soluble in ether and moderately soluble in benzene, toluene, ethanol, and dioxane. One ml. of boiling glacial acetic acid dissolves 23 mg. of VII from which solution 20 mg crystallizes on cooling. With 2,4-dinitrophenylhydrazine a bright scarlet product is formed which after repeated (4 times) recrystallizations from acetone melts at 340–345°. The analysis for nitrogen for this product was 2% low in spite of repeated attempts to obtain a pure product.

Department of Chemistry
Hunter College
New York, N. Y.

3,3′-Sulfonylbis(phenyl Isocyanates)

William F. Hart, Martin E. McGreal, and Paul E. Thurston[1]

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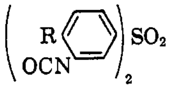
In recent years diisocyanates have become of considerable industrial importance. With the object of preparing less reactive diisocyanates, the reaction rate of which might be more easily controlled, attention was directed to the diisocyanato derivatives of diaryl sulfones. One such compound, 4,4′-sulfonylbis(phenyl isocyanate), has been described by Heymann and Fieser.[2] The reactivity of this compound has been studied by Bailey, Kirss, and Spaunburgh,[3] who found that its reaction with 2-ethylhexanol, using infrared spectroscopy to follow the reaction, was too rapid to permit calculation of the reaction rate constant.

The diisocyanates prepared for study were 3,3′-diisocyanato diphenyl sulfones, having the general formula



where R = H(I), Cl(II), CH_3(III), and $(CH_3)_3C$(IV)

They were prepared from the parent diaryl sulfones by nitration, reduction to the diamino sulfones using alcoholic stannous chloride, and phosgenation in chlorobenzene solution. The four diisocyanates and the intermediates bis(*tert*-butylphenyl) sulfone, bis(3-nitro-4-*tert*-butylphenyl) sulfone, and bis(3-amino-4-*tert*-butylphenyl) sulfone have not previously been described.

The relative reactivities of the four diisocyanates were semiquantitatively determined by following the reaction with a hindered alcohol, 2-ethylhexanol, in an infrared spectrophotometer using the technique of Bailey and co-workers.[3] Compounds I and II reacted quite rapidly and at almost exactly the same rates. In both cases the reaction was 50% completed in five minutes and was practically completed in thirty minutes. Compounds III and IV reacted relatively much more slowly. The reaction of III was 50% completed in forty minutes and practically completed in six hours. Compound IV, because of the greater steric hindrance of the *tert*-butyl groups, required two and one-half hours for 50% completion and twenty-two hours for practical completion of the reaction.

Comparison of these results with those of Bailey and coworkers[3] would lead to the conclusion that a sulfone group meta to the isocyanate group has less effect on increasing the reactivity of an isocyanate group than a sulfone group para to the isocyanate group, and confirms the observation of these workers that alkyl groups ortho to the isocyanate group exert a strong inhibiting effect due to steric hindrance.

EXPERIMENTAL[4]

Bis(4-chlorophenyl) sulfone. This compound was kindly contributed by the Stauffer Chemical Company and and the Diamond Alkali Company. The material obtained from the latter company contained about 20% water, which was removed by drying at 120°. The compound, m.p. 148–149°, was used for nitration without further purification.

Bis(p-tolyl) sulfone. This sulfone was prepared by a modification of the procedure of Meyer.[5] In a 6-l. three necked flask equipped with heating mantle, stirrer, water trap, and reflux condenser was placed 16 moles (1702 ml.) of toluene. To this was added 8 moles (436 ml.) of 98% sulfuric acid and 22 ml. of water, making the acid concentration 93% to prevent charring. This mixture was heated with stirring at the reflux temperature of toluene over a period of several days until the separation of water had practically ceased. At this point 183 ml. of water had been collected. A calculated amount of phosphorus pentoxide (357 g.) to react with the remainder of water to be removed to complete the reaction was added to the hot solution in portions with vigorous stirring to disperse the solid. The resultant mixture was refluxed for 5 hr. and then poured while hot into a large excess of ice and water.

The crude product was removed by filtration, washed several times with water, once with sufficient 5% sodium carbonate solution to neutralize residual acid, and then twice with water. The washed air-dried product weighed 1637 g., an 83% yield. Two recrystallizations from alcohol, using Darco on the first, gave a white crystalline product melting at 154°, lit.[5] 158°. The melting point can be raised to 160° by further recrystallization from glacial acetic acid or ethyl acetate.

tert-Butylbenzene. This intermediate, b.p. 167–70°, was prepared by the method of Nightingale and co-workers[6] by the reaction of *tert*-butyl chloride, benzene, and anhydrous ferric chloride catalyst.

p-tert-Butylbenzenesulfonyl chloride. This compound was made from *tert*-butylbenzene and chlorosulfonic acid by the method of Huntress and co-workers.[7] The product, m.p. 83–84°, was obtained in 70% yield.

Bis(4-tert-butylphenyl) sulfone. This sulfone was prepared

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(1) P.E.T. engaged in this work under the Undergraduate Research Participation Program of the National Science Foundation.

(2) H. Heymann and L. F. Fieser, *J. Am. Chem. Soc.*, **67**, 1979 (1945).

(3) M. E. Bailey, V. Kirss, and R. G. Spaunburgh, *J. Ind. Eng. Chem.*, **48**, 794 (1956).

(4) Melting points and boiling points are uncorrected.

(5) H. Meyer, *Ann.*, **433**, 336 (1923).

(6) D. Nightingale, R. G. Taylor, and H. W. Smelser, *J. Am. Chem. Soc.*, **63**, 258 (1941).

(7) (a) E. H. Huntress and F. H. Carten, *J. Am. Chem. Soc.*, **62**, 511 (1940); (b) E. H. Huntress and J. S. Autenrieth, *J. Am. Chem. Soc.*, **63**, 3446 (1941).

by the procedure used by Newell[8] to prepare phenyl *p*-tolyl sulfone. One-tenth mole (23.3 g.) of *p*-*tert*-butylbenzenesulfonyl chloride and 0.2 mole (26.9 g.) of *tert*-butylbenzene were placed in a three necked flask equipped with mechanical stirrer, thermometer, and condenser protected by a calcium chloride tube. Anhydrous aluminum chloride (20 g., 0.15 mole) was added in four portions while stirring the mixture which was heated to 70° on a steam bath. The dark brown mass was then heated at 70° for 2 hr. and at 80° for 1 hr.

The reaction mass was cooled, ice added to hydrolyze the excess aluminum chloride, and the mixture was then steam distilled to remove the unreacted *tert*-butylbenzene. The residue was filtered and the product which was a brown sticky mass was washed twice with petroleum ether (b.p. 30–60°). It was then dissolved in hot acetone from which it crystallized. Upon recrystallization from acetone a 79% yield of the sulfone was obtained which melted at 213–215°.

Anal. Calcd. for $C_{20}H_{26}O_2S$: C, 72.68; H, 7.93; S, 9.70. Found: C, 72.58; H, 8.02; S, 9.75.

A modification of this experiment adding the anhydrous aluminum chloride at room temperature by the procedure of Maclean and Adams[9] failed to yield any of the desired product.

An attempt to prepare bis(4-*tert*-butylphenyl) sulfone from *tert*-butylbenzene and sulfuric acid by the procedure used to prepare bis(*p*-tolyl) sulfone yielded only a very small amount of sulfone and some unchanged *tert*-butylbenzene, the chief product being *p*-*tert*-butylbenzenesulfonic acid. This was precipitated as the sodium salt from the aqueous solution by saturating with sodium chloride, filtered, and air dried. The salt was converted to *p*-*tert*-butylbenzenesulfonyl chloride with phosphorus pentachloride by the method of Adams and Marvel,[10] the yield being 57%.

Bis(3-nitrophenyl) sulfones. Nitration of the sulfones was performed by the method of Buehler and Masters.[11]

Bis(3-nitro-4-chlorophenyl) sulfone. The yield of this derivative was 97%, the melting point after recrystallization from dioxane was 201–202°. Gunnstone and Tucker[12] reported a melting point of 192–196° for this compound crystallized from glacial acetic acid; Ullman and Korselt[13] reported the melting point as 202° from the same solvent.

Bis(3-nitro-4-methylphenyl) sulfone. The yield of this derivative was also 97%; the melting point was 160–162°, which agrees with the literature.[5,11]

Bis(3-nitro-4-tert-butylphenyl)sulfone. This derivative was obtained as a light yellow solid in 85% yield. After recrystallization from glacial acetic acid it melted at 209–211°.

Anal. Calcd. for $C_{20}H_{24}O_4N_2S$: C, 57.12; H, 5.75; N, 6.66; S, 7.62. Found: C, 57.05; H, 5.98; N, 6.82; S, 7.79.

Bis(3-aminophenyl) sulfones. The general procedure used to prepare these compounds was the reduction of the corresponding bis(3-nitrophenyl) sulfones using alcoholic stannous chloride by the method of Raiziss and co-workers.[14]

This procedure was modified by the addition of 12 equivalents of concd. HCl after $^1/_2$ hr. refluxing of the alcoholic solution, followed by $1^1/_2$ hr. additional refluxing. Excess 40% sodium hydroxide solution was used in working up the reaction mixture.

Bis(3-aminophenyl) sulfone. This compound was obtained from the Tennessee Corporation as a technical grade material. It was purified by dissolving in warm 6*N* hydrochloric acid, treating with Darco, and filtering, making the filtrate alkaline with sodium hydroxide, and washing until free of alkali. After recrystallization from dioxane the compound melted at 166° (lit.[15] 168°).

Bis(3-amino-4-chlorophenyl) sulfone. This compound was obtained by the reduction procedure in yields up to 83%. It crystallized from dioxane as a flesh-colored solid, m.p. 158–160°, which agrees with the literature.[16] It is not soluble in warm 12*N* hydrochloric acid.

Bis(3-amino-4-methylphenyl) sulfone. This compound was obtained in 95% yield as a cream colored solid. Meyer[5] gives the melting point as 154°; actually this compound melts with gas evolution at 159°, very close to the melting point of the parent bis(3-nitro-4-methylphenyl) sulfone. It is readily soluble in warm 6*N* hydrochloric acid and may be purified by dissolving in the acid, treatment with Darco, and reprecipitation by alkali, followed by washing until neutral. The compound was recrystallized from alcohol or dioxane.

Bis(3-amino-4-tert-butylphenyl) sulfone. This compound was obtained from the reduction as a discolored solid contaminated with inorganic salts. It was purified by extraction with tetrahydrofuran in a Soxhlet extractor, and crystallized by concentrating the extract, m.p. 219–230°, yield 80%. The melting point was raised to 232° by repeated recrystallizations from dioxane; the product was a flesh-colored solid.

Anal. Calcd. for $C_{20}H_{28}O_2N_2S$: C, 66.63; H, 7.82; N, 7.77; S, 8.89. Found: C, 66.30; H, 7.81; N, 7.78; S, 9.28.

3,3′-Sulfonylbis(phenyl isocyanates). (Table I). These compounds were prepared by the phosgenation of the bis(3-aminophenyl) sulfones in chlorobenzene solution using established procedures.[17] Conversion of the amino groups to the hydrochloride salts in order to minimize urea formation by the reaction of the isocyanate with the starting amino compound has been recommended by Hardy.[18] Boron trifluoride complexes have been patented as phosgenation catalysts,[19] but in this preparation of these compounds the use of boron trifluoride etherate did not improve the yields or ease of preparation.

The general procedure used was to place approximately 50 g. of the pure bis(3-aminophenyl) sulfone and 750 ml. of chlorobenzene distilled from phosphorus pentoxide in a two liter three necked flask equipped with heating mantle, condenser, mechanical stirrer, inlet tube, and outlet tube. The inlet tube was connected with a wash bottle containing conc. sulfuric acid and the outlet tube with a wash bottle containing 20% potassium hydroxide solution. The sulfone was dissolved with heating and stirring and the solution saturated with dry hydrogen chloride gas. The slurry of the hydrochloride was cooled to room temperature and introduction of phosgene, dried by bubbling through conc. sulfuric acid, was begun. The gas was passed into the mixture with stirring until no more phosgene was absorbed at room temperature, which required 2–3 hr. The temperature was then slowly raised to the reflux temperature of the solvent and held there for $^1/_2$ hr. while continuing to pass a slow stream of phosgene into the reaction mixture. The slurry became thinner and in most cases nearly all solid present dissolved. The solution was then degassed by passing dried nitrogen through the stirred refluxing solution until little more phosgene and hydrogen chloride were present in the effluent gas. This required at least 3 hr. The hot solution was filtered on sintered glass and the filtrate was concentrated to approximately 100

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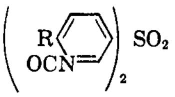
TABLE I

3,3′-SULFONYLBIS(PHENYL ISOCYANATES)



	R	Formula	Yield, %	M.P.[a]	N Calcd.	N Found	S Calcd.	S Found
I	H	$C_{14}H_8N_2O_4S$	40–50	126–129	9.32	9.13	10.67	10.70
II	Cl	$C_{14}H_6Cl_2N_2O_4S$	68	149–150	7.58	7.30	8.65	8.54
III	CH_3	$C_{16}H_{12}N_2O_4S$	77	132–134	8.53	8.52	9.76	9.96
IV	$(CH_3)_3C$	$C_{22}H_{24}N_2O_4S$	73	120	6.79	6.69	7.77	7.79

[a] Melting points are uncorrected.

ml. by distillation at atmospheric pressure. The concentrate was placed in a 250-ml. filter flask and the remaining solvent removed by heating in an oil bath under vacuum. The diisocyanates were taken up in a small volume of dry benzene and crystallized from that solvent. They were further purified by trituration with petroleum ether (b.p. 30–60°) and were obtained as white or faintly yellow solids.

The relatively low yield of I was accompanied by the formation of a considerable amount of high melting, insoluble polyurea which was removed by filtration of the hot chlorbenzene solution. The other three products were accompanied by only small amounts of such a polymer.

Compound IV was converted into the corresponding diethylurethane, 5,5′-sulfonylbis(2-*tert*-butyl)carbanilic acid, ethyl ester, by reaction with ethyl alcohol. This derivative after crystallization from carbon tetrachloride and trituration with petroleum ether (b.p. 30–60°) melted at 135°.

Anal. Calcd. for $C_{26}H_{36}N_2O_6S$: N, 5.55; S, 6.35. Found: N, 5.41; S, 6.18.

The relative reactivities of the four diisocyanates were studied by the procedure of Bailey and co-workers[3] using a Beckman IR-5 spectrophotometer with sodium chloride 0.102 mm. absorption cells. From the data obtained the times required for 50% completion and practical completion of the reaction with 2-ethylhexanol were determined for each diisocyanate.

DEPARTMENT OF CHEMISTRY
LAFAYETTE COLLEGE
EASTON, PA.

DEPARTMENT OF CHEMISTRY
ST. JOHN'S UNIVERSITY
JAMAICA 32, N. Y.

Communications TO THE EDITOR

Titanium-Catalyzed Reduction and Rearrangement in Grignard Coupling Reaction with Silicon Halides[1]

Sir:

Adding 0.1 wt. % titanium tetrachloride to triethylchlorosilane alters the course of its reaction with isopropylmagnesium bromide, producing reduction [$(C_2H_5)_3SiCl + (CH_3)_2CHMgBr \rightarrow (C_2H_5)_3SiH + C_3H_6$] and rearrangement [$(C_2H_5)_3SiCl + (CH_3)_2CHMgBr \rightarrow (C_2H_5)_3Si(CH_2)_2CH_3$]. Titanium tetrachloride also catalyzed reduction and rearrangement in the reaction of diethyldichlorolane with isopropylmagnesium bromide [$(C_2H_5)_2SiCl_2 + (CH_3)_2CHMgBr \rightarrow (CH_3)_2CHSi(C_2H_5)_2H + CH_3(CH_2)_2Si(C_2H_5)_2H + C_3H_6$)]; details of our work on this reduction and rearrangement prior to our recognizing the titanium tetrachloride catalysis and the propylene formation should appear shortly.[2] Titanium tetrachloride also catalyzed participation of hexene-1 in the reaction of diethyldichlorosilane with isopropylmagnesium bromide to produce *n*-hexyldiethylsilane [$(C_2H_5)_2SiCl_2 + (CH_3)_2CHMgBr + CH_3(CH_2)_3CH = CH_2 \rightarrow n\text{-}C_6H_{13}Si(C_2H_5)_2H + (CH_3)_2CHSi(C_2H_5)_2H + CH_3(CH_2)_2Si(C_2H_5)_2H + C_3H_6$].

Such catalyses have not been reported in over fifty years of widespread use of the Grignard reagent for synthesizing organosilicon compounds. However analogous reductions and rearrangements proceeding without known catalysis have been reported for organoboron[3,4] and organoaluminum compounds.[5]

The new reactions outlined above are described in greater detail below. They have since been shown by our associates to involve titanium-catalyzed isomerization of the Grignard reagent and titanium-catalyzed olefin exchange with the Grignard reagent.[6,7]

Refluxing 150 g. of triethylchlorosilane contain-

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