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A Base-Induced Coupling–Condensation of Aryl *o*-Methylarenesulfonates and *o*-Methylarenesulfonanilides[1]

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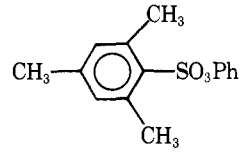
Abstract: The product, resulting from treatment of aryl *o*-methylarenesulfonates or *o*-methylarensulfonanilides with *n*-butyllithium in THF at −72 °C, has a bibenzyl backbone substituted in the 2 position with a sulfinic acid moiety and in the 2′ position with an unchanged aryl sulfonate or sulfonanilide unit. Possible mechanisms for this novel coupling-condensation are discussed.

Base-induced rearrangements of *o*-methylaryl aryl sulfones have been studied extensively in this laboratory over the last several years.[2] In attempting to extend the scope of these rearrangements to related compounds, a novel coupling–condensation reaction of aryl *o*-methylarenesulfonates and *o*-methylarenesulfonanilides has been encountered.

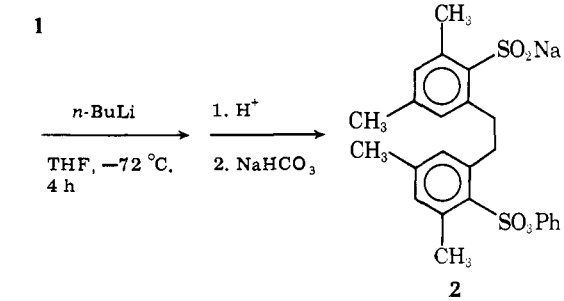
Results and Discussion

When phenyl mesitylenesulfonate (**1**) is treated with *n*-butyllithium at −72 °C for 4 h, a 63% yield of the bibenzyl condensation product **2** is isolated. The structural assignment for **2** is based on spectral and analytical data for the corresponding magnesium salt and for the 2-hydroxy-3,5-dichlorobenzyl sulfone derivative. This coupling–condensation has been extended to four additional aryl *o*-methylarenesulfonates as summarized in Table I.

When phenyl mesitylenesulfonate is treated with *n*-butyllithium at 0 °C or above, the reaction takes a different course and the major products are *n*-butyl mesityl sulfone and 1,1-bis(mesitylsulfonyl)butane (**7**). Displacement of phenoxide by the organometallic accounts for *n*-butyl mesityl sulfone, while the geminal disulfone presumably arises from a subsequent reaction of metalated *n*-butyl mesityl sulfone with phenyl



1



2

mesitylenesulfonate. Even at −72 °C displacement of phenoxide by butyl is a competing reaction, thereby limiting the overall yield of the bibenzyl condensation product.

o-Methylarenesulfonanilides also undergo this coupling condensation reaction (Table II). In addition to the requirement that there be an *N*-aryl substituent, it is also required that

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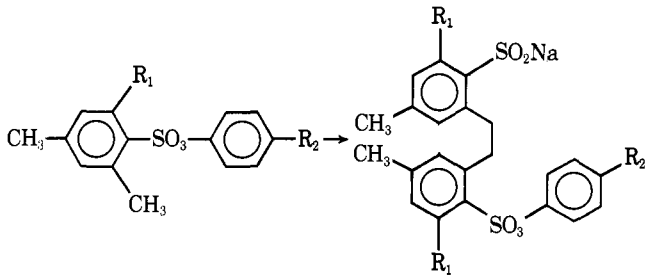
Table I. Coupling-Condensation Reaction of Aryl *o*-Methylarenesulfonates



compd	R_1	R_2	% yield[a]	mp, °C	derivative[c] mp, °C
2	Me	H	63	82-84[b]	217.5-219.0
3	H	Me	71	205-208	207.0-208.0
4	Me	Me	63	152-154[b]	171.5-173.0
5	Me	*t*-Bu	60	143-145[b]	168.0-170.0
6	Me	Ph	36[d]	143-146[b]	165.0-167.0

[a] Yields are approximate for sodium sulfinates containing an unknown amount of water of hydration. [b] Hydrated. [c] 2-Hydroxy-3,5-dichlorobenzyl sulfone. [d] The yield is improved to 68% by the use of lithium diisopropylamide as a base.

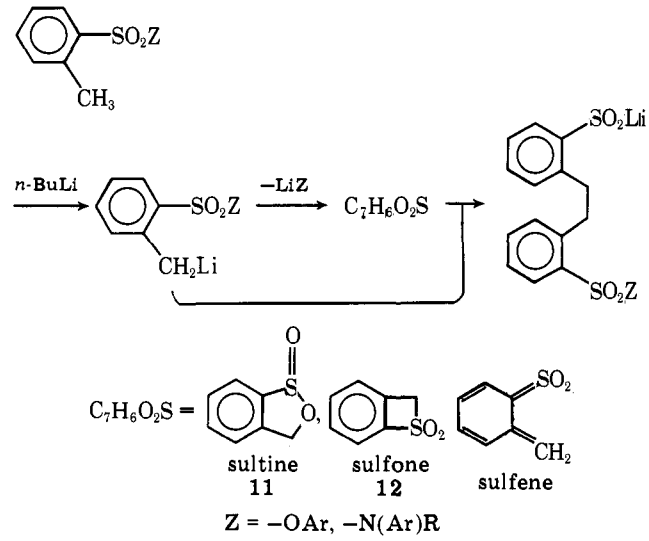
the sulfonamide be derived from a secondary amine.[3] With the sulfonanilides, displacement on sulfur is not a competing reaction as evidenced by sulfones not being found on workup. This undoubtedly is a result of anilide being a poorer leaving group than phenoxide.

Several mechanisms were considered as logical reaction pathways, and experiments were designed to limit the number of possibilities. During the course of this work it soon became obvious that this was a difficult undertaking[4] and that a definitive answer was not readily obtainable. The preliminary results from our mechanistic studies are reported here along with any conclusions we were able to draw.

The first step in the reaction is believed to be a rapid metalation of a methyl group ortho to the electron-withdrawing sulfonate (or sulfonamide) moiety.[5] From this point several different pathways are possible that would lead to the observed products. Three of these are closely related in that they involve the loss of phenoxide (or anilide) in the second step (see Scheme I).

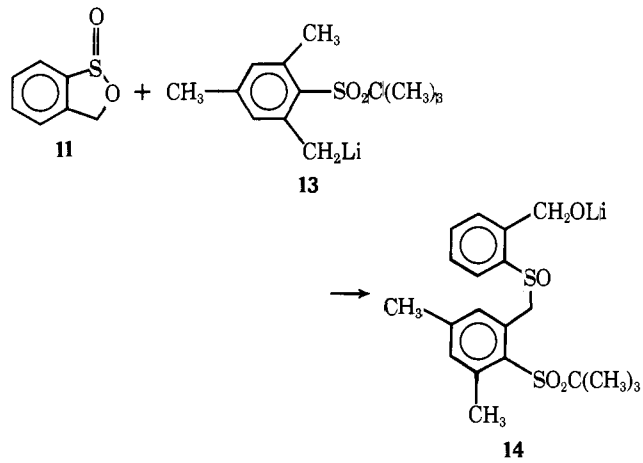
Mechanisms involving **11** and **12** were rendered unlikely by model studies. When **11** was treated with an equivalent of metalated *tert*-butyl mesityl sulfone (**13**) at −72 °C in THF, a sulfoxide **14** rather than a lithium sulfinate was produced. Like treatment of benzothiete dioxide (**12**) appeared to result

Scheme I



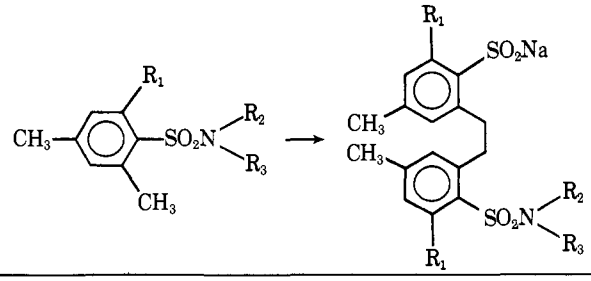
simply in proton transfer between the two substrates, with 91% of the *tert*-butyl mesityl sulfone being recovered.

An attempt was made to trap a sulfene intermediate by running the reaction in the presence of an enamine; however, no cycloadduct could be detected, and the reaction took its



normal course. Data are available suggesting vinylsulfene to be a fairly unreactive diene-like species.[6] Therefore, one might expect preferential reaction with the organometallic rather than the enamine, and the intermediacy of a sulfene cannot be ruled out on the basis of this experiment. On the other hand,

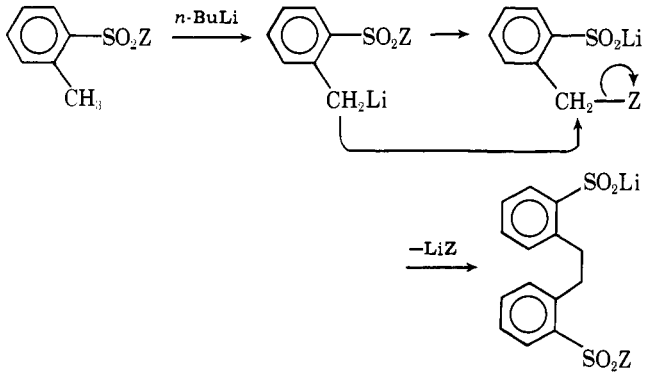
Table II. Coupling-Codensation Reaction of *o*-Methylarenesulfonanilides



compd	R_1	R_2	R_3	% yield[a]	mp, °C	derivative[c] mp, °C	derivative[d] mp, °C
8	Me	Me	Ph	81	72-75[b]	188.0-189.0	124.0-125.5
9	H	Ph	Ph	58	253-255	214.5-215.5	186.0-188.0
10	H	Me	Ph	74	254-256	213.0-214.0	153.0-155.0
	Me	Et	Et	0[e]			

[a] Yields are approximate for sodium sulfinates containing an unknown amount of water of hydration. [b] Hydrated. [c] 2-Hydroxy-3,5-dichlorobenzyl sulfone. [d] Methyl sulfone. [e] 72% starting material recovered.

Scheme II



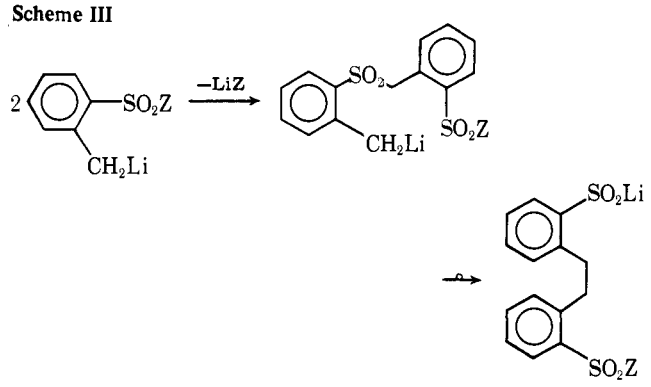
Z = –OAr, –N(Ar)R

if a vinyl-type sulfene were the intermediate, the product would need to arise from a reverse[7] conjugate addition of the nucleophile (metalated sulfonate or sulfonanilide).[8]

A fourth mechanism considered involves a benzyl aryl ether (or amine) as an intermediate (Scheme II). This pathway was considered unlikely when it was found that benzyl phenyl ether is inert to reaction with metalated *tert*-butyl mesityl sulfone at room temperature and below. Ideally the ether tested should have contained an ortho lithium sulfinate moiety as the possibility exists that the proximate lithium grouping could facilitate displacement. The substitution of the simple unsubstituted ether for a more representative intermediate was made for obvious synthetic reasons.

The possible sequence of intermolecular and intramolecular displacements (Scheme III) raised the prospect of forming a

Scheme III



Z = –OAr, –N(Ar)R

"mixed" benzyl sulfone by treating metalated *N*-phenyl-*N*-methylmesitylenesulfonamide with phenyl mesitylenesulfonate. However, no sulfone was detected, the sulfonate ester was recovered, and the condensation product **8** was isolated in normal yield.

Several, if not all, of the proposed mechanisms (Schemes I–III) involve the loss of LiZ in what might be the rate-determining step. To examine if changing the group Z has an effect on the kinetics of the reaction, a competitive reaction was run between *N*,*N*-diphenyl-2,4-dimethylbenzenesulfonamide and *N*-phenyl-*N*-methyl-2,4-dimethylbenzenesulfonamide. Ideally such an experiment should compare a sulfonamide with a sulfonate, but as a result of the competing displacement reaction in the sulfonate system (yielding sulfones), the data would be difficult to interpret. A difference in acidity of 4 pK_a units[9] for aniline vs. diphenylamine would hopefully make the leaving group potential of the Li salts large enough to observe. In the experiment the reaction was quenched before completion, and the ratio of unreacted sulfonamides was found to be essentially unchanged from the initial mixture.

The inconclusive information compiled during examination of these anionic mechanisms raises the possibility of radical or radical-anion intermediates. Again, several reasonable mechanisms can be drawn, but little evidence has been gathered either to support or refute them.

Experimental Section

The IR spectra were recorded on a Beckman IR-33. The NMR spectra were recorded on a Varian A-60A spectrometer using Me_4Si as an internal standard. The microanalyses were performed by Dr. C. S. Yeh and C. M. Lam of this department. All melting and boiling points are uncorrected.

n-Butyllithium was purchased from Alfa Inorganics (Ventron). The listed normality of the solution was checked on occasion using the procedure of Ellison et al.[10]

General Method for the Preparation of Aryl *o*-Methylarenesulfonates. Potassium hydroxide (0.05–0.15 mol) was dissolved, with warming, in 20–100 mL of absolute ethanol. An equimolar portion of the phenol was added, and the solution was stirred at room temperature. After about 5 min, an equimolar amount of the sulfonyl chloride was added in several portions over a 10-min period. The reaction was rapid as evidenced by the generation of heat and the formation of a precipitate (KCl). The mixture was heated on a steam bath for 30 min and then poured onto 3 vol of ice. Filtration followed by recrystallization from ethanol yielded the following sulfonate esters (yield in parentheses). Phenyl mesitylenesulfonate (80%): mp 101–102 °C (lit.[11] mp 100–101 °C). *p*-Methylphenyl 2,4-dimethylbenzenesulfonate (87%): mp 67–68.5 °C; IR (KBr) 1370 and 1150 cm^{-1} (sulfonate SO_2); NMR ($CDCl_3$) δ 2.2 (s, 3), 2.3 (s, 3), 2.65 (s, 3), 6.7–7.7 (m, 7). *p*-Methylphenyl mesitylenesulfonate (78%): mp 100–102 °C;'IR (KBr) 1370 and 1150 cm^{-1} (sulfonate SO_2); NMR ($CDCl_3$) δ 2.2 (s, 3), 2.23 (s, 3), 2.5 (s, 6), 6.6–7.0 (m, 6). *p-tert*-Butylphenyl mesitylenesulfonate (61%): mp 103–105 °C; IR (KBr) 1370 and 1150 cm^{-1} (sulfonate SO_2); NMR ($CDCl_3$) δ 1.25 (s, 9), 2.3 (s, 3), 2.55 (s, 6), 6.8–7.35 (m, 6). *p*-Phenylphenyl mesitylenesulfonate (86%): mp 92–93 °C; IR (KBr) 1730 and 1150 cm^{-1} (sulfonate SO_2); NMR ($CDCl_3$) δ 2.3 (s, 3), 2.6 (s, 6), 6.9–7.5 (m, 11).

General Method for the Preparation of *N*,*N*-Dialkyl- and *N*-Aryl-*N*-alkyl-*o*-methylarenesulfonamides. The following sulfonamides were prepared by the method of Pezold et al.:[12] *N*-Phenyl-*N*-methylmesitylenesulfonamide (76%): mp 97–98.5 °C (lit.[12] 95–96 °C); IR (KBr) 1310 and 1140 cm^{-1} (sulfonamide SO_2); NMR ($CDCl_3$) δ 2.25 (s, 3), 2.4 (s, 6), 3.1 (s, 3, NCH_3), 6.8 (s, 2), 7.1 (s, 5). *N*-Phenyl-*N*-methyl-2,4-dimethylbenzenesulfonamide (47%): mp 55–56 °C (lit.[13] 55 °C). *N*,*N*-Diethylmesitylenesulfonamide (72%): bp 138–141 °C (0.7 mm); IR (neat) 1300 and 1130 cm^{-1} (sulfonamide SO_2); NMR ($CDCl_3$) δ 1.05 (t, 6, J = 7 Hz), 2.2 (s, 3), 2.55 (s, 6), 3.1 (q, 4, J = 7 Hz), 6.85 (s, 2). *N*,*N*-Diphenyl-2,4-dimethylbenzenesulfonamide, prepared by the method of Wiley et al.[14] (50%), mp 122–124 °C; IR (KBr) 1310 and 1140 cm^{-1} (sulfonamide SO_2); NMR ($CDCl_3$) δ 2.3 (s, 3), 2.45 (s, 3), 6.8–7.7 (m, 13).

Reaction of Phenyl Mesitylenesulfonate with *n*-Butyllithium at 0 °C. Isolation of 1,1-Bis(mesitylsulfonyl)butane (7). Phenyl mesitylenesulfonate (5.52 g, 20 mmol) was suspended in 50 mL of dry ethyl ether and stirred in an oven-dried three-neck flask under nitrogen. This mixture was cooled to 0 °C and treated with 11 mL of 1.9 N *n*-butyllithium. After the 30-min addition period the solution was stirred for 30 min at 0 °C. The ice bath was removed and after an additional hour of reaction, the solution was quenched by pouring into dilute hydrochloric acid. The ether layer was separated and washed successively with dilute hydrochloric acid, water, and aqueous $NaHCO_3$. The organic layer was dried ($MgSO_4$) and stripped of solvent in vacuo to give 5.0 g of an oil. An NMR of this crude reaction mixture showed it to be composed of starting sulfonate, *n*-butyl mesityl sulfone, and 1,1-bis(mesitylsulfonyl)butane. A small amount of the disulfone **7** was isolated by crystallization from a 3:1 hexane–benzene mixture: mp 126.5–128 °C; IR (KBr) 1310 and 1140 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 0.7 (t, 3, J = 6 Hz), 1.25–1.6 (m, 4), 2.3 (s, 6), 2.6 (s, 12), 4.45 (t, 1, J = 5 Hz), 6.9 (s, 4). Anal. Calcd for $C_{22}H_{30}O_4S_2$: C, 62.52; H, 7.16; S, 15.17. Found: C, 62.68; H, 7.16; S, 15.00.

General Procedure for the *n*-Butyllithium-Induced Condensation Reaction of Aryl *o*-Methylarenesulfonates and *o*-Methylarenesulfonanilides. The reaction was carried out in a 100-mL three-neck flask equipped with a thermometer, stopple, nitrogen-inlet tube, and a

magnetic Teflon stirring bar. All glassware was oven-dried, assembled hot, and allowed to cool in a stream of nitrogen. Before the stopple was inserted, the sulfonate or sulfonanilide (10-20 mmol) was added to the cooled apparatus. Next, THF (30-50 mL, previously dried over Na turnings) was added via syringe, and the substrate was brought into solution with stirring. The mixture was cooled to −72 °C with a dry ice-acetone bath, and an equimolar amount of *n*-butyllithium was added via syringe. The rate of addition was controlled so that the temperature was maintained at −68 °C or lower. After 4-h reaction at −72 °C the solution generally had turned from a deep red to a light orange. The reaction mixture was allowed to warm to room temperature and quenched by pouring onto a mixture of 100 g of ice and 10 mL of concentrated HCl. Ether (50 mL) was added, and the layers were separated. The organic layer was washed with an equal volume of water and then treated with 75 mL of a saturated aqueous solution of $NaHCO_3$. At this point the sodium sulfinate product generally separated as an oil situated between the aqueous and organic phases. This layer was poured off with the aqueous phase, induced to crystallize by cooling, and isolated by suction filtration. The crystals generally were of high purity but could be recrystallized from water or a water-ethanol mixture.

The corresponding 2-hydroxy-3,5-dichlorobenzyl sulfone derivatives were prepared via standard procedures.[15] Likewise the methyl sulfone derivatives were prepared in standard fashion; the sodium sulfinate (0.8-2.6 g) in ethanol (20 mL) and an excess of methyl iodide (5 mL) were kept at room temperature in a stoppered flask for up to 7 days. The ethanol was removed in vacuo and the crude product taken up in ether. This solution was washed successively with water, an aqueous solution of $NaHSO_3$ (to remove iodine), and finally with water. The ether layer was dried ($MgSO_4$) and the solvent removed in vacuo. One recrystallization from ethanol was generally required to obtain the derivative analytically pure and free from traces of the isomeric methyl sulfinate. This contaminant (present only if the sulfinate moiety is flanked by two alkyl groups) could be detected in the NMR of the crude sulfone as a singlet at δ 3.8 [S(=O)OCH_3].

2-Phenoxysulfonyl-2′-sulfino-3,3′,5,5′-tetramethylbibenzyl sodium salt (2): 63%; mp 82-84 °C (hydrated). After workup of the product, the ether layer was washed with dilute aqueous NaOH to remove phenol, dried ($MgSO_4$), and stripped of solvent in vacuo to give 0.6 g of an oil, which slowly solidified. An NMR spectrum of this neutral material showed it to be an equimolar mixture of the starting sulfonate and mesityl *n*-butyl sulfone.

The 2-hydroxy-3,5-dichlorobenzyl sulfone derivative (57%) had mp 217.5-219 °C: IR (KBr) 3460 (OH), 1320 and 1140 (sulfone SO_2), 1370 and 1200 cm^{-1} (sulfonate SO_2); NMR ($CDCl_3$) δ 2.3 (s, 3), 2.35 (s, 3), 2.55 (s, 3), 2.6 (s, 3), 2.95-3.2 (m, 4, C_2H_4), 4.35 (s, 2, SO_2CH_2), 6.8-7.3 (m, 11). Anal. Calcd for $C_{31}H_{30}O_6S_2Cl_2$: C, 58.76; H, 4.77; Cl, 11.19. Found: C, 58.59; H, 4.97; Cl, 11.20

2-Phenoxysulfonyl-2′-sulfino-3,3′,5,5′-tetramethylbibenzyl Magnesium Salt. The corresponding sodium sulfinate **2** (1.0 g, 2.1 mmol) was dissolved in a minimal amount of 1:1 ethanol-water mixture. In a separate container 2.0 g of $MgSO_4$ was dissolved in 20 mL of water. The magnesium salt precipitated when the two solutions were mixed. The solid was collected and recrystallized from ethanol: yield 0.8 g (82%); mp 278-280 °C dec. Anal. Calcd for $C_{24}H_{25}Mg_2O_5S_2$: C, 61.36; H, 5.37. Found: C, 61.07; H, 5.23.

2-(*p*-Methylphenoxysulfonyl)-2′-sulfino-5,5′-dimethylbibenzyl sodium salt (3): 71%; mp 205-208 °C. The 2-hydroxy-3,5-dichlorobenzyl sulfone derivative was prepared (58%): mp 207-208 °C; IR (KBr) 3380 (OH), 1280 and 1130 (sulfone SO_2), 1330 and 1170 cm^{-1} (sulfonate SO_2); NMR ($CDCl_3$) δ 2.25 (s, 3), 2.35 (s, 3), 2.4 (s, 3), 2.25 (s, 4, C_2H_4), 4.4 (s, 2, SO_2CH_2), 5.8-6.0 (br s, 1, OH), 6.8-7.7 (m, 12). Anal. Calcd for $C_{30}H_{28}Cl_2O_6S_2$: C, 58.16; H, 4.56; Cl, 11.44. Found: C, 57.90; H, 4.43; Cl, 11.42.

2-(*p*-Methylphenoxysulfonyl)-2′-sulfino-3,3′,5,5′-tetramethylbibenzyl sodium salt (4) was prepared (63%): mp 152-154 °C (hydrated, melts and resolidifies with loss of water, 104-106 °C). The 2-hydroxy-3,5-dichlorobenzyl derivative (75%) had mp 171.5-173°: IR (KBr) 3390 (OH), 1300 and 1130 (sulfone SO_2), 1345 and 1150 cm^{-1} (sulfonate SO_2); NMR ($CDCl_3$) δ 2.2 (s, 3), 2.3 (s, 3), 2.35 (s, 3), 2.5 (s, 3), 2.55 (s, 3), 3.0-3.2 (m, 4, C_2H_4), 4.35 (s, 2, SO_2CH_2), 6.7-7.3 (m, 10). Anal. Calcd for $C_{32}H_{32}Cl_2O_6S_2$: C, 59.35; H, 4.98; Cl, 10.95. Found: C, 59.35; H, 4.80; Cl, 10.85.

2-(*p*-*tert*-Butylphenoxysulfonyl)-2′-sulfino-3,3′,5,5′-tetramethylbibenzyl sodium salt (5): 60%; mp 143-145 °C (hydrated). The 2-hydroxy-3,5-dichlorobenzyl derivative (66%) had mp 168-170 °C (melts and resolidifies with loss of ethanol, 110-120 °C); IR (KBr) 3500 (OH), 1290 and 1130 (sulfone SO_2), 1345 and 1150 cm^{-1} (sulfonate SO_2); NMR ($CDCl_3$) δ 1.2 (s, 9), 1.25 (t, 3, J = 7 Hz), 2.3 (s, 3), 2.4 (s, 3), 2.55 (s, 3), 2.6 (s, 3), 3.0-3.3 (m, 4, C_2H_4), 3.7 (t, 2, J = 7 Hz), 4.4 (s, 2, SO_2CH_2), 5.9-6.2 (br s, 1, ArOH), 6.8-7.4 (m, 10). Anal. Calcd for $C_{37}H_{44}O_7S_2Cl_2$: C, 60.39; H, 6.03; Cl, 9.64. Found: C, 60.62; H, 5.89; Cl, 9.65.

2-(*p*-Phenylphenoxysulfonyl)-2′-sulfino-3,3′,5,5′-tetramethylbibenzyl Sodium Salt (6). A. Standard Procedure. This sodium sulfinate (36%) had mp 143-146 °C (hydrated). After workup of the product, the ethereal layer was dried ($MgSO_4$) and evaporated in vacuo to give 2.2 g of a solid. *p*-Phenylphenol (0.8 g, mp 165-167 °C) was isolated from this mixture by recrystallization from carbon tetrachloride. The mother liquid was shown by the NMR spectrum to contain butyl mesityl sulfone in addition to more of the phenol.

B. Lithium Diisopropylamide Induced Condensation. Lithium diisopropylamide (0.01 mol) was generated from *n*-butyllithium and diisopropylamine according to the method of Wittig and Hess.[16] *p*-Phenylphenyl mesitylenesulfonate (3.5 g, 0.01 mol) was dissolved in 30 mL of THF and cooled to −72 °C as described in the general procedure. The lithium diisopropylamide solution was added via syringe while maintaining the temperature at −68 °C or lower. The mixture was stirred for 4 h at −72 °C and sodium sulfinate **6** was worked up as described in section A: yield 1.8 g (68%); mp 143-146 °C (hydrated). (Workup of the ethereal layer gave 1.1 g of a solid, which was shown to be *p*-phenylphenol and starting sulfonate by its NMR spectrum.) The 2-hydroxy-3,5-dichlorbenzyl sulfone derivative (43%) had mp 165-167 °C; IR (KBr) 3480 (OH), 1290 and 1120 (sulfone SO_2), 1340 and 1145 cm^{-1} (sulfonate SO_2); NMR ($CDCl_3$) δ 2.3 (s, 3), 2.4 (s, 3), 2.5 (s, 3), 2.6 (s, 3), 3.0-3.4 (m, 4, C_2H_4), 4.35 (s, 2, SO_2CH_2), 5.2 (br s, 1, OH), 6.8-7.6 (m, 10). Anal. Calcd for $C_{37}H_{34}O_6S_2Cl_2$: C, 62.62; H, 4.83; Cl, 9.99. Found: C, 62.43; H, 5.01; Cl, 10.00.

2-(*N*-Phenyl-*N*-methylaminosulfonyl)-2′-sulfino-3,3′,5,5′-tetramethylbibenzyl Sodium Salt (8). This sodium sulfinate (81%) had mp 72-75 °C (hydrated). Workup of the ether layer gave less than 0.2 g of neutral material. The 2-hydroxy-3,5-dichlorobenzyl sulfone derivative (77%) had mp 188-189 °C: IR (KBr) 3480 (OH), 1290 and 1120 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 2.35 (s, 3), 2.4 (s, 3), 2.55 (s, 3), 2.6 (s, 3), 3.1 (s, 4, C_2H_4), 3.25 (s, 3, NCH_3), 4.5 (s, 2, SO_2CH_2), 6.15-6.35 (br s, 1, OH), 6.9-7.4 (m, 11). Anal. Calcd for $C_{32}H_{33}Cl_2NO_5S_2$: C, 59.43; H, 5.14; Cl, 10.97. Found: C, 59.49; H, 5.42; Cl, 10.93.

The methyl sulfone derivative (40%) had mp 124-125.5 °C: IR (KBr) 1300 and 1130 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 2.25 (s, 6), 2.45 (s, 3), 2.65 (s, 3), 3.0 (s, 3, SO_2CH_3), 3.1 (s, 4, C_2H_4), 3.2 (s, 3, NCH_3), 6.9-7.25 (m, 9). Anal. Calcd for $C_{26}H_{31}NO_4S_2$: C, 64.31; H, 6.43; S, 13.20. Found: C, 64.40; H, 6.44; S, 13.00.

2-(*N*,*N*-Diphenylaminosulfonyl)-2′-sulfino-5,5′-dimethylbibenzyl sodium salt (9): 58%; mp 253-255 °C. Workup of the ether layer gave 1.4 g of a solid which appeared to be a mixture of starting sulfonamide and diphenylamine. The 2-hydroxy-3,5-dichlorobenzyl sulfone derivative (ca. quantitative) had mp 214.5-215.5 °C: IR (KBr) 3480 (OH), 1300 and 1140 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 2.3 (s, 3), 2.45 (s, 3), 3.1 (s, 4, C_2H_4), 4.4 (s, 2, SO_2CH_2), 6.0 (s, 1, OH), 6.8-7.8 (m, 18). Anal. Calcd for $C_{35}H_{31}Cl_2NO_5S_2$: C, 61.76; H, 4.59; Cl, 10.42. Found: C, 61.89; H, 4.79; Cl, 10.54.

The methyl sulfone derivative (62%) had mp 186-188°: IR (KBr) 1290 and 1140 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 2.3 (s, 3), 2.4 (s, 3), 3.0 (s, 3, SO_2CH_3), 3.1 (s, 4, C_2H_4), 6.8-7.9 (m, 16). Anal. Calcd for $C_{29}H_{29}NO_4S_2$: C, 67.03; H, 5.62; S, 12.34. Found: C, 66.80; H, 5.61; S, 12.60.

2-(*N*-Phenyl-*N*-methylaminosulfonyl)-2′-sulfino-5,5′-dimethylbibenzyl Sodium Salt (10). A. Standard Procedure. This sodium sulfinate (74%) had mp 254-256 °C. The ethereal layer was dried ($MgSO_4$) and evaporated in vacuo to give an oil (0.8 g) which soon crystallized. An NMR spectrum indicated that this was essentially pure starting material.

B. Methyl Iodide Workup. The condensation reaction was run as described in section A with the exception that methyl iodide (3 mL, an excess) was added to the reaction mixture before it was poured onto an ice-concentrated HCl mixture. Again, a 74% yield of sodium sulfinate **10** was isolated using the standard procedure. (Workup of the ether layer gave 0.8 g of a solid identified as *N*-methyl-*N*-phenylmesitylenesulfonamide, mp 94-96 °C. This product resulted from methylation of starting sulfonamide which had metalated ortho to the

sulfonyl group.)

The 2-hydroxy-3,5-dichlorobenzyl sulfone derivative (76%) had mp 213-214 °C: IR (KBr) 3480 (OH), 1290 and 1130 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 2.35 (s, 3), 2.4 (s, 3), 2.5-3.1 (m, 4, C_2H_4), 3.15 (s, 3, NCH_3), 4.4 (s, 2, SO_2CH_2), 6.0 (s, 1, OH), 6.9-7.8 (m, 13). Anal. Calcd for $C_{30}H_{29}Cl_2NO_5S_2$: C, 58.25; H, 4.73; Cl, 11.46. Found: C, 58.25; H, 4.68; Cl, 11.50.

The methyl sulfone derivative (50%) had mp 153-155 °C: IR (KBr) 1280 and 1120 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 2.4 (s, 6), 2.55-3.1 (m, 4, C_2H_4), 3.05 (s, 3), 3.2 (s, 3), 7.0-7.9 (m, 11). Anal. Calcd for $C_{24}H_{27}NO_4S_2$: C, 62.99; H, 5.95; S, 14.01. Found: C, 62.75; H, 5.95; S, 13.81.

Reaction of Metalated Mesityl *tert*-Butyl Sulfone (13) with 3*H*-2,1-Benzoxathiole 1-Oxide (11). Mesityl *tert*-butyl sulfone (prepared in 95% yield on treatment of mesityl isopropyl sulfone[17] with butyllithium followed by methyl iodide) had mp 101.5-103 °C: IR (KBr) 1310 and 1140 cm^{-1} (SO_2); NMR (CCl_4) δ 1.3 (s, 9), 2.3 (s, 3), 2.65 (s, 6), 6.85 (s, 2). A solution of 1.56 g (6.5 mmol) of sulfone in 20 mL of dry THF (distilled from $LiAlH_4$), stirred under nitrogen in an oven-dried three-neck flash, was cooled to dry ice-acetone temperature and metalated with 3 mL of 2.0 N *n*-butyllithium. The bright red mixture was stirred for 10 min; then 3*H*-2,1-benzoxathiole 1-oxide[18] (1.0 g, 6.5 mmol), dissolved in 10 mL of dry THF, was added via syringe over a 5-min period. During the addition the mixture turned to a light yellow. The reaction was stirred at −72 °C for 15 min, allowed to warm to room temperature, and was quenched by pouring into dilute aqueous HCl. The THF was removed in vacuo and replaced by 50 mL of ether. The ether layer was separated, and, on cooling, crystals precipitated. These were collected and identified as 2-hydroxymethylphenyl 2-*tert*-butylsulfonyl-3,5-dimethylbenzyl sulfoxide (**14**): yield 1.0 g (40%) mp 176-178 °C; IR (KBr) 3400 (OH), 1275 and 1105 (SO_2), 1000 cm^{-1} (SO); NMR ($CDCl_3$) δ 1.3 (s, 9), 2.3 (s, 3), 2.7 (s, 3), 4.0 (br s, 1, OH), 4.7 (s, 2, CH_2OH), 7.0-7.9 (m, 6); mass spectrum (70 eV) *m/e* (rel intensity) 394 (1), 239 (4), 183 (100), 165 (15), 138 (20), 119 (15), 109 (10), 91 (20). Anal. Calcd for $C_{20}H_{26}O_4S_2$: C, 60.88; H, 6.64; S, 16.25. Found: C, 61.08; H, 6.75; S, 16.44.

The ether layer, from which the product crystallized, was dried ($MgSO_4$) and stripped of solvent in vacuo to give 1.1 g of a semisolid. An NMR spectrum of this material showed it to be composed of 70% starting sulfone and 30% starting sultine. This corresponds to 55% recovered mesityl *tert*-butyl sulfone.

Reaction of Metalated Mesityl *tert*-Butyl Sulfone (13) with 2*H*-Benzo[*b*]thiete 1,1-Dioxide (12). Mesityl *tert*-butyl sulfone (0.72 g, 3 mmol) was dissolved in 20 mL of dry THF and was stirred under nitrogen in an oven-dried three-neck flask. The solution was cooled to dry ice-acetone temperature, and over a period of 5 min 1.5 mL of a 2.0 N *n*-butyllithium solution was added via syringe. Next, 2*H*-benzo[*b*]thiete 1,1-dioxide[19] (0.45 g, 3 mmol), dissolved in 5 mL of dry THF, was added via syringe. The red solution was allowed to warm and was stirred at room temperature for 30 min before quenching on an ice-concentrated HCl mixture. The organic layer was separated, and the aqueous fraction was extracted with ether. The combined extract and organic fraction were washed successively with water and saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and stripped of solvent in vacuo. The resulting oil, 0.65 g, quickly solidified and was identified as mesityl *tert*-butyl sulfone (91% recovery). The bicarbonate wash was acidified and extracted several times with ether. The extracts were combined, dried ($MgSO_4$), and stripped of solvent in vacuo to give 0.3 g of an oil. Because this material had the solubility properties of a sulfinic acid, an attempt was made to form a 2-hydroxy-3,5-dichlorobenzyl sulfone derivative. This was unsuccessful and, as a result, the composition of the oil was not determined.

References and Notes

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