

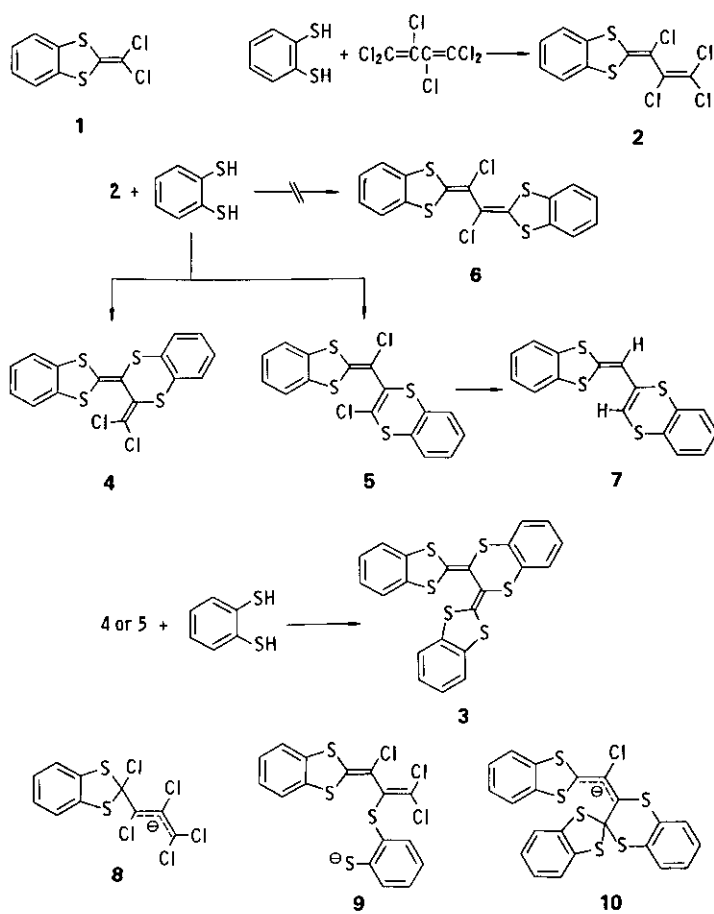
THE REACTION OF o-BENZENEDITHIOL WITH HEXACHLOROBUTADIENEMasao Mizuno and Michael P. Cava*Department of Chemistry, University of PennsylvaniaPhiladelphia, Pennsylvania 19104, U.S.A.

The reaction of o-benzenedithiol with hexachlorobutadiene in the presence of triethylamine affords four products, in ratios dependent upon the experimental conditions employed. These products are assigned the structures of the tetrachloride 2, the isomeric dichlorides 4 and 5, and the fully substituted benzodithiine 3. Dichloride 4 is resistant to zinc reduction, whereas its isomer 5 is reduced by zinc to the corresponding dithiine derivative 7.

In the course of studying the scope and mechanism of the Hurtley-Smiles tetrathiafulvalene synthesis, we recently reported a reinvestigation of the reaction of o-benzenedithiol with tetrachloroethylene, in which we found that the intermediate 2-dichloromethylene-4,5-benzo-1,3-dithiole (1) could be easily isolated.¹ We subsequently turned our attention to a study of the more complex reaction of o-benzenedithiol with hexachlorobutadiene, the results of which are reported here.

The reaction of o-benzenedithiol (2 equiv) with hexachlorobutadiene (1 equiv) in refluxing acetonitrile containing excess triethylamine afforded the expected tetrachloride 2 (20%), mp 64-65°, as well as a dichloride fraction (35%).² When the ratio of dithiol to hexachlorobutadiene was raised to 3:1, a comparable yield of dichloride fraction was isolated, but the yield of tetrachloride 2 dropped to 5-12% and a new product, the dithiine 3, mp 275-277°, was obtained in 20-26% yield.

The dichloride fraction could be separated by fractional crystallization and proved to be a 40:60 mixture of dichloride 4, mp 141-142°, and dichloride 5, mp 165-167°. Both the cmr spectrum of 4 (δ 126.9, 130.1, 131.4, 133.3, 134.7, 136.4, 138.0, 139.3, 141.3, 142.8) and of 5 (125.9, 129.9, 130.0, 132.2, 132.7, 138.7, 138.8, 139.5, 140.8) contained a sufficient number of signals



to rule out the more symmetrical structure 6. Both compounds reacted with *o*-benzenedithiol and triethylamine to give the fully substituted dithiine 3 in high yield.

Reduction of 5 with zinc and refluxing aqueous ethanol (15 hours) gave 73% of the corresponding reduced product 7, mp 167-168°. In accord with its unsymmetrical structure, the pmr structure of 7 showed, in addition to an aromatic envelope at δ 7.16-7.40 (8 H), two sharp and different olefinic protons at 6.22 and 6.40, respectively. Under similar reducing conditions, both the dichloromethylene isomer 4 and the model compound 1 were unreactive and were recovered unchanged.

Mechanistically, the formation of tetrachloride 2 is to be expected in view of the highly stabilized nature of the intermediate anion 8. Conversion of 2 to both dichlorides 4 and 5 is best explained by assuming the formation of the common intermediate anion 9. Finally, whereas the thiolation of 4 to 3 is unexceptional, the conversion of 5 to 3 requires ring opening of the original dithiine ring of 5 and formation of a new dithiine ring in 3; anion 10 is a proposed intermediate. The conversion of 5 to 3 has analogy in some previously reported transthioation reactions of 1,3-dithiole derivatives.¹

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REFERENCES AND NOTES

1. M. Mizuno and M. P. Cava, *J. Org. Chem.*, 1978, 43, 416.
2. Satisfactory elemental analyses and spectral data were obtained for all new compounds (2-5 and 7).

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