Scope and Limitations of a New Highly Selective Synthesis of Unsymmetrical Monomers for the Synthesis of Precursors toward Poly(arylenevinylene)s

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In our laboratory a precursor route to poly(*p*-phenylenevinylene) derivatives is developed in which unsymmetrically substituted *p*-xylene derivatives, possessing a benzylic sulfinylalkyl group, are used as monomers. Because of this unsymmetry, we were forced to investigate thoroughly the synthesis of these sulfoxides, as we start from symmetric and readily accessible molecules, namely, bis(halomethyl)-*p*-xylene derivatives. In a former publication, a new extremely effective route for the production of these unsymmetrically substituted sulfinyl monomers was presented. This paper expands upon these previously reported results. To examine the scope and limitations of this elegant route, this new method was applied to the synthesis of various derivatives not included in the initial work.

Introduction

To avoid the drawbacks connected to the precursor routes known from literature for the synthesis of poly(arylenevinylene) derivatives,[1−12] a new precursor route was developed in our laboratory. The monomers in this route possess a benzylic leaving group and a benzylic so-called polarizer which differs from the former. It was shown that the use of an alkylsulfinyl group as the polarizer and a halogen as the leaving group leads to stable and soluble precursor polymers.[13−15] These unsymmetric sulfoxides are readily accessible via the oxidation of the corresponding thioethers, meaning that the first step to come to these sulfoxides is the synthesis of the thioethers. These thioethers can be made via several routes, of which one is very convenient, namely, the nucleophilic substitution of a thiolate anion on a benzylic halide (Route I, Scheme 1).[16] A disadvantage bound to this method is the difficulty to synthesize unsymmetric sulfides starting from symmetrical *p*-xylene products which have two identical benzylic halogenides. Indeed, in this case a second substitution reaction only can be avoided by the use of a 5−10-fold excess of the substrate. The amount of substrate can be diminished significantly to 2 or 3 equiv of bishalogenide by working with a phase-transfer-catalyzed nucleophilic substitution. This method also avoids the use of NaH and the necessity of water-free conditions coupled therewith (Route II, Scheme 1).[17,18]

Despite this improvement, the synthesis of unsymmetric monomers remains a delicate point in our route. An excess of the substrate is necessary and bisthioalkylation, in some measure, inevitable. As a consequence column chromatography is a necessity in the purification process. So, an alternative synthesis appeared to be desirable, and a new highly selective route for the synthesis of these unsymmetrically substituted monomers was developed and recently published (Route III, Scheme 2).[19] This paper expands upon these previously reported results. To elaborate the scope and limitations of this route, we applied this new method to the synthesis of various derivatives not included in the initial work. Like depicted in Scheme 2, five steps can be distinguished in this new route. The thiolate anion (1 equiv) withdraws a benzylic proton from the bissulfonium salt **3a** (1 equiv). Then the *p*-quinodimethane system is formed by a 1,6-elimination, and the unsymmetric thioether formed when a thiol molecule attacks the *p*-quinodimethane system. Next, octane is added to remove the THT by means of an azeotropic distillation, in this way accelerating the

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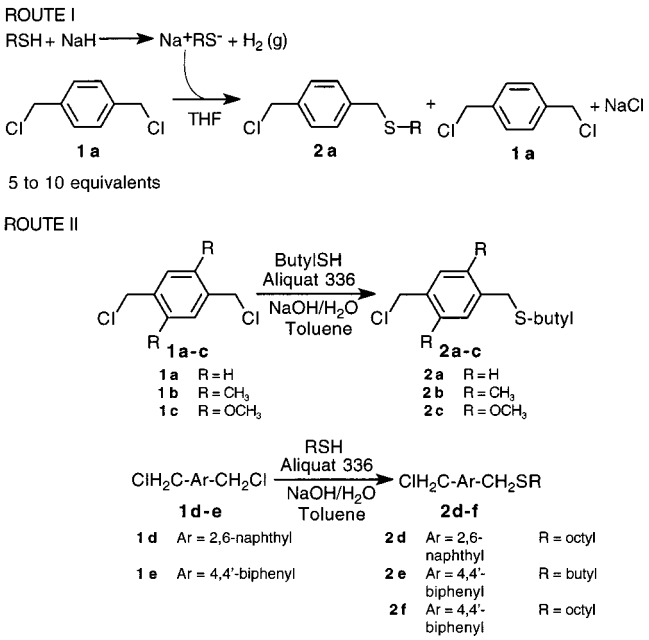
Scheme 1



substitution of the sulfonium salt by the counterion, the chloride anion.

UV−vis measurements confirmed this mechanism. Indeed, it is possible to follow the progress of the reaction because the benzoid (282 nm) and the quinoid (316 nm) structures absorb at different wavelengths. In this manner the formation and consumption of the quinoid compound was established during the reaction.[19]

In this reaction bissulfonium salts are used for three reasons. First, the pK_a of a benzylic proton next to a bissulfonium salt is low enough for a thiolate anion to remove this proton. Second, a sulfonium salt is a good leaving group, and third the halogenide is easily formed by a nucleophilic attack of the counterion on the sulfonium salt.

Former work has taught us that it is very important to keep the number equivalents of the thiol, the base, and the bissulfonium salt equal, to avoid a possible bissubstitution or polymerization. Indeed, these bissulfonium salts are known as monomers for the so-called Wessling polymerization, to synthesize precursor polymers for conjugated polymers.[8,9]

Results and Discussion

Synthesis of the Sulfides. This new method is tested on four different derivatives, which can be divided into electron-rich derivatives, electron-poor derivatives, and derivatives with an extended aromatic structure. First the synthesis of the bissulfonium salts will be discussed briefly, next the synthesis of the monosulfides, and finally the oxidation to the sulfoxides, the monomers in our precursor route (Scheme 3).

The first step in this strategy is the synthesis of the bissulfonium salts. The procedures for the syntheses of these salts are known from literature and are simple to perform. Except for the synthesis of **3d**, all of the procedures are approximately the same.[20−23] These bissulfonium salts are very hygroscopic. Because the number of equivalents of the reagents used in the next step is very critical, the amount of water bound to the salt has to be known and is determined by ^{1}H NMR measurements.

As already mentioned, we tried to synthesize the monosulfide of four different bissulfonium salts via this procedure. The mixtures obtained are analyzed by means of ^{1}H NMR (which are given as Supporting Information) or GC−MS (CI). The relative ratios of the bishalogenides, the bissulfides, and the monosulfides are presented in Table 1. We established that high relative amounts of the monosulfide of the methyl (**2h**), methoxy (**2i**), and chloride (**2j**) substituted derivatives are formed. In the last case, some water was added to the methanol because of the low solubility of this salt **2j** (with bromides as counterions) in methanol. Clearly this has not influenced the reaction. The amounts of bishalogenide and bissulfide in theory should be the same, as approximately is in accordance with the experimental results.

When the thiolate anion is added to the naphthylbissulfonium salt **3e**, dissolved in methanol, after 45 min the conversion only comes to 42%. In other words, only 42% of the thiol is converted into the sulfide. Even after 24 h the conversion only amounts to 75%. In both of the experiments no high relative amount of the monosulfide is formed. According to a simple linear regression on these results, at a conversion of 100%, the theoretical distribution of 25 (bischloride):50 (monosulfide):25 (bissulfide) is reached. Although we established that the bissulfide precipitates from the reaction mixture, apparently this phenomenon has no influence on the relative distribution of the products formed during the reaction. Thus, it is not possible to synthesize the monosulfide of the naphthyl derivative **2d** with a high relative yield via this method. This is caused by the high resonance energy of this derivative. As a matter of fact, this synthesis proceeds via its *p*-quinodimethane system, and the elimination reaction to form this *p*-quinodimethane system is a high-energy step that involves the loss of resonance energy of the aromatic system. Hence, a driving force for the formation of the quinoid compound is required, which in this case apparently is not large enough. A consequence is that other derivatives possessing high resonance energy, like the 4,4′-biphenyl derivative, cannot be used in this route. So, both the 2,6-naphthyl and 4,4′-biphenyl sulfide derivatives **2d**−**f** described in this paper, are synthesized via a phase-transfer-catalyzed nucleophilic substitution.

It can also be deduced from these two last experiments that the nucleophilic substitution reaction, under these conditions, is very slow. The other monosulfides were synthesized under equivalent conditions, and these reactions were already finished after 45 min. From this, it can be concluded that the nucleophilic substitution is hindered significantly, as it proceeds many times slower. As a consequence, the relative amounts of bissulfide found in the reaction mixtures **2g**−**j** are very low.

Oxidation to the Sulfoxides. The oxidation of thioethers can deliver both sulfoxides and sulfones.[24] Soft oxidation, which only delivers sulfoxides and avoids the

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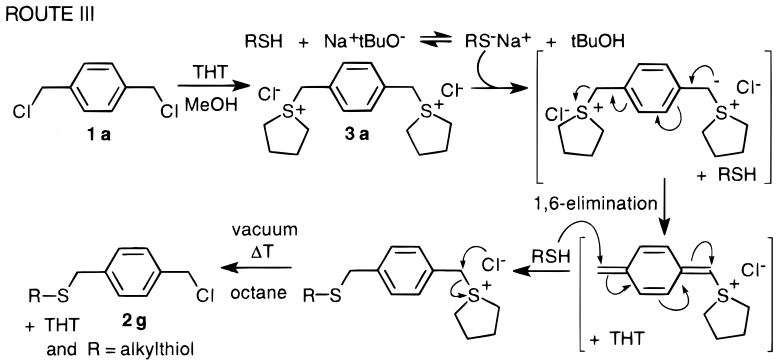
Scheme 2



Scheme 3

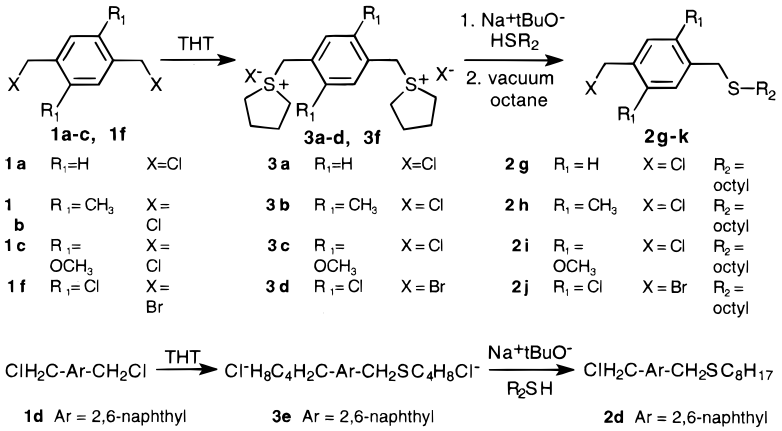


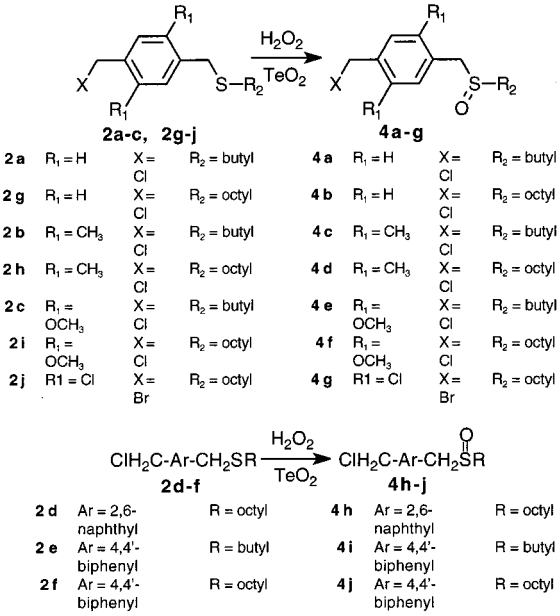
Table 1. Product Distribution of Crude Reaction Mixtures of Thioether Synthesis

derivative	MeOH/H_2O ratio	bishalogenide (%)	bissulfide (%)	monosulfide (%)
2g	1/0	5	5	90
2h	1/0	8	6	86
2i	1/0	9	11	80
2j	4/1	7	7	86
2d	1/0	60	2	38

overoxidation to sulfones, requires the appropriate reaction conditions. H_2O_2, alone or together with several solvents or catalysts, is a possible reagent for the oxidation of organic sulfides to sulfoxides.[25−27] A very simple and efficient method is the tellurium-catalyzed oxidation of the thioethers by means of H_2O_2 in methanol.[28] If the product, which must be oxidized, hardly dissolves in methanol, a mixture of methanol and dioxane or even pure dioxane is used. Because the rate of the oxidation is rather low in dioxane, a drop of concentrated HCl is added to the mixture, to accelerate the reaction (Scheme 4).

The sulfides are used impure, or only partially purified, in this reaction. The reaction is followed with TLC and terminated most of the times after 6−8 h. The sulfoxides are purified with column chromatography, although it must be possible to purify these sulfoxides without column chromatography, owing to the low amount of side

Scheme 4



products present in the crude reaction mixture. The yields of the synthesis of the sulfoxides, starting from the bishalogenide or the bissulfonium salt, are shown in Table 2. Because we started with 2−3 equiv of bishalogenide in the phase-transfer-catalyzed reaction, the yields will be rather low in these cases.

As already explained, it is possible to obtain high relative yields of the monosulfide starting from bissulfonium derivatives, substituted with electron-donating groups or inductive electron-withdrawing groups. The oxidation of the sulfide to the sulfoxide is a reaction with

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Table 2. Overall Yields of the Sulfoxides Synthesized via Route II or Route III[a]

	yield route II (%)		yield route III (%)
4a	38	**4b**	75
4c	28	**4d**	61
4e	3	**4f**	12
–	–	**4g**	70
4h	19	**4h**	0
4i	25	–	–
4j	20	–	–

[a] – = not carried out.

high yields. All of this is confirmed by the total yields of the methyl- and chloride-substituted monomers **4d** and **4g**. However, the methoxy-substituted derivative **4f** does not confirm the expectations. According to our observations, this low yield is caused by an undesirable reaction during the purification by column chromatography, because the crude mixture placed on the column mainly consisted of monosulfoxide (80%) according to ^{1}H NMR measurements.

In the meantime, it appeared that the few percentages of the side products present in the crude mixture do not interfere with the polymerization of the sulfoxides.[29] This means that is not necessary anymore to purify the sulfoxides, made via this new route, for this purpose. After the polymerization the polymer is easily purified by means of a simple precipitation in the appropriate solvent, such that the polymer precipitates and the monomers and side products stay in solution.

Conclusions

Bissulfonium salts can be used as starting materials for the synthesis of unsymmetric benzylic sulfides. Namely, it is possible to obtain high yields (90%) of the monosulfide starting from a symmetric bissulfonium salt, 1 mol equiv of Na^+tBuO^- and 1 mol equiv of a thiol, via the effective procedure described. Until now it is proven that it is possible to synthesize unsymmetric benzylic sulfides from bissulfonium derivatives substituted with electron-donating groups or inductive electron-withdrawing groups via this new and efficient route. These sulfides are easily oxidized to their corresponding sulfoxides, which are the monomers for the synthesis of poly(arylenevinylene) precursors, with H_2O_2 an TeO_2 in methanol and/or dioxane.

Experimental Section

General Methods. Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. The reagent gas was *i*-butane, and the reagent gas pressure was 3000−4000 mTorr if chemical ionization was used. For the infrared spectroscopy measurements, KBr pellets were used. ^{13}C NMR spectra were recorded at 100 MHz and ^{1}H NMR spectra at 200, 300, or 400 MHz. The chemical shift assignment was based on 1D APT, 2D COSY, and HETCOR (optimized for direct and vicinal coupling) experiments, and values are given in ppm relative to internal TMS as the standard.

Materials. All solvents and reagents were purchased from ACROS or Aldrich except NaOH, $MgSO_4$ (VEL), **1b** (Lancaster), and octane (Fluka). All of these materials are reagent grade and are used without further purification unless otherwise noted. The bischlorides **1c**,[21] **1f**,[30] **1d**,[31,32] and **1e**[31,32] were prepared as reported in the literature. Chromatographic separations were performed on Macherey−Nagel silica gel (particle size: 0.023−0.2 mm). TLC was performed on Merck silica gel 60F_{254}.

(Chloromethyl)-4-[(butylsulfanyl)methyl]benzene (2a). A mixture of 99.7 g (0.569 mol) of **1a** in 1000 mL of toluene, 60 g (1.5 mol) of NaOH in 1000 mL of H_2O, and 2.5 g of a phase-transfer catalyst, trioctylmethylammonium chloride (Aliquat 336), is vigorously stirred at room temperature. A solution of 30.5 mL (0.285 mol = 0.5 equiv) of butanethiol in 300 mL of toluene is added drop by drop to this mixture. When the thiol is added completely, the mixture is still stirred for 1 h more. The organic layer is separated, washed with water, and dried over $MgSO_4$. After the evaporation of the solvent, a white-yellow crystalline product is obtained. This mixture containing **1a**, **2a**, and 1,4-bis[(butylsulfanyl)methyl]benzene is dried under vacuum. Next it is purified partially by a recrystallization from hexane during which the bishalogenide precipitates as white crystals. These crystals are filtered of and washed with cold hexane. The mother liquor is reduced on a rotary evaporator and the oil obtained oxidized to the sulfoxide in the next step.

The following syntheses are performed in the same manner, unless otherwise stated.

(Chloromethyl)-4-[(butylsulfanyl)methyl]-2,5-dimethylbenzene (2b). A mixture of 30 g (0.148 mol) of **1b** in 450 mL of toluene, 14.88 g (0.372 mol) of NaOH in 372 mL of water, and 0.74 g (1.84 mmol) of Aliquat 336 is stirred vigorously. To this is added over 24 h a solution of 7.9 mL (0.074 mol) of butanethiol in 96.5 mL of toluene.

(Chloromethyl)-4-[(butylsulfanyl)methyl]-2,5-dimethoxybenzene (2c). A total of 60 g (0.255 mol) of **3a** is dissolved in 1875 mL of toluene and stirred together with 17.25 g (0.43 mol) of NaOH in 500 mL of water and 0.86 g (2.14 mmol) of Aliquat 336. To this is added over 24 h 9.12 mL (0.085 mol) of butanethiol in 120 mL of toluene. The excess **1c** is recuperated partially by a recrystallization from a mixture of hexane and $CHCl_3$ (ratio: 2/1).

2-(Chloromethyl-6-[(octylsulfanyl)methyl]naphthalene (2d). A total of 23 g (0.1 mol) of **1d** is dissolved in 1100 mL toluene. To this is added 10.5 g (0.263 mol) of NaOH dissolved in 230 mL, of H_2O, together with 0.44 g of Aliquat 336. A total of 8.5 mL (0.05 mol) of octanethiol dissolved in 53 mL of toluene is added slowly over 24 h. Afterward the raw mixture is recrystallized from a mixture of hexane and $CHCl_3$, during which the **1d** partially precipitates as white crystals.

4-(Chloromethyl)-4′-[(butylsulfanyl)methyl]biphenyl (2e) and 4-(Chloromethyl)-4′-[(octylsulfanyl)methyl]biphenyl (2f). These compounds were synthesized according to the procedure described for the synthesis of **2a**.

Determination of the Amount Water bound to The Sulfonium salts. First the amount of H_2O in D_2O used for the ^{1}H NMR measurement is determined. Next, the sample of the bissulfonium salt, dissolved in D_2O, is measured under equivalent conditions. The amount of H_2O in the D_2O sample is subtracted from the total amount of water in the salt sample, and the intensity of the water signal is compared with the intensity of a signal of the salt itself (for instance, an aromatic proton). From this, the amount of water bound to the salt is deduced. For the synthesis of the sulfide we work with the adapted molecular weight, including the water bound to the molecule.

1,4-Bis[(tetrahydrothiophenio chloride)methyl]-2,5-dimethylbenzene (3b). Synthesis is according to ref 20: mp 146.0−147.5 °C (lit. mp 147.0−149.0 °C); FT IR (KBr, ν, cm^{-1})

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2976, 2931, 1613, 1461, 1259; ^{1}H NMR (δ, D_2O, 400 MHz) 7.23 (s, 2H), 4.38 (s, 4H), 3.32 (m, 8H), 2.25 (m, 8H).

1,4-Bis[(tetrahydrothiophenio chloride)methyl]-2,5-dimethoxybenzene (3c). Synthesis is according to ref 21: mp 176.5−178.9 °C; FT IR (KBr, ν, cm^{-1}) 2976, 2950, 2885, 1513, 1461, 1398, 1233, 1031, 690; ^{1}H NMR (δ, D_2O, 400 MHz) 7.10 (s, 2H), 4.43 (s, 4H), 3.81 (s, 6H), 3.40 (m, 8H), 2.21 (m, 8H).

1,4-Bis[(tetrahydrothiophenio bromide)methyl]-2,5-dichlorobenzene (3d). Synthesis is according to ref 23: mp 161.6−163.8 °C (lit. mp 160.0−161.0 °C); FT IR (KBr, ν, cm^{-1}) 2994, 2927, 2888, 2822, 1479, 1411, 1371, 1260, 1083, 907; ^{1}H NMR (δ, D_2O, 200 MHz) 7.74 (s, 2H), 4.56 (s, 4H), 3.45 (m, 8H), 2.30 (m, 8H).

2,6-Bis[(tetrahydrothiophenio chloride)methyl]naphthalene (3e). Synthesis is according to ref 22: mp 146.5−149.4 °C; FT IR (KBr, ν, cm^{-1}) 2936, 1624, 1408, 1261, 897, 831; ^{1}H NMR (δ, D_2O, 300 MHz) 7.97 (s, 2H), 7.96 (d, ^3J = 8.43 Hz, 2H), 7.56 (d, ^3J = 8.36 Hz, 2H), 4.60 (s, 4H), 3.41 (m, 8H), 2.22 (m, 8H).

(Chloromethyl)-4-[(octylsulfanyl)methyl]-2,5-dimethylbenzene (2h). A total of 2 g (5.27 mmol) of **3b** is dissolved in 27 mL of MeOH and stirred. A mixture of 0.48 g (5.03 mmol) of Na^+tBuO^- and 0.7 g (4.76 mmol) of octanethiol, dissolved in 15 mL of MeOH, is added at once, while the mixture is stirred vigorously. After 45 min the mixture is neutralized by the addition of 0.1 M HCl, and MeOH is evaporated. Further octane is added to remove THT completely by azeotropic distillation. The residue is dissolved in a sufficient quantity of $CHCl_3$ whereupon this solution is filtered to remove the NaCl formed. The filtrate is reduced on a rotary evaporator and used without further purification: ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.09 (s, 1H), 7.01 (s, 1H), 4.55 (s, 2H), 3.64 (s, 2H), 2.45 (t, ^3J = 7.28 Hz, 2H), 2.35 (s, 3H), 2.33 (s, 3H), 1.56 (m, 2H), 1.34 (m, 2H), 1.25 (m, 8H), 0.87 (t, ^3J = 6.80 Hz, 3H).

The syntheses of the following thioethers are the same as the synthesis of **2h** unless otherwise stated.

(Chloromethyl)-4-[(octylsulfanyl)methyl]-2,5-dimethoxybenzene (2i). A total of 8 g (0.0185 mol, inclusive bound water) of **3c** is dissolved in 130 mL of methanol and stirred. A mixture of 1.81 g (0.019 mol) of Na^+tBuO^- and 2.76 g (0.019 mol) of octanethiol, dissolved in 60 mL of methanol, is added: ^{1}H NMR (δ, $CDCl_3$, 300 MHz) 6.86 (s, 1H), 6.85 (s, 1H), 4.62 (s, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 3.70 (s, 2H), 2.45 (t, ^3J = 7.35 Hz, 2H), 1.57 (m, 2H), 1.30 (m, 2H), 1.24 (m, 8H), 0.85 (t, ^3J = 6.86 Hz, 3H).

(Bromomethyl)-4-[(octylsulfanyl)methyl]-2,5-dichlorobenzene (2j). A total of 15.59 g (0.030 mol, inclusive bound water) of **3d** is dissolved in a mixture of 240 mL of MeOH and 67 mL of H_2O and stirred. A mixture of 2.91 g (0.030 mol) of Na^+tBuO^- and 4.34 g (0.029 mol) of octanethiol, dissolved in a mixture of 81 mL of MeOH and 21 mL of H_2O, is added: ^{1}H NMR (δ, $CDCl_3$, 200 MHz) 7.43 (s, 1H), 7.40 (s, 1H), 4.49 (s, 2H), 3.73 (s, 2H), 2.45 (t, ^3J = 7.21 Hz, 2H), 1.54 (m, 2H), 1.24 (m, 10H), 0.85 (t, ^3J = 6.49 Hz, 3H); MS (EI, *m*/*z*, relative intensity in %) 396 (M^+, 1), 317 (M^+ − Br, 1), 253 (M^+ − S − Oct, 6), 172 (M^+ − S − Oct − Br, 29), 145 (S − Oct, 100), 137 (M^+ − S − Oct − Br − Cl, 1), 102 (M^+ − S − Oct − Br − 2Cl, 5).

2-(Chloromethyl)-6-[(octylsulfanyl)methyl]naphthalene (2d). A total of 2.28 g (4.98 mmol inclusive bound water) of **3e** is dissolved in 50 mL of MeOH and stirred. A mixture of 0.48 g (4.98 mmol) of Na^+tBuO^- and 0.73 g (4.98 mol) of octanethiol, dissolved in 17 mL of MeOH, is added: MS (CI, *m*/*z*, relative intensity in %) 335 (MH^+, 100), 299 (M^+ − Cl, 9), 189 (M^+ − S − Oct, 10), 155 (M^+ − S − Oct − Cl, 3).

(Chloromethyl)-4-[(butylsulfinyl)methyl]benzene (4a). A total of 4.61 g (0.029 mol) of TeO_2 is added to a solution of the partially purified **1c** in 1200 mL of MeOH. A total of 65 mL (0.570 mol) of a H_2O_2 solution in H_2O (35 wt %) is added slowly to the stirred solution. The reaction mixture is stirred at room temperature and the reaction followed with TLC (silica, $CHCl_3$). When, after 6−8 h, the reaction is finished or a new spot as a consequence of oxidation to the sulfone appears, the reaction is stopped by the addition of 800 mL of brine. The aqueous layer is extracted several times with $CHCl_3$. The combined organic layers are dried over $MgSO_4$ and reduced on a rotary evaporator. The mixture, existing of **1a**, some 1,4-bis[(butylsulfinyl)methyl]benzene, and **4a**, is separated by means of column chromatography (silica, $CHCl_3$), after which **4a** is recrystallized from toluene and dried under vacuum (yield calculated from 38% **1a**): mp 111.0−112.0 °C; IR (KBr, ν, cm^{-1}) 3060, 2970−2870, 1450−1410, 1010, 850, 730, 660; ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.38 (d, ^3J = 8.18 Hz, 2H), 7.27 (d, ^3J = 8.18 Hz, 2H), 4.55 (s, 2H), 3.96 (d, ^2J = 13.20 Hz, 1H), 3.92 (d, ^2J = 13.20 Hz, 1H), 2.56 (t, ^3J = 7.96 Hz, 2H), 1.70 (m, 2H), 1.41 (m, 2H), 0.90 (t, ^3J = 7.34 Hz, 3H); ^{13}C NMR (δ, $CDCl_3$) 136.8, 129.9, 129.8, 128.4, 56.9, 50.2, 45.1, 23.8, 21.3, 13.1; MS (EI, *m*/*z*, relative intensity in %) 244 (M^+, 9), 209 (M^+ − Cl, 5), 139 (M^+ − S(O) − Bu, 100), 104 (M^+ − Cl − S(O) − Bu, 19), 77 (M^+ − CH_2Cl − $CH_2S(O)$ − Bu, 5).

The following syntheses are carried out in the same manner, unless otherwise stated.

(Chloromethyl)-4-[(butylsulfinyl)methyl]-2,5-dimethylbenzene (4c). A total of 1.17 g (7.33 mmol) of TeO_2 is added to a solution of the partially purified **2b** in 300 mL of MeOH. A total of 14.36 mL (0.127 mol) of a H_2O_2 solution is added. After column chromatography (silica, $CHCl_3$), **4c** is recrystallized from a mixture of hexane and CH_2Cl_2 (10/1), giving 10.9 g of white crystals (yield calculated from **1b** 28%): mp 112.9−114.0 °C; IR (KBr, ν, cm^{-1}) 2980, 2930, 2900, 2840, 1440, 1240, 1020, 880, 660; ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.15 (s, 1H), 7.03 (s, 1H), 4.53 (s, 2H), 4.02 (d, ^2J = 12.60 Hz, 1H), 3.90 (d, ^2J = 12.60 Hz, 1H), 2.64 (m, 2H), 2.35 (s, 3H), 2.34 (s, 3H), 1.74 (m, 2H), 1.44 (m, 2H), 0.92 (t, ^3J = 7.20 Hz, 3H); ^{13}C NMR (δ, $CDCl_3$) 135.62, 135.12, 135.09, 133.21, 132.12, 129.47, 56.61, 51.39, 44.23, 24.47, 21.97, 19.17, 18.11, 13.63; MS (EI, *m*/*z*, relative intensity in %) 237 (M^+ − Cl, 1), 167 (M^+ − S(O) − Bu, 100), 132 (M^+ − S(O) − Bu − Cl, 15).

(Chloromethyl)-4-[(octylsulfinyl)methyl]-2,5-dimethylbenzene (4d). A total of 0.08 g (0.48 mol) of TeO_2 is added to a solution of the partially purified **2h** in a mixture of 22 mL of MeOH and 7 mL of dioxane. A total of 0.8 mL (8.6 mmol) of a H_2O_2 solution is added. After purification by means of column chromatography, **4d** is recrystallized from hexane, giving **4d** as white crystals (yield calculated from 61% **3b**): mp 77.3−78.8 °C; FT IR (KBr, ν, cm^{-1}) 2959, 2922, 2851, 1508, 1459, 1020, 890, 663; ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.14 (s, 1H), 7.03 (s, 1H), 4.53 (s, 2H), 4.02 (d, ^2J = 12.40 Hz, 1H), 3.90 (d, ^2J = 12.40 Hz, 1H), 2.36 (m, 2H), 1.75 (m, 2H), 1.39 (m, 2H), 1.25 (m, 8H), 0.85 (t, ^3J = 7.23 Hz, 3H); ^{13}C NMR (δ, $CDCl_3$) 136.26, 135.77, 135.72, 133.86, 132.76, 130.13, 56.63, 51.69, 44.27, 31.67, 29.13, 28.95, 28.78, 22.57, 22.52, 19.24, 18.17, 14.05; MS (EI, *m*/*z*, relative intensity in %) 293 (M^+ − Cl, 6), 277 (M^+ −Cl − O, 1), 132 (M^+ − Cl − S(O) − Oct, 100), 117 (M^+ − Cl − S(O) − Oct − CH_3, 13).

(Chloromethyl)-4-[(butylsulfinyl)methyl]-2,5-dimethoxybenzene (4e). A total of 1.08 g (6.79 mmol) of TeO_2 is added to a solution of 16 g of the partially purified **2c** in 640 mL of MeOH. A total of 13.3 mL (0.117 mol) of a H_2O_2 solution is added. After purification by column chromatography, **4e** is recrystallized from a mixture of ether and hexane, giving 1.80 g of white crystals (yield calculated from **1c** 3%): mp 75.4−76.6 °C; IR (KBr, ν, cm^{-1}) 2920, 2900, 2830, 1490, 1450, 1395, 1310, 1250, 1200, 1030, 1105, 855, 660; ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 6.91 (s, 1H), 6.82 (s, 1H), 4.61 (s, 2H), 4.07 (d, ^2J = 12.40 Hz, 1H), 3.90 (d, ^2J = 12.40 Hz, 1H), 3.82 (s, ^{3}H), 3.80 (s, ^{3}H), 2.60 (m, 2H), 1.73 (m, 2H), 1.44 (m, 2H), 0.91 (t, ^3J = 7.25 Hz, 3H); ^{13}C NMR (δ, $CDCl_3$) 151.19, 150.93, 126.30, 119.71, 114.65, 112.87, 56.08, 76.68, 52.52, 51.01, 41.19, 24.38, 21.92, 13.57; MS (CI, *m*/*z*, relative intensity in %) 305 (M^+, 100), 269 (M^+ − Cl, 8), 199 (M^+ − S(O) − Bu, 22), 165 (M^+ − S(O) − Bu − Cl, 4).

(Chloromethyl)-4-[(octylsulfinyl)methyl]-2,5-dimethoxybenzene (4f). A total of 0.30 g (0.89 mol) of TeO_2 is added to a solution of 6.5 g of the partially purified **2i** in 50 mL of dioxane. A total of 3.7 mL (0.038 mol) of a H_2O_2 solution is added. After separation by column chromatography, **4f** is recrystallized from hexane, giving 0.81 g of white fluffy crystals (yield calculated from 12% **3c**): mp 88.6−90.4 °C; FT IR (KBr, ν, cm^{-1}) 2916, 2851, 1512, 1471, 1406, 1320, 1265, 1214, 1043,

1021, 871, 678; ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 6.92 (s, 1H), 6.82 (s, 1H), 4.62 (s, 2H), 4.07 (d, ^2J = 12.40 Hz, 1H), 3.91 (d, ^2J = 12.40 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 2.60 (t, ^3J = 7.83 Hz, 2H), 1.73 (m, 2H), 1.39 (m, 2H), 1.25 (m, 8H), 0.85 (t, ^3J = 6.84 Hz, 3H); ^{13}C NMR (δ, $CDCl_3$) 151.31, 351.06, 126.45, 119.78, 114.81, 112.97, 56.26, 56.04, 52.69, 51.48, 31.69, 29.18, 28.99, 28.87, 22.56, 22.56, 14.05; MS (CI, *m*/*z*, relative intensity in %) 361 (MH^+, 100), 325 (M^+ − Cl, 6), 199 (M^+ − S(O) − Oct, 20), 165 (M^+ − S(O) − Oct − Cl, 7).

(Bromomethyl)-4-[(octylsulfinyl)methyl]-2,5-dichlorobenzene (4g). A total of 0.48 g (3.03 mmol) of TeO_2 is added to a solution of the partially purified **2j** in 184 mL of dioxane. A total of 6 mL (0.060 mol) of a H_2O_2 solution and 1 drop of a concentrated HCl solution are added. After separation by column chromatography, **4g** is recrystallized from hexane, giving 8.80 g of white crystals (yield calculated from 70% **3d**): mp 60.6−61.2 °C; FT IR (KBr, ν, cm^{-1}) 2955, 2919, 2844, 1476, 1370, 1084, 892, 872, 636; ^{1}H NMR (δ, $CDCl_3$, 200 MHz) 7.50 (s, 1H), 7.43 (s, 1H), 4.49 (s, 2H), 4.13 (d, ^2J = 12.90 Hz, 1H), 3.94 (d, ^2J = 12.90 Hz, 1H), 2.69 (t, ^3J = 7.67 Hz, 2H), 1.77 (m, 2H), 1.40 (m, 2H), 1.25 (m, 8H), 0.85 (t, ^3J = 6.44 Hz, 3H); ^{13}C NMR (δ, $CDCl_3$) 136.47, 132.86, 132.54, 132.31, 131.41, 130.41, 54.63, 51.73, 31.26, 28.72, 28.55, 28.55, 28.36, 22.18, 22.18, 13.72; MS (EI, *m*/*z*, relative intensity in %) 414 (M^+, 1), 333 (M^+ − Br, 1), 253 (M^+ −S(O) − Oct, 100), 172 (M^+ − Br − S(O) − Oct, 41), 137 (M^+ − Br − Cl − S(O) − Oct, 6), 102 (M^+ − Br − 2 Cl − S(O) − Oct, 9).

2-(Chloromethyl)-6-[(octylsulfinyl)methyl]naphthalene (4h). A total of 0.80 g (0.005 mol) of TeO_2 is added to a solution of the partially purified **2d** in a mixture of 100 mL of dioxane and 400 mL of MeOH. A total of 11.5 mL (0.101 mol) of a H_2O_2 solution is added. After separation by column chromatography, **4h** is recrystallized from toluene, giving **4h** as white crystals (yield calculated from 19% **1d**): mp 133.2−134.7 °C; FT IR (KBr, ν, cm^{-1}) 2954, 2922, 2849, 1496, 1266, 1027, 902, 834, 708; ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.73 (d, ^3J = 8.56 Hz, 2H), 7.72 (s, 1H), 7.68 (s, 1H), 7.43 (d, ^3J = 8.48 Hz, 1H), 7.34 (d, ^3J = 8.44 Hz, 1H), 4.66 (s, 2H), 4.19 (d, ^2J = 13.00 Hz, 1H), 4.10 (d, ^2J = 13.00 Hz, 1H), 2.53 (m, 2H), 1.68 (m, 2H), 1.31 (m, 2H), 1.18 (m, 8H), 0.81 (t, ^3J = 6.94 Hz, 3H); ^{13}C NMR (δ, $CDCl_3$) 135.12, 132.67, 132.36, 128.80, 128.46, 128.34, 128.11, 127.80, 127.05, 126.64, 58.06, 50.87, 46.14, 31.39, 28.84, 28.67, 28.49, 22.30, 22.20, 13.82; MS (EI, *m*/*z*, relative intensity in %) 350 (M^+, 1), 334 (M^+ − O, 1), 315 (M^+ − Cl, 1), 299 (M^+ − O − Cl, 1), 189 (M^+ − S(O) − Oct, 100), 154 (M^+ − S(O) − Oct − Cl, 22).

4-(Chloromethyl)-4′-[(butylsulfinyl)methyl]biphenyl (4i). A total of 0.49 g (0.003 mol) of TeO_2 is added to a solution of the partially purified **2e** in 180 mL of MeOH. A total of 7 mL (0.062 mol) of a H_2O_2 solution is added. After separation by column chromatography, **4i** is recrystallized from a mixture of $CHCl_3$ and hexane, giving **4i** as white crystals (yield calculated from 25% **1e**): mp 175.5−176.1 °C; FT IR (KBr, ν, cm^{-1}) 2955, 2923, 2858, 1496, 1400, 1268, 1023, 831, 730, 671; ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.57 (d, ^3J = 8.22 Hz, 2H), 7.56 (d, ^3J = 8.22 Hz, 2H), 7.45 (d, ^3J = 8.22 Hz, 2H), 7.35 (d, ^3J = 8.22 Hz, 2H), 3.97 (d, ^2J = 13.00 Hz, 1H), 4.01 (d, ^2J = 13.00 Hz, 1H), 2.60 (t, ^3J = 7.57 Hz, 2H), 1.73 (m, 2H), 1.45 (m, 2H), 0.92 (t, ^3J = 7.30 Hz, 3H); ^{13}C NMR (δ, $CDCl_3$) 140.42, 140.35, 136.67, 130.45, 129.15, 129.06, 127.49, 127.30, 57.64, 50, 45.87, 24.38, 21.95, 13.61; MS (CI, *m*/*z*, relative intensity in %) 304 (M^+ − O, 1), 285 (M^+ − Cl, 1), 269 (M^+ − O − Cl, 87), 215 (M^+ − S(O) − Bu, 94), 195 (M^+ − phenyl − CH_2Cl, 17), 180 (M^+ − Cl − S(O) − Bu, 100), 152 (M^+ − $CH_2S(O)$ − Bu − CH_2Cl, 8), 90 (M^+ − phenyl − $CH_2S(O)$ − Bu, 4).

4-(Chloromethyl)-4′-[(octylsulfinyl)methyl]biphenyl (4j). A total of 1.13 g (7.11 mmol) of TeO_2 is added to a solution of the partially purified **2f** in a mixture of 40 mL of dioxane and 250 mL of MeOH. A total of 15.8 mL (0.138 mol) of a H_2O_2 solution is added. After separation by column chromatography, **4j** is recrystallized from a mixture of $CHCl_3$ and hexane, giving **4j** as white crystals (yield calculated from **1e** 20%): mp 161.5−162.9 °C; FT IR (KBr, ν, cm^{-1}) 2956, 2916, 2848, 1496, 1467, 1400, 1025, 830, 732, 673; ^{1}H NMR (δ, $CDCl_3$, 400 MHz) 7.57 (d, ^3J = 8.22 Hz, 2H), 7.55 (d, ^3J = 8.22 Hz, 2H), 7.44 (d, ^3J = 8.22 Hz, 2H), 7.35 (d, ^3J = 8.22 Hz, 2H), 4.61 (s, 2H), 3.97 (d, ^2J = 12.80 Hz, 1H), 4.02 (d, ^2J = 12.80 Hz, 1H), 2.61 (m, 2H), 1.74 (m, 2H), 1.39 (m, 2H), 1.25 (m, 8H), 0.84 (t, ^3J = 7.05 Hz, 3H); ^{13}C NMR (δ, $CDCl_3$) 140.37, 140.32, 136.64, 130.41, 129.14, 129.01, 127.45, 127.25, 57.63, 50.95, 45.84, 31.59, 29.03, 28.87, 28.71, 22.47, 22.39, 13.96; MS (EI, *m*/*z*, relative intensity in %) 360 (M^+ − O, 1), 341 (M^+ − Cl, 1), 215 (M^+ − S(O) − Oct, 100), 180 (M^+ − Cl − S(O) − Oct, 29), 152 (M^+ − CH_2Cl − $CH_2S(O)$ − Oct, 3).

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Supporting Information Available: ^{1}H NMR spectra of **2h**−**j** and **2d** for the determination of the amounts of bischloride, monosulfide, and bissulfide. ^{1}H and ^{13}C NMR spectra for new compounds **4a**−**j**. This material is available free of charge via the Internet at http:pubs.acs.org.

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