %: C 54.83; H 4.60; Cl 12.45; S 11.26.

3-Chloro-5-isopropoxy-4-(4-methylphenylsulfanyl)furan-2(5*H*)-one (IIId) was synthesized from 1.18 g (4.6 mmol) of sulfide **IIa** and 35 mL (0.46 mol) of propan-2-ol using 0.025 mL (0.46 mmol) of concd. H$_2$SO$_4$. The yellow oily residue was crystallized from hexane. Yield 1.18 g (86%), colorless crystals, mp 65–66°C, R_f 0.40 (acetone–toluene, 1:6). IR spectrum, ν, cm^{-1}: 1764 (C=O), 1628 (C^3=C^4), 1600 (C=C$_{arom}$). ^{1}H NMR spectrum (CDCl$_3$, 400 MHz), δ, ppm: 0.73 d (3H, CH$_3$, $^3J_{HH}$ = 6.2 Hz), 1.10 d (3H, CH$_3$, $^3J_{HH}$ = 6.2 Hz), 2.36 s (3H, C**H**$_3$C$_6$H$_4$), 3.53 sept (1H, CH, $^3J_{HH}$ = 6.2 Hz), 5.60 s (1H, 5-H), 7.21 m and 7.44 m (4H, H$_{arom}$, *AA′BB′*, $^3J_{AB}$ + $^5J_{AB'}$ = 8.2 Hz). ^{13}C NMR spectrum (CDCl$_3$, 100 MHz), δ$_C$, ppm: 20.90 q.q.d and 22.77 q.q.d (CH$_3$, $^1J_{CH}$ = 126.5, $^2J_{CH}$ = 0.9, $^3J_{CH}$ = 4.8 Hz), 21.16 q.t (4′-CH$_3$, $^1J_{CH}$ = 127.1, $^3J_{CH}$ = 4.4 Hz), 73.85 d.d.sept (OCH, $^1J_{CH}$ = 143.8, $^3J_{CH}$ = 4.3 Hz), 99.45 d.d (C^5, $^1J_{CH}$ = 176.4, $^3J_{CH}$ = 3.6 Hz), 116.91 d (C^3, $^3J_{CH}$ = 2.2 Hz), 121.86 t (C^i, $^3J_{CH}$ = 9.7 Hz), 130.22 d.m (C^m, $^1J_{CH}$ = 161.4 Hz), 135.22 d.m (C^o, $^1J_{CH}$ = 158.5 Hz), 140.91 q.t (C^p, $^2J_{CH}$ = $^3J_{CH}$ = 6.3 Hz), 155.80 s (C^4), 163.64 d (C^2, $^3J_{CH}$ = 3.3 Hz). Found, %: C 56.24; H 5.09; Cl 11.79; S 10.70. C$_{14}$H$_{15}$ClO$_3$S. Calculated, %: C 56.28; H 5.06; Cl 11.87; S 10.73.

3-Chloro-5-hydroxy-4-(4-methylphenylsulfonyl)-furan-2(5*H*)-one (Va). Sulfide **IIa**, 0.60 g (2.3 mmol),

was dissolved in 20 mL of glacial acetic acid, 0.57 mL (5.8 mmol) of 33% hydrogen peroxide was added under stirring, and the mixture was stirred for 4 days at room temperature (TLC). When the reaction was complete, the mixture was diluted with 30 mL of water, and the precipitate was filtered off, dried, and recrystallized from appropriate solvent. Yield 0.50 g (74%), colorless crystals, mp 155°C (from benzene), R_f 0.68 (acetone–benzene, 1:6). IR spectrum, ν, cm^{-1}: 3363 (OH), 1801 (C=O), 1623 (C^3=C^4), 1594 (C=C_{arom}), 1334 (SO_2, asym.), 1144 (SO_2, sym.). ^1H NMR spectrum, δ, ppm: in acetone-d_6 (300 MHz): 2.49 s (3H, CH_3), 6.57 d (1H, 5-H, $^3J_{HH}$ = 8.2 Hz), 7.58 d (1H, OH, $^3J_{HH}$ = 8.2 Hz), 7.54 m and 7.98 m (4H, H_{arom}, *AA′BB′*, $^3J_{AB}$ + $^5J_{AB'}$ = 8.3 Hz); in $CDCl_3$ (400 MHz): 2.48 s (3H, CH_3), 4.46 br.s (1H, OH), 6.45 s (1H, 5-H), 7.42 m and 7.95 m (4H, H_{arom}, *AA′BB′*, $^3J_{AB}$ + $^5J_{AB'}$ = 8.3 Hz). Found, %: C 45.84; H 2.83; Cl 12.43; S 11.26. $C_{11}H_9O_5ClS$. Calculated, %: C 45.76; H 3.14; Cl 12.28; S 11.11.

Compounds **Vb**–**Vf**, **VIa**–**VId**, **VIIa**–**VIIc**, and **VIIIc**–**VIIIe** were synthesized in a similar way.

3-Chloro-4-(4-chlorophenylsulfonyl)-5-hydroxyfuran-2(5*H*)-one (Vb) was synthesized by oxidation of 0.57 g (2.1 mmol) of sulfide **IIb** with 1.00 mL (10.9 mmol) of 33% H_2O_2. Yield 0.53 g (83%), colorless crystals, mp 139–141°C (from benzene), R_f 0.36 (acetone–toluene, 1:6). IR spectrum, ν, cm^{-1}: 3395 (OH), 1801 (C=O), 1625 (C^3=C^4), 1575 (C=C_{arom}), 1338 (SO_2, asym.), 1147 (SO_2, sym.). ^1H NMR spectrum, δ, ppm: in $CDCl_3$ (300 MHz): 6.48 br.s (1H, 5-H), 7.60 m and 8.01 m (4H, H_{arom}, *AA′BB′*, $^3J_{AB}$ + $^5J_{AB'}$ = 8.7 Hz); in acetone-d_6 (400 MHz): 6.59 d (1H, 5-H, $^3J_{HH}$ = 8.6 Hz), 7.57 d (1H, OH, $^3J_{HH}$ = 8.6 Hz), 7.78 m and 8.11 m (4H, H_{arom}, *AA′BB′*, $^3J_{AB}$ = $^3J_{A'B'}$ = 8.5, $^4J_{AA'}$ = $^4J_{BB'}$ = 2.3, $^5J_{AB'}$ = $^5J_{A'B}$ = 0.3 Hz). ^{13}C–{^1H} NMR spectrum (acetone-d_6, 100 MHz), δ_C, ppm: 98.71 (C^5), 131.81 and 132.58 (C^o, C^m); 134.14, 139.59, 143.29 (C^3, C^i, C^p); 153.47 (C^4), 164.71 (C^2). Found, %: C 38.65; H 1.78; Cl 23.06; S 10.45. $C_{10}H_6Cl_2O_5S$. Calculated, %: C 38.85; H 1.96; Cl 22.94; S 10.37.

4-(4-Bromophenylsulfonyl)-3-chloro-5-hydroxyfuran-2(5*H*)-one (Vc) was synthesized by oxidation of 1.50 g (4.66 mmol) of sulfide **IIc** with 1.75 mL (18 mmol) of 33% H_2O_2. Yield 1.27 g (77%), colorless crystals, mp 141–142°C (from benzene), R_f 0.46 (acetone–benzene, 1:6). IR spectrum, ν, cm^{-1}: 3394 (OH), 1798 (C=O), 1623 (C^3=C^4), 1569, 1507 (C=C_{arom}), 1333 (SO_2, asym.), 1142 (SO_2, sym.). ^1H NMR spectrum (acetone-d_6, 400 MHz), δ, ppm: 6.59 d (1H, 5-H, $^3J_{HH}$ = 8.4 Hz), 7.56 d (1H, OH, $^3J_{HH}$ = 8.4 Hz), 7.94 m and 8.03 m (4H, H_{arom}, *AA′BB′*, $^3J_{AB}$ = $^3J_{A'B'}$ = 8.4, $^4J_{AA'}$ = $^4J_{BB'}$ = 2.2, $^5J_{AB'}$ = $^5J_{A'B}$ = 0.4 Hz). ^{13}C–{^1H} NMR spectrum (acetone-d_6, 100 MHz), δ_C, ppm: 98.69 (C^5); 132.06, 134.16, 140.05 (C^3, C^i, C^p); 132.53 and 134.83 (C^o, C^m), 153.40 (C^4), 164.69 (C^2). Found, %: C 34.23; H 1.40; Br 22.91; Cl 10.32; S 9.27. $C_{10}H_6BrClO_5S$. Calculated, %: C 33.97; H 1.71; Br 22.60; Cl 10.03; S 9.07.

3-Chloro-4-(3,5-di-*tert*-butyl-4-hydroxyphenylsulfonyl)-5-hydroxyfuran-2(5*H*)-one (Vd) was synthesized by oxidation of 0.60 g (1.62 mmol) of sulfide **IId** with 0.50 mL (5.15 mmol) of 33% H_2O_2. Yield 0.45 g (69%), colorless powder, mp 221–223°C (from benzene), R_f 0.44 (acetone–benzene, 1:6). IR spectrum, ν, cm^{-1}: 3603 (4′-OH), 3473 (5-OH), 1805 (C=O), 1622 (C^3=C^4), 1576 (C=C_{arom}), 1322 (SO_2, asym.), 1140 (SO_2, sym.). ^1H NMR spectrum (acetone-d_6, 400 MHz), δ, ppm: 1.47 s (18H, CH_3), 6.56 d (1H, 5-H, $^3J_{HH}$ = 8.2 Hz), 7.28 s (1H, 4′-OH), 7.55 d (1H, 5-OH, $^3J_{HH}$ = 8.2 Hz), 7.95 s (2H, H_{arom}). ^{13}C–{^1H} NMR spectrum (acetone-d_6, 100 MHz), δ_C, ppm: 31.05 (CH_3), 36.46 [**C**$(CH_3)_3$], 98.83 (C^5), 128.43 (C^o); 130.73, 131.97, 139.97 (C^3, C^i, C^m); 155.27 and 162.21 (C^p, C^4), 165.10 (C^2). Found, %: C 53.31; H 5.83; Cl 8.92; S 8.13. $C_{18}H_{23}ClO_6S$. Calculated, %: C 53.66; H 5.75; Cl 8.80; S 7.96.

4-Benzylsulfonyl-3-chloro-5-hydroxyfuran-2(5*H*)-one (Ve) was synthesized by oxidation of 0.90 g (3.51 mmol) of sulfide **IIe** with 1.62 mL (16.7 mmol) of 33% H_2O_2. Yield 0.75 g (74%), colorless crystals, mp 167–169°C (from benzene), R_f 0.42 (acetone–toluene, 1:6). IR spectrum, ν, cm^{-1}: 3405 (OH), 1800 (C=O), 1629 (C^3=C^4), 1495 (C=C_{arom}), 1310 (SO_2, asym.), 1156 (SO_2, sym.). ^1H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 4.47 m and 4.56 m (1H each, SCH, *AB* quartet, $^2J_{AB}$ = 14.1 Hz), 6.38 br.s (1H, 5-H), 7.41 br.s (5H, H_{arom}). Found, %: C 45.41; H 3.33; Cl 12.36; S 11.23. $C_{11}H_9ClO_5S$. Calculated, %: C 45.76; H 3.14; Cl 12.28; S 11.11.

3-Chloro-5-hydroxy-4-(naphthalen-1-ylsulfonyl)-furan-2(5*H*)-one (Vf) was synthesized by oxidation of 0.44 g (1.50 mmol) of sulfide **IIf** with 0.84 mL (9.18 mmol) of 33% H_2O_2. Yield 0.28 g (58%), yellow powder, mp 183–186°C (from benzene), R_f 0.46 (acetone–benzene, 1:6). IR spectrum, ν, cm^{-1}: 3350 (OH), 1796 (C=O), 1621 (C^3=C^4), 1591, 1507 (C=C_{arom}), 1318 (SO_2, asym.), 1154 (SO_2, sym.). ^1H NMR spectrum (acetone-d_6, 300 MHz), δ, ppm: 6.56 br.s (1H, 5-H), 7.41 br.s (1H, OH), 7.66–8.83 m

(7H, H_{arom}). Found, %: C 51.56; H 2.92; Cl 10.84; S 10.05. $C_{14}H_9ClO_5S$. Calculated, %: C 51.78; H 2.79; Cl 10.92; S 9.87.

3-Chloro-5-ethoxy-4-(4-methylphenylsulfonyl)-furan-2(5*H*)-one (VIa) was synthesized by oxidation of 0.39 g (1.36 mmol) of furanone **IIIa** with 0.44 mL (4.80 mmol) of 33% H_2O_2. Yield 0.26 g (61%), colorless crystals, mp 63°C (from hexane), R_f 0.48 (acetone–toluene, 1:6). IR spectrum, ν, cm^{-1}: 1800 (C=O), 1625 (C^3=C^4), 1593 (C=C_{arom}), 1343 (SO_2, asym.), 1159 (SO_2, sym.). ^{1}H NMR spectrum (300 MHz), δ, ppm: in $CDCl_3$: 1.28 t (3H, CH_3, *X* part of ABX_3, $^3J_{AX}$ = $^3J_{BX}$ = 7.1 Hz), 2.48 s (3H, CH_3), 3.87 m (1H, OCH_2, *B* part of ABX_3, $^2J_{AB}$ = –9.4, $^3J_{BX}$ = 7.1 Hz), 3.95 m (1H, OCH_2, *A* part of ABX_3, $^2J_{AB}$ = –9.4, $^3J_{AX}$ = 7.1 Hz), 6.15 s (1H, 5-H), 7.40 m (2H, *m*-H, *AA′* part of $AA'BB'X_3$, $^3J_{AB}$ = $^3J_{A'B'}$ = 8.0, $^4J_{AA'}$ = 1.8, $^5J_{AB'}$ = $^5J_{A'B}$ = 0.2, $^5J_{AX}$ = $^5J_{A'X}$ = 0.0 Hz), 7.92 m (2H, *o*-H, *BB′* part of $AA'BB'X_3$, $^3J_{AB}$ = $^3J_{A'B'}$ = 8.0, $^4J_{BB'}$ = 1.8, $^5J_{BA'}$ = $^5J_{B'A}$ = 0.2, $^4J_{BX}$ <0.5, $^4J_{B'X}$ <0.5 Hz); in acetone-d_6: 1.24 t (3H, CH_3, *X* part of ABX_3, $^3J_{AX}$ = $^3J_{BX}$ = 7.1 Hz), 2.49 s (3H, CH_3), 3.89 q (2H, OCH_2, $^3J_{HH}$ = 7.1 Hz), 6.36 s (1H, 5-H), 7.56 m and 7.97 m (4H, H_{arom}, $AA'BB'$, $^3J_{AB}$ + $^5J_{AB'}$ = 8.3 Hz); in benzene-d_6: 0.82 t (3H, CH_3, $^3J_{AX}$ = 7.1, $^3J_{BX}$ = 7.0 Hz), 1.80 s (3H, CH_3), 3.20 m (1H, OCH_2, *B* part of ABX_3, $^2J_{AB}$ = –9.4, $^3J_{BX}$ = 7.0 Hz), 3.33 m (1H, OCH_2, *A* part of ABX_3, $^2J_{AB}$ = –9.4, $^3J_{AX}$ = 7.1 Hz), 5.46 s (1H, 5-H), 6.69 m and 7.81 m (4H, H_{arom}, $AA'BB'$, $^3J_{AB}$ + $^5J_{AB'}$ = 8.3 Hz). ^{13}C–{^{1}H} NMR spectrum (acetone-d_6, 100 MHz), δ_C, ppm: 15.62 (**C**H_3CH$_2$), 22.19 (4′-CH_3), 68.41 (OCH_2), 102.80 (C^5), 130.32 and 131.56 (C^o, C^m); 133.24, 137.22, 148.34 (C^3, C^i, C^p); 152.26 (C^4), 164.24 (C^2). Found, %: C 49.44; H 4.17; Cl 10.95; S 10.27. $C_{13}H_{13}ClO_5S$. Calculated, %: C 49.29; H 4.14; Cl 11.19; S 10.12.

4-(4-Bromophenylsulfonyl)-3-chloro-5-ethoxy-furan-2(5*H*)-one (VIb) was synthesized by oxidation of 1.46 g (4.16 mmol) of furanone **IIIb** with 2.80 mL (30.4 mmol) of 33% H_2O_2. Yield 1.00 g (63%), colorless crystals, mp 107–108°C (from CCl_4), R_f 0.65 (acetone–toluene, 1:6). IR spectrum, ν, cm^{-1}: 1790 (C=O), 1622 (C^3=C^4), 1575 (C=C_{arom}), 1344 (SO_2, asym.), 1165 (SO_2, sym.). ^{1}H NMR spectrum (acetone-d_6, 400 MHz), δ, ppm: 1.24 t (3H, CH_3, *X* part of ABX_3, $^3J_{AX}$ = $^3J_{BX}$ = 7.1 Hz), 3.918 m (1H, OCH_2, *B* part of ABX_3, $^2J_{AB}$ = 2.5, $^2J_{BX}$ = 7.1 Hz), 3.922 m (1H, OCH_2, *A* part of ABX_3, $^2J_{AB}$ = 2.5, $^3J_{AX}$ = 7.1 Hz), 6.40 s (1H, 5-H), 7.95 m and 8.02 m (4H, H_{arom}, $AA'BB'$, $^3J_{AB}$ = $^3J_{A'B'}$ = 8.4, $^4J_{AA'}$ = $^4J_{BB'}$ = 2.0, $^5J_{AB'}$ = $^5J_{A'B}$ = 0.4 Hz). ^{13}C–{^{1}H} NMR spectrum (acetone-d_6, 100 MHz), δ_C, ppm: 16.10 (CH_3), 69.05 (OCH_2), 103.19 (C^5); 132.17, 132.53, 134.83, 139.86 (C^3, C_{arom}); 151.81 (C^4), 164.53 (C^2). Found, %: C 37.71; H 2.51; Br 20.95; Cl 9.14; S 8.37. $C_{12}H_{10}BrClO_5S$. Calculated, %: C 37.77; H 2.64; Br 20.94; Cl 9.29; S 8.40.

4-Benzylsulfonyl-3-chloro-5-ethoxyfuran-2(5*H*)-one (VIc) was synthesized by oxidation of 0.34 g (1.21 mmol) of furanone **IIIc** with 0.38 mL (3.6 mmol) of 33% H_2O_2. Yield 0.19 g (50%), colorless crystals, mp 79–81°C (from hexane), R_f 0.52 (acetone–toluene, 1:6). IR spectrum, ν, cm^{-1}: 1808 (C=O), 1623 (C^3=C^4), 1497 (C=C_{arom}), 1330 (SO_2, asym.), 1153 (SO_2, sym.). ^{1}H NMR spectrum (300 MHz), δ, ppm: in $CDCl_3$: 1.41 t (3H, CH_3, *X* part of ABX_3, $^3J_{AX}$ = $^3J_{BX}$ = 7.1 Hz), 3.98 m (1H, OCH_2, *B* part of ABX_3, $^2J_{AB}$ = –9.5, $^3J_{BX}$ = 7.1 Hz), 4.12 m (1H, OCH_2, *A* part of ABX_3, $^2J_{AB}$ = –9.5, $^3J_{AX}$ = 7.1 Hz), 4.42 m and 4.49 m (1H each, CH_2, *AB* quartet, $^2J_{AB}$ = 14.0 Hz), 6.08 s (1H, 5-H), 7.33–7.49 m (5H, H_{arom}); in acetone-d_6: 1.38 t (3H, CH_3, *X* part of ABX_3, $^3J_{AX}$ = $^3J_{BX}$ = 7.1 Hz), 4.04 m (1H, OCH_2, *B* part of ABX_3, $^2J_{AB}$ = –9.7, $^3J_{BX}$ = 7.1 Hz), 4.11 m (1H, OCH_2, *A* part of ABX_3, $^2J_{AB}$ = –9.7, $^3J_{AX}$ = 7.1 Hz), 4.65 m and 4.71 m (1H each, CH_2, *AB* quartet, $^2J_{AB}$ = 14.0 Hz), 6.33 s (1H, 5-H), 7.36–7.54 m (5H, H_{arom}); in C_6D_6: 0.83 t (3H, CH_3, *X* part of ABX_3, $^3J_{AX}$ = $^3J_{BX}$ = 7.1 Hz), 3.19 m (1H, OCH_2, *B* part of ABX_3, $^2J_{AB}$ = –9.6, $^3J_{BX}$ = 7.1 Hz), 3.41 m (1H, OCH_2, *A* part of ABX_3, $^2J_{AB}$ = –9.6, $^3J_{AX}$ = 7.1 Hz), 3.78 m and 3.95 m (1H each, CH_2, *AB* quartet, $^2J_{AB}$ = 13.9 Hz), 5.29 s (1H, 5-H), 6.84–7.11 m (5H, H_{arom}). Found, %: C 49.41; H 4.46; Cl 10.96; S 10.23. $C_{13}H_{13}ClO_5S$. Calculated, %: C 49.29; H 4.14; Cl 11.19; S 10.12.

3-Chloro-5-isopropoxy-4-(4-methylphenylsulfonyl)furan-2(5*H*)-one (VId) was synthesized by oxidation of 0.60 g (2.00 mmol) of furanone **IIId** with 1.10 mL (12.0 mmol) of 33% H_2O_2. Yield 0.43 g (65%), colorless crystals, mp 76°C (from benzene–CCl_4, 1:1), R_f 0.65 (acetone–toluene, 1:6). IR spectrum, ν, cm^{-1}: 1794 (C=O), 1626 (C^3=C^4), 1594, 1493 (C=C_{arom}), 1340 (SO_2, asym.), 1164 (SO_2, sym.). ^{1}H NMR spectrum ($CDCl_3$, 300 MHz), δ, ppm: 1.24 d and 1.33 d (3H each, CH_3, $^3J_{HH}$ = 6.2 Hz), 2.46 s (3H, 4′-CH_3), 4.16 sept (1H, CH, $^3J_{HH}$ = 6.2 Hz), 6.24 s (1H, 5-H), 7.39 m and 7.91 m (4H, H_{arom}, $AA'BB'$, $^3J_{AB}$ + $^5J_{AB'}$ = 8.2 Hz). Found, %: Cl 11.01; S 9.97. $C_{14}H_{15}ClO_5S$. Calculated, %: Cl 10.72; S 9.69.

3,4-Dichloro-5-(4-methylphenylsulfonyl)furan-2(5*H*)-one (VIIa) was obtained by oxidation of 2.08 g (7.57 mmol) of furanone **IVa** with 2.28 mL

(24.88 mmol) of 33% H_2O_2. According to the ^1H NMR data, the reaction mixture contained sulfone **VIIa**, mucochloric acid (**I**), and *p*-toluenesulfonic acid (**XI**) at a ratio of 10:1:1. Compound **VIIa** was precipitated with water and recrystallized from carbon tetrachloride. Yield 1.92 g (83%), colorless crystals, mp 106–107°C, R_f 0.28 (acetone–benzene, 1:9). IR spectrum, ν, cm^{-1}: 1800 (C=O), 1616 (C^3=C^4), 1595, 1494 (C=C_{arom}), 1340 (SO_2, asym.), 1158 (SO_2, sym.). ^1H NMR spectrum (400 MHz), δ, ppm: in $CDCl_3$: 2.48 s (3H, CH_3), 5.69 s (1H, 5-H), 7.40 m and 7.80 m (4H, H_{arom}, *AA′BB′*, $^3J_{AB} + {}^5J_{AB'}$ = 8.2 Hz); in acetone-d_6: 2.49 s (3H, CH_3), 6.51 s (1H, 5-H), 7.56 m and 7.84 m (4H, H_{arom}, *AA′BB′*, $^3J_{AB} + {}^5J_{AB'}$ = 8.2 Hz). ^{13}C–{^1H} NMR spectrum (acetone-d_6, 100 MHz), δ_C, ppm: 22.69 (CH_3), 92.92 (C^5); 126.47, 131.65, 132.15, 133.04, 146.86, 149.24 (C^3, C^4, C_{arom}); 164.56 (C^2). Found, %: C 42.95; H 2.35; Cl 22.80; S 10.46. $C_{11}H_8Cl_2O_4S$. Calculated, %: C 43.01; H 2.63; Cl 23.09; S 10.44.

Signals of *p*-toluenesulfonic acid (**XI**) in the ^1H NMR spectrum of the reaction mixture (acetone-d_6, 400 MHz), δ, ppm: 2.43 s (3H, CH_3), 7.41 m and 7.78 m (4H, H_{arom}, *AA′BB′*, $^3J_{AB} + {}^5J_{AB'}$ = 8.1 Hz).

3,4-Dichloro-5-(4-chlorophenylsulfonyl)furan-2(5*H*)-one (VIIb) was synthesized in a similar way by oxidation of 0.80 g (2.70 mmol) of furanone **IVb** with 0.63 mL (6.5 mmol) of 33% H_2O_2. Yield 0.61 g (68%), colorless crystals, mp 115°C (from CCl_4), R_f 0.61 (acetone–benzene, 1:6). IR spectrum, ν, cm^{-1}: 1796 (C=O), 1613 (C^3=C^4), 1573 (C=C_{arom}), 1353 (SO_2, asym.), 1166 (SO_2, sym.). ^1H NMR spectrum (300 MHz), δ, ppm: in acetone-d_6: 6.64 s (1H, 5-H), 7.83 m and 8.00 m (4H, H_{arom}, *AA′BB′*, $^3J_{AB} + {}^5J_{AB'}$ = 8.9 Hz); in $CDCl_3$: 5.70 s (1H, 5-H), 7.61 m and 7.88 m (4H, H_{arom}, *AA′BB′*, $^3J_{AB} + {}^5J_{AB'}$ = 8.8 Hz). Found, %: C 36.61; H 1.19; Cl 32.36; S 9.47. $C_{10}H_5O_4Cl_3S$. Calculated, %: C 36.67; H 1.54; Cl 32.47; S 9.79.

5-(4-Bromophenylsulfonyl)-3,4-dichlorofuran-2(5*H*)-one (VIIc) was synthesized by oxidation of 1.20 g (3.53 mmol) of furanone **IVc** with 1.03 mL (10.6 mmol) of 33% H_2O_2. According to the ^1H NMR data, the reaction mixture contained sulfone **VIIc**, mucochloric acid (**I**), and 4-bromobenzenesulfonic acid at a ratio of 7:1:1. Sulfone **VIIc** was precipitated with water and recrystallized from carbon tetrachloride. Yield 1.04 g (79%), colorless crystals, mp 103–105°C, R_f 0.66 (acetone–benzene, 1:6). IR spectrum, ν, cm^{-1}: 1795 (C=O), 1615 (C^3=C^4), 1570 (C=C_{arom}), 1357 (SO_2, asym.), 1166 (SO_2, sym.). ^1H NMR spectrum (acetone-d_6, 400 MHz), δ, ppm: 6.61 s (1H, 5-H), 7.92 m and 7.98 m (4H, H_{arom}, *AA′BB′*, $^3J_{AB} + {}^5J_{AB'}$ = 8.8 Hz). ^{13}C–{^1H} NMR spectrum (acetone-d_6, 100 MHz), δ_C, ppm: 92.77 (C^5); 126.79, 132.69, 135.46 (C^3, C^i, C^p); 133.40 and 134.95 (C^o, C^m), 146.44 (C^4), 164.41 (C^2). Found, %: C 32.41; H 1.07; Br 21.78; Cl 18.86; S 8.75. $C_{10}H_5BrCl_2O_4S$. Calculated, %: C 32.29; H 1.35; Br 21.48; Cl 19.06; S 8.62.

3-Chloro-5-hydroxy-4-(4-methylphenylsulfinyl)-furan-2(5*H*)-one (VIIIa). A solution of 0.40 g (1.6 mmol) of sulfide **IIa** in 22 mL of diethyl ether was cooled to –15°C, a cold solution of 0.32 g (1.9 mmol) of *m*-chloroperoxybenzoic acid in 8 mL of diethyl ether was added dropwise, and the mixture was stirred for 3 h at –12°C and evaporated to dryness under reduced pressure. The solid residue containing sulfoxide **VIIIa** and *m*-chlorobenzoic acid was washed on a Schott filter with hexane–diethyl ether (3:1). The undissolved material was recrystallized from carbon tetrachloride–benzene (4:1) to isolate a mixture of two diastereoisomers at a ratio of 1:1. Yield 0.27 g (64%), colorless crystals, mp 138–142°C; published data [25]: mp 138°C. The spectral parameters of the product were consistent with those given in [25].

Compounds **VIIIb**–**VIIIe** were synthesized in a similar way.

3-Chloro-4-(4-chlorophenylsulfinyl)-5-hydroxy-furan-2(5*H*)-one (VIIIb) was synthesized by reaction of 0.44 g (1.6 mmol) of furanone **IIb** with 0.33 g (1.9 mmol) of *m*-chloroperoxybenzoic acid. According to the ^1H NMR data, the solid residue contained initial compound **IIb** and sulfoxide **VIIIb** at a ratio of 1:5 and *m*-chlorobenzoic acid. Sulfoxide (**VIIIb**) was isolated by column chromatography on silica gel (gradient elution with acetone–toluene, 1:6, to pure acetone). Yield 0.28 g (59%), colorless crystals, mp 118–121°C (from benzene), R_f 0.20 (acetone–toluene, 1:6). IR spectrum, ν, cm^{-1}: 3167 (OH), 1790 (C=O), 1630 (C^3=C^4), 1572 (C=C_{arom}), 1045 (S=O). ^1H NMR spectrum (acetone-d_6, 300 MHz), δ, ppm: 6.44 d (1H, 5-H, $^3J_{HH}$ = 8.5 Hz), 6.46 d (1H, 5-H, $^3J_{HH}$ = 8.4 Hz), 7.39 d (1H, OH, $^3J_{HH}$ = 8.4 Hz), 7.44 d (1H, OH, $^3J_{HH}$ = 8.5 Hz), 7.69, 7.90 m (4H, H_{arom}, *AA′BB′*, $^3J_{AB} + {}^5J_{AB'}$ = 8.7 Hz), 7.70 m and 7.92 m (4H, H_{arom}, *AA′BB′*, $^3J_{AB} + {}^5J_{AB'}$ = 8.5 Hz). Found, %: Cl 24.35; S 11.13. $C_{10}H_6Cl_2O_4S$. Calculated, %: Cl 24.19; S 10.94.

4-(4-Bromophenylsulfinyl)-3-chloro-5-hydroxy-furan-2(5*H*)-one (VIIIc) was synthesized by oxida-

tion of 0.40 g (1.2 mmol) of furanone **IIc** with 0.26 g (1.5 mmol) of *m*-chloroperoxybenzoic acid. Yield 0.28 g (71%), colorless crystals, mp 147–149°C (from CCl_4–benzene, 3:1), R_f 0.27 (acetone–benzene, 1:6). IR spectrum, ν, cm^{-1}: 3176 (OH), 1792 (C=O), 1626 (C^3=C^4), 1594 (C=C_{arom}), 1045 (S=O). ^{1}H NMR spectrum (acetone-d_6, 400 MHz), δ, ppm: 6.42 d (1H, 5-H, $^3J_{HH}$ = 8.8 Hz), 6.46 d (1H, 5-H, $^3J_{HH}$ = 8.4 Hz), 7.34 d (1H, OH, $^3J_{HH}$ = 8.4 Hz), 7.39 d (1H, OH, $^3J_{HH}$ = 8.8 Hz), 7.80–7.88 m (8H, H_{arom}). ^{13}C–{^{1}H} NMR spectrum (acetone-d_6, 100 MHz), δ_C, ppm: 97.97 and 98.60 (C^5); 128.07, 128.22, 128.96, 129.31, 134.63, 134.69, 140.84, 142.26, 142.59 (C^3, C_{arom}); 159.83 (C^4), 164.84 (C^2). Found, %: C 35.87; H 1.53. $C_{10}H_6BrClO_4S$. Calculated, %: C 35.58; H 1.79.

3-Chloro-4-(3,5-di-*tert*-butyl-4-hydroxyphenylsulfinyl)-5-hydroxyfuran-2(5*H*)-one (VIIId) was synthesized by oxidation of 0.40 g (1.1 mmol) of furanone **IId** with 0.22 g (1.3 mmol) of *m*-chloroperoxybenzoic acid. The mixture was evaporated to dryness under reduced pressure, and the solid residue was subjected to silica gel column chromatography using hexane–diethyl ether (1:3) as eluent to isolate 0.07 g (18%) of initial compound **IId** (R_f 0.44) and 0.26 g (60%) of sulfoxide **VIIId** (R_f 0.22). Yellow crystals, mp 155–156°C (from CCl_4–hexane, 3:1). IR spectrum, ν, cm^{-1}: 3587 (4′-OH), 3260 (5-OH), 1769 (C=O), 1626 (C^3=C^4), 1579 (C=C_{arom}), 1043 (S=O). ^{1}H NMR spectrum (acetone-d_6, 300 MHz), δ, ppm: 1.458 s (18H, CH_3), 1.462 s (18H, CH_3), 6.41 d (1H, 5-H, $^3J_{HH}$ = 9.0 Hz), 6.42 d (1H, 5-H, $^3J_{HH}$ = 8.2 Hz), 6.89 s (1H, 4′-OH), 6.90 s (1H, 4′-OH), 7.41 d (1H, 5-OH, $^3J_{HH}$ = 9.0 Hz), 7.53 d (1H, 5-OH, $^3J_{HH}$ = 8.2 Hz), 7.73 s (2H, H_{arom}), 7.79 s (2H, H_{arom}). Found, %: C 55.96; H 6.12; Cl 9.13; S 8.12. $C_{18}H_{23}ClO_5S$. Calculated, %: C 55.88; H 5.99; Cl 9.16; S 8.29.

4-Benzylsulfinyl-3-chloro-5-hydroxyfuran-2(5*H*)-one (VIIIe) was synthesized by oxidation of 0.22 g (0.8 mmol) of furanone **IIe** with 0.17 g (1.0 mmol) of *m*-chloroperoxybenzoic acid. The precipitate was filtered off and washed with diethyl ether (the product was not recrystallized). Yield 0.16 g (66%), colorless crystals, mp 130°C, R_f 0.24 (acetone–benzene, 1:6). IR spectrum, ν, cm^{-1}: 3146 (OH), 1781 (C=O), 1625 (C^3=C^4), 1500 (C=C_{arom}), 1052 (S=O). ^{1}H NMR spectrum (acetone-d_6, 300 MHz), δ, ppm: 4.49 m and 4.58 m (1H each, CH_2, *AB* quartet, $^2J_{AB}$ = 13.1 Hz), 4.70 s (2H, CH_2), 6.38 d (1H, 5-H, $^3J_{HH}$ = 7.3 Hz), 6.64 d (1H, 5-H, $^3J_{HH}$ = 6.6 Hz), 7.36–7.52 m (10H, H_{arom}), 7.67 d (1H, OH, $^3J_{HH}$ = 7.3 Hz), 8.07 d (1H, OH, $^3J_{HH}$ = 6.6 Hz). Found, %: C 48.59; H 3.61; Cl 12.96; S 11.72. $C_{11}H_9ClO_4S$. Calculated, %: C 48.45; H 3.33; Cl 13.00; S 11.76.

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