[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Cyclic Sulfones. VII. The Dimerization of 3,4-Diphenylthiophene 1,1-Dioxide[1]

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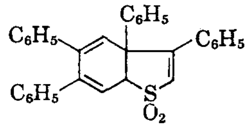
3,4-Diphenylthiophene 1,1-dioxide has been shown to dimerize *via* a Diels-Alder reaction in which it acted as both diene and dienophile. The resulting dimer immediately lost one molecule of sulfur dioxide to form 3,3a,5,6-tetraphenyl-3a,7a-dihydrobenzothiophene 1,1-dioxide (I). Pyrolysis of this product formed 1,2,4-triphenylbenzene, phenylacetylene, and sulfur dioxide. A similar cleavage was effected by Raney nickel.

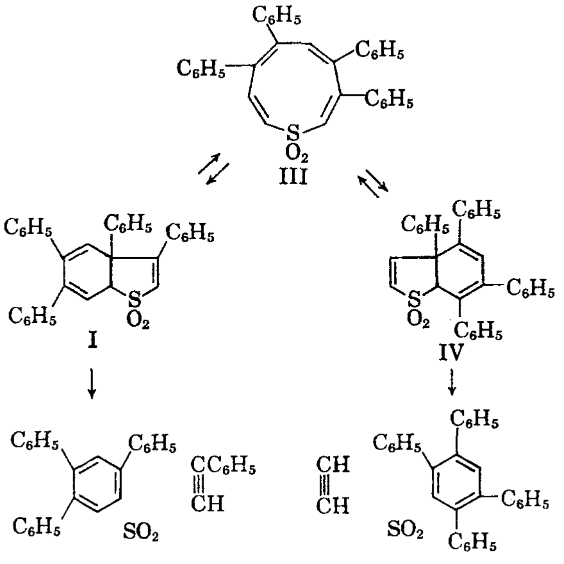
Thiophene 1,1-dioxide,[3] 3,4-dichlorothiophene 1,1-dioxide,[4] benzothiophene 1,1-dioxide,[5,6] and related compounds[7] have been shown to dimerize *via* Diels-Alder reaction, followed by loss of the bridge sulfonyl group. 3,4-Diphenylthiophene 1,1-dioxide has now been shown to undergo a similar reaction, on fusion or reflux in a high boiling solvent, to form I. This structure is analogous to that of the product formed, by a similar reaction sequence, from 3,4-diphenylcyclopentadienone.[8]



I

Both I and the carbonyl analogue II (CO in place of SO_2) readily form maleic adducts; in other respects, however, their reactions are quite different. II was quantitatively isomerized to the conjugated structure by acid at 100°[8]; I survived refluxing 10% hydrochloric acid in acetic acid for one hour. I was stable at its melting point (229°), while II was rapidly aromatized by migration of the angular phenyl group at 200.°[8] In contrast, I pyrolyzed at 280–300° to give sulfur dioxide, phenylacetylene, and 1,2,4-triphenylbenzene.

From this pyrolysis product, a small amount of 1,2,4,5-tetraphenylbenzene was isolated. A possible explanation for its formation is suggested by the fact that I may be a valence tautomer of the monocyclic 3,4,6,7-tetraphenylthiepin 1,1-dioxide (III). Isomerization to III, followed by formation of the transannular bond at an alternate site, would lead to 3a,4,6,7-tetraphenyl-3a,7a-dihydrobenzothiophene 1,1-dioxide (IV), the alternate valence tautomer. Cleavage of IV would be expected to produce sulfur dioxide, acetylene, and the observed tetraphenylbenzene.



A similar cleavage of the five-membered ring of I was effected by Raney nickel in refluxing ethanol, with formation of 1,2,4-triphenylbenzene and ethylbenzene. In this reaction, no trace of tetraphenylbenzene was found. This fact, as well as ultraviolet spectral evidence, supports the assignment of structure I, rather than III, to the dimerization product, in spite of its unexpected unreactivity. Unfortunately, the product was hydrogenated only with difficulty, under conditions which made it impossible to differentiate between double bond and phenyl ring hydrogenation. A hydrogenated derivative was isolated as a byproduct of Raney nickel desulfurization; further characterization of this may provide unequivocal evidence.

The dimerization product reacted with bromine at room temperature, and was oxidized by chromic acid in acetic acid at room temperature and by potassium permanganate in refluxing acetone.

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(1) For the previous paper in this series, see C. G. Overberger and A. Katchman, *J. Am. Chem. Soc.*, **78**, 1965 (1956); see also C. G. Overberger and A. Luisi, *J. Am. Chem. Soc.*, 81, 506 (1959).

(2) This paper comprises a portion of a thesis presented by John M. Whelan in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

(3) W. J. Bailey and E. W. Cummins, *J. Am. Chem. Soc.*, **76**, 1932, 1936, 1940 (1954).

(4) H. Bluestone, R. M. Bimber, R. A. Berkey, and Z. Mandel, *J. Org. Chem.*, **26**, 346 (1961).

(5) F. G. Bordwell, W. H. McKellin, and D. Babcock, *J. Am. Chem. Soc.*, **73**, 5566 (1951).

(6) W. Davies, N. W. Gamble, and W. E. Savage, *J. Chem. Soc.*, 4678 (1952).

(7) W. Davies and Q. N. Porter, *J. Chem. Soc.*, 2609 (1956); 826 (1957); H. J. Backer and J. L. Melles, *Proc. Koninkl. Nederland Akad. Wetenschap.*, **543**, 340 (1951).

(8) Leading reference, C. F. H. Allen and J. A. Van Allan, *J. Org. Chem.*, 20, 315 (1955).

TABLE I

DIMERIZATION OF 3,4-DIPHENYLTHIOPHENE 1,1-DIOXIDE

Solvent[a]	Concn. Moles/ Kg.	Additive, %	Reaction Time, Hr.	Yield Dimeric Compd., %	% SO_2 at Infinite Time	Rate Constituent Kg./Mole/Min.
Phenol	0.358	—	4.5	51.5	66.0	0.107
Phenol	0.714	—	2	53.4	58.0	0.103
Phenol	1.108	—	2	52.6	56.7	0.207
Phenol	0.236	.06 HQ[b]	4	57.9	62.2	0.126
Phenol	0.259	.07 HQ	4	58.2	57.0	0.0859
Phenol	0.238	0.1 PTS[c]	1.5	0	90.9[d]	0.455
Xylene	0.38	1.0 PTS	4	13.6	76.5	0.0483
Nitrobenzene	0.216	—	1.5	53.3	49.5	1.221
Diethylene glycol monobutyl ether	0.208	—	1	41.2	60.1	1.69

[a] All reactions conducted at reflux temperature. [b] Hydroquinone. [c] *p*-Toluenesulfonic acid. [d] Sulfur dioxide not removed during first three hours.

It formed an intense violet solution on treatment with potassium *t*-butoxide in benzene–*t*-butyl alcohol, which precipitated an organic product free from sulfur. The products of these reactions have thus far resisted characterization.

Sulfur dioxide evolution during dimerization of 3,4-diphenylthiophene 1,1-dioxide is not quantitative, ranging from 47–91% under varying experimental condition. In refluxing phenol, it amounts to 56–62% over a six-fold range of initial concentrations; it is lower in refluxing nitrobenzene.

Sulfur dioxide evolution, when plotted as percent of total sulfur dioxide evolution, is in excellent agreement with second order kinetics. This may be intrepreted as indicating that two competing second order reactions are occurring, one of which does not cause loss of sulfur dioxide. The reaction by-products are brown to black tars, offering no clue as to the nature of the competing reaction.

Addition of hydroquinone, a radical acceptor, changes neither the rate of sulfur dioxide evolution nor the amount involved. This appears to rule out radical polymerization as a side reaction.

Reaction in quinoline gave a much lower yield of the dimeric compound. Addition of *p*-toluenesulfonic acid to phenol solution increased the rate of sulfur dioxide evolution by a factor of 4 to 5, and raised the total sulfur dioxide evolution to 90.9% of the theoretical; however, the reaction product was a gum containing none of the dimeric compound. In refluxing xylene, acid catalysis increased total sulfur dioxide evolution by 76%, but only a low (13.6%) yield of dimeric compound was obtained (Table I).

The absence of an induction period and the close agreement to second order kinetics under all conditions indicates that the initially formed sulfonyl bridge compound loses sulfur dioxide rapidly.

EXPERIMENTAL[9]

3,4-Diphenylthiophene 1,1-dioxide. The procedure for preparing this compound was based on that used by Backer, Bolt, and Stevens,[10] using peroxyacetic acid in place of peroxybenzoic acid, and using the isolation procedure of Overberger, Mallon, and Fine.[11] To a solution of 42.8 g. (0.181 mole) of 3,4-diphenylthiophene[11] in 450 ml. chloroform was added 90 ml. (equivalent to 0.544 mole) of commercial 40% peroxyacetic acid (Buffalo Electrochemical Co.). This mixture was held at 22–25° for 24 hr. (cooling initially), and poured into excess saturated aqueous sodium bicarbonate solution. The chloroform layer was washed with sodium bicarbonate solution and then water. After adding 285 ml. of 95% ethanol, solvent was removed at room temperature under aspirator vacuum to give a volume of 300 ml. The light yellow crystals were collected by filtration and washed with 50 ml. of 95% ethanol; 31.6 g. (65.1%) m.p. 165.5–171°. Recrystallization from methanol gave a product of m.p. 171.5–172.5° (50%, m.p. 171°, by peroxybenzoic acid oxidation.[12]

3,3a,5,6-Tetraphenyl-3a,7a-dihydrobenzothiophene 1,1-dioxide (I). 3,4-Diphenylthiophene 1,1-dioxide (10.0 g., 0.0372 mole) was dissolved in 12.0 g. of freshly distilled phenol by gentle warming, and the solution was refluxed for 2 hr. Sulfur dioxide was evolved. Phenol was removed from the reaction mixture by steam distillation until the distillate no longer gave a ferric chloride test for phenol (700 ml.). The resinous distillation residue was dissolved in 125 ml. of boiling acetone. After standing for 2 days, the colorless prisms were collected; 3.21 g. (36.5%), m.p. 228–229.5°. A further 2.23 g. (25.4%) was obtained by concentration of the mother liquor and recrystallization. After repeated recrystallization from acetone, the product melted at 229–229.5°.

Anal. Calcd. for $C_{32}H_{24}O_2S$: C, 81.32; H, 5.12; S, 6.79; mol. wt. 472.7. Found: C, 81.32; H, 5.12; S, 6.71; mol. wt. (Menzies-Wright, acetone), 487.

The principal infrared absorption bands above 6μ (in Nujol mull) were (μ): 6.27m, 6.38m, 6.71s, 6.94s, 7.72vs, 8.27s, 8.43m, 8.91vs, 10.33s, 11.57m, 12.12m, 12.62m, 13.05vs, 13.30s, 13.65s, 14.06s, 14.34vs, and 14.53s. A crystalline film deposited from acetone showed, in addition, bands at 3.28m, and 7.30w. On comparison with the infrared spectra of known compounds of related structure, the following assignments appeared reasonable: phenyl, 3.28, 5.10,

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(9) All melting points are corrected. Microanalyses were performed by Drs. G. Weiler and F. B. Strauss, Microanalytical Laboratory, Oxford, England. Infrared spectra were determined using a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics; ultraviolet spectra using a Carey Model 14.

(10) H. J. Backer, C. C. Bolt, and W. Stevens, *Rec. trav. chim.*, **56**, 1063 (1937).

(11) C. G. Overberger, H. J. Mallon, and R. Fine, *J. Am. Chem. Soc.*, **72**, 4958 (1950).

(12) J. L. Melles and H. J. Backer, *Rec. trav. chim.*, **72**, 314 (1953).

5.30, 5.53, 5.70, 5.95, 6.27, 6.38, 6.71, 6.94, 13.30, 14.34; sulfone, 7.72 and 8.91; CH in-plane vibration of the trisubstituted double bonds, 7.30; CH out-of-plane vibration at positions 4 and 7, 12.62; at position 2, 12.12. A saturated solution in methanol had ultraviolet absorption maxima at 201 and 240 mμ, and inflections suggesting absorptions at 220 and 262 mμ.

A series of similar experiments were performed in which the sulfur dioxide was swept through a solution of hydrogen peroxide by a stream of nitrogen, and periodically estimated by titration of the sulfuric acid formed. Sulfur dioxide evolution, extrapolated to infinite time, varied from 57 to 66% in experiments at different concentrations, and was not markedly changed on addition of 0.06% hydroquinone. Addition of 0.1% of *p*-toluene-sulfonic acid increased the extrapolated sulfur dioxide evolution to 90.9% and almost quadrupled the rate. However, none of the desired product could be isolated from the reaction mixture. A plot of instantaneous sulfur dioxide evolution divided by the differences between instantaneous and extrapolated sulfur dioxide evolution versus time (second order plot) was linear over the entire range studied (over 90% reaction), and showed no induction period, implying very fast loss of sulfur dioxide from the sulfonyl bridge intermediate.

The same product was obtained, in lower yield, on heating 3,4-diphenylthiophene 1,1-dioxide alone to 200° for one hour, or refluxing in other high boiling solvents (xylene, nitrobenzene, monobutyl ether of diethylene glycol, or quinoline).

Maleic anhydride adduct. A solution of I (1.58 g., 0.00334 mole) and 0.66 g. (0.00673 mole) of maleic anhydride in 20 ml. of xylene was refluxed for 8 hr. A crystalline product separated from the nearly colorless solution in 99% yield (1.88 g.). It was recrystallized from acetic anhydride: 1.65 g. (86.4%) white crystals, m.p. 335–337°. Further recrystallization raised the melting point to 357–359° (sealed capillary, 1°/min. from 355°).

Anal. Calcd. for $C_{36}H_{26}O_5S$: C, 75.77; H, 4.59. Found: C, 75.97; H, 4.29.

The product dissolved very slowly in refluxing 0.1N sodium hydroxide. Attempted esterification by methanolic hydrogen chloride or refluxing methanol and sulfuric acid was unsuccessful. The principal infrared absorption bands (Nujol mull) were (μ): 5.34w, 5.41w, 5.59s, 6.24w, 6.68m, 6.90m, 7.65s, 8.07m, 8.15m, 8.20sh, 8.87s, 9.15m, 10.36m, 10.65m, 10.92m, 11.12m, 12.38m, 13.13m, 14.20s, and 14.32m.

Hydrogenation of I. Platinum dioxide (175 mg.) was prereduced in 10 ml. of acetic acid, and 0.3116 g. of I was added. After 24 hr. at room temperature, 4.2 moles of hydrogen had been absorbed; hydrogen was still being consumed slowly, and there was no break in the hydrogen absorption curve. The product was amorphous. The major changes in infrared spectrum from that of I were: appearance of aliphatic CH at 3.45 and 3.52; almost complete disappearance of the conjugated phenyl band at 6.38; disappearance of bands at 7.30, 8.43, 10.33, 11.57, 13.65, 14.06, and 14.53.

Action of potassium t-butoxide on I. A solution of 0.530 g. (0.00112 mole) of I in 14 g. of benzene was added to a solution of potassium *t*-butoxide prepared by dissolving 0.2 g. (0.0051 g.-atom) of potassium metal in 8.0 g. of dry *t*-butyl alcohol. The intense violet solution was allowed to stand at room temperature for 0.5 hr., during which time an orange solid deposited. The infrared spectrum of this material had lost the 7.72 and 8.91 μ sulfone bands. On washing with water, it melted to a tar and resolidified to a brown-yellow powder. Repeated attempts to purify this product failed.

Pyrolysis of I. I (0.8386 g., 0.00177 mole) was heated for 0.5 hr. in a Wood's metal bath at 280°. The oily brown residue was dissolved in petroleum ether (b.p. 30–60°), chromatographed on alumina (Alcoa F-20), and eluted with a 4:1 mixture of petroleum ether and benzene. The eluate was desolvated and recrystallized from 1 ml. of petroleum ether; 0.2354 g. (43.2%) of white crystals were obtained. Extraction with methanol left a crystalline residue, 9.8 mg. (1.4%) of 1,2,4,5-tetraphenylbenzene, m.p. 249–255°; after two recrystallizations from heptane, this melted at 270–272°. The melting point was not depressed on admixture with an authentic sample prepared by the method of Dilthey and Hurtig[13]; infrared spectra of the two samples were identical.

The methanolic extract deposited 0.152 g. (28%) of white solid, m.p. 81–84.5°. After a second recrystallization from methanol, the melting point was 98.5–100° (52.3 mg., 9.6%). Further quantities of less pure material were recovered from the mother liquors. The infrared spectrum was identical with that of authentic 1,2,4-triphenylbenzene.[14]

In another experiment, 0.4656 g. (0.000985 mole) of I was held at 300° for 0.5 hr. in an evacuated and sealed bent tube, one end of which was cooled in a Dry Ice–acetone bath. Neutral 3% hydrogen peroxide was admitted to the cooled tube, and sulfur dioxide estimated by titration (94%). The organic material was extracted with carbon tetrachloride, the extract distilled, the distillate concentrated by fractional distillation, and an infrared spectrum obtained. By comparison of the absorbance at 3.03 μ with that of authentic phenylacetylene in carbon tetrachloride, the yield of phenylacetylene was estimated at 22%. The carbon tetrachloride solution was shaken with mercuric iodide solution, following the procedure of Johnson and McEwen[15]; this gave 31.4 mg. (17.2%) of mercury bisphenylacetylide. The infrared spectrum of the recrystallized product was identical with that of a sample similarly prepared from authentic phenylacetylene. The carbon tetrachloride mother liquor from the mercurous iodide treatment, on distillation and treatment with aqueous silver nitrate, deposited needles of silver phenylacetylide, whose infrared spectrum was identical to that of an authentic sample.

Infrared absorbance at 6.79 μ of a carbon tetrachloride solution of the total pyrolysis product from a similar experiment, compared with that of authentic 1,2,4-triphenylbenzene and 1,2,4,5-tetraphenylbenzene, was in accord with a combined yield of 60–97% (this band is absent in other chromatographic fractions of the pyrolysis product).

Action of Raney nickel on I. Finely powdered I, 1.244 g. (0.00263 mole) was mixed with an excess of W-7 Raney nickel[16] and allowed to stand for 12 hr. the mixture was then refluxed gently in the alcohol introduced with the nickel for 8 hr. After filtration, the solvent was distilled, leaving a colorless, viscous oil which partially solidified on standing.

The distillate was concentrated to 2 ml. by fractional distillation, the distillation residue taken up on carbon tetrachloride, and washed with water to remove residual ethanol. After drying over sodium sulfate, the solution was concentrated by fractional distillation to 1 ml. An infrared spectrum was identical with that of a 0.7% solution of authentic ethylbenzene in carbon tetrachloride.

The oil residue from the initial distillation was combined with the desolvated acetone extract of the Raney nickel residue, and extracted with a 4:1 mixture of petroleum ether and benzene, leaving a white solid which was recrystallized from acetone; 0.1696 g. (13.5%), m.p. 233–244°. This was extracted with hot heptane, and the residue recrystallized three times from acetone; m.p. 243–245°. The infrared spectrum suggested that this was a hydrogenated derivative of I: principal absorption bands of a crystalline film were at (μ): 3.33m, 3.45m, 6.26m, 6.33m, 6.70s, 6.91s, 7.72vs, 8.00m, 8.95 vs, 9.32m, 9.73m, 10.01m, 11.85m, 13.12vs, 13.40s, and 14.40 vs.

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[13] W. Dilthey and G. Hurtig, *Ber.*, **67**, 2004 (1934).

[14] C. G. Overberger and J. M. Whelan, *J. Org. Chem.*, **24**, 1155 (1959).

[15] J. R. Johnson and W. L. McEwen, *J. Am. Chem. Soc.*, **48**, 469 (1926).

[16] H. Adkins and A. A. Pavlic, *J. Am. Chem. Soc.*, **69**, 3039 (1947).

Anal. Calcd. for $C_{32}H_{28}O_2S$: C, 80.64; H, 5.92; S, 6.73. Found: C, 80.28, 80.46; H, 5.74, 5.64; S, 6.84, 7.10.

The benzene-petroleum ether extracts were chromatographed on alumina (Alcoa F-20) and the column eluted with a 4:1 mixture of petroleum ether and benzene. The desolvated eluate, twice recrystallized from petroleum ether, gave 0.1149 g. (14.2%) of 1,2,4-triphenylbenzene; four more recrystallizations raised the melting point to 99.4–100°. An infrared spectrum was identical to that of an authentic sample of 1,2,4-triphenylbenzene.[14]

Anal. Calcd. for $C_{22}H_{18}$: C, 94.08; H, 5.92. Found: C, 93.88; H, 5.92.

A similar experiment using aged (145 days at room temperature) Raney nickel gave a 14.6% yield of 1,2,4-triphenylbenzene, m.p. 97.5–98.5°. Unchanged starting material (60.5%, m.p. 216.5–221.5°; recrystallized, 50.6%, m.p. 227–227.5°) was also recovered; no hydrogenated product was found.

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Rearrangements of Aryl Sulfones. IV. Substituted Phenyl Mesityl Sulfones[1]

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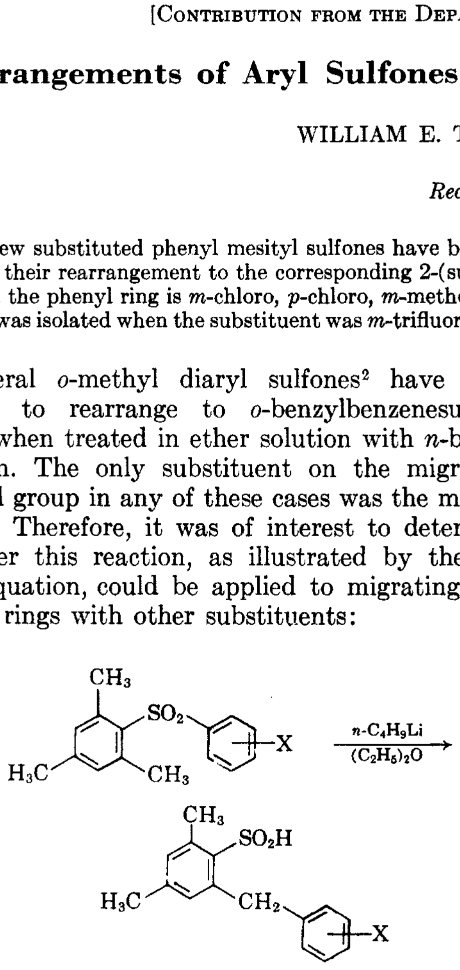
Six new substituted phenyl mesityl sulfones have been synthesized. Treatment of these sulfones with *n*-butyllithium results in their rearrangement to the corresponding 2-(substituted benzyl)-4,6-dimethylbenzenesulfinic acids when the substituent on the phenyl ring is *m*-chloro, *p*-chloro, *m*-methoxy, *p*-methoxy, *p*-trifluoromethyl, and 3,4,5-trimethyl. Only a trace of acid was isolated when the substituent was *m*-trifluoromethyl.

Several *o*-methyl diaryl sulfones[2] have been shown to rearrange to *o*-benzylbenzenesulfinic acids when treated in ether solution with *n*-butyllithium. The only substituent on the migrating phenyl group in any of these cases was the methyl group. Therefore, it was of interest to determine whether this reaction, as illustrated by the follow equation, could be applied to migrating aromatic rings with other substituents:



The results obtained in the present series of sulfones have demonstrated an expanded usefulness for this reaction. The sulfinic acids which were formed can be converted to sulfonic acids, diphenylmethanes, and chloromercuridiphenylmethanes; thiosulfonates may also be obtained as well as various sulfone derivatives.[3]

The substituents on the phenyl ring in this set of phenyl mesityl sulfones were: *m*-chloro, *p*-chloro, *m*-methoxy, *p*-methoxy, *m*-trifluoromethyl, *p*-trifluoromethyl, and 3,4,5-trimethyl. Each of the starting materials was characterized by physical constants such as melting point and infrared spectrum. Although a few of the sulfones (see Experimental) were prepared by Friedel-Crafts condensation of a sulfonyl chloride with mesitylene, most were prepared by the hydrogen peroxide oxidation of sulfides obtained from the condensation of cuprous mesitylenethiolate with a suitability substituted aromatic bromide as described by Adams, Reifschneider, and Nair.[4] Although these authors report the reaction as proceeding at 200–210°, temperature did not appear to be a critical factor; in half of our experiments the temperature of the reactants did not rise above 180° and in many it was lower. Duplicate preparations of the sulfides differed in internal temperatures by as much as 50° without any decrease in yield. Cuprous mesitylenethiolate, prepared from cuprous oxide and mesitylenethiol, was insoluble in most organic solvents and decomposed on addition to polar liquids such as dimethylformamide. Its identity was shown by treatment with bromobenzene and oxidation of the resulting sulfide to the known phenyl mesityl sulfone.

The general technique for rearranging the sulfones with *n*-butyllithium is described in the Experimental section along with procedures developed for making satisfactory derivatives of the sulfinic acid products. Inspection of Table I shows the following propensity to rearrange (on the basis of yield of crude acids and the time required to ob-

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(1) Abstracted from M. M. G.'s Ph.D. thesis.

(2) Mesityl phenyl, mesityl *p*-tolyl, *o*-tolyl phenyl, 2,4-xylyl phenyl, 2,6-xylyl phenyl, and dimesityl sulfones. (a) W. E. Truce, W. J. Ray, Jr., C. L. Norman, and D. B. Eickemeyer, *J. Am. Chem. Soc.*, **80**, 3625 (1958). (b) W. E. Truce and W. J. Ray, Jr., *J. Am. Chem. Soc.*, **81**, 481 (1959). (c) *J. Am. Chem. Soc.*, **81**, 484 (1959).

(3) Precautions should be taken to avoid high temperatures, exposure to air, and long storage in solvents since many of the acids were decomposed under those conditions.

(4) R. Adams, W. Reifschneider, and M. D. Nair, *Croatica Chem. Acta*, **29**, 277 (1957).