

**Reactions of
S,S'-[2,2'-Dithiobis(nitrophenyl)] Bis(N,N-dimethyl-
carbamothioates) with Hydroxide and Hydrosulfide
Anions. A Synthesis of Nitrobenzotriphioles**

Summary: Reactions of the title compounds with hydroxide and hydrosulfide anions in Me_2SO result in an initial cyclization to nitro-1,3-benzodithiol-2-ones followed by conversion of the latter to nitrobenezotetrathiocins and nitrobenzotriphioles.

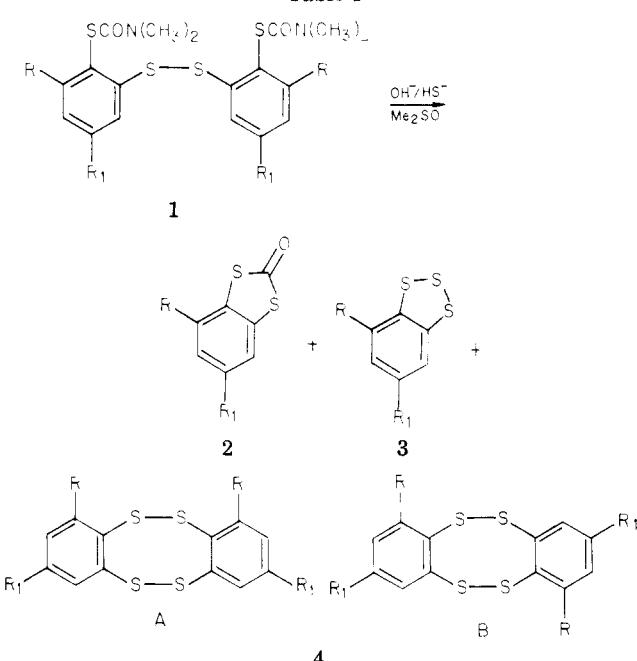
Sir: We have described the thermal cyclization of 2,6-dinitro- and 2,4-dinitrophenyl-*N,N*-dimethylthiocarbamates and shown that this reaction represents a general synthetic route to nitro-1,3-benzodithiol-2-ones.^{1,2} In some cases the title carbamothioates were also isolated. The relative amounts of these two products depend both on the nature of alkyl groups of the dithiocarbamate moiety as well as the nature and position of substituents on the benzene ring. The carbamothioates can in some instances become the major or even the sole products of these reactions.^{2,3}

Our continuing interest in these reactions has led us to examine the behavior of disulfides **1a-d** with hydroxide and hydrosulfide anions in Me_2SO . The results of this study are the subject of this communication. Table I summarizes the results obtained.

The products **2a-d** were identified by comparison with authentic materials already described.² The dibenzoc $[c,g]$ [1,2,5,6]tetrathiocin structure for **4a** was deduced from its elemental analysis and NMR (multiplet at 8.0 ppm in acetone- d_6) and mass spectra (*m/e* 506). A distinction between structures A and B for **4a** cannot be made at this time; an X-ray diffraction study is planned to resolve this point.

The most unexpected result of these reactions was the isolation of benzotriphioles **3a**, **3c**, and **3d**. These were isolated as colored (**3a** brick red, **3c** dark red, **3d** rust) crystalline materials, melting without decomposition. Their structural assignments are based on elemental analyses, NMR (CDCl_3) spectra [**3a**, 1 proton multiplets at 8.43 and 8.03 ppm; **3c**, 1 proton doublets at 8.1 and 7.7 ppm ($J = 2\text{H}_2$); **3d**, multiplet at 7.3-8.3 ppm], and mass spectra [**3a**, *m/e* 285 (96%), 237 (100%); **3c**, *m/e* 251 (82%), 203 (100%); **3d**, *m/e* 217 (85%), 169 (100%)]. The mass spectral data of all three benzotriphioles show the loss of 48 mass units, presumably SO , to give the base peaks. Similar effects of nitro groups have been observed in the mass spectra of ortho-substituted nitrobenzenes.⁴ As expected benzotriphiole **3a** was rapidly oxidized with peroxyacetic acid to benzotriphiole oxide **5** (80%). The reaction of **3a** with triethyl phosphite produced dibenzotetrathiocin **4a** (80%) and triethyl thiophosphate (60%), a result which is further confirmation for the benzotriphiole structure **3a** (eq 1).

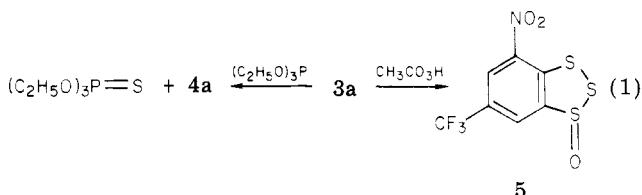
Table I



a, R = NO_2 , $\text{R}_1 = \text{CF}_3$; **b**, R = CF_3 , $\text{R}_1 = \text{NO}_2$;
c, R = NO_2 , $\text{R}_1 = \text{Cl}$; **d**, R = NO_2 , $\text{R}_1 = \text{H}$

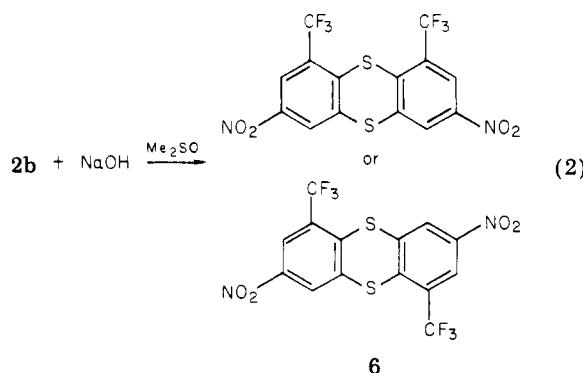
disulfide (1 mol)	nucleophile (moles)	products, % yield		
		2	3	4
1a	NaOH (2)	59	trace	ND
1a	NaOH (4)	12	trace	34
1b	NaOH (2)	74.5	ND ^a	ND
1a	NaSH (2)	50	10	ND
1b	NaSH (2)	72	ND	ND
1c	NaSH (2)	66	14	ND
1d	NaSH (2)	48	31	ND

^a ND = not detected.



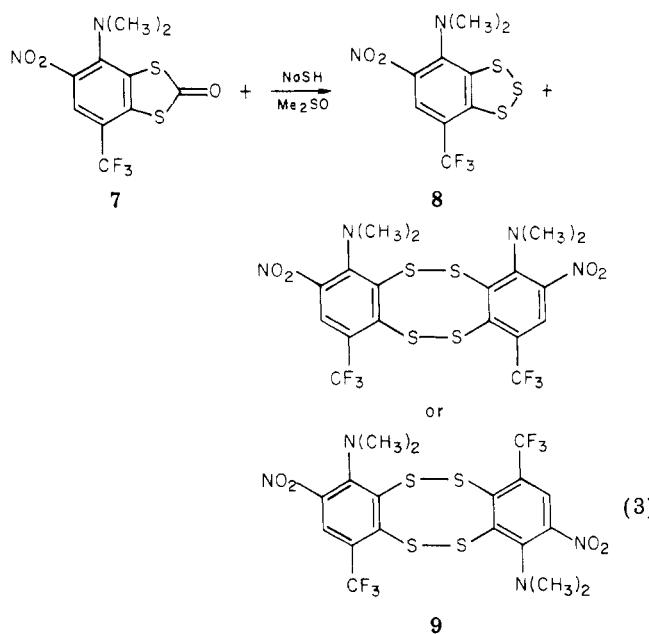
We have evidence that the conversions of disulfides **1a-d** to products shown in Table I take the course: disulfide \rightarrow 1,3-benzodithiol-2-one \rightarrow dibenzotetrathiocin \rightarrow benzotriphiole. For example, reaction of 1,3-benzodithiol-2-one **2a** with 1 equiv of NaSH in Me_2SO at room temperature yielded dibenzotetrathiocin **4a** in 50% yield whereas the use of 5 equiv of NaSH with **4a** gave **3a** in 77% yield. It is also possible to convert 1,3-benzodithiol-2-one **2a** directly to **3a** in 80% yield, using 5 equiv of NaSH. This constitutes a simple high-yield synthesis of benzotriphiole **3a**. Although we have not confirmed this sequence of reactions with respect to disulfides **1c** and **1d**, we feel that the same sequence of reactions is operative in these cases. Disulfide **1b**, isomeric with disulfide **1a**, is unique in that the formation of the corresponding benzotriphiole was not observed. In contrast 1,3-benzodithiol-2-one **2b** on reaction with 1 molar equiv of NaOH in Me_2SO yielded the thianthrene **6** (16%),⁶ mp 166-167 °C [NMR (acetone- d_6), doublets at 8.39 and 8.18 ppm; *m/e* 442] (eq 2). This

(6) For the synthesis of an isomeric thianthrene, see J. J. D'Amico et al., *J. Org. Chem.*, **42**, 2896 (1977).



constitutes further evidence that dibenzotetrathiocins are intermediates in the formation of benzotrichioles **3a**, **3c**, and **3d**. The stereochemistry of **6** remains to be established.

Although the presence of a nitro group in the starting material appears to be a requirement for the 1,3-benzodithiol-2-one \rightarrow benzotrichiole conversion, the presence of other, even electron-donating, substituents results in the formation of the corresponding benzotrichiole. For example, **7**² was converted to benzotrichiole **8** (45%) and dibenzotetrathiocin **9** (13%) (eq 3).



The series of conversions described represent useful synthetic routes to the benzotrichiole and dibenzotetrathiocin ring systems. The isolation of benzotrichioles **3a**, **3c**, **3d**, and **8**, in particular, represents the first unequivocal synthesis of this ring system. The only other report known to us is that of Fehér and co-workers who obtained 5,6-dimethylbenzotrichiole from the reaction of dimercapto-*o*-xylene with sulfur dichloride.⁷ The product isolated was reported to be impure and unstable and the structure of the product was deduced from its mass spectrum. Fields has reported the synthesis of a number of benzotrichioles by the reaction of halobenzenes with sulfur and sulfuric acid, based on mass spectra of product mixtures; pure compounds were not isolated.⁸ The synthesis of the related 5-methylbenzotrichiole oxide from the reaction of 4-methyl-*o*-phenylenedithiole with thionyl chloride has

been described by Steinle and Schmidt.⁹

The synthesis and reactions of other benzotrichioles as well as the mechanism of these reactions are currently being investigated.

4-Nitro-6-(trifluoromethyl)benzotrichiole (3a). To a stirred and tap-water cooled solution of 28.1 g (0.1 mol) of 4-nitro-6-(trifluoromethyl)-1,3-benzodithiol-2-one (**2a**)¹² in Me₂SO (200 mL) under nitrogen was added 44.5 g (0.5 mol) of NaSH as a powder. After the dark red mixture was allowed to stir (12 h) it was poured into water (600 mL) and acidified with 1 N HCl (hood, H₂S evolution). The mixture was extracted with CH₂Cl₂ (3 \times 100 mL) and the organic extract washed with water (3 \times 500 mL) and dried (Na₂SO₄). The solvent was distilled to dryness in vacuo and the red crystalline residue was triturated with ethanol and suction filtered to yield 23 g (80.7%) of **3a**, mp 107–109 °C. Recrystallization of crude **3a** from ethanol gave analytically pure material as a brick red solid: mp 110–111 °C; NMR (CDCl₃) δ 8.43 (m, 1 H), 8.03 (m, 1 H); mass spectrum, *m/e* 285. Anal. Calcd for C₇H₂F₃NO₂S₃: C, 29.47; H, 0.70; N, 4.91; S, 33.68. Found: C, 29.40; H, 0.75; N, 4.72; S, 33.76.

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Registry No. **1a**, 59983-45-8; **1b**, 68151-94-0; **1c**, 68151-95-1; **1d**, 68200-48-6; **2a**, 62558-16-1; **2b**, 62558-22-9; **2c**, 63417-83-4; **2d**, 62558-20-7; **3a**, 70001-71-7; **3c**, 70001-71-7; **3d**, 70001-75-1; **4a**, 75083-33-9; **5**, 75101-74-5; **6**, 75101-70-1; **7**, 62558-23-0; **8**, 70001-74-0; **9**, 75083-34-0.

(9) K. Steinle and M. Schmidt, *Z. Naturforsch.*, **B**, 28, 686 (1973). See also L. Field and W. B. Lacefield, *J. Org. Chem.*, **31**, 3555 (1966).

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Carbon-13 and Oxygen-17 Nuclear Magnetic Resonance Studies of Organosulfur Compounds: The Four-Membered-Ring Sulfone Effect

Summary: As revealed by carbon-13 and oxygen-17 NMR spectroscopy, thietane 1,1-dioxides and related four-membered-ring sulfonyl compounds show unusual α -carbon and sulfonyl oxygen deshielding and β -carbon shielding when compared to other thiacycloalkane 1,1-dioxides and acyclic counterparts.

Sir: We report that 1,1-dioxides of thietanes, 1,2-dithietanes, and 1,3-dithietanes and a sulfoximide derived from a thietane display carbon-13 chemical shifts which are notably at variance with the bulk of the published chemical shift data on other organosulfur compounds and that this NMR effect is apparently uniquely associated with sulfur-containing four-membered rings. We also report the first oxygen-17 chemical shift data for sulfoxides (other than dimethyl sulfoxide)¹ and sulfones, note that the oxygen-17 shifts for a homologous series of thiacycloalkane 1-oxides and 1,1-dioxides also exhibit an anomaly for the four-membered rings, and point out that discrete oxy-

(7) F. Fehér, M. Langer, and R. Volkert, *Z. Naturforsch.*, **B**, 27, 1006 (1972).

(8) E. K. Fields, U. S. Patent 3 491 119 (to Standard Oil Company, Chicago), Jan 20, 1970.

(1) H. A. Crist, P. Diehl, H. R. Schneider, and H. Dahn, *Helv. Chim. Acta*, **44**, 865 (1961). Also see: W. G. Klemperer, *Angew. Chem., Int. Ed. Engl.*, **17**, 246 (1978); T. St. Armour and D. Fiat, *Bull. Magn. Reson.*, **1**, 118 (1980).