

Communications

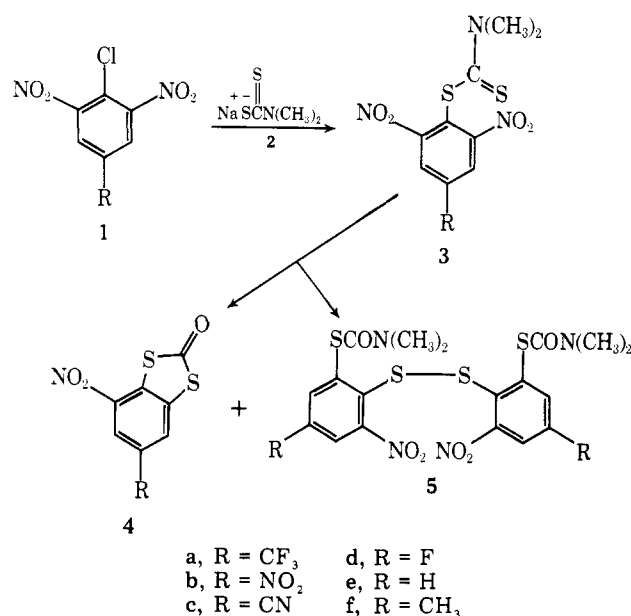
The Thermal Cyclization of Dinitrophenyl *N,N*-Dimethyldithiocarbamates. A Novel Synthesis of 1,3-Benzodithiol-2-ones¹

Summary: The title compounds, in particular those possessing additional electron-withdrawing substituents on the benzene ring, undergo intramolecular cyclizations involving displacement of a nitro group. The major products of this reaction are substituted 1,3-benzodithiol-2-ones.

Sir: A series of reports²⁻⁴ by D'Amico and co-workers on the reactions of 4-chloro-3,5-dinitrobenzotrifluoride (**1a**) and salts of dialkyldithiocarbamic acids prompt us to describe our work on the reactions of **1a** and other dinitrohalobenzenes **1** with the sodium salt of dimethyldithiocarbamic acid (**2**). For example, addition of **2** to a solution of **1a** in Me₂SO at room temperature produced the carbamate **3a** which undergoes an intramolecular displacement of the nitro group as evidenced by evolution of nitrogen oxides. Two products, 4-nitro-6-trifluoromethyl-1,3-benzodithiol-2-one (**4a**) and the disulfide **5a** were isolated in yields of 43 and 40%, respectively (Scheme I). Essentially the same results were obtained using acetone or DMF as solvent. The structures of **4a** and **5a** are based on elemental analyses, mass spectral data, and NMR spectra. The reactions of a variety of substituted dinitrohalobenzenes with **2**, followed by thermal decomposition of the carbamates thus formed yielded in all cases the corresponding 1,3-benzodithiol-2-ones **4a-f**; in a few instances the corresponding disulfides were also isolated (Table I).

In contrast to **3a** which begins to cyclize at room temperature the isomeric carbamate **6**, obtained by reacting 2-chloro-3,5-dinitrobenzotrifluoride and **2** in DMF, is more stable. Heating a solution of **6** in DMF to 75 °C results in evolution of nitrogen oxides and formation of the 1,3-benzodithiol-2-one **7** (11%) and the disulfide **8** (54%) (Scheme II). The presence of a dialkylamino substituent ortho to both nitro groups, as in **9**, has a profound effect on the cyclization. Very good yields of the corresponding 1,3-benzodithiol-2-ones were readily obtained. For example, **9a** on refluxing in acetone furnishes **10a** in 77% yield (Scheme III).

Scheme I



Scheme II

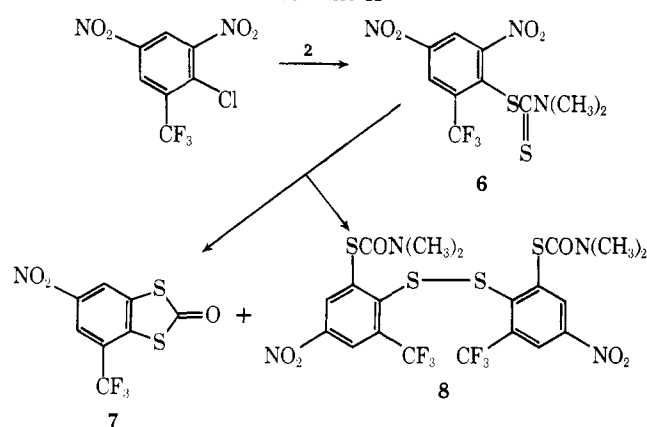
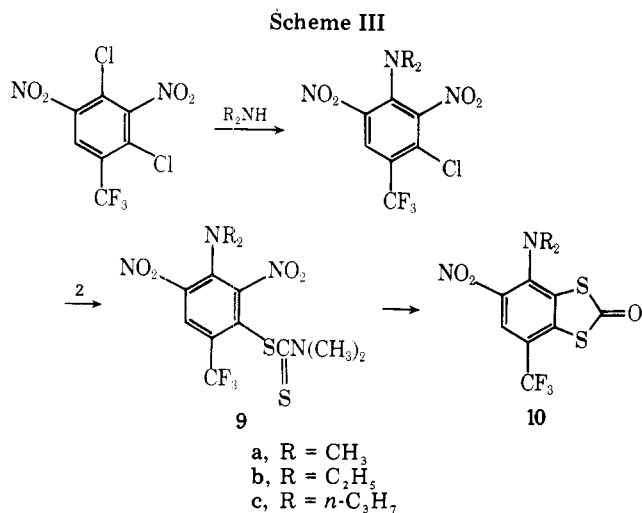


Table I. Products of Decomposition of Dinitrophenyl *N,N*-Dimethyldithiocarbamates

| No | Dithiocarbamates ^a Substituents | Procedure | | | Products, ^b % yield (mp, °C) | |
|-----------|-----------------------------------------------------------------------------------------------------------------------|-----------|-----|--------------------|-----------------------------------------|--------------------------|
| | | °C | h | Solvent | 1,3-Benzodithiol-2-one | Disulfide |
| 3a | 2,6-(NO ₂) ₂ , 4-CF ₃ | 25 | 3 | Me ₂ SO | 4a , 43 (111-112) | 5a , 40 (222-224) |
| 3b | 2,6-(NO ₂) ₂ , 4-NO ₂ | 25 | 16 | Acetone | 4b , 35 (129-131) | |
| 3c | 2,6-(NO ₂) ₂ , 4-CN | 25 | 16 | Acetone | 4c , 46 (177-178) | |
| | | 56 | 2 | | | |
| 3d | 2,6-(NO ₂) ₂ , 4-F | 90-100 | 2.5 | Me ₂ SO | 4d , 37 (98-100) | 5d , 12 (192-195) |
| 3e | 2,6-(NO ₂) ₂ , 4-H | 90-100 | 18 | Me ₂ SO | 4e , 43 (110-111) | 5e , 16 (201-202) |
| 3f | 2,6-(NO ₂) ₂ , 4-CH ₃ | 90-100 | 3 | Me ₂ SO | 4f , 26 (163-164) | |
| 6 | 2,4-(NO ₂) ₂ , 6-CF ₃ | 75 | 1.5 | DMF | 7 , 11 (117-118) | 8 , 53 (222-224) |
| 9a | 2,4-(NO ₂) ₂ , 6-CF ₃ , 3-N(CH ₃) ₂ | 56 | 16 | Acetone | 10a , 77 (106-107) | |
| 9b | 2,4-(NO ₂) ₂ , 6-CF ₃ , 3-N(C ₂ H ₅) ₂ | 56 | 16 | Acetone | 10b , 76 (58-60) | |
| 9c | 2,4-(NO ₂) ₂ , 6-CF ₃ , 3-N(<i>n</i> -C ₃ H ₇) ₂ | 56 | 16 | Acetone | 10c , 80 (60-61) | |

^a In general the dithiocarbamates were generated in solution and except for **3f** and **6** were not isolated. ^b All products were isolated by column chromatography of crude mixtures on silica gel, eluting with hexane (**10a**, **10b**, **10c**), 50% hexane in benzene (**4b**, **4c**, **4d**, **4e**, **7**), and chloroform (**4f**, **5a**, **5d**, **5e**, **8**). Satisfactory elemental analyses and NMR spectra were obtained for all compounds; in addition mass spectral data obtained for **4a**, **5a**, and **8** confirmed the structures assigned to them.

Scheme III



The thermal cyclizations of dinitrophenyl *N,N*-dimethylthiocarbamates are greatly facilitated by the presence of additional electron-withdrawing substituents and by the presence of nitro groups ortho to the dialkyldithiocarbamate functionality. Thus, 2,4-dinitrophenyl *N,N*-dimethylthiocarbamate had to be heated to 130 °C before evolution of nitrogen oxides could be detected and yielded 5-nitro-1,3-benzodithiol-2-one in only 5% yield.

Previous synthetic routes to 1,3-benzodithiol-2-ones^{5,6} have started with phenylene ortho dithiols which are available only via a difficult multistep synthesis. The novel cyclizations that we have described represents a facile synthetic route to a variety of substituted 1,3-benzodithiol-2-ones using readily available starting materials.

D'Amico, Tung, and Dahl¹ originally reported that the reaction of **1a** with **2** yielded 6,6'-thiobis(5-nitro-3-trifluoromethylphenyl) dimethylthiocarbamate. This structural assignment was subsequently revised^{2,3} and is now in agreement with structure **5a** proposed by us. However these workers did not report the 1,3-benzodithiol-2-one **4a**, which is one of the major products of this reaction.⁷

The mechanism of these cyclizations and other related work will be the subject of future communications.

General Procedure. To a stirred and cooled solution of 16.2 g (60 mmol) of **1a**⁸ in Me₂SO (60 mL) was added dropwise a solution of 10.74 g (60 mmol) of **2**⁹ in Me₂SO (60 mL) at a rate so as to maintain the temperature of the reaction mixture below 20 °C. The reaction is exothermic and accompanied by evolution of nitrogen oxides. After stirring (3 h) at room temperature, water (450 mL) was added and the mixture was extracted with CHCl₃ (3 × 150 mL). The combined CHCl₃ extracts were washed with water (3 × 50 mL), dried (Na₂SO₄), and concentrated in vacuo. The residue was chromatographed over silica gel (180 g). Elution with benzene gave 7.3 g of **4a** (43%), mp 104–107 °C. Recrystallization from EtOH yielded **4a**: mp 111–112 °C; NMR (CDCl₃) δ 8.60 (m, 1 H), 8.16 (m, 1 H); mass spectrum *m/e* 281. Anal. Calcd for C₈H₂F₃NO₃S₂: C, 34.16; H, 0.71; N, 4.98; S, 22.77. Found: C, 33.91; H, 0.90; N, 4.94; S, 22.55. Elution with CHCl₃ yielded 8.0 g (40%) of **5a**: mp 222–224 °C;¹⁰ NMR (CDCl₃) δ 8.35 (m, 2 H), 8.07 (m, 2 H), 3.24 (s, 12 H); mass spectrum *m/e* 650. Anal. Calcd for C₂₀H₁₆F₆N₄O₆S₄: C, 36.92; H, 2.46; N, 8.59. Found: C, 36.77; H, 2.56; N, 8.52.

References and Notes

- (1) Patent applications have been filed on these compounds.
- (2) J. J. D'Amico, C. C. Tung, and W. E. Dahl, Abstracts of Papers, First Chemical Congress of the North American Continent, Mexico City, Mexico, Nov 30–Dec 5, 1975, Organic Section, paper no. 39.
- (3) J. J. D'Amico, C. C. Tung, and W. E. Dahl, Abstracts of Papers, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 29–Sept 3, 1976, Organic Section, paper no. 235.
- (4) J. J. D'Amico, C. C. Tung, W. E. Dahl, and D. J. Dahm, *J. Org. Chem.*, **41**, 3564 (1976).
- (5) W. R. H. Hurttley and S. Smiles, *J. Chem. Soc.*, 1820 (1926).
- (6) S. Huenig and E. Fleckenstein, *Justus Liebig's Ann. Chem.*, **738**, 192 (1970).
- (7) Dr. D'Amico, who was one of the reviewers, ran the reaction of **1a** with **2** in Me₂SO and isolated **4** in 4.15% yield. The failure of D'Amico and co-workers to isolate **4** in their work⁴ is to be attributed to washing their crude product with ethyl ether, in which solvent **4** is very soluble, and discarding the ethyl ether wash.
- (8) Commercially available from Peninsular ChemResearch, Gainesville, Fla.
- (9) Commercially available from Aldrich Chemical Co., Milwaukee, Wis.
- (10) D'Amico and co-workers⁴ report a melting point of 242–243 °C for this product. Under our conditions, in an open capillary and using a Thomas-Hoover melting point apparatus, their sample melted at 225–227 °C. The higher value reported by D'Amico and co-workers was determined on a Fisher-Johns block. The identity of this material with **5a** isolated by us was confirmed by a mixture melting point. We thank Dr. D'Amico for supplying us with their sample of **5a**.

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