An aqueous solution of barium chloride caused some turbidity when it was added to a portion of the unextracted aqueous layer. Not enough sulfate anion was present in the aqueous layer for a gravimetric determination as barium sulfate.

Reaction of *cis*-1,2-Cyclopentylene Sulfate (3) with Phenyllithium.—A solution of **3** (16 g., 0.10 mole) in ether (50 ml.) was added dropwise over a 30-min. period with stirring and cooling in an ice bath to a solution of phenyllithium in ether (400 ml.) prepared from bromobenzene (48 g., 0.31 mole) and lithium (4.8 g., 0.70 g.-atom). The apparatus and technique described above were used. The reaction mixture was stirred for 10 hr. and then hydrolyzed with an aqueous ammonium chloride solution. The ether layer was separated, dried over magnesium sulfate, filtered, and concentrated on the steam bath using a 30 × 2 cm. Vigreux column to give a brown oil (26.5 g.). The ether which distilled gave only one peak in a vapor phase chromatogram using a 2-m. column packed with polyethylene glycol.

A portion (16.4 g.) of the reaction oil (26.5 g.) was distilled through a 15 × 1 cm., spiral-wire column to give 1-phenylcyclopentene (6.6 g., b.p. 130–132° at 30–32 mm., lit. b.p. 107–108° at 12 mm).[18] Water codistilled with this material. A portion of the reaction oil (26.5 g.) was redried over calcium sulfate. 1-Phenylcyclopentene and water codistilled from this mixture as above. A vapor phase chromatogram of the 1-phenylcyclopentene using a 2-m. column packed with Apiezon L grease gave two peaks. The large peak occupied 99% of the peak area, while the small peak occupied 1%. The retention time for the small peak was equal to that for biphenyl. The infrared spectra of the synthetic 1-phenylcyclopentene and of an authentic sample were identical. The freezing point of the synthetic sample was 19.4° and for an authentic sample 23.6°; the mixture freezing point was 21.4°; lit.[17] m.p. 22–23°. The total yield of 1-phenylcyclopentene (12.8 g., 0.0889 mole) was 89%.

The aqueous hydrolysis layer was continuously extracted with ether. No *cis*-1,2-cyclopentanediol was isolated but only a trace of unidentified oil.

The presence of benzenesulfonic acid in the aqueous layer was confirmed as above.

A 1.3% recovery of the sulfate anion from the aqueous hydrolysis layer was made gravimetrically as barium sulfate.

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(18) G. Baddeley, J. Chadwick, and H. T. Taylor, *J. Chem. Soc.*, 448 (1956).

Grignard Reagents of Sulfones. VIII. Reactions of Alkylene Disulfones with Ethylmagnesium Bromide[1]

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Reactions were studied between ethylmagnesium bromide and alkylene disulfones of the structure $ArSO_2(CH_2)_nSO_2Ar$. With $n = 2$, no stable metalated product could be demonstrated by addition to benzaldehyde, but the presence of such a product could not be altogether discounted; vigorous conditions resulted in difficultly reproducible elimination and reduction reactions which gave mixtures of products. With $n = 5$, formation of bis-Grignard reagents was demonstrated by reaction with ketones and bromine. Grignard reagents apparently were formed also with $n = 3$ and 4. Appropriate conditions for formation of Grignard reagents of alkylene disulfones are suggested. No indications were found of discrete monometalation of alkylene disulfones. Certain Grignard reagents of sulfones were found to be soluble in solutions of ethylmagnesium bromide, although such reagents usually are virtually insoluble in organic solvents; reasons for this solubility are considered.

Products obtained by metalating sulfones with Grignard reagents are most simply regarded as Grignard reagents themselves and are most conveniently formulated as shown by structure **1**. Previous work from our laboratories has dealt with the preparation, properties, and reactions of such substances obtained by metalating monosulfones. This paper extends these studies to α,ω-alkylene disulfones.

$$\underset{\textbf{1}}{R_1SO_2CR_2R_3MgX}$$

Reaction of ethylmagnesium bromide (**2**) with 1,2-bis(phenylsulfonyl)ethane (**3**) gave no clear-cut evidence of formation of a stable Grignard reagent (**4**), which might occur according to the following equation. It should be mentioned that a major obstacle to smooth reactions of **3** lay in its sparing solubility in solvents commonly used for Grignard reactions, *e.g.*, benzene, ether, anisole, and tetrahydrofuran; more soluble substituted derivatives should be more amenable to study.

$$\underset{\textbf{2}}{2EtMgBr} + \underset{\begin{array}{l}\textbf{3}, n = 2\\ \textbf{5}, n = 5\\ \textbf{7}, n = 3\\ \textbf{9}, n = 4\end{array}}{ArSO_2(CH_2)_nSO_2Ar} \longrightarrow$$

$$\underset{\begin{array}{l}\textbf{4}, n = 2\\ \textbf{6}, n = 5\\ \textbf{8}, n = 3\\ \textbf{10}, n = 4\end{array}}{ArSO_2CH(MgBr)(CH_2)_{n-2}CH(MgBr)SO_2Ar} + 2C_2H_6$$

Reaction of **3** with about 2 molar proportions of ethylmagnesium bromide (**2**) resulted in about twice the amount of gas which had been found in metalation of methyl phenyl sulfone,[2] suggesting that the reagent **4** might have been formed. Furthermore, recovery after acidification of the sulfone **3** (59%) suggested that **4** might have survived reasonably well. Nevertheless, attempted demonstration of the presence of **4** by trapping it with benzaldehyde[3] failed, nearly all of the benzaldehyde and 53% of sulfone **3** being recovered. Since a reagent of structure **1** gave poorer results upon heating,[3] there seemed little point in trying to force addition to benzaldehyde in this way.

The formation of **4** conceivably might be demonstrated using other trapping agents, but the failure with an aldehyde, representing the most active common functional group to which Grignard reagents add,[4] shows at least that synthetically useful addition reactions of **4** are unlikely.

Since elimination reactions seemed probable in reaction of the sulfone **3** with **2**, vigorous conditions and ex-

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(1) (a) Paper VII: L. Field and E. T. Boyd, *J. Org. Chem.*, **26**, 1787 (1961). (b) Results are abstracted from a portion of the Ph.D. Dissertation of E. T. B., Vanderbilt University, Jan., 1961. This investigation was supported in part by the U. S. Army Research Office, Durham, N. C.

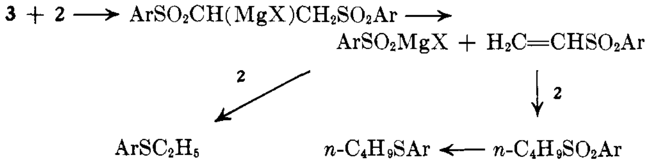
(2) L. Field, *J. Am. Chem. Soc.*, **78**, 92 (1956).

(3) L. Field, *ibid.*, **74**, 3919 (1952).

(4) C. E. Entemann, Jr., and J. R. Johnson, *ibid.*, **55**, 2900 (1933).

cess **2** were used to force such secondary reactions to completion so that their nature could be determined. At least six products resulted. Very little of sulfone **3** was recovered.

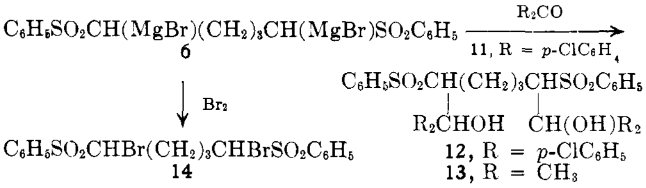
Ethyl phenyl sulfide usually was formed in about 14–21% yield. Its formation can be explained by metalation and subsequent elimination, as follows.



Truchet found that a mixture of ethyl phenyl sulfoxide and ethyl phenyl sulfide resulted from reaction of benzenesulfinic acid and **2**.[5] Using a large excess of **2** with benzenesulfinic acid, we obtained ethyl phenyl sulfide in 50% yield, showing that the postulated reduction of a sulfinate salt can indeed occur under conditions resembling those used with ethylene disulfone **3**. If the equations are correct, **2** would be expected to add to the intermediary vinyl sulfone with formation of the *n*-butyl aryl sulfone, which subsequently might be converted by unusual species present under the vigorous conditions to the sulfide. Substances with consistent properties were isolated (5–11% yields). Phenyl disulfide also was isolated (24%) but probably was an artifact produced during distillation, because a disulfide should react with a Grignard reagent to form a sulfide.[6] Two unidentified substances also were isolated; these apparently contained phenyl groups (infrared spectra), but efforts to determine their structures did not seem worthwhile because of the small amounts formed.

In a reaction of a large excess of **2** with the sulfone **3**, titration showed that nearly 2 molar proportions of basic magnesium were consumed in about 2 hr. after the initially rapid gas evolution was virtually complete and that after about 20 hr. nearly 3 molar proportions had been consumed. Since **4** should behave in titration exactly like **2**, the results suggest rapid metalation and rapid gas evolution during about 5 min.; at this point, **4** might be present, even though it could not be trapped. Elimination, addition, and reduction evidently then occur during 1–2 hr., followed finally by reduction of more difficultly reducible species (*e.g.*, sulfones) during about 18 hr. more.

With the hope of minimizing elimination, attention next was focused on the pentamethylene disulfone **5**. This disulfone when heated with about 2 molar proportions of **2** evolved 39% of 2 molar equiv. of gas, an amount consistent with either monometalation or incomplete dimetalation. Good recovery (78%) of sulfone **5** after acidification made it worthwhile to determine whether the mono-Grignard reagent of **5** did indeed predominate. Benzaldehyde apparently reacted with the metalated product, even though the metalation period was quite short (that used with methyl phenyl sulfone[3] and seemingly effective with the ethylene sulfone **3**). No products could be crystallized, perhaps because of the presence of numerous diastereoisomers as well as a metalation time which later results suggest may have been too short. To reduce the number of diastereoisomers possible, ketones were used. *p,p'*-Dichlorobenzophenone (**11**) was tried first for reasons given elsewhere.[1a] The biscarbinol **12** shown in the equations was obtained in 11% yield. Since extremely vigorous conditions are necessary for effecting addition to the chlorophenyl ketone **11**,[1a] acetone was used. Again, a biscarbinol (**13**, 16%) resulted, as shown by the equations. The yields isolated in reactions of these kinds are rather poor indications of the amounts actually formed because of the difficulty of separating the diastereoisomers; in all reactions of the sulfone **5**, only one crystalline diastereoisomer could be isolated.



The results with both ketones pointed to the probability that the bis-Grignard reagent **6** predominated and that the relatively low gas evolution was a consequence simply of incomplete formation of **6**. Larger excesses than usual of **2** thus seemed called for in the metalation of alkylene disulfones. Reaction of sulfone **5** with 8 molar proportions of **2** was followed gasometrically for 5 hr., at which time recovery of the **5** by acidification suggested that at least half of the bisreagent **6** survived. There was a marked change in the slope of the gas volume–time curve at about 50 min., at a gas evolution corresponding to 72% of 2 molar equiv. This result implied that dimetalation was substantially complete at this point and that secondary reactions which involved evolution of gas thereafter became increasingly significant.

The time required for metalation of **5** is comparable to that of ethyl *p*-tolyl sulfone,[7] but the apparent desirability of the large excess of **2** for metalation of **5** was unexpected and is intriguing. The explanation probably relates to complexes involving the sulfone groups of **5** and the Grignard reagent **2**.[2] An observation which may be germane was the apparent inhibition of dimetalation of a β-hydroxysulfone, which was attributed to interaction of $-OMgBr$ with the sulfonyl group.[1a] The greater difficulty of metalating **5** in comparison with the ethylene homolog **3** suggests that a quasi-cyclic coordination complex may be possible for the pentamethylene sulfone **5**, which is prohibited for the ethylene homolog; however, the participation of both sulfonyl groups in increasing the acidity of the α-hydrogen atoms also could be a major factor in the easier metalation of **3**.

Another interesting point in the same vein is that the Grignard reagent **6** is completely soluble in benzene when it is prepared by metalating **5** with 8 molar proportions of ethereal **2**. This behavior differs notably from several reagents of structure **1**, which are virtually insoluble in usual solvents.[2,7] Solubility also was noted for the tetramethylene homolog discussed below, but not for the trimethylene. Even phenylsulfonylmethylmagnesium bromide formed a homogeneous solution at 25° when it was prepared in benzene by metalating methyl phenyl sulfone with 8 molar proportions of

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[5] R. Truchet, *Compt. rend.*, **191**, 296 (1930).

[6] *Cf.* L. Field, J. R. Holsten, and R. D. Clark, *J. Am. Chem. Soc.*, **81**, 2572 (1959).

[7] L. Field and J. W. McFarland, *ibid.*, **75**, 5582 (1953).

ethereal **2**. The solutions are colloidal (Tyndall effect). These phenomena can be explained by assuming that insoluble polymeric aggregates resulting from intermolecular association of $-SO_2-$ and $-MgX$, to which insolubility has been attributed,[2] are destroyed by large amounts of **2**. Association then presumably is between molecules **1** and **2**, affording more soluble species, instead of between a number of molecules only of structure **1**.

It is also noteworthy that the gas volume–time plot during metalation of **5** showed no indication of an appreciable inflection which would signify monometalation. The conclusion that dimetalation predominates, suggested by the isolation only of biscarbinols, thus is supported.

Deductions from the gas volume–time plot as to an optimum time for dimetalation of about an hour were affirmed by reaction of the Grignard reagent **6** with bromine. Although only one solid diastereoisomeric dibromosulfone of structure **14** was isolated (8% yield), an oil was nearly pure **14** (22% yield) and, indeed, bromine analysis showed that the crude reaction product itself, obtained quantitatively as shown by the equations, was almost entirely **14**.

Preliminary exploration was done to determine whether the trimethylene disulfone **7** and the tetramethylene homolog **9** could be metalated without decomposition.

Gas volume–time plots were obtained with **7** and **9** using 8 molar proportions of **2**. Both sulfones showed definite plateaus in time, during which gas evolution was quite slow, after evolution of about 76–102% of 2 molar equiv. of gas which signified dimetalation; the plateau was particularly notable for the tetramethylene homolog **9**, and the evolution (75%) seemed more consistent with a minimum of subsequent reactions than did the plateau for **7** (102% of 2 equiv.). In later experiments, acidification after estimated gas evolution amounting to 75–76% of 2 molar equiv. (*i.e.*, after about 0.5 hr. when dimetalation was presumed complete) resulted in recoveries of 70% for **7** and of 96% for **9**; presumably therefore, the Grignard reagents **8** and **10** had been formed at this point and were reasonably stable. Heating after the time of plateau caused resumption of gas evolution; owing to the associated secondary reactions, the recovery of **7** was only 34% after 8 hr. and of **9** only 19% after 6 hr. Dimetalation of **7** and **9** by heating with 8 molar proportions of **2** for 35–40 min. thus seems to afford a feasible means of obtaining the Grignard reagents **8** and **10**. As with **5**, no inflections appeared in the gas volume–time plot which would point to discrete monometalation of **7** or **9**.

It is of interest to compare the attractiveness of reagents **6**, **8**, and **10** for synthesis: **8** offers an advantage of insolubility, which should permit removal of excess **2**; **10** offers an advantage of apparent greater stability and of a better defined time plateau after dimetalation before secondary reactions become serious.

Experimental[8]

Reactions of Ethylmagnesium Bromide (2) with 1,2-Bis-(phenylsulfonyl)ethane (3).—Ethylmagnesium bromide (**2**, 25 mmoles) was added to a slurry of 3.88 g. (13 mmoles, m.p. 183–183.5°) of sulfone **3** in 125 ml. of benzene. A precipitate formed, but no gas appeared. Heating at reflux for 5 min. and cooling resulted in 60% of 2 molar equiv. of gas. After acidification, 2.29 g. (59%, m.p. 181–183°) of **3** was recovered; a heating period of 5 hr. gave little additional gas (67%) but lower recovery of **3** (43%).

The original experiment was repeated, but with addition of 25 mmoles of benzaldehyde after the 5-min. heating period. After 1.5 hr., hydrolysis resulted in 2.06 g. of **3** (53%, m.p. and m.m.p. 181–183°) and in 87% recovery of the benzaldehyde.

In a reaction fairly typical of those under vigorous conditions, 56.1 g. (181 mmoles) of sulfone **3** was mixed with 1080 mmoles of **2** in 500 ml. of benzene. Ether was removed by distillation and the mixture then was heated at 72° for 18.5 hr. After addition of 150 mmoles more of **2** and 1.5 hr. of additional heating (to assure complete reaction), acidification resulted in recovery of 15% of **3** and an oil. Distillation of the oil gave ethyl phenyl sulfide (3.48 g.) in 14% yield,[10] b.p. 55° (2.7 mm.), $n^{25}\mathrm{D}$ 1.5609 (identity established by infrared spectrum and oxidation to the sulfone in 80% yield). Also obtained were three other materials: (a) 1.7 g., b.p. 60–66° (2.6 mm.), $n^{25}\mathrm{D}$ 1.5422; (b) 1.8 g., b.p. 122–124° (2.5 mm.), $n^{25}\mathrm{D}$ 1.5935, rapidly reduced aqueous permanganate; (c) 9.5 g., b.p. 129–130° (0.2 mm.), which solidified and upon recrystallization proved to be phenyl disulfide, m.p. and m.m.p. 59.5–60.5°. The yield of 9.5 g. thus was 24%.[11]

In other experiments under vigorous conditions two more substances were isolated. (a) After a reaction time of 1 hr. with excess **2** (molar ratio, *ca.* 12:1), a substance resulted which had b.p. 115–125° (0.6 mm.); $n^{25}\mathrm{D}$ 1.5399–1.5429 (5% if *n*-butyl phenyl sulfone); infrared absorption typical of $-SO_2-$ at 1150 and 1300 cm.$^{-1}$ and in good agreement with the spectrum of *n*-butyl phenyl sulfone[12]; melting point for the derivative *n*-butyl *m*-(3-bromobenzoylamino)phenyl sulfone, lit.[12] 130–131.5° (uncor.), found 131.5–132.5°. (b) After a reaction time of several days with excess **2** (molar ratio, *ca.* 12:1), a substance resulted which had b.p. 90–100° (1.4 mm.), $n^{25}\mathrm{D}$ 1.5388–1.5402 (11%, if *n*-butyl phenyl sulfide); for *n*-butyl phenyl sulfide, lit.[13] b.p. 96–98° (4 mm.), $n^{20}\mathrm{D}$ 1.5458.

To determine loss of basic magnesium, ether was distilled from a mixture of 60 mmoles of **3**, 750 mmoles of **2**, and 400 ml. of benzene, and was replaced with benzene until the reflux temperature was 72°. The mixture was heated for 20 hr. while 1-ml. aliquots of the slurry were removed and titrated[14]; decrease in basic magnesium began *ca.* 1 hr. after addition of the **2** (**4** should behave like **2** in titration and its formation should not cause a decrease in basic magnesium), and after 2 hr. about 110 mmoles had disappeared. After *ca.* 20 hr., *ca.* 170 mmoles of basic magnesium had disappeared.

In the reaction of benzenesulfinic acid with ethylmagnesium bromide, 1440 mmoles of **2** was added during 1.5 hr. to 35.0 g. of the acid in 200 ml. of ether. Ether was distilled and replaced with benzene until the reflux temperature was 72°. After 19 hr. of heating, the mixture was cooled and acidified. The benzene layer and a benzene extract were dried and distilled; the yield of slightly impure ethyl phenyl sulfide was 17.0 g. (50%), b.p. 51° (3 mm.), $n^{25}\mathrm{D}$ 1.5600; identity was confirmed by oxidation to ethyl phenyl sulfone (79% yield).

Preparation of 1,5-Bis(phenylsulfonyl)pentane (5) and 1,4-Bis(*p*-tolylsulfonyl)butane (9).—Sulfone **5** was prepared, using the general procedure of Otto,[15] by heating 358 g. of sodium benzenesulfinate and 200 g. of 1,5-dibromopentane in 1.2 l. of ethanol at 78° for 118 hr. The mixture was poured onto ice (700 g.), and **5** was removed by filtration and recrystallized twice from

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[8] General procedures, etc., are summarized in the following reference[9]; as before, *ca.* 3.0 *N* ethereal ethylmagnesium bromide was used throughout. Gas evolution was measured using either a wet-test meter (Precision Scientific Co.) or a gas buret, which were connected through a Dry Ice trap to the apparatus; volumes of gas were corrected to 0° and 760 mm. It should be added that monometalation of monosulfones in benzene–ether results in measurement of *ca.* 57% of 1 molar equiv. of gas, probably because of solubility of the gas.[2] Infrared spectra were determined using a Perkin-Elmer Model 137 spectrophotometer with Nujol mulls or neat liquids. Analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

[9] L. Field, J. E. Lawson, and J. W. McFarland, *J. Am. Chem. Soc.*, **78**, 4389 (1956), footnote 19.

[10] Assuming that 1 mole of **3** produces only 1 of ethyl phenyl sulfide.

[11] Assuming that 1 mole of **3** leads to 1 mole of phenyl disulfide.

[12] A. C. Cope, D. E. Morrison, and L. Field, *J. Am. Chem. Soc.*, **72**, 59 (1950).

[13] H. Gilman and F. J. Webb, *ibid.*, **71**, 4062 (1949).

[14] L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1955, p. 269.

[15] R. Otto, *Ber.*, **13**, 1274 (1880).

ethanol, yielding 161.6 g. (53%), m.p. 91–93°. Further recrystallization from 2-propanol, ethanol, and *n*-butyl chloride gave 1,5-bis(phenylsulfonyl)pentane (**5**) with a constant melting point of 92.5–93.5°.

Anal. Calcd. for $C_{17}H_{20}O_4S_2$: C, 57.93; H, 5.72; S, 18.19. Found: C, 57.55; H, 5.42; S, 18.34.

Sulfone **9** was prepared similarly by heating 445 g. of sodium *p*-toluenesulfinate and 127 g. of 1,4-dichlorobutane in 2 l. of ethanol for 98 hr. After the mixture had been poured onto ice, the gummy solid was recrystallized from 2-propanol and from aqueous acetone; yield of 1,4-bis(*p*-tolylsulfonyl)butane (**9**) was 123.9 g. (34%), m.p. 152.5–153.5°, unchanged by further recrystallization.

Anal. Calcd. for $C_{18}H_{22}O_4S_2$: C, 59.26; H, 6.05. Found: C, 59.34; H, 6.23.

Reactions of 1,5-Bis(phenylsulfonyl)pentane (5) with about 2 Molar Proportions of Ethylmagnesium Bromide (2).—A mixture of 43 mmoles of **5** and 110 mmoles of **2** in 200 ml. of benzene was heated at 72° for 6 hr. Gas evolved was 39% of 2 molar equiv. and evolution was essentially complete after 1.5 hr. Acidification and recrystallization gave 11.8 g. (78%) of **5**, m.p. 91.5–93°.

Reaction of **5** (15 g., 43 mmoles) with **2** and then with benzaldehyde (9.12 g.), essentially as before[3] but with 110 mmoles of **2** (later work showed this heating period in metalation of **5** to be undesirably short), resulted in 25.5 g. (106%) of yellow oil. Strong infrared absorption at 3570 cm.$^{-1}$ indicated addition had occurred, but no crystalline products could be isolated even after 1 year, nor could the adduct be dehydrated[3] to crystalline material; one would expect that any large amounts of unchanged **5** would have been detected in the attempts at crystallization.

In the reaction of the Grignard reagent **6** with *p,p'*-dichlorobenzophenone (**11**), a mixture of 7.5 g. (21 mmoles) of the sulfone **5** and 50 mmoles of **2** in 100 ml. of benzene was heated at 72° for 1 hr., treated with 12.6 g. (50 mmoles) of ketone **11** in benzene (200 ml.), and then heated for 24 hr. more. Acidification and extraction gave 19.5 g. of solid, which when slurried in ethanol gave 1.95 g. (11%) of crude 1,1,7,7-tetrakis(*p*-chlorophenyl)-2,6-bis(phenylsulfonyl)-1,7-heptanediol (**12**), m.p. 229–231°. This **12** was identical with similarly prepared **12**, which was nearly insoluble in most solvents but was recrystallized for analysis to a constant melting point of 252–253° from 1:1 nitromethane–dimethylformamide.

Anal. Calcd. for $C_{43}H_{36}Cl_4O_6S_2$: C, 60.42; H, 4.24; S, 7.50. Found: C, 60.35; H, 4.17; S, 8.05.

When the heating period after addition of **11** was only 5.3 hr., the yield of adduct **12** was 5%. No **12** could be isolated when anisole was used as a solvent for the reaction.

For the reaction of **6** with acetone, 3.01 g. (52 mmoles) of purified[7] acetone in 15 ml. of benzene was added to the **6** prepared by heating 7.5 g. (21 mmoles) of **5** and 50 mmoles of **2** in 60 ml. of benzene for 1 hr. The mixture was stirred at 25° for 3.5 hr. and acidified. A benzene extract gave an oil, part of which was chromatographed on acid-washed alumina but with negligible benefit. Crystallization from 2-propanol of part of the chromatographed material separated the starting material **5** and product in amounts consistent, over-all, with recovery of 33% of **5**, m.p. and m.m.p. 88–91°, and a yield of 16% of crude 2,8-dimethyl-3,7-bis(phenylsulfonyl)-2,8-nonanediol (**13**), m.p. 159–164°, with appropriate infrared absorption at 3590, 1300, and 1145 cm.$^{-1}$. Recrystallization of adduct **13** (2-propanol, ethyl acetate) gave material with a constant melting point of 182.5–183.5°.

Anal. Calcd. for $C_{23}H_{32}O_6S_2$: C, 58.95; H, 6.88. Found: C, 58.95; H, 6.86.

Reactions of Sulfone 5 with 8 Molar Proportions of 2.—A solution of 3.52 g. (10 mmoles) of sulfone **5** and 80 mmoles of **2** in 50 ml. of benzene was heated for 5 hr. at 72°, at which time gas evolution was 88% of 2 molar equiv. Recovered **5** obtained by acidification amounted after recrystallization to 1.79 g. (51%), m.p. 92.5–93.5°; the residue rapidly reduced aqueous permanganate. A plot of gas evolution against time showed a definite change in slope, the inflection of which was estimated by intersection of tangents as being at a time of *ca.* 50 min. and at an evolution of 72% of 2 molar equiv. (suggesting that dimetalation was complete after about 50 min.).

The reaction of **6** with bromine was based on a procedure used with a monosulfone.[16] A mixture of 17.60 g. (50 mmoles) of **5** and 400 mmoles of **2** in 200 ml. of benzene was heated at 70° for 1 hr. The mixture then was cooled at 5–15° while 64 g. of bromine in 75 ml. of benzene was added. After the mixture had warmed to 25°, it was stirred for 2 hr. and 400 ml. of water was added. Excess bromine was destroyed with aqueous sodium bisulfite. The benzene layer gave 27.7 g. of oil [Br, 28.2%, equivalent to a yield of 98% of 1,5-dibromo-1,5-bis(phenylsulfonyl)-pentane (**14**)]. Chromatography of 15.2 g. of the oil on acid-washed alumina (950 g., elution with carbon tetrachloride–chloroform) gave seven major fractions. Fraction 3 was dissolved in *n*-butyl chloride; after several days at 0°, 1.45 g. of solid separated, which after recrystallization amounted to 1.15 g. (8%) of **14**, m.p. 137.5–139°, and which after further recrystallization from ethyl acetate had a constant melting point of 140–140.5°.

Anal. Calcd. for $C_{17}H_{18}Br_2O_4S_2$: C, 40.01; H, 3.55; Br, 31.32. Found: C, 40.26; H, 3.49; Br, 31.44.

Fraction 4, an oil, amounted to 3.10 g. (22%, if pure **14**); Br, 30.4%. No other crystalline products could be isolated.

Reactions of 1,3-Bis(phenylsulfonyl)propane (7) and of 1,4-Bis(*p*-tolylsulfonyl)butane (9) with 2.—A mixture of 3.24 g. (10 mmoles, m.p. 126.5–128°) of **7** and 80 mmoles of **2** in 150 ml. of benzene was heated at 74° for 8 hr. and gas evolution was plotted as a function of time. A fairly definite plateau developed in the plot after about 2 hr. (gas evolution then was 102% of 2 molar equiv.) and continued to about 4 hr. before gas evolution again began to increase markedly. After 8 hr., acidification and recrystallization gave 1.10 g. (34%) of **7**, m.p. 128.5–129.5°. The plot indicated a gas evolution after 35 min. of 75% of 2 molar equiv.; hydrolysis at this point in another experiment gave 2.28 g. (70% recovery) of **7** after recrystallization; m.p. 127–128°.

Essentially as described for **7**, a mixture of 3.66 g. (10 mmoles) of **9** and 80 mmoles of **2** was heated at 74° but only for 6 hr. A nearly flat plateau occurred after *ca.* 20 min. (gas evolution then was 76% of 2 molar equiv.) and continued to about 1 hr. before gas evolution again began to occur rather rapidly. After 6 hr., only 19% of **9** was recovered by acidification (m.p. 150–152.5°); the residual oil rapidly consumed large amounts of aqueous permanganate. The plot indicated gas evolution after 38 min. of 76% of 2 molar equiv.; acidification at this point, and recrystallization, resulted in a recovery of 3.54 g. of **9** (97%), m.p. 151–152°.

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(16) W. M. Ziegler and R. Connor, *J. Am. Chem. Soc.*, **62**, 2596 (1940).