Convenient Methods for the Preparation of Sulfur Substituted Allenecarboxylates[1]

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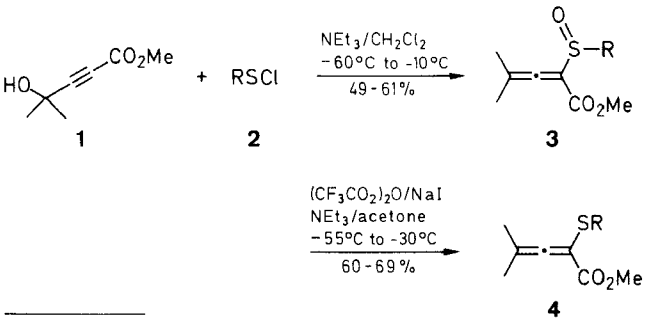
2-Sulfinyl- and 2-sulfonylallenecarboxylates, as new 1,1-diacceptor substituted allenes, were prepared starting from methyl 4-hydroxy-4-methyl-2-pentynoate by a [2,3]-sigmatropic rearrangement. The sulfoxides could be reduced to the corresponding allenyl sulfides. A 2(5*H*)-furanone derivative was prepared by a side-reaction.

As part of our research program on donor–acceptor systems, we required a method to introduce sulfur functionalities in the α-position to the ester group of an allenecarboxylate. The reason for the use of sulfur substituents lies in the fact that the reactivity may be modulated by changing the oxidation state of the sulfur atom. Furthermore the sulfinyl and the sulfonyl group attract increasing attention as useful functionalities in organic synthesis. Of particular interest are the applications of these groups as temporary transformers of chemical reactivity in the synthesis of eventually sulfur-free compounds.[3]

The synthesis of α-thioallenecarboxylates by metallation of an allene sulfide, followed by treatment with methyl chloroformate was mentioned by Viehe[4] as an approach to capto-dativ (*c,d*) substituted allenes, however, without giving experimental details. In this paper we present an alternative procedure which enables the preparation of thio-, sulfinyl- and sulfonyl derivatives. This new route starts from methyl 4-hydroxy-4-methyl-2-pentynoate (**1**), and the cumulated double bonds are generated by a [2,3]-sigmatropic rearrangement. We favored this procedure since both the starting materials are ready available and the reagents are easy to handle.



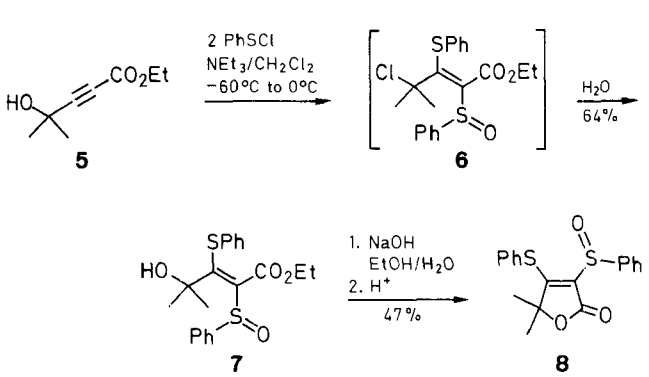
2-4	R
a	4-ClC$_6$H$_4$
b	Ph

Scheme A

For the preparation of the allenyl sulfoxides **3a** and **3b** the alkynol **1** is treated with *p*-chlorobenzenesulfenyl chloride **2a** or benzenesulfenyl chloride **2b**[5] in the presence of triethylamine at −60 °C, according to the procedure of Horner[6] (Scheme **A**). The crystalline sulfoxides **3a** and **3b** are isolated in 49% and 61% yield, respectively. After some days at 25 °C both products showed slight decomposition.

Unfortunately, treatment of these compounds with common reducing agents (e.g. aluminum chloride/sodium iodide,[7] titanium(III) chloride/ethanol,[8] *tert*-butyl bromide[9] failed to give good yields of the desired allenyl sulfides **4a,b**. Reasoning that the allenyl sulfoxides, or the corresponding sulfides, might be unstable to the harsh conditions sometimes used under these reactions, we tried the reduction with sodium iodide/trifluoroacetic anhydride in the presence of triethylamine at −55 °C as described by Buynak.[10] These conditions cleanly produce the allenyl sulfides **4a,b** in good yields (60–69%). The crude products are purified by column chromatography and isolated as yellow oils.

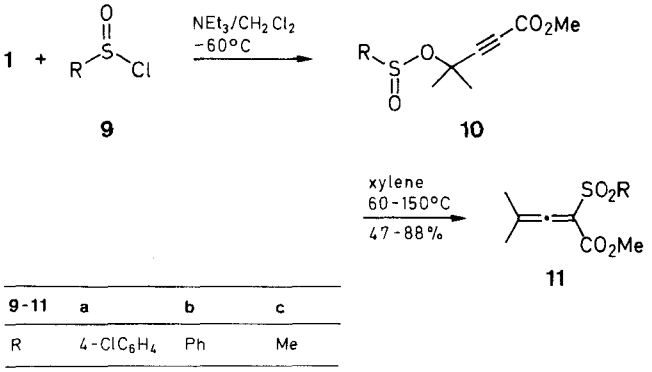
If the alkynol **1** is treated with excess of sulfenyl chloride **2** or if the sulfenyl chloride **2** is added too fast, the isolated sulfoxides **3** are contaminated with a byproduct, resulting from the addition of the sulfenyl chloride **2** to the sulfoxide **3**. During the reduction procedure this byproduct is transformed to a 2(5*H*)-furanone derivative. For the investigation of this side-reaction we treated the alkynol **5** with two equivalents benzenesulfenyl chloride **(2b)** (Scheme **B**). The primary formed allyl chloride **6** is hydrolyzed during aqueous workup to the γ-hydroxy ester **7**, which is saponified with sodium hydroxide. Acidification leads to lactonization, yielding the 2(5*H*)-furanone **8**.



Scheme **B**

α-Ester sulfones are generally prepared by oxidation of the corresponding allenyl sulfides or sulfoxides[11] or by alkylation of benzenesulfinate salts with α-halo esters.[12,13] Furthermore the oxidation of allenyl sulfides or sulfoxides represents a common method for the preparation of allenyl sulfones.[14] In the case of the α-ester sulfoxides **3a,b** several attempts with different oxidizing agents (e.g. 3-chloroperoxybenzoic acid, hydrogen peroxide, magnesium monoperoxophthalate) failed. The IR- and ^{13}C-NMR spectra of the crude products showed no cumulated double bonds.

For that reason we prepared the allenyl sulfones **11a–c** directly from the alkynol **1** by treatment with a sulfinyl chloride **9a–c** followed by thermal isomerization of the propargylic sulfinates **10a–c**[15] (Scheme **C**). The sulfinate esters from the reaction with 4-chlorbenzenesulfinyl chloride or benzenesulfinyl chloride rearrange after warming in toluene for 2 h at 60–80 °C. The sulfone **11a** is even formed, if the corresponding sulfinate is allowed to stand at room temperature for some days. The methyl sulfinate **10c** rearranges only at higher temperatures (refluxing xylene). All sulfones are isolated as crystalline powders, which can be stored in the refrigerator for weeks without decomposition.



9-11	a	b	c
R	4-ClC$_6$H$_4$	Ph	Me

Scheme **C**

All reagents were of commercial quality from freshly opened containers. Et_2O and THF were dried (KOH) and distilled over $LiAlH_4$. CH_2Cl_2 was distilled from CaH_2. All other solvents were purified by distillation. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on either a Varian VXR 300 spectrometer (300/75 MHz) or a Bruker WM 300 spectrometer (300/75 MHz) using TMS as internal standard. IR-spectra were obtained using a Perkin-Elmer 257 or Perkin-Elmer 1750 spectrophotometer. Mass spectra were recorded at 70 eV on a Varian Mat 212 instrument. Melting points were taken using a Büchi 510 apparatus and are uncorrected. Microanalyses were performed at Mikroanalytisches Labor der RWTH Aachen and Analytisches Labor des Organisch-Chemischen Instituts der WWU Münster. GC-analyses were performed on a Siemens Sichromat 3 with 25 m HP Ultra 2. Silica gel 60 (230–400 mesh) was purchased from Macherey und Nagel. Analytical TLC plates Merck were used. HPLC was performed with Kontron HPLC-Pump 420, Kontron UV-Detector 432, and RI-Detector 8110 (Bischoff) and a column Lichrosorb Si 60-5 (2 × 25 cm) (Chromatographie-Service).

Ethyl 4-Hydroxy-4-methyl-2-pentynoate (5):
A solution of 3-methyl-3-tetrahydropyranyloxy-1-butyne[16] (16.8 g, 0.1 mol) in THF (50 mL) is added to the Grignard reagent from EtBr (11.5 g, 0.106 mol) and Mg (2.6 g, 0.107 mol) in Et_2O (50 mL) in such a rate that the Et_2O slightly refluxes. In order to complete the conversion the mixture is heated on a steam bath for 1 h. The flask is flushed with Ar and cooled in an ice-bath. At 0 °C ethyl chloroformate (10.3 g, 0.095 mol) is added in five equal portions during 5 min. A rise of temperature must be avoided, but if the ester is added in a longer period of time the yield decreases. After 2 h at r.t. the mixture is hydrolyzed with a sat. solution of $NaHCO_3$ and extracted with cyclohexane (4 × 75 mL). The combined organic layers are washed with water (50 mL) and brine (50 mL) and dried ($MgSO_4$). The solvents are removed *in vacuo*, and the residue is dissolved in EtOH and treated with an acidic ion-exchange resin (Lewatit SC 108, 1 g) for 3 h to remove the protecting group. Then the resin is filtered and the solvent is evaporated. This procedure is repeated once.

Distillation of the crude product affords **5** as a colourless oil; yield: 8 g (54%); bp 120°C/13 mbar.

$C_8H_{12}O_3$ (156.2) calc. C 59.15 H 7.09 found 59.24 7.24

IR (cap): ν = 3420 (OH), 2985–2958, 2940 (CH), 2238 (C≡C), 1720 cm^{-1} (C=O).

^{1}H-NMR ($CDCl_3$): δ = 1.3 (t, 6H, J = 7 Hz, 2x CH_3), 1.58 (s, 6H, 2x CH_3), 3.75 (s, 1H, OH), 4.23 (q, 2H, J = 7 Hz, CH_2O).

^{13}C-NMR ($CDCl_3$): δ = 13.99 ($\underline{C}H_3CH_2$), 30.74 (CH_3), 62.02 (CH_2O), 64.82 (C-4), 73.95 (C-3), 91.59 (C-2), 153.9 (C=O).

MS: m/z (%) = 142 (7.7), 141 (M^+-CH_3, 100).

Methyl 4-Hydroxy-4-methyl-2-pentynoate (**1**)[17] is prepared analogously; yield: 70%; bp 80°C/3 mbar (Lit.[17] bp not reported).

^{1}H-NMR ($CDCl_3$): δ = 1.57 (s, 6H, 2x CH_3), 3.78 (s, 4H, OH + CH_3O).

^{13}C-NMR ($CDCl_3$): δ = 30.74 (CH_3), 52.83 (CH_3O), 64.82 (C-4), 73.6 (C-3), 92.04 (C-2), 154.29 (C=O).

MS: m/z (%) = 128 (6.6), 127 (M^+-CH_3, 100).

4-Chlorobenzenesulfinyl Chloride (9a):

Sodium 4-chlorobenzene sulfinate[18] (60 g, moist, contaminated with Na_2CO_3) is suspended in water (100 mL) at 50°C and treated with 2N HCl (200 mL). The stirred mixture is allowed to cool to r.t. and the sulfinic acid is isolated by filtration. The acid is washed with a small amount of cold water and dried in vacuum; yield: 30 g.

A suspension of the crude acid (5 g, 25.6 mmol) in pentane (50 mL) is treated with $SOCl_2$ (15 mL). After the vigorous reaction has subsided, the mixture is filtered through a glasswool filter. The filtrate is warmed on a steam bath to remove the pentane. Residual $SOCl_2$ is removed by pumping under vacuum for 2 h to leave 4-chlorobenzenesulfinyl chloride as an oil, which solidifies slowly and is used without further purification; yield: 4.4 g (89%).

Benzenesulfinyl chloride (**9b**) is prepared in a similar manner. Both, the chloride and the dry benzenesulfinic acid are very instable and decomposition occurs even at −20°C.

Methyl 2-(4-Chlorophenylsulfinyl)-4-methyl-2,3-pentadienoate (3a); Typical Procedure:

In an Ar flushed flask, a solution of alkynol **1** (3.4 g, 24 mmol) and NEt_3 (2.4 g, 24 mmol) in CH_2Cl_2 (50 mL) is cooled to −78°C. At this temperature a solution of 4-chlorobenzenesulfenyl chloride (**2a**;[5] 4.6 g, 26 mmol) in CH_2Cl_2 (20 mL) is added dropwise in such a rate that the orange colour of the sulfenyl chloride immediately disappears. Half way through the addition, the mixture becomes gelatinous and is warmed to −10°C for the rest of the addition. The mixture is stirred for an additional hour at this temperature before water (20 mL) is added to quench the reaction. The organic layer is separated and washed with dilute HCl (10 mL) water (2 × 50 mL), and brine (50 mL). After drying ($MgSO_4$), the solvent is removed to afford a yellow, viscous residue. Crystallization from Et_2O/pentane (1:3) at −15°C furnishes **3a** as white crystals; mp 108–110°C.

$C_{13}H_{13}ClO_3S$ (284.8) calc. C 54.83 H 4.60 found 54.70 4.70

IR (KBr): ν = 3080, 3060, 2955, 2910 (C–H), 1900 (C=C=C), 1708 (C=O), 1570, 1470 cm^{-1} (Ar C–C).

^{1}H-NMR ($CDCl_3$): δ = 1.82 1.93 (2 s, each 3H, CH_3), 3.74 (s, 3H, CH_3O), 7.46 (d, 2H_{arom}, J = 8.7 Hz), 7.66 (d, 2H_{arom}, J = 8.7 Hz).

^{13}C-NMR ($CDCl_3$): δ = 19.39, 19.57 (C-5, 6), 52.54 (C-7), 110.0 (C-2), 112.24 (C-4), 126.5 129.1 (C-2′, 3′ and C-5′, 6′), 137.3 (C-4′), 143.17 (C-1′), 163.04 (C-1), 204.5 (C-3).

Methyl 4-Methyl-2-phenylsulfinyl-2,3-pentadienoate (**3b**); yield: 61%; mp 73–74°C (Et_2O).

$C_{13}H_{14}O_3S$ (250.3) calc. C 62.38 H 5.64 found 62.28 5.52

IR (KBr): ν = 3060, 2985, 2910 (CH), 1950 (C=C=C), 1713 (C=O), 1584 cm^{-1} (Ar C–C).

^{1}H-NMR ($CDCl_3$): δ = 1.73, 1.78 (2 s, each 3H, 2x CH_3), 3.73 (s, 3H, CH_3O), 7.45–7.49 (m, 3H, H-3′-5′), 7.67–7.7 (m, 2H, H-2′, 6′).

^{13}C-NMR ($CDCl_3$): δ = 19.24, 19.42 (C-5, 6), 52.46 (C-7), 110.15 (C-4), 111.33 (C-2), 124.97 (C-2′, 6′), 128.9 (C-3′, 5′), 131.2 (C-4′), 144.2 (C-1′), 163.1 (C-1), 204.7 (C-3).

MS: m/z (%) = 250 (M^+, 23), 125 (100).

Methyl 2-[(4-Chlorophenyl)thio]-4-methyl-2,3-pentadienoate (4a); Typical Procedure:

A solution of **3a** (0.7 g, 2.5 mmol), NEt_3 (1.6 mL, 11.4 mmol), anhydrous NaI (0.96 , 6.4 mmol) and anhydrous acetone (14 mL) in a 100 mL 3-necked flask equipped with overhead stirrer is cooled to −50°C. Trifluoracetic anhydride (0.98 mL, 6.9 mmol) is then added during 1 min and the mixture is stirred for 0.5 h. The bath temperature is gradually allowed to rise to −30°C in the course of 15 min, and then the cold mixture is poured into a two-phase system consisting of hexane (15 mL), 5% $NaHCO_3$-solution (10 mL) and 5% Na_2SO_3-solution (10 mL). The separatory funnel is shaken vigorously for 2 min, the layers are separated, and the aqueous layer is extracted with hexane (2 × 20 mL). The combined hexane layers are washed with water (3 × 15 mL), brine (20 mL), and dried ($MgSO_4$). The solution is concentrated and immediately purified by column chromatography (silica gel, Et_2O) to afford **4a** as a yellow oil in 95% purity; yield: 0.4 g (60%).

$C_{13}H_{13}ClO_2S$ (268.8) calc. C 58.10 H 4.88 found 57.60 4.95

IR (cap): ν = 2984, 2950, 2908 (C–H), 1948 (C=C=C), 1720 (C=O), 1574, 1476 cm^{-1} (ArC–C).

^{1}H-NMR ($CDCl_3$): δ = 1.29 (s, 6H, 2x CH_3), 2.16 (s, 3H, CH_3O), 7.23–7.34 (m, 4H_{arom}).

^{13}C-NMR ($CDCl_3$): δ = 19.33 (2x CH_3), 52.78 (CH_3O), 96.73 (C-2), 104.59 (C-4), 129.07, 133.61 (C-2′, 3′ and C-5′, 6′), 132.6 (C-4′), 133.7 (C-1′), 165.1 (C-1), 207.8 (C-3).

MS: m/z (%) = 270 (M^{+37}Cl, 14.5), 268 (M^{+35}Cl, 37.1), 201 (100).

Methyl 4-Methyl-2-(phenylthio)-2,3-pentadienoate (**4b**); the crude product, which contains benzenethiol, is purified by HPLC (Si 60, EtOAc/cyclohexane, 10:90, 10 mL/min); yield 1.3 g (69%); yellow oil.

$C_{13}H_{14}O_2S$ (234.3) calc. C 66.64 H 6.02 found 66.80 5.96

IR (cap): ν = 3060, 2990, 2955, 2855 (C–H), 1950 (C=C=C), 1720 cm^{-1} (C=O).

^{1}H-NMR ($CDCl_3$): δ = 1.61 (s, 6H, 2x CH_3), 3.75 (s, 3H, CH_3O), 7.25–7.32 (m, 3H_{arom}), 7.36–7.4 (m, 2H_{arom}).

^{13}C-NMR ($CDCl_3$): δ = 19.29 (C-5, 6), 52.73 (C-7), 97.27 (C-4), 104.5 (C-2), 127.7 (C-4′), 128.8 (C-3′, 5′), 132.6 (C-2′, 6′), 165.37 (C-1), 207.51 (C-3).

MS: m/z (%) = 234 (M^+, 33.7), 39 (100).

Methyl 4-Methyl-2-(methylsulfonyl)-2,3-pentadienoate (10c):

To a mixture of **1** (2.8 g, 20 mmol), NEt_3 (2.9 g, 29 mmol) and anhydrous CH_2Cl_2 (30 mL) is added methanesulfinyl chloride (**9c**)[20] (2.4 g, 24 mmol) within 10 min. with cooling at −50°C. The cooling bath is removed and after 15 min a mixture of water (40 mL) and conc HCl (0.6 mL) is added with vigorous stirring. The lower layer is separated, washed with water (2 × 10 mL) and dried ($MgSO_4$). The residue remaining after evaporation of the solvent in a water-pump vacuum is dissolved in xylene (16 mL). The solution is refluxed for 2 h, and the xylene is distilled out at 15–30 mbar. The oily residue is crystallized from Et_2O; yield: 3.6 g (88%); white crystals; mp 64–66°C.

$C_8H_{12}O_4S$ (204.2) calc. C 47.05 H 5.94 found 46.57 5.83

IR (KBr): ν = 3020, 2975 (CH), 1956 (C=C=C), 1720 (C=O), 1310, 1318, 1143, 1150 cm^{-1} (SO_2).

^{1}H-NMR ($CDCl_3$): δ = 1.98 (s, 6H, CH_3), 3.22 (s, 3H, SO_2CH_3), 3.82 (s, 3H, CH_3O).

^{13}C-NMR ($CDCl_3$): δ = 19.15 (2x CH_3), 43.0 (SO_2CH_3), 52.9 (CH_3O), 106.0 (C-2), 109.8 (C-4), 161.99 (C-1, C=O), 202.4 (C-3).

MS: m/z (%) = 204 (M^+, 16.0), 125 (100).

Methyl 2-(4-Chlorophenylsulfonyl)-4-methyl-2,3-pentadienoate (11a); Typical Procedure:

A solution of the alkynol **1** (3.2 g, 22.5 mmol), 4-(dimethylamino)-pyridine (50 mg) and NEt_3 (2.3 g, 22.5 mmol) in CH_2Cl_2 (50 mL) is treated with a solution of 4-chlorobenzenesulfinyl chloride (**9a**; 4.4 g, 22.5 mmol) in CH_2Cl_2 (20 mL) according to the procedure described for the preparation of **10c**. Before quenching with dil HCl, the mixture must be stirred for 2 h at 0 °C in order to complete the conversion. The crude sulfinate **10a** (5.2 g) is dissolved in toluene (50 mL), and heated for 2 h at 60–80 °C; yield: 3.2 g (47 %) mp 85 °C (Et_2O).

$C_{13}H_{13}ClO_4S$	calc.	C 51.92	H 4.36
(300.8)	found	51.94	4.31

IR ($CDCl_3$): ν = 3090, 2990, 2955, 2910, 2850 (CH), 1960 (C=C=C), 1735 (C=O), 1586, 1479, 1460 cm^{-1} (C=C).

^{1}H-NMR ($CDCl_3$): δ = 1.97 (s, 6 H, 2x CH_3), 3.72 (s, 3 H, CH_3O), 7.52 (d, 2 H, J = 8.7 Hz, H-3′, 5′), 7.91 (d, 2 H, J = 8.7 Hz, H-2′, 6′).

^{13}C-NMR ($CDCl_3$): δ = 18.69 (CH_3), 52.298 (CH_3O), 106.42 (C-2), 109.66 (C-4), 128.75 (C-2′, 6′), 129.81 (C-3′, 5′), 138.86 (C-1′), 139.64 (C-4′), 160.72 (C=O), 208.61 (C-3).

Methyl 4-Methyl-2-(phenylsulfonyl)-2,3-pentadienoate (**11b**); the first formed sulfinate ester is rearranged by heating in toluene at 90 °C for 2 h; yield: 2.5 g (48 %); mp 93 °C (Et_2O).

$C_{13}H_{14}O_4S$	calc.	C 58.63	H 5.30
(266.3)	found	58.50	5.29

IR (KBr): ν = 3081, 3060, 3038, 3000, 2960, 2850 (CH), 1952 (C=C=C), 1725 (C=O), 1255, 1155 cm^{-1} (S=O).

^{1}H-NMR ($CDCl_3$): δ = 1.92 (s, 6 H, 2x CH_3), 3.7 (s, 3 H, CH_3O), 7.51–7.65 (m, 3 H, H-3′-5′), 7.97–8.00 (m, 2 H, H-2′, 6′).

^{13}C-NMR ($CDCl_3$): δ = 19.09 (C-5, 6), 52.62 (C-7), 107.12 (C-4), 109.7 (C-2), 128.55 (C-2′, 6′), 128.8 (C-3′, 5′), 133.52 (C-4′), 140.61 (C-1′), 161.16 (C-1), 208.8 (C-3).

Ethyl 4,4-Dimethyl-4-hydroxy-2-phenylsulfinyl-3-phenylthio-2-pentenoate (7):

A solution of **5** (5 g, 35 mmol) and NEt_3 (7.2 g, 70 mmol) in CH_2Cl_2 (80 mL) is cooled to −78 °C. At this temperature a solution of benzenesulfenyl chloride (**2b**;[5] 11.6 g, 80 mmol) in CH_2Cl_2 (50 mL) is added. The mixture is stirred for 1 h at −20 °C and then quenched with water (25 mL). The organic layer is separated and washed with dil HCl (10 mL), water (2 × 50 mL), and brine (50 mL). After drying (K_2CO_3) the solvent is removed and crystallized from Et_2O; yield: 8.8 g (64 %); white powder; mp 156 °C.

$C_{20}H_{22}O_4S_2$	calc.	C 61.5	H 5.6
(390.2)	found	61.0	5.59

IR (KBr): ν = 3280 (OH), 2950, 3020 (C–H), 1720 cm^{-1} (C=O).

^{1}H-NMR ($CDCl_3$): δ = 1.05 (s, 3 H, CH_3), 1.19 (t, 3 H, J = 6 Hz, CH_3CH_2O), 1.40 (s, 3 H, CH_3), 4.19 (m, 2 H, CH_2O), 4.77 (s, 1 H, OH), 7.05–7.09 (m, 2 H_{arom}), 7.26–7.32 (m, 3 H_{arom}), 7.51–7.56 (m, 3 H_{arom}), 8.14–8.17 (m, 2 H_{arom}).

5,5-Dimethyl-3-phenylsulfinyl-4-phenylthio-2(5*H*)-furanone (8):

A solution of **7** (2 g, 5 mmol) in EtOH (30 mL), is stirred with a solution of NaOH (0.8 g, 20 mmol) in water (30 mL) for 12 h. The resulting nearly clear mixture is filtered and treated with 2 N H_2SO_4 until pH 2 is reached. The white precipiate is filtered, washed with cold water and dried *in vacuo* at room temperature; yield: 0.8 g (47 %); mp 165 °C.

$C_{18}H_{16}O_3S$	calc.	C 62.77	H 4.68
(344.4)	found	62.24	4.63

^{1}H-NMR ($CDCl_3$): δ = 1.49, 1.51 (2 s, each 3 H, 2x CH_3), 7.44–7.54 (m, 8 H_{arom}), 7.71–7.73 (m, 2 H_{arom}).

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Muth, F., in: *Houben-Weyl*, 4th Ed., Vol. IX, Georg Thieme Verlag, Stuttgart 1955, p. 304.
(19) Benzenesulfenyl chloride tends to spontaneous decomposition with generation of sulfur dichloride.
(20) Hearst, P.J.; Noller, C.R. *Org. Synth. Coll. Vol. IV*, **1963**, 571.