Cyclization of Dinitrophenyl *tert*-Butyl Trithiocarbonates. A Novel Synthesis of Nitro-1,3-benzodithiole-2-thiones

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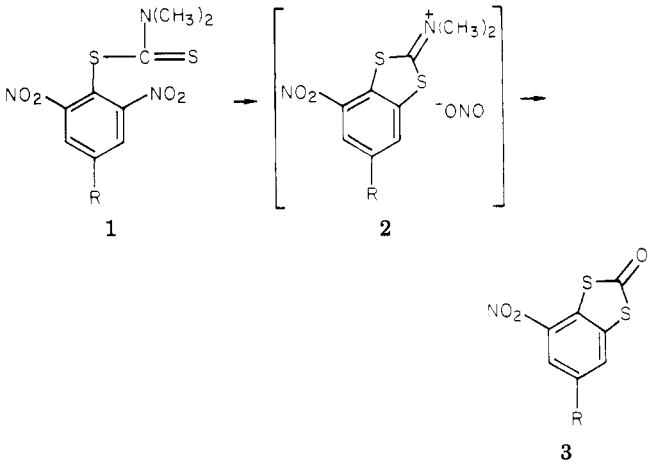
Reaction of the sodium salt of *tert*-butyl trithiocarbonic acid with chlorodinitrobenzenes yields dinitrophenyl *tert*-butyl trithiocarbonates. The latter cyclize on heating in glacial acetic acid to nitro-1,3-benzodithiole-2-thiones.

During the course of work relating to the synthesis of heterocyclic systems we required a method for the synthesis of nitro-1,3-benzodithiole-2-thiones and their derivatives. Although 1,3-benzodithiole-2-thiones and some of their derivatives are available,[1] the nitro derivatives have not been described;[2] this is due mainly to the sensitivity of the 1,3-dithiole-2-thione functionality to oxidative degradation under normal nitration conditions. For example, whereas 1,3-benzodithiol-2-one can be readily nitrated to its 5-nitro derivative (70%)[3] the nitration of 1,3-benzodithiole-2-thione in our hands resulted in a very complex reaction mixture. The reaction of alicyclic 1,3-dithiol-2-ones with potassium ethyl xanthate has been shown to produce the corresponding 1,3-dithiole-2-thiones in good yields.[4] Our attempts at applying this method to convert, for example, 4-nitro-6-(trifluoromethyl)-1,3-benzodithiol-2-one to 4-nitro-6-(trifluoromethyl)-1,3-benzodithiole-2-thione were unsuccessful.

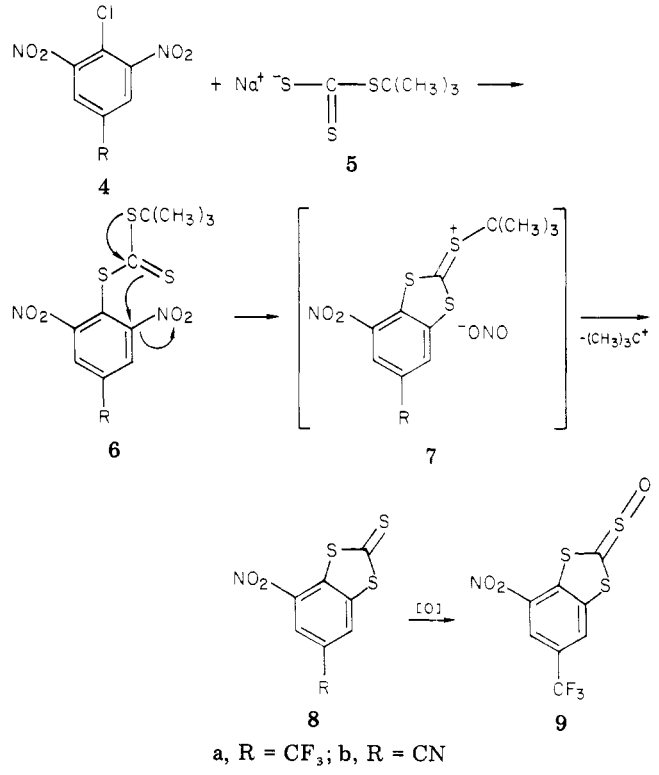
An alternative approach to nitro-1,3-benzodithiole-2-thiones is based on our earlier work on the cyclization of dinitrophenyl *N,N*-dimethyldithiocarbamates.[5,6] This procedure represents a general synthesis of nitro-1,3-benzodithiol-2-ones (Scheme I). It was pointed out[6] that the intramolecular displacements of nitro groups from dithiocarbamates such as 1 proceed through the nitrite salt **2** as an intermediate to produce **3** as the final product. On the basis of these observations we began to investigate whether the sequence of reactions represented in Scheme I could be modified so as to generate a nitro-1,3-benzodithiole-2-thione as the final product. Scheme II shows the planned synthetic route. We had reason to expect that, in analogy with reactions of Scheme II, *tert*-butyl trithiocarbonates such as **6** would cyclize to the nitrite salt **7**. The latter could be expected to lose *tert*-butyl cation, hopefully before attack by nitrite ion could occur, to yield the desired nitro-1,3-benzodithiole-2-thiones **8**. As expected, the reaction of *n*-butyl trithiocarbonates resulted in the isolation of products derived from attack of nitrite (vide infra).

The sodium salt of *tert*-butyl trithiocarbonic acid (**5**) required for the synthesis of trithiocarbonates **6** has not been previously described but is easily prepared as a nicely crystalline solid by reaction of *tert*-butyl mercaptan with sodium hydroxide and CS_2.

Scheme I



Scheme II



a, R = CF_3; b, R = CN

Reaction of the chlorodinitrobenzenes **4a** and **4b** with **5** in acetone at room temperature did not result in the isolation of the expected trithiocarbonates **6a** and **6b**. We were pleased to find that most of the product consisted of the 1,3-benzodithiole-2-thiones **8a** and **8b** contaminated with smaller amounts of trithiocarbonates **6a** and **6b** (NMR spectra). Reaction was completed by heating the crude reaction mixtures in glacial acetic acid at 70–80 °C

(1) R. Huisgen and V. Weberndoerfer, *Experientia*, **17**, 566 (1961). S. Huenig and E. Fleckenstein, *Justus Liebigs Ann. Chem.*, **738**, 192 (1970). For a heterocyclic example, see S. Gronowitz and P. Moses, *Acta Chem. Scand.*, **16**, 105 (1962).

(2) A *Chemical Abstracts* search did not uncover any nitro-1,3-benzodithiole-2-thiones. H. Hagen and H. Fleig [(BASF A.-G.) Ger. Offen. 2460783] describe the synthesis of the related 5-nitro-1,2-benzodithiole-3-thione via reaction of 2-halo-5-nitrobenzyl halides with sulfur.

(3) W. R. H. Hurtley and S. Smiles, *J. Chem. Soc.*, 1821 (1926). For proof of structure see ref 6.

(4) N. G. Kardouche and L. N. Owen, *J. Chem. Soc., Perkin Trans. 1*, 754 (1975).

(5) K. Rasheed and J. D. Warkentin, *J. Org. Chem.*, **42**, 1265 (1977).

(6) K. Rasheed and J. D. Warkentin, *J. Org. Chem.*, **44**, 267 (1979).

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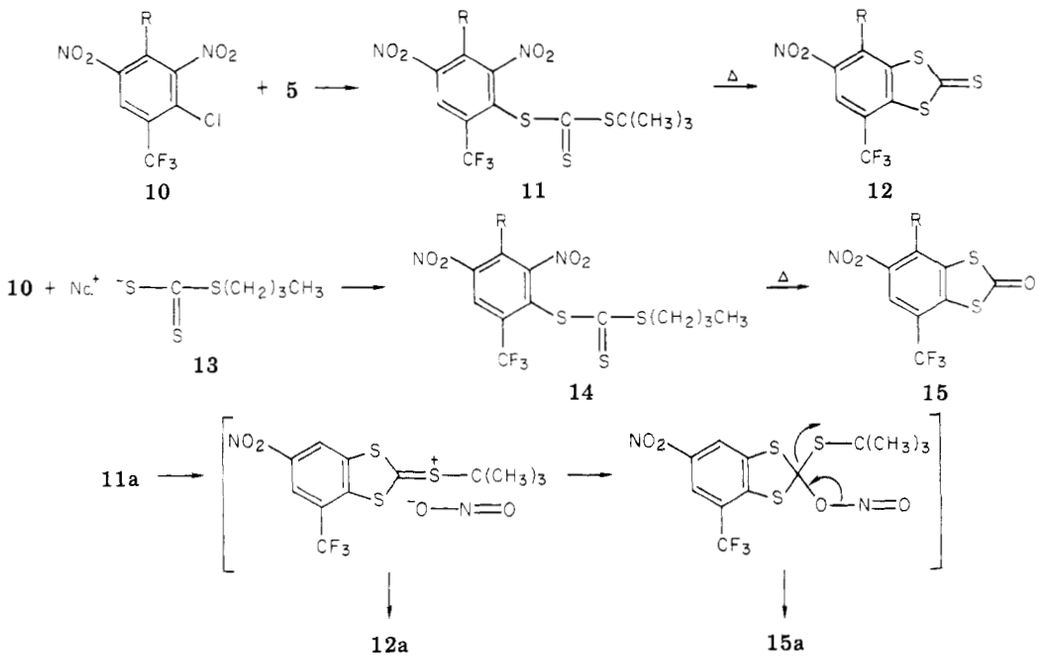
Scheme III



a, R = H; b, R = $N(CH_3)_2$; c, R = $NHCH_2CH_2CH_3$

for 1 h. This produced **8a** and **8b** in yields of 38% and 32%, respectively. The structure assignment for **8a** is based on its mass spectrum, NMR spectrum, elemental analysis and conversion to the thione oxide **9** on reaction with peracetic acid, a reaction characteristic of 1,3-dithiole-2-thiones.[7] The successful realization of this synthetic route (Scheme II) represents a novel and simple synthesis of nitro-1,3-benzodithiole-2-thiones from readily available starting materials.

Further examples of the application of this reaction include the reaction of **5** with chlorodinitrobenzenes **10a–c** (Scheme III). In these instances the intermediate trithiocarbonates can be isolated as stable crystalline solids; however, attempts at recrystallization should be avoided since at temperatures above 70 °C significant decomposition was observed. On refluxing **11c** in glacial acetic acid, **12c** was produced in 38% yield. Also isolated was *tert*-butyl acetate in 40% yield, indicating the intermediate formation of *tert*-butyl cation. Cyclization of **11c** in Me_2SO gave **12c** in 42% yield. The formation of isobutylene (64%) was demonstrated by trapping it as isobutylene dibromide. Heating solutions of **11a** and **11b** in glacial acetic acid also produced the 1,3-benzodithiole-2-thiones **12a** (42%) and **12b** (45%).

We have evidence that the presence of the *tert*-butyl group in these intramolecular cyclizations is essential to the success of this reaction. Attempts at cyclizations of the isomeric *n*-butyl trithiocarbonates **14a** and **14b** by heating in glacial acetic acid or Me_2SO resulted in the isolation of 1,3-benzodithiol-2-ones **15a** (33%) and **15b** (31%). The presence in these mixtures of the corresponding 1,3-benzodithiole-2-thiones could not be detected (TLC). Similarly, decomposition of **14a** in Me_2SO also gave **15a** in 28% yield (Scheme III). The structures of **15a** and **15b** were confirmed by comparison with authentic materials[6] (mixture melting point, TLC, NMR).

The isolation of **15a** and **15b** in the cyclizations of *n*-butyl trithiocarbonates **14a** and **14b** led us to reexamine the cyclization of the *tert*-butyl trithiocarbonate **11a** in glacial acetic acid. For purposes of comparison this cyclization was also studied in Me_2SO and DMF. These reactions were carried out in order to ascertain whether the decomposition of *tert*-butyl trithiocarbonates also resulted in the formation of some nitro-1,3-benzodithiol-2-ones, a reaction which might have been overlooked in our earlier decompositions owing to our method of workup which involved recrystallization of crude product mixtures. Crude reaction mixtures obtained from the decomposition of **11a** in DMF and Me_2SO were judged by TLC to contain small amounts of 6-nitro-4-(trifluoromethyl)-1,3-benzodithiole-2-thione (**12a**) and 6-nitro-4-(trifluoromethyl)-1,3-benzodithiol-2-one (**15a**). These mixtures were chromatographed over silica gel and **12a** and **15a** eluted quantitatively from the column. The two fractions were analyzed by gas-liquid chromatography. The reaction mixture obtained from the decomposition of **11a** in glacial acetic acid was found to contain fewer impurities and was therefore analyzed directly for **12a** and **15a**. Table I shows the results obtained. It is interesting that **15a** was formed in three solvents used; in DMF and Me_2SO it was the major product. Also significant are the poor yields observed in Me_2SO and DMF, although the decompositions of **11c** in acetic acid and in Me_2SO produced comparable yields (40–45%) of thione **12c**. These results suggest that the reaction sequence is not as straightforward as depicted in Scheme II but that the intermediate nitrite salt **7** undergoes varying degrees of attack by nitrite ion (Scheme III). Expectedly this attack becomes predominant when the leaving group is the less stable *n*-butyl cation. In Me_2SO and DMF the attack of nitrite ion can become predominant even when the leaving group is the *tert*-butyl

Table I. Decomposition of 2,4-Dinitro-6-(trifluoromethyl)phenyl *tert*-Butyl Trithiocarbonate (11a)

	products, % yield	
solvent	12a	15a
CH_3CO_2H	54	13
DMF	7.7	16.6
Me_2SO	4.2	8.8

(7) E. Klingsberg, *J. Am. Chem. Soc.*, 86, 5290 (1964).

cation. We have no explanation for the poor yields of products observed in DMF and Me_2SO (Table I). This synthetic procedure becomes practical, however, when the decompositions are carried out in glacial acetic acid where the nitrite is presumably well-solvated or protonated to the less nucleophilic nitrous acid.

The cyclizations of dinitrophenyl *tert*-butyl trithiocarbonates in glacial acetic acid represent a useful synthetic route to nitro-1,3-benzodithiole-2-thiones. Although small amounts of nitro-1,3-benzodithiol-2-ones are formed, the nitro-1,3-benzodithiole-2-thiones are generally obtained pure on recrystallization. The decomposition of 2-nitrophenyl *tert*-butyl trithiocarbonate was also investigated and gave only complex reaction mixtures which were not further investigated.

Experimental Section[8]

Sodium Salt of *tert*-Butyl Trithiocarbonic Acid (5). To a mechanically stirred and cooled (ice bath) solution of 90 g (1.0 mol) of *tert*-butyl mercaptan in THF (1 L) was added dropwise 80 g (1.0 mol) of 50% aqueous sodium hydroxide. To the thick slurry formed was added dropwise 76 g (1.0 mol) of carbon disulfide, keeping the temperature of the reaction mixture at 5–10 °C. Stirring was continued until a clear orange-yellow solution was obtained which was filtered and added dropwise to mechanically stirred hexane (2 L). The precipitated crystalline solid was suction filtered and dried in a vacuum desiccator over calcium chloride (24 h). **5** (183 g) was obtained which was assayed to be approximately 85% material (70%); NMR (acetone-d_6) δ 2.95 (H_2O), 1.13 (s). The material was assayed by dissolving a weighed amount (~3.5 g) in water (~100 mL), allowing it to stir (2 h) with an excess of 1 N HCl (stench, hood), and back titrating excess acid with 0.5 N sodium hydroxide to pH 7.

Sodium Salt of *n*-Butyl Trithiocarbonic Acid (13). This was prepared by using the procedure described for **5** except that after filtration of the THF solution most of the solvent was removed on a rotary evaporator in vacuo at 45 °C. The resulting viscous residue was stirred with hexane (500 mL for a 0.5-mol run) and the resulting crystalline solid was suction filtered and dried over calcium chloride in a vacuum desiccator. There was obtained 63.7 g of solid which assayed for 75% **13** (50%); NMR (acetone-d_6) δ 3.18 (H_2O), 2.70 (t, 2 H), 1.10 (m, 4 H), 0.50 (t, 3 H).

4-Nitro-6-(trifluoromethyl)-1,3-benzodithiole-2-thione (8a). To a stirred and cooled (ice–salt bath) solution of 13.6 g (50 mmol) of 2-chloro-1,3-dinitro-5-(trifluoromethyl)benzene (**4a**) in acetone (100 mL) was added dropwise a filtered solution of 12.7 g (52 mmol) of **5** in acetone (80 mL). The temperature of the reaction mixture during addition of **5** was not allowed to exceed 0 °C. After being stirred at 0–5 °C (2 h), the mixture was stirred at room temperature overnight, the solvent was distilled in vacuo, and the residue was extracted with methylene chloride. The extract was washed with water (3 × 200 mL) and dried (Na_2SO_4) and the solvent was removed in vacuo. The residual oil crystallized and was triturated with cold ethanol and suction filtered. This solid was added to glacial acetic acid (100 mL) and heated to 80–85 °C (1 h). After the mixture stood at room temperature the crystalline solid obtained was filtered, washed with water, and dried in a vacuum desiccator over $CaCl_2$. This yielded 4.8 g of **8a**, mp 166–168 °C. The acetic acid filtrate was poured into water and extracted with methylene chloride, and after the solution was washed with water and dried, the solvent was distilled to dryness. The residual solid was recrystallized from glacial acetic acid to yield an additional 0.8 g of **8a**, mp 165–167 °C. This gave an overall yield of 5.6 g of **8a** (38%): NMR ($CDCl_3$) δ 8.73 (m, 1 H), 8.13 (m, 1 H); mass spectrum, *m/e* 297. Anal. Calcd for $C_8H_2F_3NO_2S_3$: C, 32.32; H, 0.67; N, 4.71; S, 32.32. Found: C, 32.18; H, 0.74; S, 32.21.

6-Cyano-4-nitro-1,3-benzodithiole-2-thione (8) was prepared as described for **8a** by adding a solution of 49.2 g (0.22 mol) of **5** in acetone (320 mL) to a solution of 47.5 g (0.21 mol) of 4-chloro-3,5-dinitrobenzonitrile in acetone (210 mL). Acetone was distilled to dryness in vacuo and the residue heated in glacial acetic acid (200 mL) at 100 °C (1 h). The cooled reaction mixture was poured into water (2 L) and the precipitated solids were suction filtered and purified by dissolving in hot acetone (2.2 L) and concentrating the acetone solution to 1.5 L. After the mixture stood overnight, 17 g (32%) of **8b**, mp 232–233 °C, was obtained; NMR (Me_2SO-d_6) δ 9.05 (d, 1 H), 8.85 (d, 1 H, J = 2 Hz). Anal. Calcd for $C_8H_2N_2O_2S_3$: C, 37.80; H, 0.79; S, 37.80. Found: C, 37.88; H, 0.85; S, 37.93.

4-Nitro-6-(trifluoromethyl)-1,3-benzodithiole-2-thione *S*-Oxide (9). To a stirred solution of 0.89 g (3 mmol) of 1,3-benzodithiole-2-thione **8a** in chloroform at 10 °C (ice–water bath) was added dropwise a solution of 0.63 g (3.3 mmol) of 40% peracetic acid. The mixture was stirred at room temperature (15 min), chloroform (25 mL) was added, the solution was washed with water (2 × 150 mL) and dried (Na_2SO_4), and the solvent was removed in vacuo. The residual solid on recrystallization from ethanol yielded 0.6 g (65%) of **9**, mp 166–168 °C dec. A mixture melting point with starting material gave a depression of melting point; NMR (Me_2SO-d_6) δ 8.70 (m, 1 H), 8.45 (m, 1 H). Anal. Calcd for $C_8H_2F_3NO_3S_3$: C, 30.67; H, 0.64; S, 30.67. Found: C, 30.89; H, 0.77; S, 30.86.

***tert*-Butyl 2,4-dinitro-6-(trifluoromethyl)phenyl trithiocarbonate (11a)** was prepared as described for **11c**, using 20 g (74 mmol) of 2-chloro-3,5-dinitro(trifluoromethyl)benzene (**10a**) and 19.0 g (78 mmol) of **5** in acetone. The crude product was triturated with cold ethanol, suction filtered, and air-dried to yield 24 g (81%) of **11a**: mp 86–88 °C; NMR ($CDCl_3$) δ 8.98 (s, 2 H), 1.66 (s, 9 H).

***tert*-Butyl 2,4-dinitro-3-(dimethylamino)-6-(trifluoromethyl)phenyl trithiocarbonate (11b)** was prepared as described for **11c**, using 13.9 g (44 mmol) of 2-chloro-4-(dimethylamino)-3,5-dinitro(trifluoromethyl)benzene (**10b**) and 10.3 g (46 mmol) of **5** in acetone. This yielded 14.1 g (72%) of **11b**: mp 108–109 °C dec; NMR (acetone-d_6) δ 8.10 (s, 1 H), 2.50 (s, 6 H), 1.20 (s, 9 H).

***tert*-Butyl 2,4-Dinitro-3-(*n*-propylamino)-6-(trifluoromethyl)phenyl Trithiocarbonate (11c).** To a stirred and cooled (ice bath) solution of 27.0 g (82 mmol) of 2-chloro-4-(n-propylamino)-3,5-dinitro(trifluoromethyl)benzene (**10c**) in acetone (125 mL) was added dropwise a filtered solution of 21.1 g (86 mmol) of 77% **5** in acetone (160 mL); the temperature of the reaction mixture was maintained at 5–10 °C. After the mixture was allowed to stir at room temperature (2.5 h), acetone was distilled in vacuo at 30 °C and the residue shaken with methylene chloride (300 mL)–water (200 mL). The organic phase was washed with water (300 × 200 mL) and dried (Na_2SO_4), and the solid residue obtained after distillation of solvent in vacuum was triturated with cold hexane and suction filtered. The bright yellow solid was air-dried to yield 26.7 g (71%) of **11c**: mp 115–116 °C dec; NMR ($CDCl_3$) δ 8.79 (s, 1 H), 8.48 (br, NH), 3.29 (q, 2 H), 1.68 (m, 11 H), 1.10 (t, 3 H).

Cyclization of *tert*-Butyl Trithiocarbonate (11c). (a) In Glacial Acetic Acid. A stirred mixture of 26.4 g (58 mmol) of trithiocarbonate **11c** and glacial acetic acid (200 mL) was heated to 110–115 °C for 80 min (evolution of nitrogen oxides). After cooling, the reaction mixture was poured into water (500 mL) and extracted with CH_2Cl_2. The organic extract was washed with water, dried (Na_2SO_4), and filtered into a flask containing silica gel (25 g), and the methylene chloride was distilled in vacuo into a receiver cooled in ice. The methylene chloride distillate was fractionated on a spinning-band column and yielded 2.7 g (40%) of *tert*-butyl acetate, bp 96–98 °C, identical with a sample obtained from Aldrich (GLC, IR). The powder obtained on removal of solvent was chromatographed over silica gel (250 g). Elution with 20% benzene in hexane eluted a yellow fraction (450 mL) which was discarded. The orange-red band was next eluted and this fraction (1 L) on distillation of solvent in vacuo gave an orange

(8) Melting points were determined in open capillaries and are uncorrected. NMR spectra were recorded on Varian Associates T-60 Model spectrometer using Me_4Si as an internal standard. Elemental analyses were carried out by Spang Microanalytical Laboratory, Eagle Harbor, MI. Mass spectra were run on a Varian MAT CH-4 single-focusing mass spectrometer by Dr. J. J. Downs of Midwest Research Institute, Kansas City, MO. GLC analyses were carried out on a Hewlett-Packard gas chromatograph Model 5840A. Silica used for chromatography was E. Merck, silica gel 60, 70–230 mesh.

solid (13.2 g) which was recrystallized from hot ethanol (200 mL) to give 7.8 g (38%) of 1,3-benzodithiole-2-thione **12c**, mp 93–94 °C. A second recrystallization gave analytically pure material: mp 94–95 °C; NMR ($CDCl_3$) δ 9.0 (br, NH), 8.76 (s, 1 H), 3.97 (q, 2 H), 1.97 (m, 2 H), 1.39 (s, 3 H). Anal. Calcd for $C_{11}H_9F_3N_2O_2S_3$: C, 37.28; H, 2.54; N, 7.90; S, 27.11. Found: C, 37.09; H, 2.76; N, 8.12; S, 26.98.

(b) In Dimethyl Sulfoxide. A solution of 15.0 g (33 mmol) of **11c** in Me_2SO (150 mL) was heated at 115–120 °C (1 h) in a stream of nitrogen which was bubbled through a cooled (freezing mixture) trap containing 4 g of bromine in chloroform (50 mL). On completion of reaction the trap solution was shaken with water (2 × 50 mL), the light yellow chloroform phase was dried (Na_2SO_4), and the solvent was distilled in vacuum. This yielded 4.6 g (65%) of a pale yellow liquid characterized as isobutylene dibromide by NMR (neat, δ 4.13 (s, 2 H), 2.13 (s, 6 H)). The reaction mixture was worked up by pouring it into water, extracting with methylene chloride, and chromatographing over silica gel (170 g) as described for the reaction in glacial acetic acid. The solid obtained on distillation of the fraction obtained on elution of the orange band was recrystallized from ethanol. This yielded 5.0 g (43%) of 1,3-benzodithiole-2-thione **12c**, mp 92–93 °C.

(c) In Dimethylformamide. A solution of 15.0 g (33 mmol) of trithiocarbonate **11c** in DMF (150 mL) was heated at 110–120 °C (2 h) and the apparatus swept by a slow stream of nitrogen into a cold trap containing 5 g of bromine in chloroform (60 mL). The reaction mixture was worked up exactly as described under method b. This gave 2.1 g (29%) of isobutylene dibromide and 2.7 g (23%) of 1,3-benzodithiole-2-thione **12c**, mp 89–91 °C, after two recrystallizations from ethanol.

4-(Dimethylamino)-5-nitro-7-(trifluoromethyl)-1,3-benzodithiole-2-thione (12b). A solution of 13.0 g (29 mmol) of *tert*-butyl 2,4-dinitro-3-(dimethylamino)-6-(trifluoromethyl)-phenyl trithiocarbonate **11b** in glacial acetic acid (100 mL) was heated to 100–110 °C (2 h). The cooled reaction mixture was poured into water (700 mL) and extracted with methylene chloride. The organic extract was washed with water and dried and the solvent distilled to dryness in vacuo. The solid residue on recrystallization from ethanol yielded 4.8 g (45%) of **12b**, mp 86–87 °C. A second recrystallization from ethanol furnished an analytical sample: mp 87–88 °C; NMR (acetone-d_6) δ 7.90 (s, 1 H), 2.60 (s, 6 H). Anal. Calcd for $C_{10}H_7F_3N_2O_2S_3$: C, 35.29; H, 2.06; S, 28.23. Found: C, 35.43; H, 2.18; S, 28.35.

5-Nitro-7-(trifluoromethyl)-1,3-benzodithiole-2-thione (12a). A solution of 20 g (50 mmol) of *tert*-butyl 2,4-dinitro-6-(trifluoromethyl)phenyl trithiocarbonate **11a** in glacial acetic acid (180 mL) was heated to 110–115 °C (3.5 h). The crystalline material obtained on cooling was suction filtered to give 3.4 g of solid, mp 136–138 °C. The filtrate was poured into water (1 L) and extracted with methylene chloride and the extract distilled to dryness. The residual solid on recrystallization from glacial acetic acid yielded 2.9 g of crystalline solid, mp 135–137 °C. The total yield of 1,3-benzodithiole-2-thione **12a** was 6.3 g (42%); NMR (acetone-d_6) δ 8.58 (d, 1 H), 8.20 (d, 1 H). Anal. Calcd for $C_8H_2F_3NO_2S_3$: C, 32.32: H, 0.67; S, 32.32. Found: C, 32.40; H, 0.70; S, 32.45.

***n*-Butyl 2,4-Dinitro-6-(trifluoromethyl)phenyl Trithiocarbonate (14a).** This was obtained as a viscous oil in 94% yield on dropwise addition of a solution of sodium *n*-butyl trithiocarbonate **13** in acetone to a cooled (ice–salt bath) solution of 2-chloro-3,5-dinitro(trifluoromethyl)benzene as described for the corresponding *tert*-butyl trithiocarbonates; NMR (acetone-d_6) δ 8.86 (d, 1 H), 8.67 (d, 1 H), 3.06 (t, 2 H), 1.20 (m, 4 H), 0.53 (t, 3 H).

***n*-Butyl 2,4-Dinitro-3-(dimethylamino)-6-(trifluoromethyl)phenyl Trithiocarbonate (14b).** This was obtained as a viscous oil (80%) on addition of sodium *n*-butyl trithiocarbonate **13** to 2-chloro-3,5-dinitro-4-(dimethylamino)(trifluoromethyl)benzene (**10b**) in acetone. The oil crystallized on standing; trituration with cold ethanol yielded **14b** as a solid: mp 46–48 °C; NMR ($CDCl_3$) δ 8.33 (s, 1 H), 3.43 (t, 2 H), 2.98 (s, 6 H), 1.70 (m, 4 H), 1.03 (s, 3 H).

Decomposition of Trithiocarbonates 14a and 14b. In separate experiments 9 g (22.5 mmol) of **14a** was dissolved in glacial acetic acid (100 mL) and in Me_2SO (100 mL). The solutions were heated to 120–125 °C (3 h in glacial acetic acid and 2 h in Me_2SO). Both runs were worked up as described for **12b**. The residues obtained on distillation of the methylene chloride extract to dryness were recrystallized from ethanol and yielded 2.1 g (33%) of **15a**, mp 118–120 °C, for the glacial acetic acid run and 1.8 g (28%) of **15a**, mp 118–120 °C, for the Me_2SO run. The identity of **15a** was confirmed by comparison (mixture melting point, TLC, NMR) with an authentic sample.[6]

Similarly, decomposition of 10.2 g (23 mmol) of trithiocarbonate **14b** in glacial acetic acid (150 mL) for 3 h followed by the usual workup procedure gave after recrystallization from ethanol 2.3 g (31%) of **15b**, mp 108–110 °C, identical with an authentic sample (mixture melting point, TLC, NMR).[6]

Quantitative Determination of 12a and 15a in the Decomposition of Trithiocarbonate 11a by GLC. In three separate runs a solution of 11 g (27.5 mmol) of **11a** in 100 mL of solvent (glacial acetic acid, DMF, or Me_2SO) was heated to 110–115 °C (3 h). The reaction mixtures were worked up as described for **12b**. The residues obtained on distillation of the methylene chloride extract to dryness were chromatographed over silica gel (190 g) and eluted with 30% benzene in hexane. The orange-yellow band was eluted (1250 mL) until **12a** and **15a** were completely removed from the column (TLC). This fraction was distilled to dryness and the residue obtained was assayed for **12a** and **15a**. In the case where glacial acetic acid was used as solvent, the crude mixture obtained on distillation of the methylene chloride extract to dryness was assayed for **12a** and **15a** without going through the silica gel chromatographic purification step. The results are shown in Table I. GLC assay was carried out on a Hewlett-Packard 5840A gas chromatograph using a 6 ft × 1/8 in. i.d. glass column packed with 5% S-30 on 80–100-mesh Chromosorb WHP at a column temperature of 240 °C and gas flow rate of 30 mL min^{-1} of nitrogen, using a F.I.D. detector and triallyl trimesate as an internal standard. Acetone was used as a solvent.

Registry No. **4a**, 393-75-9; **4b**, 1930-72-9; **5**, 71127-42-9; **8a**, 63417-82-3; **8b**, 74511-97-0; **9**, 70344-40-0; **10a**, 392-95-0; **10b**, 59431-66-2; **10c**, 59431-93-5; **11a**, 74511-98-1; **11b**, 74511-99-2; **11c**, 74512-00-8; **12a**, 70344-41-1; **12b**, 70344-43-3; **12c**, 74512-01-9; **13**, 64773-45-1; **14a**, 74512-02-0; **14b**, 10156-75-9; **15a**, 62558-22-9; **15b**, 62558-23-0; *tert*-butyl mercaptan, 75-66-1; carbon disulfide, 75-15-0; *tert*-butyl acetate, 540-88-5; isobutylene dibromide, 594-34-3.