TABLE I

Analytical results of the 1:1 composition complexes

	% Nb		% Cl		% C		% H		
Ligands	Anal.	Theor.	Anal.	Theor.	Anal.	Theor.	Anal.	Theor.	Colors
Ph_3N	18.12	18.02	34.12	34.38	41.80	41.93	2.81	2.93	Green
Ph_3P	17.66	17.44	22.10	22.02	40.30	40.60	2.76	2.85	Amber
Ph_3As	15.92	16.10	20.32	20.35	37.71	37.50	2.50	2.62	Orange
Ph_3Sb	14.76	14.90	18.76	18.81	34.60	34.68	2.30	2.42	Brown
Ph_3Bi	13.13	13.07	16.61	16.50	30.21	30.42	2.21	2.12	Orange

TABLE II

Analytical results of the 2:1 composition complexes

	% Nb		% Cl		% C		% H		
Ligands	Anal.	Theor.	Anal.	Theor.	Anal.	Theor.	Anal.	Theor.	Colors
Ph_3N	23.26	23.65	44.78	45.12	27.32	27.51	2.01	1.92	Dark green
Ph_3P	23.29	23.14	43.91	44.17	26.79	26.93	1.90	1.88	Brown
Ph_3As	22.60	21.94	42.12	41.88	25.61	25.53	1.89	1.78	Red
Ph_3Sb	20.31	20.79	39.13	39.68	24.30	24.19	1.54	1.69	Blue
Ph_3Bi	18.15	18.94	36.42	36.15	22.11	22.04	1.80	1.54	Red

The precipitates were filtered off and the filtrates used to isolate the complexes by evaporation of the solvent under vacuum. Crystalline precipitates were obtained which were filtered, washed several times with normal hexane, dried under vacuum, and analyzed for carbon, hydrogen, niobium, and chloride as for the 1:1 complexes. The analytical results are listed in Table II and compared with the theoretical values for the 2:1 complexes.

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SYNTHESIS AND REACTIVITY OF SOME ORTHO-SUBSTITUTED DIPHENYL SULFONES

O. FRANCIS BENNETT[1]

The influence of the sulfone group on the reactivity of substituents (including hydrogen) at the ortho positions in diaryl sulfones has been noted in several cases. For example, 5-nitro-2-(*p*-nitrophenylsulfonyl)benzaldehyde fails to cyclize to the corresponding thiaxanthone dioxide, whereas 5-nitro-2-(*p*-nitrothiophenoxy)benzaldehyde readily ring closes to the corresponding thiaxanthone. The resistance of the former towards cyclization has been attributed to the oxidation state of sulfur (1). Furthermore, the sulfone group which is normally considered a meta directing substituent in electrophilic substitution reactions, promotes ortho substitution when diphenyl sulfones are metalated by *n*-butyl lithium (2). Resonance and inductive effects of the sulfone group have been invoked to

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explain the observed orientation in this latter example (2*a*). Indeed, these effects adequately explain the reactivity found for a variety of substituted diphenyl sulfones.*

Many years ago, Weedon and Doughty (4) gave brief mention to their observation that 2-carbomethoxyphenyl phenyl sulfone was resistent to alkaline saponification. They offered no explanation for these findings. Since that time, as far as we are aware, no further observations of the effect of the sulfone group on the reactivities of 2-carboalkoxyphenyl phenyl sulfones towards saponification have been reported. Moreover, the susceptibilities of substituted 2-carboxyphenyl phenyl sulfones to esterification have also been neglected.

Recently we had occasion to prepare a number of substituted diphenyl sulfones for use as intermediates. Several of these new compounds clearly demonstrated that for diaryl sulfones, a carboxyl group or carbomethoxy group in the 5-position—which is not affected by neighboring groups—is much more reactive than the corresponding group in the 2-position in esterification and saponification reactions, respectively. Thus, methanolic esterification of the mixture obtained from nitric acid oxidation of 2,5-dimethylphenyl phenyl sulfone (5) afforded 5-carbomethoxy-2-methylphenyl phenyl sulfone, I, and 5-carbomethoxy-2-carboxyphenyl phenyl sulfone, V, in a weight ratio of 1:10, respectively. Compounds I and V were readily converted to their corresponding acids, II and VI, by treatment with dilute base. To demonstrate the difference in reactivity of the 2-carbomethoxy group relative to the 5-carbomethoxy group, 2,5-dicarbomethoxyphenyl phenyl sulfone, III, prepared by reaction of either V or VI with diazomethane, was reacted with 1 equiv of aqueous base. As expected, 2-carbomethoxy-5-carboxyphenyl phenyl sulfone, IV, was the principal product.

Our findings parallel the reactivities found for ortho- and meta-nitrobenzoic acids (6) and their esters (7) as well as the reactivities found for 2-nitroterephthalic acid (8) and its esters (9) in esterification and saponification reactions, respectively. For these latter cases, the refractory nature of the ortho groups has been attributed primarily to steric effects (6–11). It appears likely that similar effects, attributable to the large sulfone group, provide a major contribution to the observed reactivities reported in this paper.

The equations on the next page summarize this work.

EXPERIMENTAL†

2,5-Dimethylphenyl Phenyl Sulfone

This compound (5) was prepared in 92% yield by reaction of benzenesulfonyl chloride with excess *p*-xylene in the presence of aluminium chloride; m.p. 109–110°.

Nitric Acid Oxidation of 2,5-Dimethylphenyl Phenyl Sulfone

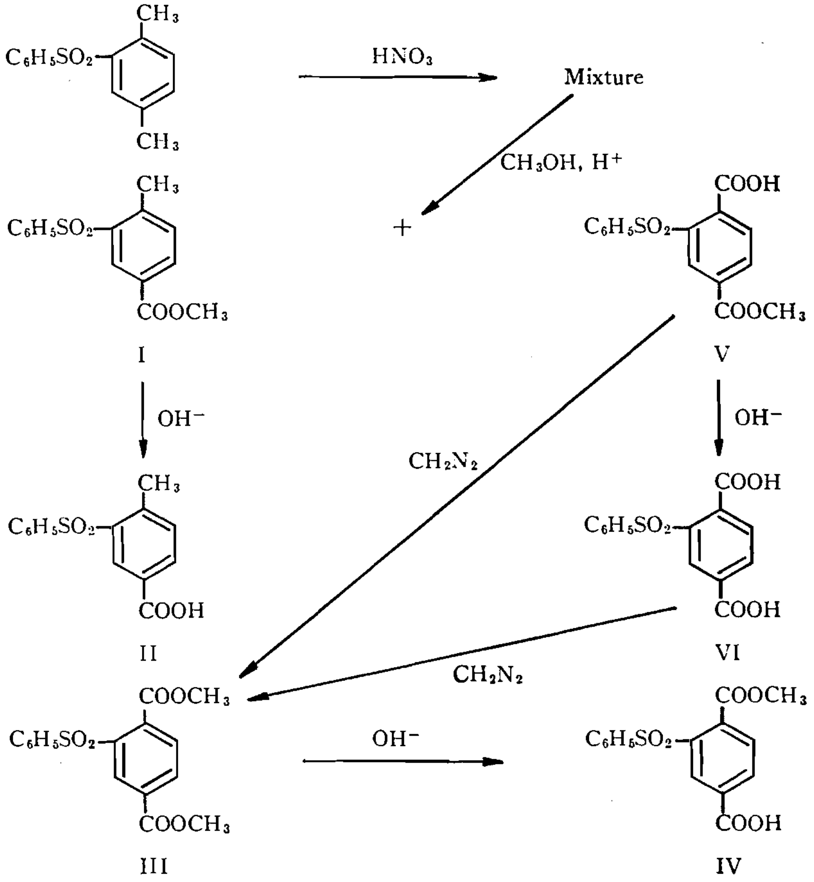
Aqueous nitric acid (580 ml, 35%) and 2,5-dimethylphenyl phenyl sulfone, 187.3 g (0.762 mole) were charged into a 2 l stainless steel pressure vessel. An initial pressure of 150 p.s.i.g. of nitrogen was placed on the system which was heated at 190° until no further increase in pressure was evident (3 h). The pressure vessel was cooled, vented to the atmosphere, and the contents allowed to degas overnight. The insoluble materials were collected by suction filtration, washed with cold water, and air dried. Attempts to separate and purify the oxidation products by crystallization from common solvents were not successful.

Separation of Principal Oxidation Products as Methyl Esters

The above oxidation mixture (10.0 g) was treated with 300 ml of methanol containing 10 drops of concentrated sulfuric acid. The stirred reactants were heated to reflux with occasional distillation of methanol until the volume of the reaction mixture was about 75 ml (6 h). Ether (150 ml) was added to the methanolic solution, and the resulting ethereal solution was washed with three 50 ml portions of 10% sodium bicarbonate and two 50 ml portions of water. The combined washings were set aside for subsequent work-up.

**An excellent discussion of both the resonance and the inductive effects of the sulfone group in diphenyl sulfones may be found in ref. 3.*

†All melting points are corrected. Infrared spectra were obtained on a Perkin-Elmer model 221 spectrophotometer.



5-Carbomethoxy-2-methylphenyl Phenyl Sulfone (I)

The neutral ethereal solution obtained from the esterification described above was dried over anhydrous magnesium sulfate and filtered, and the ether was removed by evaporation. The oily residue crystallized to a yellow solid (0.85 g) after gentle scratching with a glass rod. Three crystallizations from methanol–water afforded a white solid with m.p. 106–108°.

Anal. Calcd. for $C_{15}H_{14}O_4S$: C, 62.0; H, 4.86; S, 11.0. Found: C, 61.8; H, 4.88; S, 10.71.

Saponification of I in 0.1 *N* sodium hydroxide gave the corresponding acid, 5-carboxy-2-methylphenyl phenyl sulfone, II, m.p. 230.5–231.5°.

Anal. Calcd. for $C_{14}H_{12}O_4S$: C, 61.0; H, 4.38; neut. equiv, 276. Found: C, 60.74; H, 4.53; neut. equiv, 278.

Independent Synthesis of Compounds I and II; 3-Chlorosulfonyl-4-methylbenzoic Acid (VII)

This compound was prepared by modifying the procedure used by Hansch and co-workers (12) to make 3-chlorosulfonyl-4-ethylbenzoic acid.

Chlorosulfonic acid, 200 g (1.71 moles), was added to 66 g (0.426 mole) of *p*-toluoyl chloride at such a rate that the reaction temperature did not exceed 40°. After complete addition of the chlorosulfonic acid, the reactants were heated to 80° for 3 h and then poured cautiously, with stirring, onto cracked ice. The solid was collected by suction filtration and washed thoroughly with cold water. Crystallization of the air-dried product from toluene gave VII as a white solid in 74% yield; m.p. 166–167.6°.

Anal. Calcd. for $C_8H_7O_4SCl$: C, 41.0; H, 3.02; neut. equiv, 78.2. Found: C, 41.07; H, 3.29; neut. equiv, 79.3.

The Friedel–Crafts procedure starting with 100 g (1.28 moles) of benzene, 30 g (0.127 mole) of VII, and 38 g (0.286 mole) of aluminium chloride gave II as silvery plates after crystallization of the crude reaction product from methanol; m.p. 229–231°.

Anal. Calcd. for $C_{14}H_{12}O_4S$: C, 61.0; H, 4.38; neut. equiv, 276. Found; C, 60.68; H, 4.69; neut. equiv, 280.

Methanol esterification of this acid afforded the methyl ester, identical to I in all respects, in 89% yield, m.p. 106.4–108°.

5-Carbomethoxy-2-carboxyphenyl Phenyl Sulfone (V)

Acidification with 5% sulfuric acid of the combined bicarbonate–water washings from the esterification of the oxidation products afforded 8.5 g of crude V. This product, after crystallization from methanol–water, had m.p. 182.2–183.6°.

Anal. Calcd. for $C_{15}H_{12}O_6S$: C, 56.2; H, 3.78; S, 10.0; neut. equiv, 320. Found: C, 55.93; H, 4.09; S, 9.73; neut. equiv, 323.

Alkaline saponification readily converted V to the known 2,5-dicarboxyphenyl phenyl sulfone, VI (5); m.p. 265–266.5°.

Treatment of both V and VI with ethereal diazomethane gave the known 2,5-dicarbomethoxyphenyl phenyl sulfone, III (5); in each instance, m.p. 110.4–112°. In addition, reaction of both V and VI with thionyl chloride followed by treatment with excess methanol afforded III in each case.

Structure Proof of V

3-Carbomethoxyphenyl Phenyl Sulfone (VIII); Polymorphs of VIII

One gram (0.00313 mole) of V was heated at 180° with 10 ml of quinoline containing a trace of copper powder until gas evolution ceased ($\frac{1}{2}$ h). Ether (100 ml) was added to the cooled reaction mixture and the ethereal solution was filtered. The filtrate was washed successively with four 30 ml portions of 3% hydrochloric acid, one 30 ml portion of water, two 50 ml portions of 10% sodium bicarbonate, and one 50 ml portion of water. The neutral ethereal solution was dried over anhydrous magnesium sulfate and filtered, and the ether was evaporated. The dark residual oil crystallized from methanol–water, following treatment with Norite, as a white solid; m.p. 64.5–66.5°. A yield of 50% (0.43 g) was obtained.

Anal. Calcd. for $C_{14}H_{12}O_4S$: C, 61.0; H, 4.38. Found: C, 61.11; H, 4.40.

The following data show that this compound was an unstable polymorphic form (A) of VIII:

When A was heated above its melting point, 64.5–66.5°, solidification occurred at about 68° and the new solid (B) melted at 84–85.2°. Subsequent decarboxylations of V, performed as above, gave only the stable form of VIII, B, m.p. 84–85.2°; the unstable form, A, was not isolated in later preparations.

Anal. Calcd. for $C_{14}H_{12}O_4S$ (B): C, 61.0; H, 4.38. Found: C, 60.88; H, 4.38.

A mixture melting point of forms A and B showed no depression of the melting point of the stable form, B (m.p. of B, 84–85.2°; mixed m.p. 84–85°). The solid phase (Nujol mull) infrared spectrum of A was different from that of B. However, their solution spectra (carbon tetrachloride) were identical in all respects. The unstable form, A, spontaneously converted to the more stable form, B, after standing at room temperature for several months as shown by its m.p. (84–85.2°), and by its solid phase infrared spectrum.

3-Carboxyphenyl Phenyl Sulfone (IX) (2a)

This substance was prepared in almost quantitative yield by saponification of VIII in 0.1 *N* sodium hydroxide, m.p. 184–185.2°.

Infrared and melting point comparisons of IX with a sample of 2-carboxyphenyl phenyl sulfone showed them to be different compounds.

The m.p.'s of VIII and IX were not depressed, in either case, when mixed with authentic samples prepared by the procedures described below. In addition, infrared comparison showed VIII and IX to be identical with the authentic samples.

The Friedel–Crafts procedure starting with 20 g (0.0884 mole) of 3-chlorosulfonyl benzoic acid (13) m.p. 132–133°, 100 g (1.28 moles) of benzene, and 28 g (0.21 mole) of aluminium chloride gave a 43% yield of 3-carboxyphenyl phenyl sulfone; m.p. 184.5–185.5°.

The corresponding methyl ester had a m.p. of 84–85°.

2-Carbomethoxy-5-carboxyphenyl Phenyl Sulfone (IV)

Saponification of 2,5-dicarbomethoxyphenyl phenyl sulfone (2.0 g, 0.0006 mole) in 55 ml of 0.1067 *N* sodium hydroxide afforded this compound in 84% yield; m.p. 200.3–201° from methanol.

Anal. Calcd. for $C_{15}H_{12}O_6S$: C, 56.3; H, 3.78; S, 10.0. Found: C, 56.16; H, 3.84; S, 9.72.

Structure Proof of IV

5-Bromo-2-carbomethoxyphenyl Phenyl Sulfone (X)

2-Carbomethoxy-5-carboxyphenyl phenyl sulfone, IV, 2.7 g (0.0084 mole), was neutralized with 1 equiv of cold 0.3325 *N* sodium hydroxide, and the resulting solution was treated with 10% excess of aqueous silver nitrate solution. The silver salt of IV precipitated at once and was collected by suction filtration, washed with water, and air dried. An 81% yield of the silver salt was obtained.

The procedure of Barnes and Prochaska (14) was followed to convert the silver salt of IV to X.

The silver salt of IV (2.9 g, 0.0068 mole), 50 ml of dried carbon tetrachloride, and 1.085 g (0.0068 mole) of dry bromine were refluxed for 1 h. The warm pale-orange reaction mixture was filtered. Ether (200 ml) was added to the cooled filtrate and the ethereal solution was washed successively with 50 ml of water, two 50 ml portions of 10% sodium bicarbonate, and 50 ml of water. The dried (anhydrous magnesium sulfate) organic solution was evaporated to dryness, and the white solid residue was crystallized from methanol–water. The resultant white needles (55% yield) had m.p. 131.5–133.5°.

Anal. Calcd. for $C_{14}H_{11}O_4SBr$: C, 47.3; H, 3.13. Found: C, 47.3; H, 3.35.

5-Bromo-2-carboxyphenyl Phenyl Sulfone (XI)

Heating under reflux (5 h) of 0.8 g (0.00225 mole) of X with 60 ml of 0.5 *N* sodium hydroxide containing 40 ml of methanol gave the known (3*a*) XI in 89% yield, m.p. 195–196.3°.

A mixture m.p. of XI and an authentic sample was not depressed; the infrared spectra of both samples were totally superimposable.

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THE STRUCTURE OF BIS-DIMETHYLAMINOBERYLLIUM

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INTRODUCTION

In connection with other work, bis-dimethylaminoberyllium was prepared from the reaction of dimethylamine with diethylberyllium. Although the method of preparation was slightly different from that described by Coates and Glockling (1), it was noted on several occasions that the melting points of our preparations did not agree with those (1, 2) reported by these authors. Also, nuclear magnetic resonance (n.m.r.) data indicate that $Be(NMe_2)_2$ is not cyclic, but is trimeric as reported by Coates and Glockling (1).

EXPERIMENTAL

We prepared bis-dimethylaminoberyllium by two slightly different methods and with one of them it was possible to obtain $Be(NMe_2)_2$ with the literature (1) melting point.

In the first method, a typical preparation involved adding, under vacuum, a large excess of $HNMe_2$ in four equal portions to 2.5 g (37 mmole) of Et_2Be at 25 °C. After removal of the ethane formed and the excess dimethylamine, the solid product was vacuum sublimed (0.01 mm) at 90 °C onto a cold surface