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.

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

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

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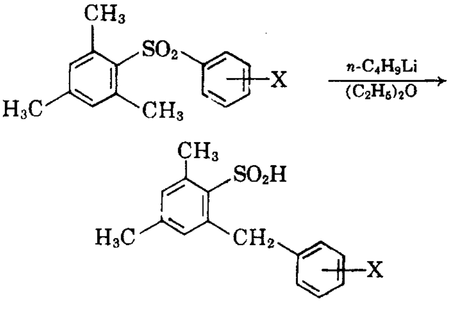
Six new substituted phenyl mesityl sulfones have been synthesized. Treatment of these sulfones with *n*-butyllithium results in their rearrangement to the corresponding 2-(substituted benzyl)-4,6-dimethylbenzenesulfinic acids when the substituent on the phenyl ring is *m*-chloro, *p*-chloro, *m*-methoxy, *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.

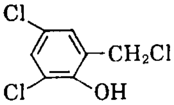
(2) Mesityl phenyl, mesityl *p*-tolyl, *o*-tolyl phenyl, 2,4-xylyl phenyl, 2,6-xylyl phenyl, and dimesityl sulfones. (a) W. E. Truce, W. J. Ray, Jr., C. L. Norman, and D. B. Eickemeyer, *J. Am. Chem. Soc.*, **80**, 3625 (1958). (b) W. E. Truce and W. J. Ray, Jr., *J. Am. Chem. Soc.*, **81**, 481 (1959).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

TABLE I

Typical Results on Rearrangement of Substituted Phenyl Mesityl Sulfones

				% Yield				M.P. Derivatives		
Substituent Group	Moles Sulfone	Moles n-C_4H_9Li	Length of Reaction (Hr.)	Crude Recovered Sulfone	Crude Acid	Neut. Equiv. Calcd.	Neut. Equiv. Found	S-Benzylthiouronium	Chloromercuridiphenylmethane	Sulfone from 
m-Cl	0.009	0.009	18	22	64[a]				144.5–145.3[b]	
p-Cl	0.025	0.027	18	30	69	295	298	168.5–169.5[c]	151.3–151.8[d]	169–172[e]
m-OCH_3	0.024	0.025	1.1	29	68				113–113.5[f]	170–171.3[g]
p-OCH_3[h]	0.025	0.027	18	78	21				[h]	
m-CF_3	0.01	0.01	18	85[i]	3					
p-CF_3	0.02	0.021	18.5	58	36	328	324			169.5–172.3[j]
3,4,5-$(CH_3)_3$	0.0067	0.0128	1.0	30	75	302	306		167–168[k]	183.5–186.5[l]

[a] An additional 5.3% of unidentified solid containing sulfur and chlorine but insoluble in aqueous base or ether was obtained. [b] *Anal.* Calcd. for $C_{15}H_{14}Cl_2Hg$: C, 38.68; H, 3.03; Cl, 15.23. Found: C, 38.94; H, 3.25; Cl, 15.13. [c] *Anal.* Calcd. for $C_{23}H_{25}ClN_2O_2S_2$: C, 59.91; H, 5.47; Cl, 7.69. Found: C, 59.77; H, 5.68; Cl, 7.82. [d] *Anal.* Calcd. for $C_{15}H_{14}Cl_2Hg$: C, 38.68; H, 3.03; Cl, 15.23. Found: C, 38.38; H, 2.99; Cl, 15.00. [e] *Anal.* Calcd. for $C_{22}H_{19}Cl_3O_3S$: C, 56.24; H, 4.08; Cl, 22.64; S, 6.82. Found: C, 56.53; H, 4.13; Cl, 22.82; S, 6.90. [f] *Anal.* Calcd. for $C_{16}H_{17}ClHgO$: C, 41.65; H, 3.71; Cl, 7.68. Found: C, 41.70; H, 3.96; Cl, 7.79. [g] *Anal.* Calcd. for $C_{23}H_{22}Cl_2O_4S$: C, 59.23; H, 4.95; Cl, 15.21. Found: C, 59.54; H, 4.80; Cl, 15.48. [h] Although the addition of 3% aqueous ferric chloride solution to an alcoholic solution of the crude acid formed a characteristic orange salt and S-benzylthiouronium and chloromercuri derivatives were prepared, their analytical values did not provide satisfactory checks with the calculated values. Crude ferric 2-(4′-methoxybenzyl)-4,6-dimethylbenzenesulfinate was obtained by treating p-methoxyphenyl mesityl sulfone with commercial n-butyllithium in hexane followed by addition of excess 3% ferric chloride solution to the aqueous solution of the lithium sulfinate. One and one-quarter grams of the ferric salt was hydrolyzed with 3% ammonium hydroxide and the filtrate, after adjusting the pH to 7, was treated according to the general procedure for preparation of chloromercuri derivatives. After repeated recrystallizations from 95% ethanol, long fine white needles were isolated which melted at 109–111° and resolidified to prisms melting at 115.3–116°. *Anal.* Calcd. for $C_{16}H_{17}ClHgO$: C, 41.65; H, 3.71; Cl, 7.68. Found: C, 41.91; H, 3.87; Cl, 8.04. [i] Every attempt at rearrangement of this sulfone produced a small amount of base-soluble material, a large amount of recovered sulfone, and an unidentified solid containing sulfur and fluorine. A pronounced red flame test indicated the presence of lithium. This solid was insoluble in ether or aqueous base and increased from 8.5% of the products to 18% when the reaction was carried out for 54 hr. [j] *Anal.* Calcd. for $C_{23}H_{19}Cl_2F_3O_3S$: C, 54.88; H, 3.80. Found: C, 54.90; H, 3.82. [k] *Anal.* Calcd. for $C_{18}H_{21}ClHg$: C, 45.67; H, 4.47; Cl, 7.49. Found: C, 45.84; H, 4.51; Cl, 7.29. [l] *Anal.* Calcd. for $C_{25}H_{26}Cl_2O_3S$: C, 62.90; H, 5.49; Cl, 14.85. Found: C, 63.04; H, 5.75; Cl, 14.80.

tain comparable yields: m-$CH_3OC_6H_4$— > 3,4,5-$(CH_3)_3C_6H_2$— > p-ClC_6H_4— > m-ClC_6H_4— > p-$CF_3C_6H_4$— > p-$CH_3OC_6H_4$— > m-$CF_3C_6H_4$—. When the sulfones were treated with commercially prepared n-butyllithium in hexane,[5] followed by isolation of the sulfinic acid in the form of its ferric salt, the same order was observed except that the yield of the p-$CH_3C_6H_4$— compound was comparable to that from the chlorine-containing sulfones and the amount of acid from the p-$CH_3OC_6H_4$— compound increased two-fold. Increased yields were observed throughout the series when the commercial base was used and the sulfinic acid was isolated as the ferric salt, but it was not determined whether these increases represented a true value or whether they were due to impurities in the base or occluded impurities in the ferric salt. Probably the resistance toward rearrangement on the part of the m-substituted trifluoromethyl sulfone is due to a particularly facile metalation at the comparatively acidic open position between the sulfonyl and the trifluoromethyl substituents.

Ferric sulfinates were employed for isolating, purifying, or identifying the acids being studied; at low pH the formation of an insoluble ferric salt is characteristic of sulfinic acids.[6] Ferric salts prepared from pure sulfinic acids, as with 2-benzyl-4,6-dimethylbenzenesulfinic and 2-(4′-chlorobenzyl)-4,6-dimethylbenzenesulfinic acid, gave analyses which agreed well with calculated values. However, the ferric salts decomposed without melting at nearly the same temperatures, and, when prepared from crude acids, gave analytical results which were not in agreement with the calculated values. Nevertheless, these materials did have some utility as a means of purifying the acids which could be regenerated by treating the powdered salt with excess dilute ammonium hydroxide at room temperature.[7] The satisfactory derivatizing methods are listed in the Experimental section. 3,5-Dichloro-2-hydroxybenzyl chloride had several advantages as a derivatizing agent, the foremost being the fact that it reacted quickly with sodium sulfinates in methanol at room temperature. The hydroxyl group introduced a new characteristic band in the infra-

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(5) n-Butyllithium in hexane was purchased from the Lithium Corp. of America. Its normality as determined by the method of R. G. Jones and H. Gilman [*Org. Reactions*, VI, 339 (1951)], was 2.025, representing 70% of the total base present.

(6) S. Krishna and H. Singh, *J. Am. Chem. Soc.*, **50**, 729 (1928).

(7) The sodium salts of the acids in the present series are not very soluble in aqueous solutions.

red spectrum of the derivative while the chlorine present permitted an additional analytical check. The conversion of the sulfinic acids into their chloromercuri derivatives was the most generally satisfactory method used. However, it could not be applied to the fluorine-containing compounds.

A useful crystalline derivative was obtained in good yield from the acid product of *m*-methoxyphenyl mesityl sulfone *via* the apparently rapid disproportionation, $3RSO_2H \longrightarrow RSO_3H + RSO_2SR$.

The two acid products formed by rearrangement of the isomeric *m*- and *p*-chlorophenyl mesityl sulfones were chosen as model compounds for structure proof. It had been shown in this laboratory[8] that lithium in methylamine reduces a sulfinic acid to the corresponding thiol, and that ring-substituted chlorine atoms were removed during the reduction. Accordingly, known 2-benzyl-4,6-dimethylbenzenesulfinic acid was reduced to the corresponding 2-benzyl-4,6-dimethylbenzenethiol by lithium in methylamine and converted into a 2,4-dinitrophenyl sulfide derivative. The acids obtained by rearrangement of the *m*- and *p*-chlorophenyl mesityl sulfones were likewise reduced to the same 2-benzyl-4,6-dimethylbenzenethiol. This was shown by infrared spectra, retention times on a chromatographic column, and preparation of a 2,4-dinitrophenyl sulfide derivative. It seems appropriate to note here that the facile rearrangement of 3,4,5-trimethylphenyl mesityl sulfone supports the argument of Truce and Ray[2c] and that the slow rearrangement of dimesityl sulfone results from steric interference by the 2′- and 6′-methyl groups.

EXPERIMENTAL[9]

Cuprous Mesitylenethiolate. Mesitylenesulfonyl chloride (m.p. 53.5–57°, lit.[10] m.p. 57) was prepared from mesitylene and practical grade chlorosulfonic acid[11] and reduced to mesitylenethiol (b.p. 65–66.5° at 1 mm., lit.[10] b.p. 228–229°) in 85–93% yields by lithium aluminum hydride.[12] Reaction with freshly prepared[13] or commercial cuprous oxide in 95% ethanol under a nitrogen atmosphere[4] gave crude cuprous mesitylenethiolate in 83% yield. Mesityl disulfide which was also formed in small amounts was soluble in the amount of ethanol used for preparations on a 0.4-mole scale. The cuprous thiolate, 11.4 g., was condensed with 7.85 g. (0.050 mole) of bromobenzene in a solution of synthetic quinoline and dry pyridine. The technique of Adams, Reifschneider, and Nair[4] was followed. Of the resulting phenyl mesityl sulfide (8.8 g., 0.038 mole, 76%, b.p. 132–135° at 1 mm.) 7.8 g. (0.034 mole) were oxidized with 30% hydrogen peroxide in glacial acetic acid to give 65.5% yield of the known phenyl mesityl sulfone (6.0 g., 0.026 mole, m.p. 76.5–78° after one recrystallization from methanol; lit.[2a] m.p. 80–80.5°).

Preparation of substituted phenyl mesityl sulfides and their sulfones. Using an adaptation of the method of Adams, Reifschneider, and Nair[4] crude cuprous mesitylenethiolate and a suitably substituted bromobenzene were refluxed in a quinoline pyridine solution for 6 hr. longer than was necessary to obtain a homogeneous solution of the organic materials. The reaction flask was inserted into a sand bath heated by a free flame. The solid sulfides were purified by recrystallization from methanol or 95% ethanol; liquids were purified by distillation under reduced pressure. The sulfide was dissolved in 1:1 acetic anhydride–glacial acetic acid and was treated with 30% hydrogen peroxide in a ratio of 1 meq. of sulfide: 1.67 ml. of solvent: 2.2 ml. of peroxide. The variably exothermic stage of the reaction was controlled with an ice bath, and after 6 hr. of refluxing the solid which deposited as the solution cooled was separated by filtration, washed with 5% sodium bisulfite solution followed by water, and recrystallized from methanol to produce white prisms or needles of the sulfone.

m-Chlorophenyl mesityl sulfide and sulfone. Crude cuprous mesitylenethiolate, 9 g., was condensed with 7.0 g. (0.04 mole) of *m*-bromoaniline to form 5.6 g. (0.02 mole, 47.5%) of a very thick yellow oil (b.p. 151–161° at less than 1 mm.) whose infrared spectrum showed the expected bands for a primary amine at 3550 cm.$^{-1}$, 2.82 μ, 3450 cm.$^{-1}$, 2.90 μ, and 3330 cm.$^{-1}$, 3.05 μ. This amino sulfide was diazotized in the presence of hydrochloric acid and cuprous chloride[4] to give 1.90 g. (0.007 mole, 36%) of an orange oil (b.p. 132–140° at 0.5 mm.) that was oxidized in 48.5% yield to *m*-chlorophenyl mesityl sulfone (m.p. 107–109.5°). This material was the same as the sulfone prepared by a Friedel-Crafts method. (See below.)

m-Chlorophenyl mesityl sulfone. *m*-Aminobenzenesulfonic acid (metanilic acid) was prepared in 70–79% yields by hydrolysis and reduction[14] of 0.34-molar quantities of Eastman *m*-nitrobenzenesulfonyl chloride using finely divided iron for the second step. The method described by Forster[15] was used for quantitatively converting metanilic acid to sodium *m*-chlorobenzenesulfonate. After drying at 96° overnight, the sodium salt was heated 14 hr. at 170–180° with phosphorus pentachloride[16] forming *m*-chlorobenzenesulfonyl chloride (b.p. 85–89° at 1 mm., lit.[17] b.p. 134° at 12 mm., yield 36–54%). In a typical condensation 4.75 g. (0.0355 mole) of anhydrous C.P. aluminum chloride in 25 ml. of dry, redistilled nitrobenzene were added dropwise to a stirred mixture of 6.88 g. (0.032 mole) of *m*-chlorobenzenesulfonyl chloride and 11.7 g. (0.097 mole) of mesitylene at room temperature and stirred for 11 hr. before hydrolyzing with ice and concentrated hydrochloric acid. The acid mixture was extracted with ether which was dried over anhydrous sodium sulfate. Removal of the ether was followed by distillation of the remaining liquid at 1 mm. (final head temp. 50–60°). Recrystallization and decolorization of the solid residue in petroleum ether (b.p. 90–100°) followed by recrystallization from methanol yielded 2.64 g. (0.0088 mole, 27.7%) of white crystals (m.p. 110–112°). A mixture with the *p*-chloro isomer showed a 30° depression in melting point. A sample prepared for analysis melted at 110–111.3°.

Anal. Calcd. for $C_{15}H_{15}ClO_2S$: C, 61.11; H, 5.13; Cl, 12.03. Found: C, 60.96; H, 4.84; Cl, 12.20.

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[8] W. E. Truce, D. P. Tate, and D. N. Burdge, *J. Am. Chem. Soc.*, 82, 2872 (1960); J. J. Breiter, unpublished work.

[9] Microanalyses were carried out by Mrs. C. S. Yeh, Mrs. I. Groten, and Mrs. V. Keblys. Melting and boiling points are uncorrected.

[10] A. Holtmeyer, *Z. für Chem. u. Pharm.*, 686 (1867).

[11] E. H. Huntress and F. H. Carten, *J. Am. Chem. Soc.*, 62, 511 (1940).

[12] L. Field and F. A. Grunwald, *J. Org. Chem.*, 16, 946 (1951).

[13] A. King, *Inorganic Preparations*, D. Van Nostrand, Co., New York, N. Y., 1930, p. 39.

[14] E. Wertheim, *Org. Syntheses*, Coll. Vol. II, 471 (1943).

[15] R. B. Forster, *J. Soc. Chem. Ind.*, 53, 258T (1934).

[16] R. Adams and C. S. Marvel, *Org. Syntheses*, Coll. Vol. I, 84 (1941).

[17] M. Meerwein, G. Dittmar, R. Gollner, K. Hafner, F. Mensch, and O. Steinfort, *Ber.*, 90, 831 (1957).

m-Methoxyphenyl mesityl sulfide and sulfone. Fifty-nine grams (0.29 mole) of *m*-anisidine[18] was converted to *m*-bromphenol (65.5%) following the directions of Koelsch.[19] Treatment of the phenol with dimethyl sulfate[20] gave a quantitative yield of *m*-bromoanisole (b.p. 38–40° at less than 1 mm., lit.[19] b.p. 100° at 20 mm.). One-tenth-mole quantities of the ether were condensed with cuprous mesitylenethiolate[21] to give a thick yellow oil (b.p. 133–144° at less than 1 mm., n_D^{20} 1.6079–1.6084, yield 77–82%). Oxidation of the oil gave *m*-methoxyphenyl mesityl sulfone (m.p. 101–102°, yield 33.5–54%).

Anal. Calcd. for $C_{16}H_{18}O_3S$: C, 66.18; H, 6.25. Found: C, 66.40; H, 6.18.

m-Trifluoromethylphenyl mesityl sulfide and sulfone. In a typical preparation 18 g. (0.08 mole) of *m*-bromobenzotrifluoride (Pierce Chemical Co.) were condensed with 15 g. of crude cuprous mesitylenethiolate to yield an orange oil containing sulfur and fluorine (b.p. 101–112° at 1 to 2 mm., n_D^{21} 1.5540–1.5566, yield 55–71%). Oxidation of the oil followed by several recrystallizations from methanol furnished crystals (m.p. 132–132.5°, yield 62.5–75%).

Anal. Calcd. for $C_{16}H_{15}F_3O_2S$: C, 58.52; H, 4.60. Found: C, 58.58; H, 4.71.

p-Trifluoromethylphenyl mesityl sulfide and sulfone. A one-tenth-mole quantity of Pierce Chemical Co. *p*-bromobenzotrifluoride was condensed with crude cuprous mesitylenethiolate, supplying, after repeated recrystallations from methanol, white needles (m.p. 68–69°, yield 71–77%). Sodium fusion showed the presence of sulfur and fluorine. Oxidation gave the sulfone (m.p. 96.8–97.8°, yield 52–72%).

Anal. Calcd. for $C_{16}H_{15}F_3O_2S$: C, 58.52; H, 4.60. Found: C, 58.40; H, 4.84.

3,4,5-Trimethylphenyl mesityl sulfide and sulfone. Following the procedure described by Beringer and Ugelow[22] redistilled isophorone was converted *via* treatment of the oxime with acetyl chloride into a 10% yield of 3,4,5-trimethylaniline[23] (m.p. 77–80°, lit.[22] b.p. 245°, m.p. 67–68°, 77–78°, 75°, 79–80°). Diazotization[24] of 20 g. (0.15 mole) of the amine in 48% hydrobromic acid followed by treatment with a solution of cuprous bromide in 48% hydrobromic acid and steam yielded 8.5 g. (42%) of hemimellitol (m.p. 105–107°, lit.[25] m.p. 107°) and 6.45 g. (20%) of 3,4,5-trimethylbromobenzene (b.p. 58–60° at 1 mm., solid at refrigerator temp., lit.[26] b.p. 117–118° at 17 mm.). Condensation of 3,4,5-trimethylbromobenzene with crude cuprous mesitylenethiolate gave sulfur-containing crystals, m.p. 121.8–125° (57–75%). A mixture melting point with mesityl disulfide (m.p. 125°[10]) was depressed below 100°. The sulfide was insoluble in cold or hot 1:1 glacial acetic acid–acetic anhydride but oxidation of a suspension of it produced white crystals (m.p. 176–177.5°, yield 30–33%).

Anal. Calcd. for $C_{18}H_{22}O_2S$: C, 71.49; H, 7.33. Found: C, 71.20; H, 7.56.

p-Methoxyphenyl mesityl sulfone. One part of redistilled anisole in chloroform solution was treated at 0° with 4.6 parts of practical grade chlorosulfonic acid according to the method of Huntress and Carten[27] to form *p*-methoxybenzenesulfonyl chloride (m.p. on recrystallization from chloroform or petroleum ether (b.p. 60–70°), 39–41°, lit.[28] m.p. 42–43°, yield 41.5–49.5%). The sulfonyl chloride was refluxed for 6 hr. with anhydrous C.P. aluminum chloride and mesitylene in carbon disulfide in a ratio of 1:1.1:1.2 with 1 l. of solvent per mole of sulfonyl chloride. Hydrolysis with ice and concentrated hydrochloric acid was followed by extraction with benzene which was washed successively with 3% ammonium hydroxide and water. The crude product was isolated by concentration of the benzene solution; several recrystallizations from methanol gave the desired sulfone (m.p. 135–136°, yield 47–67.5%), lit.[29] m.p. 134–136°).

Anal. Calcd. for $C_{16}H_{18}O_3S$: C, 66.18; H, 6.25. Found: C, 66.28; H, 6.19.

p-Chlorophenyl mesityl sulfone. p-Chlorobenzenesulfonyl chloride (m.p. 52–53°, lit.[11] m.p. 53°, yield 62.5%), was prepared following the directions of Pummerer[30] by the reaction of 1 part of chlorobenzene with 6 parts of practical grade chlorosulfonic acid at 15°. The condensation of 1 part of this sulfonyl chloride with 1.2 parts of mesitylene and 1.1 parts anhydrous aluminum chloride in carbon disulfide produced several products including chloromesitylene (b.p. 47–49° at approximately 1 mm., lit. b.p. 204–206° at atm. pressure,[31] 104°, at 25 mm.[32]), and the desired sulfone (yield *ca.* 20%, m.p. after one recrystallization from petroleum ether (b.p. 90–100°) and one from methanol, 106.5–107°).

Anal. Calcd. for $C_{15}H_{15}ClO_2S$: C, 61.11; H, 5.13; Cl, 12.03. Found: C, 61.24; H, 5.27; Cl, 12.11.

General procedure followed in the n-butyllithium-induced rearrangement of the sulfones. The rearrangements were carried out in three-neck, round-bottom flasks equipped with mechanical stirrer, Friedrichs condenser, drying tube, 60 ml. vapor by-pass addition funnel and a mantle. All glassware had standard taper joints and was dried at 140°, assembled hot, and allowed to cool in a stream of high purity nitrogen. A nitrogen atmosphere was maintained throughout the reaction; the gas was passed through a drying tower containing concentrated sulfuric acid so that it was pos-

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(18) Prepared by reduction of *m*-nitroanisole in a 5:1 absolute ethanol–acetone solvent at 40 p.s.i. of hydrogen over a platinum oxide catalyst.

(19) C. F. Koelsch, *J. Am. Chem. Soc.*, **61**, 969 (1939).

(20) J. S. Buck, *Org. Syntheses*, **Coll. Vol. II**, 619 (1943).

(21) The so-called "Ziegler" method, J. H. Ziegler, *Ber.*, **23**, 2469 (1890), whereby the diazonium chloride was treated with the sodium thiolate, produced large percentages of mesityl disulfide which boiled in the same range as the desired sulfide and could not be separated readily from it by fractional crystallizations.

(22) F. M. Beringer and I. Ugelow, *J. Am. Chem. Soc.*, **75**, 2635 (1953).

(23) Our product could not be distilled as described by the authors cited. Instead it showed a marked tendency to sublime. It formed about a 10% saturated solution in hot petroleum ether (b.p. 35–37°) from which it readily could be recrystallized. Preparation of the formanilide according to L. F. Fieser and J. E. Jones, *Org. Syntheses*, **Coll. Vol. III**, 590 (1955), gave crystals melting at 98–100° (lit.[22] m.p. 99–100°). Three preparations of the *p*-toluenesulfonanilide had melting points between 150.5–152° (lit.[22] m.p. 155.5–156°). An infrared spectrum of our compound indicated clearly that it was a primary aromatic amine. (There were three medium bands at 3402 cm.$^{-1}$, 2.94 μ; 3310 cm.$^{-1}$, 3.03 μ; and 3210 cm.$^{-1}$, 3.12 μ. There was a strong band at 1627 cm.$^{-1}$, 6.15 μ, which had a shoulder at 1605 cm.$^{-1}$, 6.23 μ, and another at 1326 cm.$^{-1}$, 7.55 μ.) An NMR spectrum showed clearly that only one kind of aromatic proton was present. 2,3,5-Trimethylaniline, which Beringer and Ugelow state is also formed by this method, would have two distinguishable aromatic hydrogens.

(24) J. L. Hartwell, *Org. Syntheses*, **Coll. Vol. III**, 185 (1955).

(25)(a) K. von Auwers and K. Saurwein, *Ber.*, **55**, 2372 (1922). (b) The amount of hemimellitol was reduced somewhat if no steam was introduced until all the diazonium salt solution had been added to the hot solution of cuprous bromide in 48% hydrobromic acid.

(26) N. Porowska, *Roczniki Chem.*, **32**, 677 (1957); *Chem. Abstr.*, **52**, 5334g (1958).

(27) E. H. Huntress and F. H. Carten, *J. Am. Chem. Soc.*, **62**, 603 (1940).

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sible to regulate the flow rate visually. The sulfones were dissolved in anhydrous ether using a fresh supply for each run. The *n*-butyllithium reagent was always standardized immediately before use by the method of Jones and Gilman[5] and generally it was prepared fresh from redistilled *n*-butyl bromide following the directions of the same authors.

Color changes and/or the appearance of precipitates were used as guides to the course of the reaction. Aliquots of the reaction mixtures were also removed, hydrolyzed with water, and tested for the presence of acid product by acidification of the aqueous layer to *p*H 1. The reactions were quenched by the addition of water in sufficient amount to dissolve the lithium salt of the acid which had been formed. The ether layer was then separated and washed several times with water before being dried over anhydrous magnesium sulfate. Evaporation of the ether followed by drying over phosphorus pentoxide at 1-2 mm. isolated the neutral products of the rearrangement which often consisted of unchanged sulfone in a high state of purity. This was recrystallized from methanol and checked for identity by a mixture melting point with the starting material and often by its infrared spectrum. In a few runs the infrared spectrum was the only criterion used.

The combined aqueous layer and washings were acidified to *p*H 1 with hydrochloric acid and the organic acid, which separated as a sticky solid or as an oil, was either filtered off or extracted with ether. Since the sulfinic acid products generally were unstable to heat and air the procedure involved extraction of the acid product with ether, drying the ether 4 hr. over anhydrous magnesium sulfate at 1°, and evaporation of the solvent and removal of the last traces of volatile contaminants over phosphorus pentoxide at 1–2 mm. During the last drying period the acid product would often begin to decompose and turn the same red color which appeared in melting point determinations on pure sulfinic acids. It was possible to purify a few of the acids by recrystallizing them from acetone-water solutions. The acids were always stored in the refrigerator.

Ferric sulfinates. These compounds were prepared by adding an excess of 3% ferric chloride solution to an aqueous solution of the sodium salt of the acid.[6] The *p*H was adjusted to 1 by the addition of hydrochloric acid and the finely divided, orange-brown salt was collected by vacuum filtration. It was washed repeatedly with hot water and finally rinsed with cold ethanol. The powdered salt appeared stable at room temperature. The acid was regenerated by treating the salt with excess dilute ammonium hydroxide at room temperature and acidifying the filtrate with hydrochloric acid. The ammoniacal solution could be used directly for the preparation of the chloromercuri derivative but for equivalent determinations it was often necessary to purify the acid further by alternate extractions with aqueous ammonia followed by acidification and ether extraction, or by recrystallization from acetone to which water was added.

General procedure for the preparation of S-benzylthiouronium salts of complex aromatic sulfinic acids. These compounds were prepared by adapting previously published directions.[33,34] One-tenth- to 1-g. samples of the sulfinic acid were just neutralized with dilute sodium hydroxide and mixed at room temperature with a concentrated aqueous solution of an equal weight of *S*-benzylthiouronium chloride (m.p. 171–173°, lit.[35] m.p. 174°). The products often separated as oils which solidified on standing in the cold. They were recrystallized from 95% ethanol which was heated in a water bath. Purification was difficult because decomposition took place after periods of moderate heating.

General procedure for the preparation of the 3,5-dichloro-2-hydroxyphenylmethyl sulfones. This method was adapted from the work published by Beachem, *et al.*[36] One-half gram of the sulfinic acid was dissolved in a small amount of methanol and neutralized to phenolphthalein with 1*N* methanolic sodium hydroxide. An equimolar amount of 2-hydroxy-3,5-dichlorobenzyl chloride,[37] m.p. 83–85°, lit.[37] m.p. 81–84°, was dissolved in a very small amount of methanol and was added to the filtered solution of the sodium salt. After a short period of vigorous stirring with a glass rod, fine crystals separated which were recrystallized from methanol.

Disproportionation product of 2-(3′-methoxybenzyl)-4,6-dimethylbenzenesulfinic acid. Two and one-half grams of the crude acid isolated from the rearrangement of *m*-methoxyphenyl mesityl sulfone was dissolved in 7 ml. of methanol. A copious white precipitate formed immediately. This solid was insoluble in 5% sodium bicarbonate solution, contained sulfur and melted at 107–109°. After several recrystallizations from methanol it melted at 109–110°.

Anal. Calcd. for $C_{32}H_{34}O_4S_2$ (the expected $ArSO_2SAr$ disproportionation products): C, 70.38; H, 6.27; S, 11.72. Found: C, 70.45; H, 6.26; S, 11.96, 11.70.

2-Benzyl-4,6-dimethylbenzenethiol and its 2,4-dinitrophenyl sulfide derivative. The reduction[8] of 5.25 g. (0.021 mole) of freshly prepared 2-benzyl-4,6-dimethylbenzenesulfinic acid[2a] with 0.57 g. (0.084 mole) of lithium metal in methylamine supplied 2.44 g. of the corresponding thiol (b.p. 134–135° at 1 mm.). Its infrared spectrum showed a weak absorption band at 2600 cm.$^{-1}$, 3.85 μ and a 30-μl. sample of a 13% (by weight) solution of the thiol in dry, distilled benzene showed only one peak besides that for the solvent when it was run through a 4-ft. silicone-rubber column on an F and M model 500 gas chromatograph programmed at 30° per min. from 50° to 350°. The thiol rapidly turned yellow on exposure to air. Following the method of Bost, Turner, and Norton[38] 0.5 g. of this thiol in absolute ethanol was converted to its sodium salt and treated with 0.46 g. of 2,4-dinitrochlorobenzene dissolved in warm absolute ethanol. The yellow sulfide derivative precipitated immediately. After several recrystallizations from absolute alcohol the translucent yellow crystals melted at 147–148°, followed by resolidification and permanent melting at 152.5–153.5°.

Anal. Calcd. for $C_{21}H_{18}N_2O_4S$: C, 63.94; H, 4.60; N, 7.10. Found: C, 63.82; H, 4.64; N, 7.07.

One gram (0.0033 mole) of pure, dry acid from the rearrangement of *p*-chlorophenyl mesityl sulfone was reduced with 0.12 g. (0.016 mole) of lithium. The 0.18 g. of clear distilled product had an infrared spectrum identical with the spectrum of the thiol from the known 2-benzyl-4,6-dimethylbenzenesulfinic acid. A mixed sample of the two thiols in benzene was put through the F and M model 500 gas chromatograph and there was only one major peak besides that for the solvent. Less than 1% impurities were present. The thiol also quickly yellowed on exposure to air. After two recrystallizations from absolute ethanol a 2,4-dinitrophenyl sulfide derivative gave clear yellow crystals melting at 146.5–147.5°. Slight cooling (bath temp. 142°) plus agitation with a fine wire caused resolidification and remelting occurred at 151.5–153°. Some of these crystals were fused with the analytical sample of the sulfide; their mixture melting point was 151.5–153°.

A similar reduction was carried out on 0.68 g. (0.0026 mole) of crude dry acid obtained from a rearrangement of *m*-chlorophenyl mesityl sulfone. Sixty-five milligrams of a light yellow oil was isolated which had the same infrared spectrum as the thiol of known structure. Treatment of this thiol with

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2,4-dinitrochlorobenzene gave a sulfide with the same infrared spectrum in 10% chloroform solution as the derivative of known structure. Three recrystallizations of this derivative from absolute ethanol yielded crystals melting first at 145–146° and, on resolidification, at 150.3–151°. A mixture melting point with the analytical sample of the sulfide did not show a depression.

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LAFAYETTE, IND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MASSACHUSETTS]

Examination of Synthetic Routes to Monosubstituted Diimides. II. Synthesis of *t*-Butyl Aryl- and Acylazoformates. Acid-Induced Cleavage of the Thionocarbo-*t*-butoxy Group[1,2]

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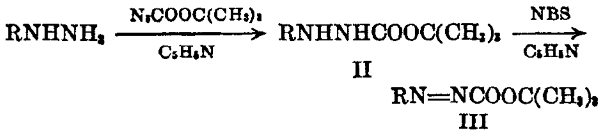
t-Butyl 2-substituted carbazates have been prepared by acylation of substituted phenylhydrazines by means of *t*-butyl azidoformate in pyridine or by alkylation or acylation of *t*-butyl carbazate. Oxidation of the appropriate hydrazo derivatives by means of *N*-bromosuccinimide and pyridine gave *t*-butyl phenyl-, *p*-bromophenyl-, *p*-nitrophenyl-, *o*-methoxyphenyl- and benzoylazoformates. *t*-Butyl hydrazodiformate gave *t*-butyl azodiformate. A description of the rapid acid-induced cleavage of the thionocarbo-*t*-butoxy and other alkyloxythiocarbonyl groups is presented.

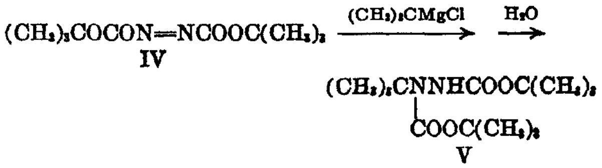
Diimide (I) has recently been identified by mass spectrometry[3] as a product of the electric discharge decompositions of hydrazoic acid and hydrazine although no definitive evidence for the isolation of I or its monosubstituted derivatives has been presented.

Recently studies of acid-induced cleavages of substituted azoformates have been initiated[4] as routes to monosubstituted diimidium salts. Because of the moderate oxidizing properties of the azo linkage it was necessary to have available a protective group of the carbalkoxy type which could be cleaved by nonreducing acids such as hydrogen fluoride or trifluoroacetic acid. Such a blocking function is the carbo-*t*-butoxy group,[5] and consequently a number of azo compounds (III) protected by this group have been prepared for study. The substituted *t*-butyl azoformates were prepared by *N*-bromosuccinimide oxidation of the corresponding hydrazo derivatives (II) which were obtained by treatment of the appropriate hydrazine derivative with *t*-butyl azidoformate[6] or by alkylation or acylation of *t*-butyl carbazate. The hydrazo compounds not described in the experimental section are recorded in Table I.



$$\mathrm{RNHNH_2} \xrightarrow[\mathrm{C_5H_5N}]{\mathrm{N_3COOC(CH_3)_3}} \underset{\mathrm{II}}{\mathrm{RNHNHCOOC(CH_3)_3}} \xrightarrow[\mathrm{C_5H_5N}]{\mathrm{NBS}} \underset{\mathrm{III}}{\mathrm{RN{=}NCOOC(CH_3)_3}}$$

No difficulty was encountered in the *N*-bromosuccinimide-pyridine oxidation of the 2-arylcarbazates (see Table II) although of the 2-acyl derivatives (III, R = $(CH_3)_3COCO$—, C_6H_5CO—, p-$NO_2C_6H_4CO$—, and CH_3CO—) only the first two gave azo compounds which were stable enough to be isolated under the conditions used. *t*-Butyl benzoylazoformate (III, R = C_6H_5CO—) was unstable at room temperature but could be stored for extended periods in a freezer (−18°). No precautions were necessary in the preparation and storage of *t*-butyl azodiformate (IV), a unique azo compound of considerable synthetic promise.[7]



$$\underset{\mathrm{IV}}{\mathrm{(CH_3)_3COCON{=}NCOOC(CH_3)_3}} \xrightarrow{\mathrm{(CH_3)_3CMgCl}} \xrightarrow{\mathrm{H_2O}} \underset{\mathrm{V}}{\mathrm{(CH_3)_3C}\underset{\mathrm{COOC(CH_3)_3}}{\mathrm{N}}\mathrm{NHCOOC(CH_3)_3}}$$

The azodiformate (IV) exhibits reactions typical of such esters, modified however by the bulk of the *t*-butyl groups. *t*-Butylmagnesium chloride adds slowly to the azo linkage of IV yielding V, cleavage of which gives *t*-butylhydrazine hydrochloride. In contrast to the exothermic reaction of ethyl azodiformate with reactive dienes, IV reacts sluggishly under Diels-Alder conditions. No reaction was observed under the usual conditions

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(2) Taken in part from the M.S. theses of P.H.T. and P.J.C.

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