

axis projection does not permit the determination of interatomic distances since none of the bonds is believed to be directed exactly perpendicular to the *c*-axis. However, the sulfur-oxygen projection distance is equal to the reported value of 1.50 Å. for the sulfates.

Summary.—The primary result of this investigation of the crystal structure of trimethylamine sulfur trioxide using X-ray diffraction is that, in the crystalline state, the SO₃ groups rotate about the molecular axes while the N(CH₃)₃ groups rotate very little, if at all. The basic unit cell was found to be a rhombohedron with *a* = 5.71 Å. and $\alpha = 107^\circ 40'$ and containing one molecule. The space group is $C_{3v}^5 = R\bar{3}m$ and the calculated density is 1.52 g./cm.³.

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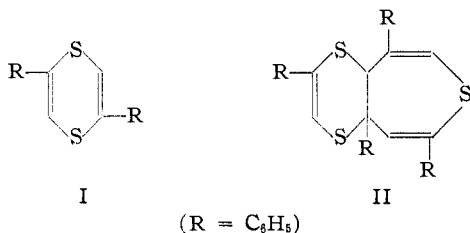
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The Oxidation Products of 2,5-Diphenyl-1,4-dithiadene

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The recent publication concerning the chemistry of the 1,4-dithiadene system¹ and the reports of the Diels-Alder type condensation reactions in the course of the oxidation of thiophene² and benzothiophene^{3,4} prompts us to report the results obtained in the study of the oxidation of 2,5-diphenyl-1,4-dithiadene (I).



When I was treated with an equimolar amount of hydrogen peroxide, there was obtained a compound C₃₂H₂₄S₃. Analogy with reactions previously studied^{2,3,4} leads to the tentative assignment of structure II to this compound.

Further study is planned, but the behavior of II on vigorous oxidation is in agreement with the structure assigned. With excess hydrogen peroxide acting for a long time, 0.11 g. of II gave 0.025 of the disulfone of I, 0.093 g. of benzoic acid and 0.051 g. of barium sulfate. These amounts are 34, 174 and 169% of the expected ones, if one molecule of the disulfone were formed from each molecule of II. The deficiency in the yield of the disulfone and the excess of benzoic acid and sulfate

(1) W. E. Parham, T. M. Roder and W. R. Hasek, *THIS JOURNAL*, **75**, 1647 (1953).

(2) W. Davies, N. W. Gamble, F. C. James and W. E. Savage, *Chem. Ind.*, 804 (1952).

(3) W. Davies, *et al.*, *J. Chem. Soc.*, 4678 (1952).

(4) F. G. Bordwell, W. H. McKellin and D. Babcock, *THIS JOURNAL*, **73**, 5566 (1951).

ion indicates that the disulfone itself is not completely stable.

The disulfone was obtained directly from I, with excess hydrogen peroxide, but in only 50% yield, and accompanied by benzoic and sulfuric acids. This may indicate that even under these conditions II is an intermediate in the oxidation of I to its disulfone.

Experimental⁵

2,5-Diphenyl-1,4-dithiadene-1,4-tetroxide.—I, 5.55 g., was heated with an excess of hydrogen peroxide in glacial acetic acid until the yellow color of the starting material faded. On cooling there was isolated 50.5% of desired disulfone of I, m.p. 232°.

Anal. Calcd. for C₁₈H₁₂O₄S₂: C, 57.82; H, 3.61. Found: C, 57.63; H, 3.78.

The filtrates from the oxidation reaction were concentrated and finally diluted with water in order to isolate additional material. There was obtained only benzoic acid and sulfate ion (precipitated as barium sulfate).

Oxidation of I with Equimolar Hydrogen Peroxide.—Equimolar amounts of I and hydrogen peroxide were heated in glacial acetic acid for one hour and the reaction mixture was poured on ice. The precipitate was crystallized repeatedly from isopropyl alcohol to give yellow crystals, m.p. 128° (II).

Anal. Found: C, 76.12; H, 4.64; S, 19.20; mol. wt. (Rast), 510-560. The repetition of this experiment gave the same results. Found: C, 76.28; H, 4.90. Calcd. for C₃₂H₂₄S₃: C, 76.16; H, 4.79; S, 19.09; mol. wt., 502.7.

Quantitative Oxidation of II with Hydrogen Peroxide.—II, 0.1094 g., was heated with an excess of hydrogen peroxide in glacial acetic acid, and nitrogen was used to sweep any carbon dioxide produced in the reaction into a solution of barium hydroxide. The reaction mixture gave on cooling 0.0247 g. (34%) of the disulfone of I, m.p. 232°. The filtrate on concentration gave no additional disulfone and was diluted with water. The aqueous solution was extracted with ether and the ether layer was dried and concentrated. The residual liquid was placed in a desiccator containing sodium hydroxide pellets, and after several days *in vacuo* the residue became solid and there was isolated 0.0928 g. of benzoic acid. The aqueous portion from the extraction was boiled to expel carbon dioxide and then was treated with barium hydroxide to give 0.0507 g. of barium sulfate.

(5) All melting points are uncorrected. Microanalyses by Mr. George Stragand, University of Pittsburgh.

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Studies in Low Concentration Chemistry. IV. The Radiocolloidal Properties of Beryllium

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In 1950, Haymond, Garrison and Hamilton¹ noted the radiocolloidal behavior of beryllium when they found that they could separate carrier-free² beryllium-7 from lithium solutions by making such solutions basic and then filtering them through a glass frit. This paper constitutes a further investigation of the radiocolloidal properties of beryllium, using beryllium-7 as a tracer nuclide.

Experimental

Materials.—All inactive chemicals were of analytical reagent quality. All water was triply distilled and was pre-

(1) H. R. Haymond, W. M. Garrison and J. G. Hamilton, *J. Chem. Phys.*, **18**, 1685 (1950).

(2) The term carrier-free is used to indicate that no inert beryllium has been intentionally added.