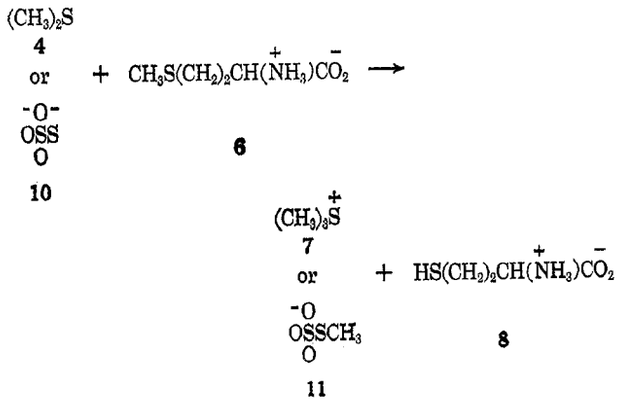
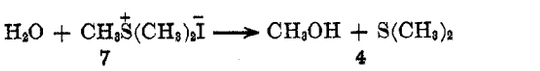
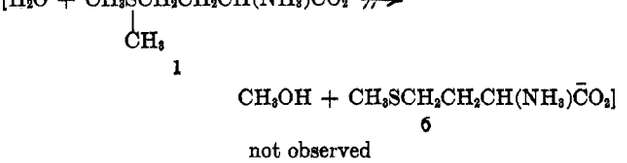
to acid catalysis in the form of protonation of the sulfur of methionine, since HCl seems to be more effective than H_3PO_4 at comparable normalities. As expected, thiosulfate **10** also caused the slow demethylation of methionine (**6**).



In conclusion, the formation of the lactone **3** as an intermediate in the hydrolytic decomposition of SMM (**1**) into homoserine (**5**) and dimethyl sulfide (**4**) is in accord with the observation that the rate of disappearance of SMM in water at neutral pH is significantly faster than solvolysis of trimethylsulfonium iodide[20] (**7**) under comparable conditions.



A neighboring group participation by the carboxylate anion would explain why the nucleophilic substitution at the methylene group of SMM (**1**) is faster than the substitution at the methyl group of the trimethylsulfonium cation (**7**). Moreover, the intermediacy of the lactone **3** also accounts for the nonoccurrence of the hydrolytic pathway for SMM that leads to methanol and methionine.



As the nucleophile becomes more effective, *i.e.*, when dimethyl sulfide is involved, the occurrence of the intermolecular nucleophilic substitution at the methyl group, with formation of trimethylsulfonium salt and methionine, becomes competitive with the intramolecular substitution at the methylene group.

Registry No.—**1** chloride, 3493-12-7; **1** nitrate, 33515-34-3; **4**, 75-18-3; **5**, 1927-25-9; **6**, 59-51-8; **7**, 676-84-6; **8**, 454-29-5; **9**, 870-93-9; **10**, 7772-98-7; **11**, 40463-71-6.

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Functionalization of Bis(phenylsulfonyl)methane

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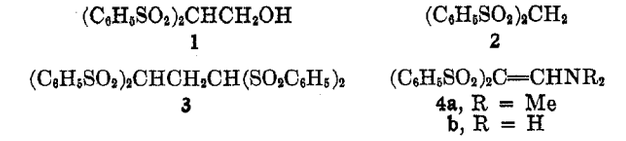
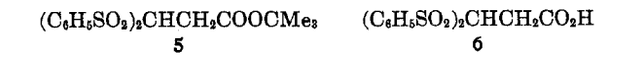
A convenient method is described for the single-carbon functionalization of bis(phenylsulfonyl)methane *via* thiomethylation with *N*-(benzoylthiomethyl)piperidine hydrochloride (**9**). The thiomethyl derivative **10** was easily converted to olefin **12** and thence to the disulfone alcohol **1**. In studying a similar approach to the tosyl analog of **12** some discrepancies with earlier structural assignments were noted and clarified.

As a possible precursor of reagents suitable for the development of new amino-protecting groups,[1] a disulfone alcohol such as **1** was of considerable interest. A readily available, logical precursor of **1** is **2** and

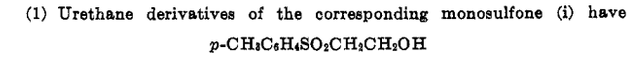


therefore a general study of the one-carbon functionalization of **2** was undertaken. Of the various techniques studied, only one proved suitable for the conversion to **1**. The most direct route, aldol condensation of **2** with formaldehyde,[1a] gave only the bis adduct **3**, which was also obtained as the sole product by alkylation of metallic salts of **2** with chloromethyl ether or *N*-chloromethylphthalimide or by application of the Mannich reaction to **2**.[2] Alkylations of the anion of **2** by means of *tert*-butyl α-bromoacetate or bromoacetic acid readily gave **5** and **6**, respectively. However, neither



of these compounds lent itself readily to conversion to **1** because of the presence of the extra carbon atom. Single-carbon functionalization of **2** was achieved *via*

(1) Urethane derivatives of the corresponding monosulfone (**i**) have been recommended as amino-protecting groups removable by base-catalyzed β elimination [A. T. Kader and C. J. M. Stirling, *J. Chem. Soc.*, 258 (1964)]. Use of the disulfone alcohol was expected to lead to much greater base sensitivity. For other examples of protective groups based on β-elimination processes, see (a) L. A. Carpino and G. Y. Han, *J. Amer. Chem. Soc.*, **92**, 5748 (1970); *J. Org. Chem.*, **37**, 3404 (1972); (b) T. Wieland, G. J. Schmitt, and P. Pfaender, *Justus Liebigs Ann. Chem.*, **694**, 38 (1966); (c) E. Wünsch and R. Spangenberg, *Chem. Ber.*, **104**, 2427 (1971).



(1a) NOTE ADDED IN PROOF (MAY 7, 1973).—After the submission of this work a paper appeared [H. Stetter and B. Riberi, *Monatsh. Chem.*, **103**, 1262 (1972)] which reported that the aldol condensation between **2** and formaldehyde gave 1,1-bis(phenylsulfonyl)ethene (**12**). However, the properties reported for **12** did not correspond to those we observed for this compound. Professor Stetter has kindly informed us that the compound obtained by his group is actually the isomeric 1,2-bis(phenylsulfonyl) analog.

(2) Lack of success with Mannich condensations involving **2** has previously been reported. See W. L. Nobles and B. B. Thompson, *J. Pharm. Sci.*, **54**, 576 (1965).

reaction with *O,N,N*-trimethylformimidium methylsulfate or formamidine acetate to give **4a** or **4b**, but reduction of either of these compounds with sodium borohydride gave not the expected Mannich base but instead the overreduction product **7**, which was

$(C_6H_5SO_2)_2CHCH_3$ (**7**) $(C_6H_5SO_2)_2CHCOOC_2H_5$ (**8**)

also obtained by reduction of ester **8** by means of lithium aluminum hydride.

In view of these disappointing results it is especially gratifying that Smissman's recently described thiomethylation process[3] proved successful with **2** and provided not only an indirect approach to the Mannich bases[2] such as **11**, but also, *via* the route shown in Chart I,[4] a convenient route to alcohol **1**. The structure of the 1,1-disulfonyl olefin **12** was established by spectral techniques and an alternate synthesis which involved peracid oxidation of the corresponding sulfide **14** (Ar = C_6H_5).[5] For synthetic purposes this latter technique was used more successfully in the synthesis of the tosyl analog **15**, as outlined in Chart II. During this investigation a discrepancy was noted between our results and those of Fromm.[6] Upon oxidation of **13** by means of hydrogen peroxide in acetic acid Fromm obtained a compound, mp 222–223°, described as 1,1,2-tritosylethane (**17**). Since early in the present work[7] we presumed that treatment of **17** with alkali might lead to the tosyl analog of **1**, we attempted to obtain this compound by Fromm's method. When alkaline treatment failed to yield an alcohol we were led to question structure **17** and found that, in our

CHART I

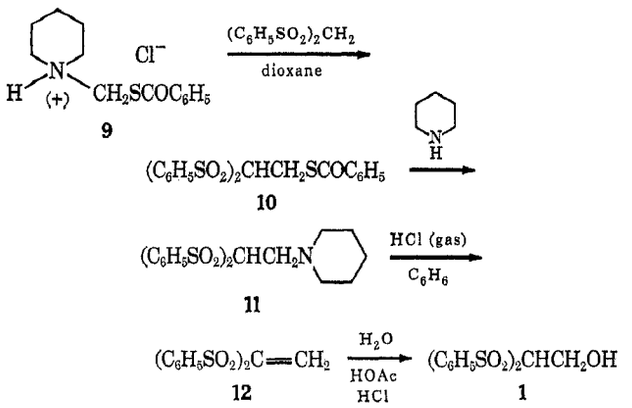
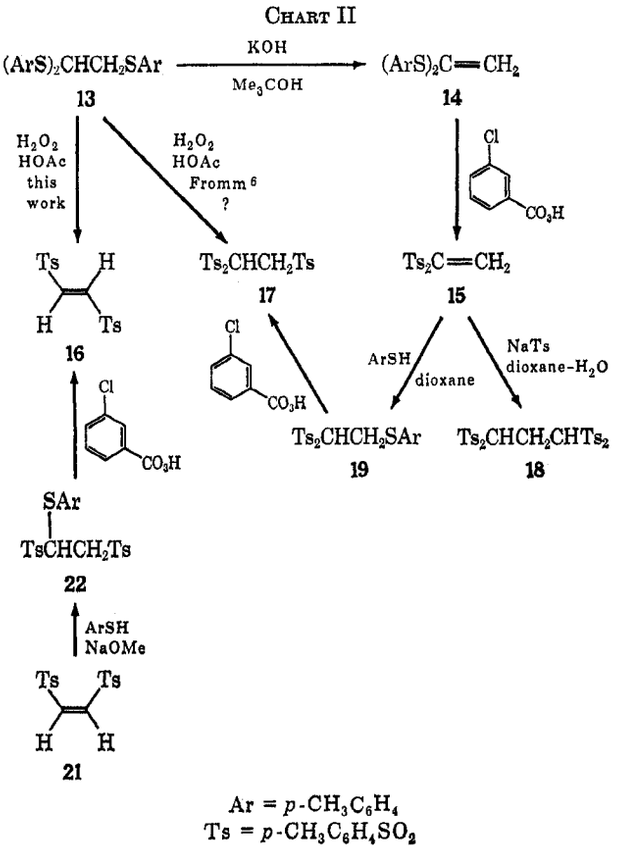


CHART II



Ar = *p*-$CH_3C_6H_4$
Ts = *p*-$CH_3C_6H_4SO_2$

hands at any rate, even though we tried to reproduce Fromm's conditions as closely as possible, oxidation of **13** gave **16**,[8a] mp 229–230°, rather than **17**, reported mp 222–223°. The structure of **16** was established by spectral examination and its alternate synthesis from the corresponding cis isomer by base-catalyzed isomerization.[8b] The availability of **15** suggested a possible alternate route to **17** and, in a search for further clarification of Fromm's results, **15** was treated with 1 equiv of sodium *p*-toluenesulfinate in dioxane–water solution. However, this reaction gave only the methylene bissulfone **18**. Other bases, such as sodium hydroxide, sodium acetate, sodium benzenesulfinate, sodium cyanate, or triethylamine, effected the same conversion. Presumably this reaction proceeds by a reverse aldol process followed by addition of the displaced methylene bissulfone anion to the unreacted disulfonylethylene.

Authentic 1,1,2-tritosylethane (**17**), mp 155–157°, could be made, however, by prior addition of *p*-thiocresol to **15** to give sulfide **19** followed by oxidation by means of *m*-chloroperbenzoic acid. Structure **17** was established by elemental analysis and spectral data (see Experimental Section). The fact that the melting point of **17** is far different from that reported by Fromm suggests that Fromm also probably isolated **16** from the oxidation of **13**. It is instructive to note in this connection that **22**, an isomer of **19** which is obtainable by addition of *p*-thiocresol to *cis*-1,2-ditosylethane (**21**), upon attempted oxidation with *m*-chloroperbenzoic acid, gives only **16**. Stepwise oxidation of **13** might well yield **22** as a first-formed product. Strangely enough, Fromm reports the synthesis of a

(3) E. E. Smissman, J. R. J. Sorenson, W. A. Albrecht, and M. W. Creese, *J. Org. Chem.*, **35**, 1357 (1970).

(4) The conversion of **10** to **11** represents the deblocking of a protected thio ester by means of the β-elimination process which inspired this work. As yet we have been unable to study the possible utility of **1** as a protectant for carboxylic acids (*via* the simple esters) or amines (*via* the urethanes) because of the relative lack of reactivity of alcohol **1** (possibly because of the strong inductive effect of the two sulfone groups) toward acid chlorides, anhydrides, or isocyanates under conditions which avoid conversion to the corresponding olefin **12**. If a base such as triethylamine is present during these attempted acylations, bissulfone **3** is formed rather than **12**. By a similar effect, whereas it is possible to recrystallize **11** from benzene without difficulty, recrystallization from ethanol leads to the formation of **3**.

(5) Obtained by the method of T. Otsu, K. Tsuda, T. Fukumizu, and H. Inoue, *Nippon Kagaku Zasshi*, **89**, 892 (1968), except that the precursor **13** (Ar = C_6H_5) was prepared by a method analogous to that of Fromm and Siebert.[6]

(6) E. Fromm and E. Siebert, *Ber.*, **55**, 1014 (1922).

(7) On the basis of our current knowledge of the chemistry of these compounds we now realize that the reaction could not have taken place in this sense. Indeed it was shown that treatment of **12** with sodium hydroxide gave **3**, presumably *via* the reverse aldol reaction described for the homolog **15**.

(8) (a) W. E. Truce and R. J. McManimie, *J. Amer. Chem. Soc.*, **76**, 5745 (1954); (b) J. S. Meek and J. S. Fowler, *J. Org. Chem.*, **33**, 985 (1968).

compound of structure 22 by permanganate oxidation of 13. However the melting point (119–120°) reported by Fromm differs somewhat from that which we obtained (127.5–129.5°) for this compound, and we made no attempt to compare these two substances directly.

Experimental Section[9]

S-[2,2-Bis(phenylsufonyl)ethyl] Thiobenzoate (10).—A mixture of 39 g of 9[4] and 44.8 g of bis(phenylsulfonyl)methane[10] in 500 ml of dioxane was refluxed for about 17 hr. Dilution to 3 l. with H_2O gave an oil which on seeding and cooling in an ice bath gave after 6–8 hr 50.5 g (77%) of cream-colored solid, mp 108–115°. A portion was recrystallized from ligroin (bp 60–70°)–benzene (3:1) to give a white, crystalline powder: mp 118–120°; ir (Nujol) 6.00 (C=O), 7.52, 8.72 μ (SO_2); nmr ($CDCl_3$) δ 3.82 (d, J = 6.5 Hz, 2, $CHCH_2$), 4.73 (t, 1, J = 6.5 Hz, $CHCH_2$), 7.7 (m, 15, phenyl).

Anal. Calcd for $C_{21}H_{18}S_3O_5$: C, 56.48; H, 4.06; S, 21.54. Found: C, 56.54; H, 4.05; S, 21.50.

1-[2,2-Bis(phenylsulfonyl)ethyl]piperidine (11).—In small portions 12.9 g of 10 was added over 2 min to 60 ml of piperidine. The resulting mixture was stirred magnetically for 20 min, diluted to 500 ml with H_2O, stirred 20 min longer, and filtered to give 10 g (89%) of the adduct as a white solid, mp 129–132°. Recrystallization from benzene gave an analytical sample: mp 128–130°; ir (Nujol) 7.57, 7.65, 8.69, 8.75 μ (SO_2); nmr ($CDCl_3$) δ 1.23 [m, 6, $(CH_2)_3$], 2.15 (m, 4, CH_2N), 3.07 (d, 2, $CHCH_2$), 4.6 (t, 1, $CHCH_2$), 7.75 (m, 10, phenyl).

Anal. Calcd for $C_{19}H_{23}NO_4S_2$: C, 57.99; H, 5.89. Found: C, 58.33; H, 5.72.

1,1-Bis(phenylsulfonyl)ethene (12).—A suspension of 35.8 g of crude 11, mp 129–132°, in 600 ml of benzene was treated with a stream of dry HCl gas for 15 min, which caused complete solution of the solid. The solution was refluxed with stirring for 3 hr, cooled to room temperature, and filtered to remove piperidine hydrochloride, and the filtrate was evaporated *in vacuo* to a volume of 75–100 ml. Addition of an equal volume of ligroin caused separation of an oil which soon solidified. Benzene was then added with heating until most of the solid dissolved, and the solution was filtered and allowed to stand overnight at room temperature. There was obtained 18.9 g (67.5%) of the disulfone, mp 120–125.5°. Recrystallization from ligroin–benzene (1:5) gave 15.5 g (55.5%): mp 126–127°; ir (Nujol) 7.55, 8.69 μ (SO_2); nmr ($CDCl_3$) δ 7.19 (s, 2, $=CH_2$), 7.5, 7.85 (m, 10, phenyl).

Anal. Calcd for $C_{14}H_{12}S_2O_4$: C, 54.53; H, 3.92; S, 20.79. Found: C, 54.49; H, 3.86; S, 20.85.

2,2-Bis(phenylsulfonyl)ethenol (1). A. From 1,1-Bis(phenylsulfonyl)ethene.—A mixture of 0.25 g of 12, 3 ml of H_2O, 0.25 ml of concentrated HCl, and 2 ml of dioxane was stirred at room temperature for 1 hr and diluted to 50 ml with H_2O. The mixture was stirred for 5–10 min until the tacky material became granular and filtered to give 0.13 g (49%) of the crude alcohol, mp 115–123.5°. Recrystallization from benzene gave 0.067 g (25%), of the alcohol, mp 121–122°.

B. From 1-[2,2-Bis(phenylsulfonyl)ethyl]piperidine.—A solution of 10 g of 11 in 100 ml of acetic acid and 50 ml of concentrated HCl was heated just below the boiling point on a hot plate for 5 min. The solution was diluted to 1 l. and stirred for 60 sec to coagulate some tacky material, and the mixture was filtered rapidly through a Büchner funnel. The filtrate was allowed to stand in a refrigerator for 24 hr and filtered to remove 2.5 g (30%) of flaky white crystals, mp 120–123°. An analytical sample was obtained by recrystallization from benzene: mp 121–123°; ir (Nujol) 2.86 (OH), 7.5, 8.62 μ (SO_2); nmr ($CDCl_3$) δ 3.1 (broad s, 1, OH), 4.29 (d, 2, $CHCH_2$), 4.69 (t, 1, $CHCH_2$), 7.6, 7.9 (m, 10, phenyl).

Anal. Calcd for $C_{14}H_{14}O_5S_2$: C, 51.52; H, 4.32; S, 19.65. Found: C, 51.59; H, 4.25; S, 19.60.

1,1-Bis(*p*-toluenesulfonyl)ethene (15).—To a solution of 2 g of 1,1-bis(*p*-tolylthio)ethene[11] in 60 ml of CH_2Cl_2 was added over a period of 6–7 min with stirring at room temperature 6 g of *m*-chloroperbenzoic acid (85%). After stirring for 15 hr the pasty mixture was shaken in a separatory funnel with three 75-ml portions of sodium bicarbonate solution, each containing 4 g of $NaHCO_3$. The dried ($MgSO_4$) solution was allowed to evaporate and the residue was recrystallized from ligroin–benzene (1:2) to give 1.53 g (62%) of the crude sulfone, mp 136–142°. Another recrystallization gave 1.25 g (50.6%), mp 140–143.5°. The analytical sample had mp 141.5–143.5°; ir (Nujol) 7.49, 8.61 μ (SO_2); nmr ($CDCl_3$) δ 2.44 (s, 6, CH_3), 7.17 (s, 2, $=CH_2$), 7.6 (q, 8, aryl).

Anal. Calcd for $C_{16}H_{16}S_2O_4$: C, 57.12; H, 4.79; S, 19.06. Found: C, 57.00; H, 4.70; S, 19.00.

Ethyl Bis(phenylsulfonyl)acetate (8).—A mixture of 31.4 g of ethyl *S*-phenylthioglycolate,[12] 28.6 g of *N*-bromosuccinimide, 160 ml of dry CCl_4, and a pinch of benzoyl peroxide was refluxed with stirring for 2 hr while irradiating with a Hanau sun lamp (Sole d'alta montagna 99, type 1005). The mixture was cooled to room temperature and filtered, and the CCl_4 was removed at reduced pressure. The residual oil was dissolved in 180 ml of CH_3OH and 36.4 g of sodium benzenesulfinate was added. After refluxing for 2.5 hr the solution was diluted with H_2O to 500 ml and extracted with three 25-ml portions of CH_2Cl_2. The extracts were washed with H_2O and dried ($MgSO_4$), and the solvent was removed to give an oil which was dissolved in 110 ml of acetic acid. After the addition of 45.5 ml of 30% H_2O_2 the mixture was stirred at room temperature for 20 hr, diluted to 500 ml with H_2O, filtered, dried in air, and recrystallized from 80 ml of benzene to give 12.5 g (21.2%) of the disulfone as white crystals, mp 141.5–143.5° (lit.[13] mp 140–142°).

1,1-Bis(phenylsulfonyl)ethane (7).—Reduction of ethyl bis(phenylsulfonyl)acetate (8) in ether by means of lithium aluminum hydride gave in 40% yield the disulfone: mp 98–99.5° (from benzene); ir (Nujol) 7.58, 8.65 μ (SO_2); nmr ($CDCl_3$) δ 1.72 (d, 3, CH_3), 4.55 (q, 1, $CHCH_3$), 7.7 (m, 10, phenyl).

Anal. Calcd for $C_{14}H_{14}O_4S_2$: C, 54.17; H, 4.54; S, 20.65. Found: C, 54.10; H, 4.61; S, 20.64.

1,1-Bis(phenylsulfonyl)-2-dimethylaminoethene (4a).—To a solution of 14.8 g of bis(phenylsulfonyl)methane[10] in 50 ml of dry DMF there was added 4.7 g of sodium methoxide (Matheson) followed by dropwise addition of 17.5 g of the adduct of dimethylformamide and dimethyl sulfate.[14] After stirring at room temperature for 7 hr the mixture was diluted to 500 ml with H_2O, and the solid was filtered, dried in air, and recrystallized from MeOH–$MeNO_2$ (5:1) to give 7.2 g (41%) of the enamine as yellow crystals, mp 198–199°. The analytical sample had mp 198–198.5°; ir (Nujol) 6.17 (C=C), 7.59, 8.79 μ (SO_2); nmr ($CDCl_3$) δ 3.06 (s, 6, CH_3), 7.4, 7.9 (m, 11, phenyl and =CH).

Anal. Calcd for $C_{16}H_{17}NO_4S_2$: C, 54.68; H, 4.88; N, 3.99. Found: C, 54.76; H, 4.91; N, 3.85.

1,1-Bis(phenylsulfonyl)-2-aminoethene (4b).—To a solution of 7.4 g of bis(phenylsulfonyl)methane (2) in 25 ml of dry DMF there was added 1.35 g of NaOMe (Matheson) followed by 2.5 g of formamidine acetate. The mixture, protected from moisture, was stirred at room temperature for 24 hr. Dilution with H_2O to 250 ml, filtration, and recrystallization from C_2H_5OH–$MeNO_2$ (1:4) gave 5 g (62%) of the disulfone as yellow crystals, mp 227–229°. The analytical sample had mp 228–229°; ir (Nujol) 2.90, 2.99 (NH_2), 6.12 (C=C), 7.56, 7.65, 7.8, 8.62, 8.77 μ (SO_2).

Anal. Calcd for $C_{14}H_{13}NO_4S_2$: C, 52.00; H, 4.05; N, 4.33. Found: C, 52.04; H, 4.18; N, 4.08.

tert-Butyl 3,3-Bis(phenylsulfonyl)propanoate (5).—To a solution of 1.5 g of bis(phenylsulfonyl)methane in 10 ml of dry DMF there was added 0.27 g of NaOMe followed by 0.98 g of *tert*-butyl α-bromoacetate. The mixture was stirred at room temperature for 8 hr, diluted carefully to the cloud point with water, seeded, and set aside for several hours. Filtration, washing with C_2H_5OH, and recrystallization from C_2H_5OH–$MeNO_2$ (8:1) gave 1.3 g (79%) of the ester as white crystals, mp 144.5–148°. Further recrystallization from the same solvent gave an analytical sample: mp 146–147°; ir (Nujol) 5.80 (C=O), 7.54, 8.61 μ (SO_2);

(9) Melting and boiling points are uncorrected. Infrared spectra were obtained on Perkin-Elmer 237B and 337 instruments and nmr spectra on Varian A-60, A-56/60, and Perkin-Elmer R-12 units. Elemental analyses were carried out by Charles Meade and associates, University of Massachusetts Microanalytical Laboratory.

(10) E. P. Kohler and M. Tishler, *J. Amer. Chem. Soc.*, **57**, 217 (1935).

(11) W. E. Truce and R. J. Steltenkamp, *J. Org. Chem.*, **27**, 2816 (1962).

(12) R. Pummerer, *Ber.*, **43**, 1401 (1910).

(13) R. Breslow and E. Mohacsi, *J. Amer. Chem. Soc.*, **83**, 4100 (1961).

(14) H. Bredereck, F. Effenberger, and G. Simchen, *Chem. Ber.*, **96**, 1350 (1963).

nmr ($CDCl_3$) δ 1.45 (s, 9, CH_3), 3.10 (d, 2, CH_2), 5.20 (t, 1, CH), 7.5–8 (m, 10, phenyl).

Anal. Calcd for $C_{19}H_{22}O_6S_2$: C, 55.59; H, 5.40; S, 15.62. Found: C, 55.44; H, 5.08; S, 15.80.

3,3-Bis(phenylsulfonyl)propanoic Acid (6).—To a solution of 2.86 g of KOH in 250 ml of CH_3OH there was added 7.15 g of bromoacetic acid, and after complete solution had occurred 17.1 g of the potassium salt of bis(phenylsulfonyl)methane was added and the mixture was stirred magnetically and refluxed for 20 hr and diluted to 1.7 l. with water. After 2 hr, unreacted disulfone was removed by filtration and the filtrate was acidified with concentrated HCl (Congo Red). After 24 hr at room temperature filtration gave 5.93 g (29.5%) of white solid, which after recrystallization from benzene containing a few drops of nitromethane gave 5.1 g (25.4%) of crusty white crystals, mp 159–162°. Recrystallization from the same solvent gave an analytical sample: mp 161–161.7°; ir (Nujol) 2.78, 2.83 (OH), 5.82 (C=O), 7.6, 7.66, 8.7, 8.8 μ (SO_2); nmr ($CDCl_3$) δ 3.25 (d, 2, CH_2), 5.18 (t, 1, CH), 6.75 (s, 1, OH, erased by D_2O), 7.5–8 (m, 10, phenyl). The same compound could be obtained by treatment of the *tert*-butyl ester with hydrochloric acid in acetic acid.

Anal. Calcd for $C_{15}H_{14}O_6S_2$: C, 50.83; H, 3.98; S, 18.09. Found: C, 50.81; H, 3.91; S, 17.80.

1,2-Bis(*p*-toluenesulfonyl)-1-*p*-toluenethioethane (22).—A mixture of 3.36 g of *cis*-1,2-ditosylethene (21), 2.48 g of *p*-toluenethiol, and 0.1 g of NaOMe (Matheson) in 25 ml of MeOH was stirred at room temperature for 24 hr. The mixture was filtered and the residual solid was washed with MeOH to give 2 g of white powder, mp 95–118°. Several recrystallizations of this crude material, which appeared to be a mixture of the desired compound and *cis*-$TsCH{=}CHSC_6H_4CH_3$-*p*, gave 0.51 g (11%) of the sulfide: mp 127.5–129.8°; ir (Nujol) 7.6, 8.78 μ (SO_2); nmr ($CDCl_3$) δ 2.3 (s, 3, CH_3), 2.41 (s, 6, CH_3), 3.7 (distorted dq, 2, CH_2), 4.55 (dd, 1, CH), 3.4 (m, 12, aryl); uv (95% C_2H_5OH) λ_{max} 228 nm (ε 34,100), 258 (6800), 275 (3890).

Anal. Calcd for $C_{23}H_{24}O_4S_3$: C, 59.97; H, 5.25; S, 20.88. Found: C, 60.05; H, 5.55; S, 20.70.

Attempted oxidation of **22** by means of *m*-chloroperbenzoic acid by the method described for **19** gave only *trans*-1,2-bis(*p*-toluenesulfonyl)ethene, mp 229–230°, identified by comparison with an authentic sample.[8] The same compound was obtained by oxidation of **13** with *m*-chloroperbenzoic acid or according to the method of Fromm.[6]

1,1-Bis(*p*-toluenesulfonyl)-2-*p*-toluenethioethane (19).—A mixture of 3.36 g of **15** and 1.24 g of *p*-toluenethiol was dissolved in 24 ml of warm dioxane and the solution was allowed to stand at room temperature for 24 hr. Upon dilution with 250 ml of H_2O an oil separated which solidified after several days standing or more readily on seeding. Filtration and recrystallization from methanol gave 3.56 g (77.5%) of the sulfide as white crystals, mp 106–108°. The analytical sample had mp 107–109° (MeOH); ir (Nujol) 7.49, 8.55 μ (SO_2); nmr ($CDCl_3$) δ 2.39 (s, 3, CH_3), 2.54 (s, 6, CH_3), 3.69 (d, 2, CH_2, J = 6.5 Hz), 4.66 (t, 1, CH, J = 6.5 Hz), 7.33 (s, 4, ArS–), 7.8 (q, 8, $ArSO_2$); uv (95% C_2H_5OH) λ_{max} 232 nm (ε 33,600), 264 (6150), 275 (4030).

Anal. Calcd for $C_{23}H_{24}O_4S_3$: C, 59.97; H, 5.25; S, 20.88. Found: C, 60.26; H, 5.52; S, 20.59.

1,1,2-Tris(*p*-toluenesulfonyl)ethane (17).—A solution of 3.56 g of **19** in 35 ml of CH_2Cl_2 was cooled in an ice bath and with stirring there was added over about 15 min 3.5 g of *m*-chloroperbenzoic acid. The mixture was stirred in the ice bath for 2 hr and at room temperature for 24 hr and then washed in a separatory funnel with two 75-ml portions of 1 *M* $NaHCO_3$ solution. Evaporation of the dried ($MgSO_4$) solution left a tacky white solid which was recrystallized from MeOH to give 0.55 g (14.5%) of the crude sulfone as white needles, mp 145–155°. Several recrystallizations from ethanol, from which an ethanol solvate was obtained, followed by $MeNO_2$–MeOH (1:10) and finally MeOH, gave an analytical sample: mp 155.5–157.5°; ir (Nujol) 7.43, 8.62 μ (SO_2); nmr ($CDCl_3$) δ 2.45 (s, 9, CH_3) 4.0 (d, 2, CH_2, J = 4.5 Hz), 5.09 (t, 1, CH, J = 4.5 Hz), 7.5 (q, 12, aryl); uv (95% C_2H_5OH) λ_{max} 264 nm (ε 2960), 275 (2195).

Anal. Calcd for $C_{23}H_{24}O_6S_3$: C, 56.08; H, 4.91; S, 19.53. Found: C, 55.82; H, 4.75; S, 19.77.

1,1,3,3-Tetrakis(*p*-toluenesulfonyl)propane (18).—A mixture of 1.01 g of **15** and 0.54 g of sodium *p*-toluenesulfinate in 15 ml of dioxane and 1.5 ml of H_2O was stirred at room temperature for 18 hr, 100 ml of H_2O was added, and the solid was filtered, dried in air, and recrystallized from C_2H_5OH–$MeNO_2$ (1:1) to give 0.75 g (76%) of white crystals: mp 225.5–227.5°; ir (Nujol) 8.62, 8.72 μ (SO_2); nmr ($CDCl_3$) δ 2.55 (s, 12, CH_3), 3.0 (t, 2, $CHCH_2CH$), 5.87 (t, 2, $CHCH_2$), 8.0 (q, 16, aryl); uv (95% C_2H_5OH–CH_2Cl_2, 65:35 v/v) λ_{max} 267 nm (ε 3930), 275 (3170); mass spectrum (80 eV) M^+ *m/e* 660.

Anal. Calcd for $C_{31}H_{32}O_8S_4$: C, 56.34; H, 4.88; S, 19.41. Found: C, 56.10; H, 4.72; S, 19.25.

Registry No.—**1**, 39837-25-7; **2**, 3406-02-8; **2** potassium salt, 19472-81-2; **4a**, 39837-27-9; **4b**, 39082-61-6; **5**, 39837-29-1; **6**, 39837-30-4; **7**, 33419-26-;0 **8**, 39837-32-6; **9**, 886-07-7; **10**, 39837-34-8; **11**, 39837-35-9; **12**, 39082-53-6; **14**, 39837-37-1; **15**, 39837-38-2; **17**, 39837-39-3; **18**, 39837-40-6; **19**, 39837-41-7; **21**, 15645-75-7; **22**, 39837-43-9; piperidine, 110-89-4; *m*-chloroperbenzoic acid, 937-14-4; ethyl *S*-phenylthioglycolate, 7605-25-6; *N*-bromosuccinimide, 128-08-5; formamidine acetate, 3473-63-0; *tert*-butyl α-bromoacetate, 5292-43-3; bromoacetic acid, 79-08-3; *p*-toluenethiol, 106-45-6; sodium *p*-toluenesulfinate, 824-79-3.

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