of anhydrous ether, to 10.1 g. (0.42 mole) of magnesium turnings. The resulting mixture was refluxed 90 minutes to complete the reaction and to this solution was then added 24.0 g. (0.20 mole) of trimethylene sulfite in 125 ml. of anhydrous ether. The addition was made during 2.5 hours and the reaction mixture then refluxed for 90 minutes. The mixture was hydrolyzed by adding 350 ml. of saturated ammonium chloride solution, the ether layer was separated and the aqueous layer was extracted twice with 200-ml. portions of ether. After drying the combined ethereal solutions over Drierite the solvent was removed and the residue distilled to give the following fractions: (1) b.p. 80–100° (55 mm.), $n^{26}\text{D}$ 1.4986; (2) b.p. 90–115° (4 mm.) solidified; (3) residue, solidified. Fraction 1 on redistillation gave 3.5 g. of trimethylene bromohydrin (12.6%), b.p. 75–80° (35 mm.), $n^{25}\text{D}$ 1.4834. Fraction 2 was recrystallized from methanol to give 2.0 g. (6.4%) of biphenyl, m.p. 65–68°. The residue was dissolved in benzene and crystallized to give 19.5 g. (50.8%) of phenyl sulfoxide, m.p. 68–69°. The identities of the solids were confirmed by mixture melting points.

Except for changes in ratios of the phenylmagnesium bromide to sulfite, and the order of addition, the Grignard reactions were carried out and worked up as described above. The results are summarized in Table I.

In a blank run to check the yield of biphenyl obtained under the above conditions it was found that 8.3% of biphenyl could be isolated.

To check the formation of methyl bromide during the reaction of phenylmagnesium bromide and methyl sulfite the reaction was carried out under the above conditions using 0.5 mole of phenylmagnesium bromide and 0.154 mole of methyl sulfite. The sulfite dissolved in ether was added to the Grignard reagent while a slow stream of nitrogen swept the gaseous products into two absorption flasks containing 30 cc. of a solution obtained by dissolving 5 g. of potassium hydroxide in 95% ethanol. The absorption flasks were maintained at 0°, and the nitrogen stream was continued during the two-hour reflux period following the completion of the addition of the sulfite. The reaction mixture was worked up in the usual way to give 65% of phenyl sulfoxide. The solution in the absorption flasks was allowed to come to room temperature and then was neutralized by addition of acetic acid, and finally a solution of silver nitrate was added until no further precipitation was observed. The precipitate was filtered, washed with dilute nitric acid, water and dried to give 0.1012 g. of silver bromide (0.00053 mole). Assuming a theoretical yield of 0.308 mole, the actual yield of silver bromide corresponds to 0.6%. Since in three control experiments this analytical procedure detected between 35 and 55% of methyl bromide from a methanolic solution, it is estimated that the maximum yield of methyl bromide is 1.8%.

**Infrared Data.**—The infrared data were obtained with a Perkin–Elmer model 12-C single beam infrared spectrophotometer using a sodium chloride cell. The spectra were taken in 0.5–2.0 *M* solutions in carbon tetrachloride in a 0.0025- or 0.0100-cm. cell.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

# Derivatives of 1-Thia-4,5-diazacyclohepta-2,4,6-triene. II.[1] Dibenzo-1-thia-4,5-diazacyclohepta-2,4,6-triene-1,1-dioxide and the Trifluoromethyl-substituted Dibenzo System Containing Sulfur in Unoxidized Form

BY H. HARRY SZMANT AND RONALD L. LAPINSKI[2]

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Controlled reduction of di-(2-nitro-4-trifluoromethylphenyl) sulfide was successful in the preparation of the 1-thia-4,5-diazacyclohepta-2,4,6-triene system containing sulfur in the unoxidized form. The oxidation of *o,o'*-diamino phenyl sulfone and its trifluoromethyl substitution product by means of phenyliodoso acetate represents an excellent synthetic method for the formation of derivatives of 1-thia-4,5-diazacyclohepta-2,4,6-triene-1,1-dioxide.

The discovery that under conditions of controlled hydrogenation an *o,o'*-dinitro phenyl sulfone can yield the seven-membered heterocyclic ring 1-thia-4,5-diazacyclohepta-2,4,6-triene, and that this ring system does not tend to decompose with elimination of nitrogen, prompted further study of compounds of this type. Of immediate interest was the synthesis of analogous compounds in which the sulfur atom was present in the unoxidized form in order to ascertain if such a ring system is less stable and tends to produce dibenzothiophene derivatives with the loss of nitrogen. Also, it was desirable to prepare dibenzo-1-thia-4,5-diazacyclohepta-2,4,6-triene without the trifluoromethyl substituents which were present in the first examples of this series of compounds. The results of these studies are reported in the present publication.

After many unsuccessful attempts to bring about the reduction of di-(2-nitro-4-trifluoromethylphenyl) sulfide with simultaneous ring closure, it was found that the use of zinc in the presence of sodium acetate, and of activated aluminum in an alcoholic medium, gave the cyclic azoxy I and azo II compounds, respectively. The identity of these compounds was proven by the conversion to the previously described cyclic azoxy sulfone III. The cyclic sulfides I and II were found to be stable and heating above their melting points did not induce any loss of nitrogen.

In the search for better synthetic methods yielding the 1-thia-4,5-diazacyclohepta-2,4,6-triene system, the recently described oxidation of anilines by means of phenyliodoso acetate was utilized.[3] The application of this procedure to di-(2-amino-4-trifluoromethylphenyl) sulfone gave an excellent yield of the cyclic azo compound IV, which was

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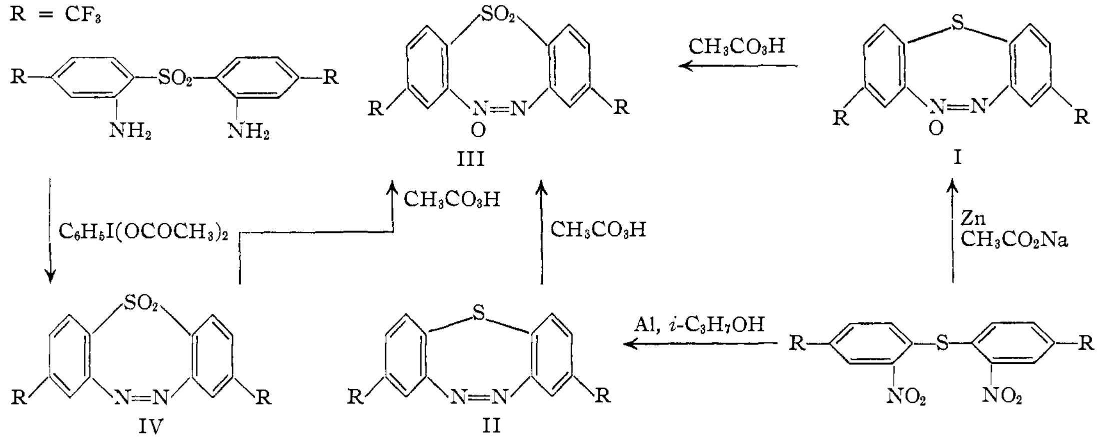
[1] The publication in THIS JOURNAL, **75**, 6338 (1953), is considered the first in this series.

[2] Taken from the Ph.D. thesis of R. L. L., Duquesne Univ., 1954. Financial aid of the Research Corporation is gratefully acknowledged.

[3] K. H. Pausacker, *J. Chem. Soc.*, 1989 (1953).

previously obtained in poor yield by the controlled reduction of the corresponding nitro sulfone.

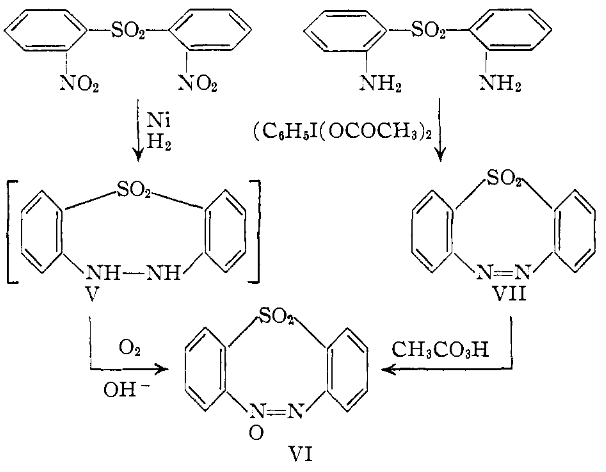
The preparative methods employed in the syntheses of the above mentioned compounds, and the reactions by which they were related to each other, are summarized as



The partial hydrogenation of di-(*o*-nitrophenyl) sulfone in the presence of Raney nickel gave, as in the case of the corresponding trifluoromethyl derivative,[1] the cyclic hydrazo sulfone (V). The latter could not be obtained in satisfactory purity because of spontaneous decomposition in air, but its identity was deduced from the colorless nature of the crystals, their violent decomposition near 125°, and their conversion by oxidation to the stable azoxy sulfone VI. The air oxidation of V gave VI and this result is of interest since the cyclic hydrazo compound derived from di-(2-nitro-4-trifluoromethylphenyl) sulfone gave, under identical conditions, the corresponding azo compound IV. The direct conversion of a hydrazo to an azoxy system by air oxidation appears to be a novel observation. It can be attributed to the fact that we are dealing here with a *cis*-azo system which is more susceptible to oxidation than the more common *trans*-azo system. The isolation of IV from the air oxidation of the hydrazo sulfone containing trifluoromethyl substituents seems to have been fortuitous and to have resulted from the presence of the electron-withdrawing substituents.[4]

The application of phenyliodoso acetate to the oxidation of di-(*o*-aminophenyl) sulfone gave an excellent yield of VII, which could be oxidized to VI obtained from the air oxidation of the cyclic hydrazo system V.

In view of the favorable results obtained in the oxidation of *o,o'*-diamino phenyl sulfones by means of phenyliodoso acetate, there were made several attempts to extend this reaction to the corresponding *o,o'*-diamino phenyl sulfides. These attempts have proven, so far, unsuccessful and no crystalline products can be isolated from the tarry reaction products. In a series of control experiments it was shown that, while phenyl sulfide was oxidized by phenyliodoso acetate to the sulfoxide, the sulfides containing electron-withdrawing substituents, such as di-(*o*-nitrophenyl) and di-(2-nitro-4-trifluoromethylphenyl) sulfides, were recovered unchanged. Thus, it appears that the oxidizing ability of phenyliodoso acetate depends greatly on the electron-density at the sulfur atom of the given sulfide, and one would therefore expect the aminophenyl sulfides to become oxidized at both the amine and sulfide functions.



Since aryl azides are known to form azo compounds under pyrolytic conditions[5] an attempt was made to bring about the decomposition of di-(*o*-azidophenyl) sulfone, di-(2-azido-4-trifluoromethylphenyl) sulfide and sulfone with simultaneous formation of a cyclic azo compound. The thermal and photochemical decompositions took place as evidenced by the evolution of nitrogen, but the products of these reactions turned out to be insoluble, high-melting materials. Apparently, in place of cyclization, the intermediates of the decomposition of the azides participated instead in intermolecular coupling reactions.

Additional studies of derivatives of 1-thia-4,5-diazacyclohepta-2,4,6-triene are in progress.

## Experimental[6]

**The Reduction of Di-(2-nitro-4-trifluoromethylphenyl) Sulfide. (A) With Zinc and Sodium Acetate.**—A mixture containing 5 g. of the sulfide,[1] 2.5 g. of zinc, 3.0 g. of sodium

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[4] This conclusion is based on other observations concerning the oxidation of cyclic hydrazo to azoxy compounds encountered in work which will be described in the near future.

[5] A. Bertho, *J. prakt. Chem.*, **120**, 119 (1929).

[6] All melting points are uncorrected. Microanalyses by Drs. Strauss and Weiler, Oxford, England.

acetate and 200 cc. of isopropyl alcohol was refluxed with vigorous stirring for 50 minutes and the hot solution was filtered and concentrated to give yellow crystals melting 178–179°. After several crystallizations from isopropyl alcohol 0.5 g. of pure I, m.p. 181–182°, was obtained.

*Anal.* Calcd. for $C_{14}H_6N_2OSF_6$: C, 46.16; H, 1.67. Found: C, 46.41; H, 1.91.

The oxidation of 0.15 g. of this compound by means of 40% peracetic acid gave an essentially quantitative yield of III, m.p. 267–268°, identical with the previously reported azoxy sulfone.[1]

(B) **With Aluminum and Isopropyl Alcohol.**—Aluminum foil, 3 g., was treated with 10% sodium hydroxide until the hydrogen evolution became very vigorous. The aqueous portion was decanted and the aluminum was washed several times with distilled water and then amalgamated by adding 100 cc. of a 2% solution of mercuric chloride. The amalgamated aluminum was washed with water and isopropyl alcohol and then added to a warm solution of 5 g. of the sulfide in 200 cc. of isopropyl alcohol. The reaction mixture was heated until hydrogen evolution became vigorous and then the mixture was allowed to stand until hydrogen evolution subsided. The reaction mixture was poured into a mixture of 300 cc. of water and 50 cc. of concentrated hydrochloric acid, and the resulting solution was extracted with benzene. The benzene extract upon concentration yielded 0.5 g. of yellow crystals, m.p. 151°, which after several crystallizations from isopropyl alcohol gave pure II, m.p. 154°.

*Anal.* Calcd. for $C_{14}H_6N_2SF_6$: C, 48.26; H, 1.74. Found: C, 48.14; H, 1.94.

The oxidation of a sample of this compound with peracetic acid gave the previously[1] described III.

**The Oxidation of Di-(2-amino-4-trifluoromethylphenyl) Sulfone with Phenyliodoso Acetate.**—To the solution obtained by warming 150 cc. of dry toluene and 2.7 g. of phenyliodoso acetate there was added 1.5 g. of the amino sulfone[1] and the resulting solution was allowed to stand for three days. Upon removal of the toluene and iodobenzene by steam distillation IV was isolated in a 95% yield. The product on crystallization from acetic acid gave a constant melting point of 231–232°. While this m.p. is lower than that reported previously,[1] the product of this preparation gave a more satisfactory analysis than the product of the reduction of the nitro sulfone.

*Anal.* Calcd. for $C_{14}H_6N_2O_2SF_6$: C, 44.21; H, 1.59. Found: C, 44.05; H, 1.65.

The oxidation of IV with peracetic acid gave the previously[1] described III.

**The Reduction of Di-(*o*-nitrophenyl) Sulfone.**—Five grams of Raney nickel was added to a solution of 3.0 g. of the nitro sulfone in 300 cc. of isopropyl alcohol and the mixture was hydrogenated under atmospheric pressure until 415 cc. of hydrogen was absorbed. Nickel was first removed by filtration of the mixture and the alcoholic solution was then gradually concentrated *in vacuo*. After the unreacted starting material ceased to precipitate, the residual solution was mixed with some benzene and the solution was dried by distillation of the benzene–water azeotrope. The residual solution gave crystals which decomposed violently with liberation of gas when heated to 125°. Since a number of attempts to purify this material by crystallization failed, the hydrazo compound V was oxidized by passing air into a solution of the compound in isopropyl alcohol containing a few drops of dilute sodium hydroxide. The solution turned orange and gave yellow crystals, m.p. 245°, which on further crystallization from isopropyl alcohol had a constant m.p. 250–251°. The analysis of this material agreed with that calculated for VI rather than VII.

*Anal.* Calcd. for $C_{12}H_8N_2O_3S$: C, 55.38; H, 3.09. Found: C, 55.03; H, 2.91.

The product resisted vigorous oxidation with peracetic acid and was recovered unchanged.

**The Oxidation of Di-(*o*-aminophenyl) Sulfone with Phenyliodoso Acetate.**—The amino sulfone, 1.50 g., was added to a solution of 1.58 g. of phenyliodoso acetate in 200 cc. of toluene and the resulting mixture was allowed to stand for 24 hours. The toluene solution was filtered to remove a small amount of a black precipitate and was concentrated by distillation. The resulting tar was dissolved in isopropyl alcohol and after a charcoal treatment addition of ethyl acetate and slow cooling gave orange crystals, m.p. 158°. Crystallization from isopropyl alcohol gave a 78% yield of VII, m.p. 170–171°.

*Anal.* Calcd. for $C_{12}H_8N_2O_2S$: C, 59.00; H, 3.35. Found: C, 59.22; H, 3.46.

A small portion of this product was oxidized by heating with peracetic acid until the solution color faded; the product of the oxidation was identical with VI obtained as described above from di-(*o*-nitrophenyl) sulfone.

**Oxidation of Phenyl Sulfide with Phenyliodoso Acetate.**—Diphenyl sulfide, 2.0 g., was added to a solution of 3.2 g. of phenyliodoso acetate in 90 cc. of dry toluene and the mixture was allowed to stand for two days. After heating on a water-bath for two hours, the reaction mixture was concentrated and there was recovered 1.3 g. of phenyliodoso acetate. Further concentration yielded an oil which was crystallized from a small amount of petroleum ether to give 0.8 g. of material, m.p. 69–70°, which produced no depression in melting point when mixed with pure diphenyl sulfoxide (m.p. 70°).

A mixture of 2.0 g. of diphenyl sulfoxide and 3.2 g. of phenyliodoso acetate in 100 cc. of toluene was allowed to stand for 24 hours. After heating on a water-bath and concentrating the solution, unreacted diphenyl sulfoxide, m.p. 69–70°, was recovered.

**Preparation of Azides. Di-(*o*-azidophenyl) Sulfone.**—To a mixture of 100 cc. of concentrated sulfuric acid and 50 cc. of water there was added 2.0 g. of di-(*o*-aminophenyl) sulfone and the solution was cooled to 5° by addition of ice. While maintaining the temperature between 5 and 10° 6 g. of sodium nitrite dissolved in a minimum amount of water was added and the mixture was maintained at below 10° for six hours. The di-(*o*-aminophenyl) sulfone slowly dissolved and, after excess nitrous acid was destroyed by means of urea, 3.0 g. of sodium azide was added as an aqueous solution. When the evolution of nitrogen subsided, the reaction mixture was diluted with water and the precipitate was collected. There was obtained 2.0 g. of di-(*o*-azidophenyl) sulfone, m.p. 196° dec. after crystallization from isopropyl alcohol.

*Anal.* Calcd. for $C_{12}H_8N_6O_2S$: C, 47.95; H, 2.68; N, 27.9. Found: C, 48.23; H, 2.94; N, 28.1.

**Di-(2-azido-4-trifluoromethylphenyl) Sulfide.**—The solution of 3.0 g. of di-(2-amino-4-trifluoromethylphenyl) sulfide in a mixture of 100 cc. of concentrated sulfuric acid and 200 cc. of water was maintained below 10° while an aqueous solution of 6 g. of sodium nitrite was added gradually; the resulting mixture was stirred for six hours. An aqueous solution of urea was added until the evolution of nitrogen ceased and this was followed by the addition of 3.0 g. of sodium azide. There was obtained 3.0 g. of di-(2-azido-4-trifluoromethylphenyl) sulfide, m.p. 111° dec., after crystallization from isopropyl alcohol.

*Anal.* Calcd. for $C_{14}H_6N_6SF_6$: C, 41.58; H, 1.49; N, 20.7. Found: C, 42.02; H, 1.43; N, 20.2.

**Di-(2-azido-4-trifluoromethylphenyl) Sulfone.**—A solution of 3.04 g. of di-(2-amino-4-trifluoromethylphenyl) sulfone in 195 cc. of concentrated sulfuric acid and 195 cc. of water was cooled to 5° by addition of ice. Sodium nitrite, 0.54 g., dissolved in a little water was then added and after the reaction mixture was stirred for six hours there was added 2.0 g. of sodium azide dissolved in water. Upon dilution of the solution with water and allowing it to stand overnight, 2.31 g. of di-(2-azido-4-trifluoromethylphenyl) sulfone was obtained, m.p. 193–194° dec. after crystallization from isopropyl alcohol.

*Anal.* Calcd. for $C_{14}H_6N_6O_2SF_6$: C, 38.57; H, 1.39; N, 19.3. Found: C, 38.86; H, 1.65; N, 19.6.

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