but significant deviation from the Brønsted relationship for strongly basic thiols. The slope for weakly basic thiols (excluding thioacetic acid[29]) is 0.65, corresponding to a β_{nuc} of ~0.35 for anion attack on the protonated semicarbazone. It has been shown that aliphatic and aromatic thiol anions exhibit no systematic differences in nucleophilic behavior toward thiol or oxygen esters.[17] Hence, the deviation of the most weakly basic thiol anions probably reflects a change in rate-determining step or transition-state structure for these compounds.[30] We speculate that this may result from a shift in transition-state structure for the RS^{-}- - -C=N^{+}(H)- system toward a more product-like transition state with a significant amount of carbon–sulfur bond formation for the more weakly basic thiols. Consistent with this idea is the observation that attack of aliphatic thiol and benzenethiol anions on a less electrophilic iminium species, the benzylidenedimethyliminium ion,[14] exhibits an even larger β_{nuc} of 0.43. These variations in β_{nuc} may possibly be a fairly straightforward manifestation of a "Hammond effect" for a system in which only one bond is being formed along the reaction coordinate.

Registry No.—**1**, 17539-52-5; **2**, 17539-53-6.

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Study of the Thermal Decomposition of Dinitrophenyl *N,N*-Dialkyldithiocarbamates and Related Compounds[1] +

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The thermal cyclization of substituted dinitrophenyl *N,N*-dimethyldithiocarbamates is shown to be a general method for the synthesis of a variety of nitro-1,3-benzodithiol-2-ones. The mechanism of this reaction is discussed.

In an earlier communication[2] we described the reaction of 3,5-dinitro-4-chlorobenzotrifluoride (**1a**) and other dinitrochlorobenzenes **1b–f** with the sodium salt of *N,N*-dimethyldithiocarbamic acid (**2**). The intermediate dithiocarbamates could not be isolated in all cases. For example, dithiocarbamates **3a–d** cyclized at 15–20 °C to produce 1,3-benzodithiol-2-ones **4a–d**, and in some cases the formation of disulfides **5a** and **5d** was also observed. D'Amico and coworkers[3] have also studied the reaction of **1a** with **2** and reported the formation of **5a**. Their structural assignment for **5a** is based on an X-ray crystal diffraction study. We regret that in our earlier note[2] the structures assigned to **5a, 5d,** and **9a** were in error, although the identity of **5a** with the disulfide isolated by D'Amico and co-workers had been confirmed.

The 2,4-dinitrophenyl *N,N*-dimethyldithiocarbamates **7a** and **7b** show greater thermal stability than the isomeric dithiocarbamates **3a** and **3e**. In particular **7b** required comparatively drastic conditions for cyclization and yielded 5-nitro-1,3-benzodithiol-2-one (**8b**) in 5% yield (Scheme I). Product **8b** was shown to be identical with that obtained by Hurtley and Smiles[4] on nitration of 1,3-benzodithiol-2-one; the isomeric 4-nitro-1,3-benzodithiol-2-one (**4e**) was found by TLC to be absent. We were able to isolate the dithiocarbamate **7c**, but it was observed to evolve nitrogen oxides slowly at room temperature as a solid, indicating ready cyclization. The excellent conversions of **7c** and analogous dithiocar-

+ Dedicated to Professor Georg Wittig.

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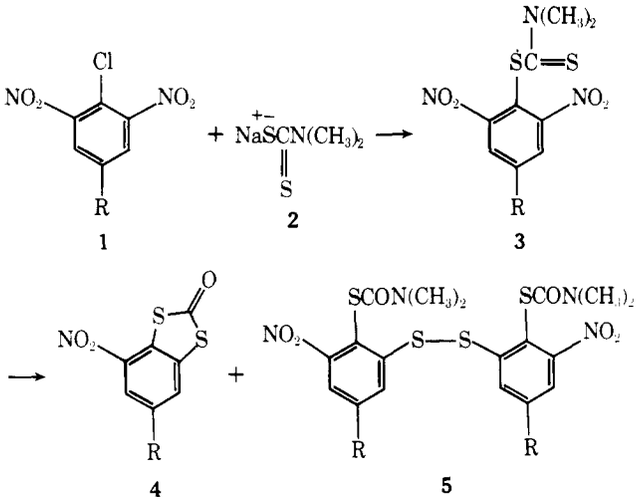
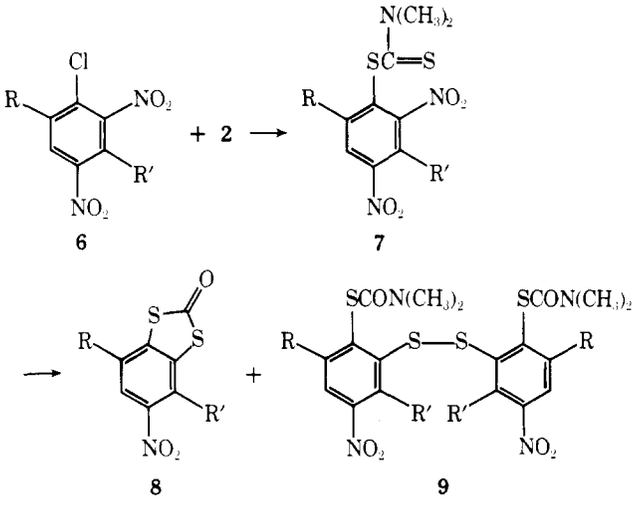
Scheme I



a, R = CF_3; b, R = NO_2; c, R = CN; d, R = F; e, R = H; f, R = CH_3

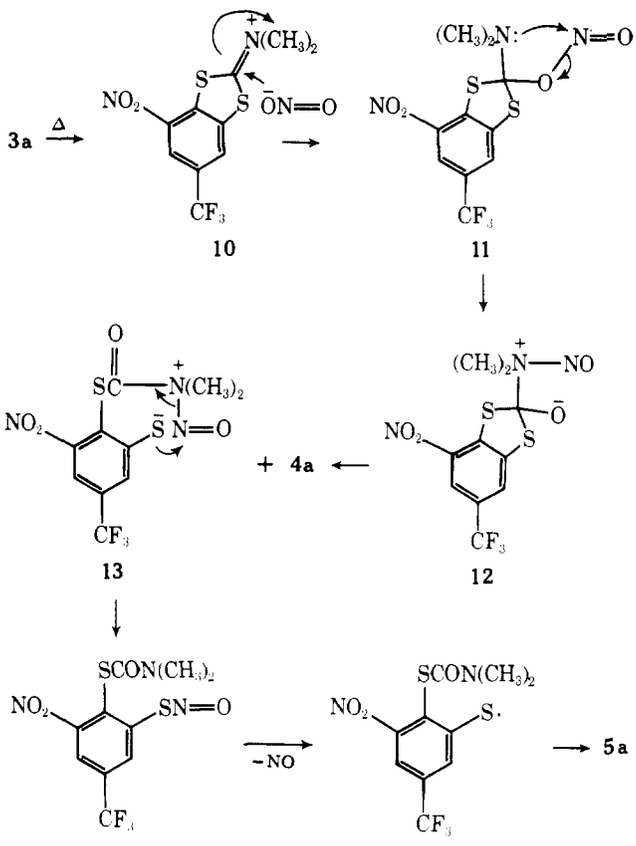


a, R = CF_3; R′ = H
b, R = R′ = H
c, R = CF_3; R′ = $N(CH_3)_2$

bamates bearing aminoalkyl substituents to the corresponding 1,3-benzodithiol-2-ones have already been described.[2] We have carried out these conversions with a total of 25 dithiocarbamates and in each case the corresponding 1,3-benzodithiol-2-one was isolated. In five cases disulfide products were also isolated. These conversions represent a general and very useful synthetic route to a variety of substituted 1,3-benzodithiol-2-ones. The applicability of this reaction is limited only by the availability of the starting dinitrohalobenzenes and is therefore capable of generating 1,3-benzodithiol-2-ones with a wide variety of substituents on the aromatic ring. The reaction conditions and yields for the products isolated are summarized in Table I.

Although 1,3-benzodithiol derivatives have been extensively investigated,[5] the synthetic methods available for preparing 1,3-benzodithiol-2-ones are tedious, requiring multistep procedures to generate benzene-1,2-dithiol intermediates. The latter have been obtained by reduction of the relatively inaccessible benzene-1,2-disulfonic acids,[4] and from the reaction of lithium thiophenoxide with sulfur.[6] More recently improved procedures utilizing 1,3-dipolar additions to CS_2[7] and reaction of CS_2 with benzyne[8] have been devised for preparing benzene-1,2-dithiols and 2-alkoxy-1,3-benzodithioles. The latter route in particular shows promise for the synthesis of a variety of 1,3-benzodithiole derivatives, although the conversion of

Scheme II



2-alkoxy-1,3-benzodithioles to 1,3-benzodithiol-2-ones has not been demonstrated.

On further investigation of the reaction of **1a** with **2** we found that in anhydrous methanol the reaction yields **4a** (51%) and **5a** (25%), which ruled out the formation of these products by attack of water on intermediate **10.** We have evidence that attack of nitrite ion, which converts the salt **10** to the nitrite ester **11,** is responsible for the formation of **4a** and **5a** (Scheme II). It is noteworthy that the disulfide **5a** isolated, and indeed others isolated by us, was not a mixture of isomers, indicating that cleavage of the carbon–sulfur bond in the postulated zwitterionic intermediate **12** occurs exclusively to generate the 2-(*N,N*-dimethylthiocarbamoyl)-3-nitro-5-(trifluoromethyl)thiophenoxide **13.**[9]

In order to test the participation of nitrite ion, 1 molar equiv of sodium nitrite was added to a solution of **3a** generated at 0 °C in anhydrous methanol. This reaction gave **4a** (6%) and **5a** (65%). In addition to this dramatic change in the ratio of **4a** and **5a,** a new product was isolated in 15% yield. On the basis of an elemental analysis, NMR spectrum, and a mass spectrum, we assign structure **17** to this product. The EI mass spectrum of **17** has the molecular ion at *m/e* 624 and a fragment at *m/e* 312, which represents the product of a symmetrical cleavage of the peroxide bond. Loss of a methoxy radical from the *m/e* 312 fragment represents the ion of **4a** at *m/e* 281. The base peak at *m/e* 253 results from loss of CO from **4a.** Additional evidence for this structural assignment was obtained by treating **17** with sodium hydride in DMF, which gave **4a.** These results are rationalized in Scheme III. Excess nitrite competes with the intramolecular attack of the dimethylamino nitrogen on the nitrite ester moiety to produce alkoxide **14,** which prefers to ring open to give **5a,** in contrast to zwitterion **12,** in which elimination of dimethylnitrosamine is competitive with ring opening. Formation of **17** apparently proceeds via oxidation of **14** to **15** followed by dimerization to **16** and subsequent methanolysis to **17.**

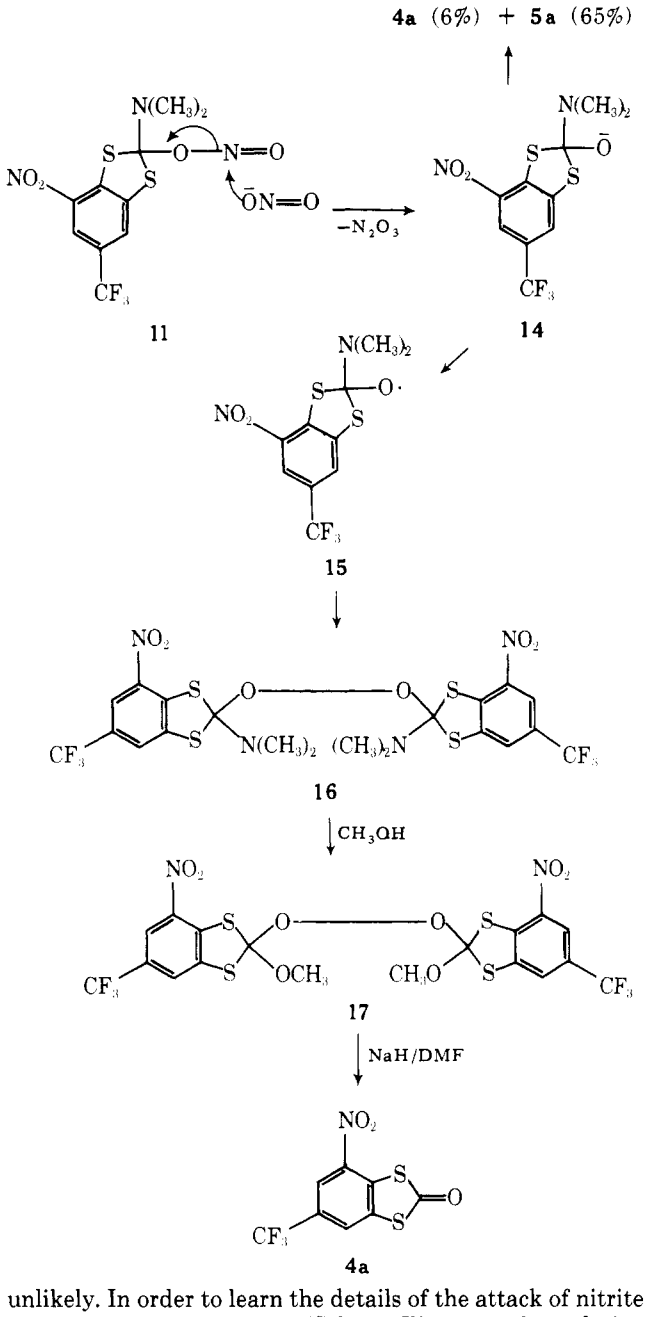
Table I. Products of Decomposition of Dinitrophenyl *N,N*-Dimethyldithiocarbamates

dithiocarbamates[a] no.	substituents	registry no.	procedure temp, °C	time, h	solvent	products,[b] % yield (mp, °C) 1,3-benzodithiol-2-one	registry no.	disulfide	registry no.
3a	2,6-$(NO_2)_2$, 4-CF_3	62558-29-6	25	3	Me_2SO	**4a**, 43 (111–112)	62558-16-1	**5a**, 40 (222–224)	59983-45-8
3b	2,4,6$(NO_2)_3$	62558-30-9	25	16	acetone	**4b**, 35 (129–131)	62558-17-2		
3c	2,6-$(NO_2)_2$, 4-CN	62558-31-0	25	16	acetone	**4c**, 46 (177–178)	62558-18-3		
3d	2,6-$(NO_2)_2$, 4-F	62558-32-1	90–100	2.5	Me_2SO	**4d**, 37 (98–100)	62558-19-4	**5d**, 12 (192–195)	68200-49-7
3e	2,6-$(NO_2)_2$	62558-33-2	90–100	4	Me_2SO	**4e**, 43 (110–111)	62558-20-7	**5e**, 16 (201–202)	68200-48-6
3f	2,6-$(NO_2)_2$, 4-CH_3	62558-34-3	85–90	12	Me_2SO	**4f**, 26 (163–164)	62558-21-8		
7a	2,4-$(NO_2)_2$, 6-CF_3	62558-35-4	75	1.5	DMF	**8a**, 11 (117–118)	62558-22-9	**9a**, 53 (222–224)	68151-94-0
7b	2,4-$(NO_2)_2$	89-37-2	100–110	15	Me_2SO	**8b**, 5 (131–136)	63418-00-8		
7c	2,4-$(NO_2)_2$, 3-$N(CH_3)_2$, 6-CF_3	62558-36-5	56	16	acetone	**8c**, 77 (106–107)	62558-23-0		
36	2,4-$(NO_2)_2$, 3-$N(C_2H_5)_2$, 6-CF_3	62558-37-6	56	16	acetone	**37**, 76 (58–60)	62558-24-1		
38	2,4-$(NO_2)_2$, 3-$N(n\text{-}C_3H_7)_2$, 6-CF_3	62558-38-7	56	16	acetone	**39**, 80 (60–61)	62558-25-2		
40	2,4-$(NO_2)_2$, 3-HN-*n*-C_3H_7, 6-CF_3	68151-79-1	56	16	acetone	**41**, 68 (72–74)	63417-89-0		
42	2,4-$(NO_2)_2$, 3-N(allyl)$_2$, 6-CF_3	68151-80-4	56	40	acetone	**43**, 38 (liquid)	63417-92-5		
44	2,4-$(NO_2)_2$, 3-N(*n*-Bu)$_2$, 6-CF_3	68151-81-5	80–85	2.0	Me_2SO	**45**, 53 (liquid)	63417-95-8		
46	2,4-$(NO_2)_2$ 3-HN-*n*-Bu, 6-CF_3	68151-82-6	80–85	2.5	Me_2SO	**47**, 30 (liquid)	63417-94-7		
48	2,4-$(NO_2)_2$, 3-HN-*i*-Pr, 6-CF_3	68151-83-7	56	16	acetone	**49**, 58 (72–73)	63417-88-9		
50	2,4-$(NO_2)_2$, 3-HNC_6H_5, 6-CF_3	68151-84-8	80–85	2	Me_2SO	**51**, 13 (121–122)	63417-96-9		
52	2,4-$(NO_2)_2$, 3-*N*-pyrrolidino, 6-CF_3	68151-85-9	60–70	3	Me_2SO	**53**, 40 (104–105)	63417-99-2		
54	2,4-$(NO_2)_2$, 3-*N*-morpholino, 6-CF_3	68151-86-0	80–85	2.5	Me_2SO	**55**, 14 (178–180)	63417-98-1		
56	2,4-$(NO_2)_2$, 3-$HNCH_3$, 6-CF_3	68151-87-1	80–85	2.5	Me_2SO	**57**, 12 (171–173)	63417-93-6		
58	2,4-$(NO_2)_2$, 3-S-*n*-C_3H_7, 6-CF_3	68151-88-2	56	5.5	acetone	**59**, 68 (87–88)	63417-90-3		
60	2,4-$(NO_2)_2$, 3-S-*i*-C_3H_7, 6-CF_3	68151-89-3	56	5.5	acetone	**61**, 53 (79–80)	63417-91-4		
62	2,6-$(NO_2)_2$, 4-Cl	68151-90-6	90–100	2.5	Me_2SO	**63**, 39 (152–153)	63417-83-4	**64**, 20 (237–239)	68151-95-1
65	2,6-$(NO_2)_2$, 4-Cl, 5-CH_3	68151-91-7	90–100	2.5	Me_2SO	**66**, 36 (147–148)	68151-93-9		
67	2,4,6-$(NO_2)_3$, 3,5-$(CH_3)_2$	68151-92-8	90–100	2.5	Me_2SO	**68**, 45 (130–131)	63417-87-8		

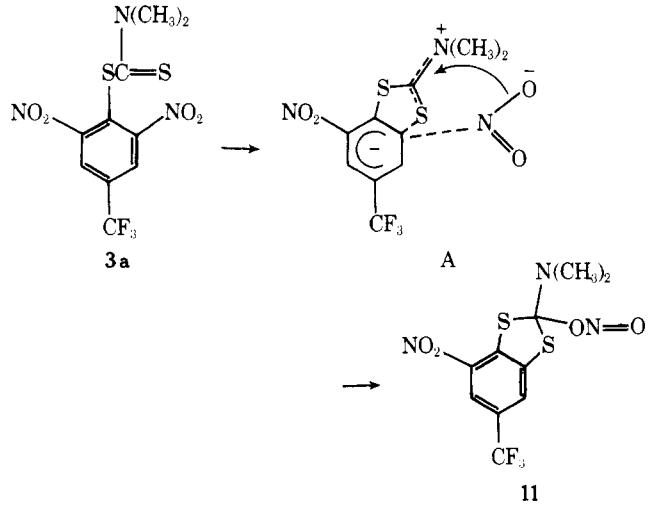
[a] In general all dithiocarbamates were generated in solution at ice-bath temperatures by dropwise addition of a solution of **2** to a stirred solution of the dinitrochlorobenzene in the solvent indicated. In cases where Me_2SO was used as solvent the temperature was controlled at 15–20 °C (see Experimental Section for more details). [b] Products were isolated by column chromatography of crude mixtures on silica gel, eluting with hexane (**8c, 37, 39, 41, 49**), 50% hexane in benzene (**4a, 4b, 4c, 4d, 4e, 8a, 51, 53, 55, 57, 59, 61, 63, 66, 68**), and chloroform (**5a, 4f, 5e, 5d, 9a, 64**). Analytically pure samples were obtained by recrystallizing from hexane (**37, 41**), ethanol (**4a, 4f, 4e, 4d, 8a, 8c, 39, 49, 51, 53, 57, 59, 61, 63, 66, 68**), ethanol–acetone (**4b, 5e, 55**), and acetone (**5a, 4c, 9a, 64**). Satisfactory elemental analyses were obtained for all products.

The nucleophilic character of the ambident nitrite anion in aliphatic[10] and more recently in aromatic systems[11,12] has been well investigated. Kornblum[10] has pointed out that attack by the oxygen atom of nitrite on carbon is pronounced when the transition state has a well-developed positive charge on carbon and that attack by nitrogen is favored in S_N2 transition states where the carbon is "softer" and carries little if any positive charge. This view suggests that in our system the displacement of the nitro group is not synchronous with attack by nitrite, making a transition state such as A seem

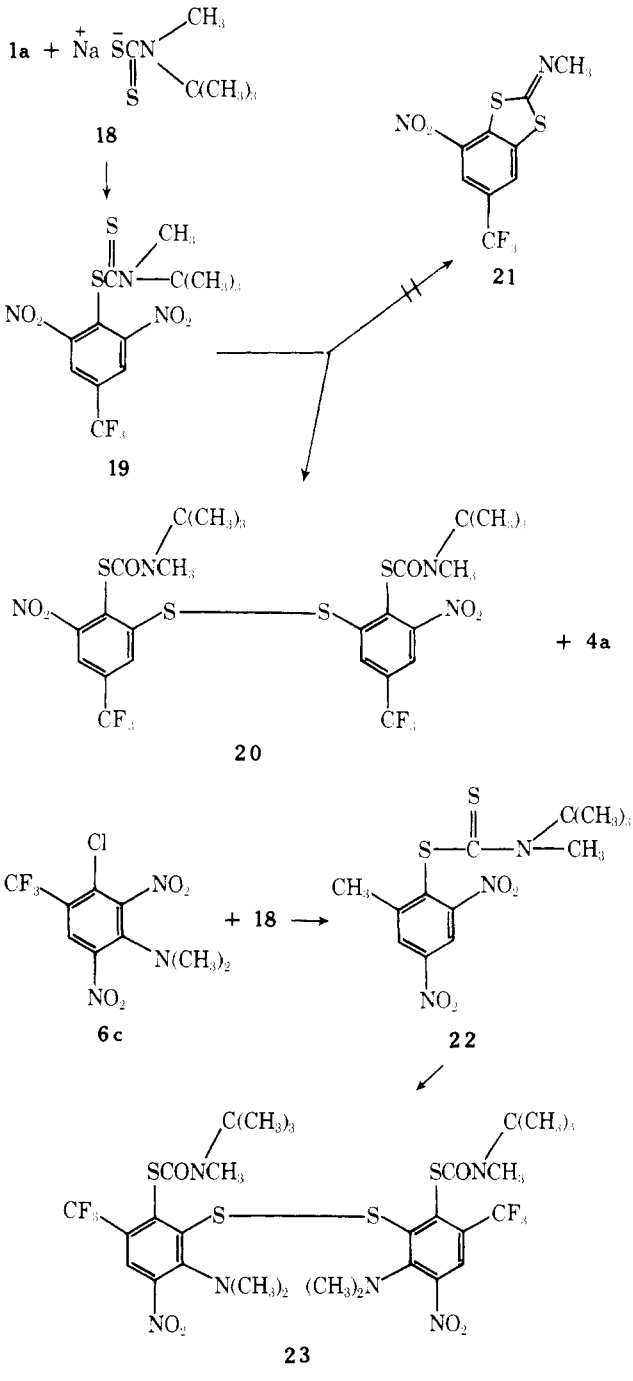
Scheme III



unlikely. In order to learn the details of the attack of nitrite ion, i.e., conversion **10** → **11** (Scheme II), we sought to design an experiment in which this attack could be prevented or at least be made competitive with other processes. This could

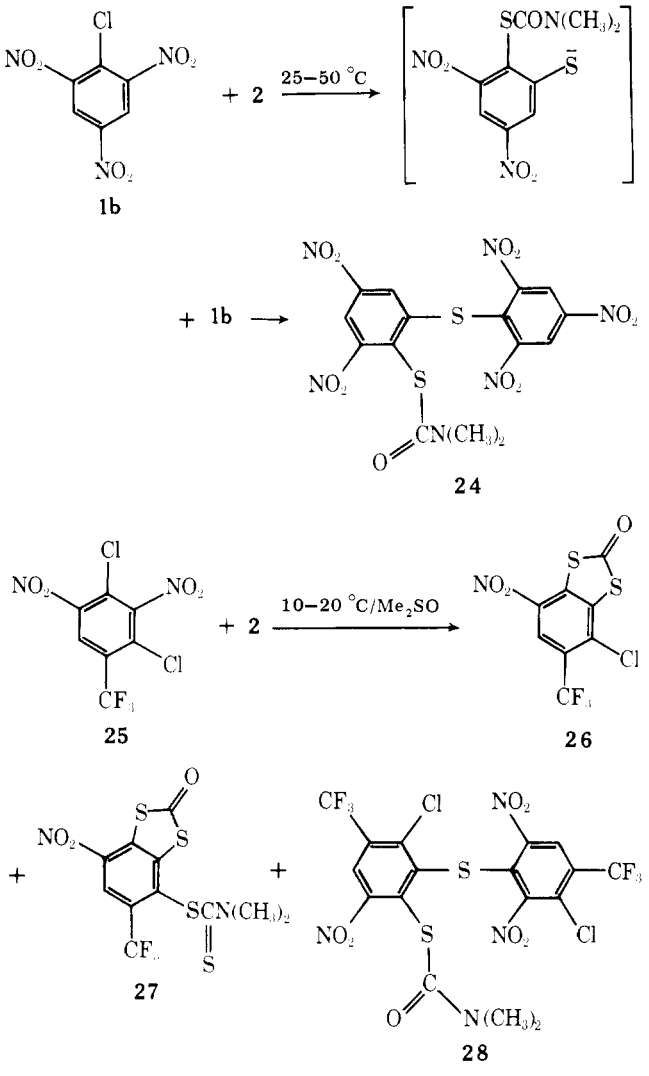


Scheme IV

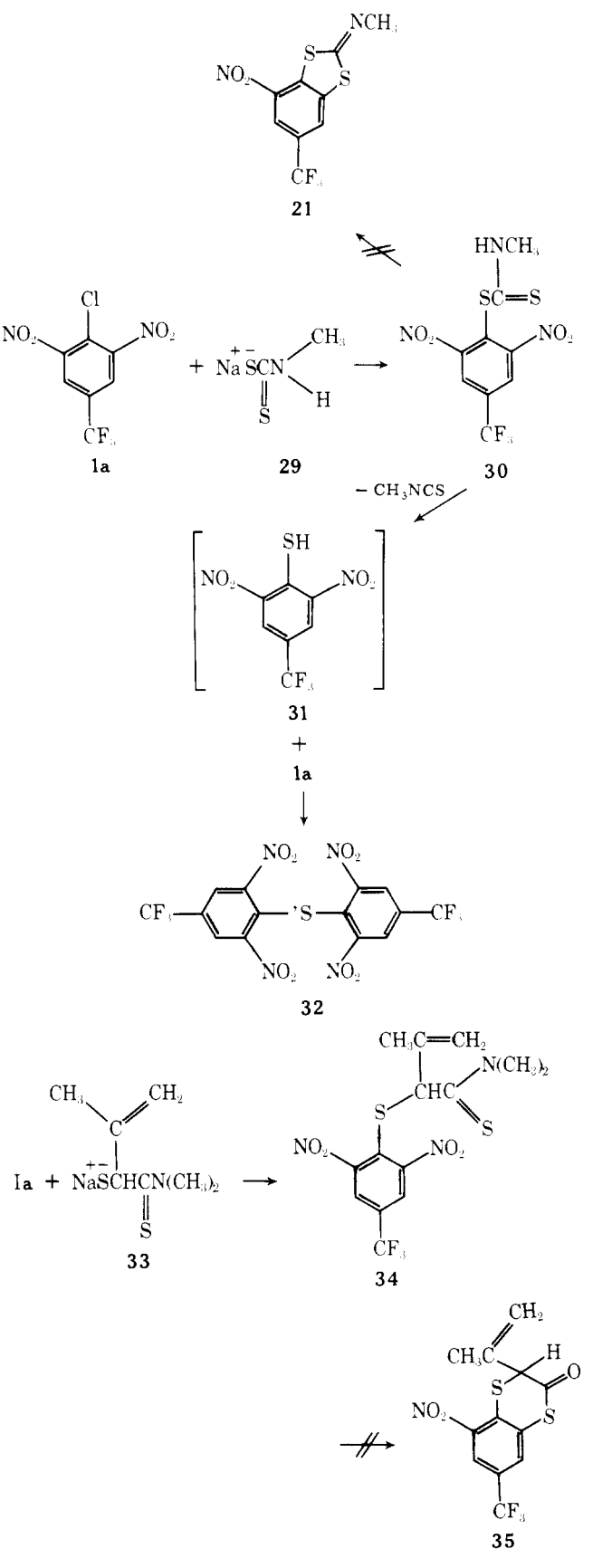


be realized by carrying out the reaction in the presence of a reagent that rapidly scavenges nitrite ions. Since we were unable to find reagents that are known to specifically complex or otherwise react with nitrite ions under neutral conditions, we have as an alternative utilized the potential for loss of a *tert*-butyl cation. Thus, when **1a** was reacted with sodium *N*-methyl-*N*-*tert*-butyldithiocarbamate (**18**), the initially formed condensation product **19** cyclized at room temperature and we isolated **4a** (2%) and disulfide **20** (37%). Heterocycle **21**, which would have been formed by loss of *tert*-butyl cation from the intermediate nitrite salt corresponding to **10**, was not isolated. A similar cyclization of dithiocarbamate **22** at room temperature produced 42% of disulfide **23** (Scheme IV). These results are indicative of rapid attack of nitrite ion. The almost exclusive formation of disulfides **20** and **23** in these reactions is noteworthy because the cyclizations of the corresponding *N*,*N*-dimethyldithiocarbamates **3a** and **7c** yield the corresponding 1,3-benzodithiol-2-ones in yields of 40 and 77%,

Scheme V



Scheme VI



respectively. This result suggests that attack of the *N*-methyl-*N*-*tert*-butylamino group, as indicated for the dimethylamino group in **11**, would on account of the bulky *tert*-butyl substituent be made sterically unfavorable.

We also have evidence to show that thiophenoxides such as **13** (Scheme II) are the precursors to the disulfides isolated in this work. When a Me_2SO solution of **2** is added to a solution of picryl chloride (**1b**) without external cooling, the sulfide **24** can be isolated in fair yield (Scheme V). Similarly, addition of **2** to 2,4-dichloro-3,5-dinitrobenzotrifluoride (**25**) yields the sulfide **28** as well as the 1,3-benzodithiol-2-ones **26** and **27**.[13] The structures of the sulfides **24** and **28** are based on their elemental analyses and NMR spectra.

The reaction of **1a** with the sodium salt of *N*-methyldithiocarbamic acid (**29**) was carried out in the expectation that cyclization of the resulting dithiocarbamate **30** would give rise to an intermediate analogous to **10**, but this could be expected to lose a proton rapidly to give the heterocycle **21**. Instead the reaction yielded the sulfide **32**, indicating that thiol **31**, which is obtained by loss of methyl isothiocyanate from dithiocarbamate **30**, reacts with **1a** to give the observed product. D'Amico and co-workers have also observed this reaction[3] (Scheme VI).

In order to extend the scope of this cyclization reaction, we have carried out the reaction of **1a** with the sodium salt of *N,N*-dimethyl-2-mercapto-3-methylbut-3-enethioamide (**33**)[14] in methanol. The condensation product **34** was isolated in 46% yield and characterized by its elemental analysis and NMR spectrum. Attempts to cyclize **34** by heating in acetone and toluene gave a very complex mixture in which the expected product of cyclization (**35**) was not detected.

Intramolecular nucleophilic displacements of aromatic nitro groups by oxygen,[15] sulfur,[16] nitrogen,[17] and carbon[18] nucleophiles is well documented. In these reactions the nucleophilic atom is an anion and temperatures of 70–200 °C have been

employed. On the other hand the nucleophilic displacement of nitro groups by sulfur nucleophiles in dinitrohalobenzenes is particularly facile, as has been shown in this work and more recently by Beck and Yahner.[19] In contrast the addition of carbon, oxygen, and nitrogen anions to polynitrobenzenes under mild conditions does not generally result in the displacement of nitro groups, but rather in the attack of the nucleophile to the unsubstituted aromatic carbon atom to yield anionic σ complexes, a reaction that has been effectively used for the construction of heterobicyclic systems.[20] The cyclizations we have described are related to the cyclization of *O*-(2,4,6-trihalophenyl) *N,N*-dimethylthiocarbamates reported by Reinecke and Goralski,[21] where nucleophilic displacement of an ortho halogen substituent by sulfur was observed at elevated temperatures. The case where such ortho substituents are lacking had earlier been investigated by Newman and Karnes[22] in the rearrangement of phenyl *N,N*-dimethylthiocarbamates, a reaction that can be used to convert phenols to thiophenols. We believe that we have developed a general synthetic route to a variety of nitro-1,3-benzodithiol-2-ones utilizing the displacement of nitro groups from electron-deficient aromatics. The presence of a nitro group lends added versatility to this method in view of the many well-known transformations of the nitro group[23] into other functionalities. The results of related work for the synthesis of other heterocyclic systems will be the subject of future communications.

Experimental Section[24]

Preparation of Starting Materials. 4-Chloro-3,5-dinitrobenzotrifluoride (**1a**) was prepared by nitration of 4-chlorobenzotrifluoride as described[25] and is also available commercially.[26] 2-Chloro-3,5-dinitrobenzotrifluoride (**6a**) was prepared by nitration of 2-chlorobenzotrifluoride as described for **1a**. Similarly, nitration of 2,4-dichlorobenzotrifluoride yielded 2,4-dichloro-3,5-dinitrobenzotrifluoride (**25**). Reactions of **25** (1 mol) with amines (2 mol) were carried out in chloroform or THF at ice bath temperatures. Essentially quantitative yields of the amino derivatives was obtained. 2,6-Dinitro-4-fluorochlorobenzene (**1d**) was prepared by refluxing 2,6-dinitro-4-fluorophenol (0.4 mol), DMF (0.4 mol), and thionyl chloride (0.6 mol) in benzene (300 mL) for 6 h. The solid residue obtained after removal of solvent was recrystallized from ethanol to yield **1d**, mp 65–67 °C, in 68% yield. 1,4-Dichloro-2,6-dinitrobenzene (60%), mp 99–100 °C, was similarly prepared via chlorination of 2,6-dinitro-4-chlorophenol. 3,6-Dichloro-2,4-dinitrotoluene was obtained by heating a mixture of 4-chloro-2,6-dinitro-3-methylphenol (0.1 mol), $POCl_3$ (75 g), and DMF (30 g) for 12 h at 90 °C. The solid obtained on pouring the reaction mixture into water was purified by filtering through a short silica gel column. Elution with 50% benzene in hexane gave the product (40%), mp 90–92 °C. Dimethylpicryl chloride was prepared as described.[27] 4-Cyano-2,6-dinitrochlorobenzene (**1c**) was obtained (93%) by refluxing 4-chloro-3,5-dinitrobenzamide (0.12 mol), anhydrous NaCl (20 g), and $POCl_3$ (300 mL).[28] 2-Chloro-3,5-dinitro-4-(*n*-propylthio)benzotrifluoride was obtained by dropwise addition of an equimolar solution of 1-propanethiol and sodium methoxide in dry methanol to a stirred and ice-cooled solution of 2,4-dichloro-3,5-dinitrobenzotrifluoride (**25**) in dry methanol under nitrogen. After stirring at room temperature (1 h), removal of solvent in vacuum and recrystallization of the residue from hexane gave the product (60%), mp 81–82 °C. The isomeric 2-chloro-3,5-dinitro-4-(isopropylthio)-benzotrifluoride, mp 85–86 °C, was similarly prepared (60%). The sodium salt of *N,N*-dimethyldithiocarbamic acid (**2**) is commercially available.[29]

4-Methyl-2,6-dinitrophenyl *N,N*-Dimethyldithiocarbamate (3f). A solution of 5.3 g (30 mmol) of **2** in Me_2SO (25 mL) was added dropwise to a stirred solution of 6.5 g (30 mmol) of 3,5-dinitro-4-chlorotoluene (**1f**) in Me_2SO (25 mL) at room temperature. After the mixture was stirred for 3 h it was diluted with water (150 mL) and extracted with chloroform (3 × 50 mL). The combined chloroform extracts were washed with water (3 × 200 mL) and dried (Na_2SO_4) and solvent was removed in vacuum. Recrystallization of the residue from chloroform–hexane yielded 7.7 g (85%) of **3f**, mp 135–136 °C dec. Anal. Calcd for $C_{10}C_{11}N_3O_4S_2$: N, 13.95. Found: N, 13.70. NMR (Me_2SO-d_6) δ 8.2 (s, 2 H), 3.4 (d, 6 H), 2.53 (s, 3 H).

6-Methyl-4-nitro-1,3-benzodithiol-2-one (4f). A solution of 6.0 g (0.02 mol) of **3f** in Me_2SO (50 mL) was heated to 85–90 °C (12 h). Nitrogen oxides were evolved. The resulting mixture was poured into water (200 mL) and extracted with chloroform (5 × 50 mL). The combined chloroform extracts were washed with water (4 × 100 mL) and dried (Na_2SO_4) and solvent was removed in vacuum. The residue was chromatographed over silica gel (100 g). Chloroform eluted 1.2 g (26%) of **4f**, mp 163–164 °C. Anal. Calcd for $C_8H_5NO_3S_2$: C, 42.29; H, 2.20; N, 6.16. Found: C, 42.19; H, 2.19; N, 6.12. NMR (acetone-d_6) δ 7.82 (m, 1 H), 7.60 (m, 1 H), 2.10 (s, 3 H).

4-Nitro-6-(trifluoromethyl)-1,3-benzodithiol-2-one (4a) and Disulfide 5a. To a stirred solution of 16.2 g (60 mmol) of 4-chloro-3,5-dinitrobenzotrifluoride (**1a**) in Me_2SO (60 mL) was added dropwise a solution of 10.74 g (60 mmol) of sodium dimethyldithiocarbamate (**2**) in Me_2SO (60 mL); the temperature of the reaction mixture was maintained at 15–20 °C. The reaction is mildly exothermic and accompanied by evolution of nitrogen oxides. After being stirred for 3 h water (450 mL) was added and the mixture was extracted with chloroform (3 × 150 mL). The combined chloroform extracts were washed with water (3 × 500 mL) and dried (Na_2SO_4) and chloroform was removed in vacuum. 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 ethanol yielded **4a**, mp 111–112 °C. Anal. Calcd for $C_8H_2F_3NO_3S_2$: 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. NMR ($CDCl_3$) δ 8.60 (m, 1 H), 8.16 (m, 1 H). Elution with chloroform yielded 8.0 g (40%) of **5a**, mp 222–224 °C. Anal. Calcd for $C_{20}H_{16}F_6N_4O_6S_4$: C, 36.92; H, 2.46; N, 8.59. Found: C, 36.77; H, 2.56; N, 8.52. NMR ($CDCl_3$) δ 8.35 (m, 2 H), 8.07 (m, 2 H), 3.24 (s, 12 H).

Cyclization of 3a in Methanol. To a stirred solution of 10.81 g (40 mmol) of **1a** in absolute methanol (100 mL) at 5–10 °C (ice bath) was added dropwise a solution of 5.73 g (40 mmol) of anhydrous **2** in absolute methanol (40 mL) under nitrogen. After addition of **2** was complete the mixture was stirred at 0–5 °C (2 h) and thereafter at room temperature (24 h). Silica gel (15 g) was added to the mixture and the solvent was removed in vacuum. The residual powder was chromatographed over silica gel (200 g). Elution with hexane–benzene (1:1) gave a fraction (650 mL) which was distilled to dryness in vacuum and the residual solid was triturated with hexane and suction filtered. **4a** (5.71 g, 50.8%), mp 106.5–108.5 °C, was obtained (TLC, mixture melting point with authentic **4a**). Elution with chloroform (850 mL) and removal of solvent yielded a solid, which was triturated with ethanol and filtered to yield 3.3 g (25.4%) of **5a**, mp 221–223 °C (TLC, mixture melting point with authentic **5a**).

Cyclization of 3a in Methanol in the Presence of Sodium Nitrite. The reaction was carried out as described in the preceding experiment except that after stirring the reactants at 0–5 °C (2 h), 2.76 g (40 mmol) of finely powdered sodium nitrite was added and the mixture was allowed to stir at room temperature (48 h). Methanol was removed in vacuum, and the residue was extracted with warm chloroform (125 mL) and filtered from insoluble material. Silica gel (15 g) was added to the chloroform extract and solvent was removed in vacuum. The residual powder was chromatographed over silica gel (200 g). Elution with hexane–benzene (1:1) gave a fraction (200 mL) from which solvent was removed in vacuum and the residual solid was recrystallized from hot hexane–benzene (1:1). Peroxide **17** (250 mg), mp 172–175 °C, was obtained. The hexane–benzene mother liquor was evaporated to dryness and the residue was recrystallized from ethanol. Impure **4a** (700 mg, 6.2%), mp 100–108 °C, was obtained. TLC indicated that this sample of **4a** contained **17** as an impurity. The second hexane–benzene (1:1) eluate (200 mL) was evaporated to dryness and the residue on recrystallization from hot hexane–benzene (1:1) gave 500 mg of **17**, mp 177–178.5 °C. Elution with chloroform (150 mL) gave on removal of solvent 1.1 g of **17**, mp 170–180 °C. Recrystallization from acetone yielded 700 mg of **17**, mp 175–179 °C. This sample by TLC contained small amounts of disulfide **5a** as an impurity. Total yield of **17** was 1.85 g (14.8%). Anal. Calcd for $C_{18}H_{10}F_6N_2O_8S_4$: C, 34.61; H, 1.60; N, 4.48; S, 20.51. Found: C, 34.65; H, 1.76; N, 4.35; S, 20.43. NMR ($CDCl_3$) δ 8.36 (m, 1 H), 8.20 (m, 1 H), 4.17 (s, 3 H); mass spectrum *m/e* 624. Further elution with chloroform (1 L) gave, after removal of solvent, 8.7 g (66.9%) of crude **5a**, mp 210–214 °C. One recrystallization from acetone gave 6.0 g of **5a**, mp 216–218 °C (mmp).

Reduction of Peroxide 17 with Sodium Hydride. To a stirred and tap water cooled solution of 206 mg (0.33 mmol) of peroxide **17** in dry DMF (10 mL) under nitrogen was added 50 mg of a 50% sodium hydride dispersion in oil (1.0 mmol). After being stirred for 2 h the mixture was acidified with 1 N HCl, poured into water, and extracted with chloroform (3 × 20 mL). The organic extract was washed with water (3 × 50 mL), dried (Na_2SO_4), and filtered. After addition of silica gel (2 g), the solvent was removed in vacuum and the residual

powder was chromatographed over silica gel (20 g) and eluted with 30% benzene in hexane. The first orange-yellow fraction (20 mL) was distilled to dryness and the residual solid was triturated with warm hexane and filtered. This gave 40 mg (21%) of **4a**, mp 107–109 °C (mmp, TLC).

5-Nitro-1,3-benzodithiol-2-one (8b). Decomposition of 10.5 g (68 mmol) of 2,4-dinitrophenyl *N,N*-dimethyldithiocarbamate in Me_2SO (100 mL) at 100–110 °C (15 h) followed by the usual workup and chromatography over silica gel (240 g) with hexane–benzene (1:1) as eluant gave 1.7 g of solid. This solid was dissolved in a hot ethanol–acetone mixture and concentrated till crystals began to separate. The crystalline solid was filtered and the filtrate was concentrated to half its volume and allowed to crystallize. **8b** (0.8 g, 5.5%), mp 131–136 °C, was obtained and was identical with the product obtained from the nitration of 1,3-benzodithiol-2-one[4] (mmp, NMR spectrum).

Sulfide 24. To a stirred solution of 49.48 g (0.2 mol) of picryl chloride (**1b**) in Me_2SO (200 mL) was added a solution of 35.84 g (0.2 mol) of **2** in Me_2SO (200 mL) dropwise. Shortly after the start of addition (5 min) nitrogen oxides were evolved and by the end of addition (45 min) the reaction mixture had warmed to 50 °C. The mixture was now allowed to stir with tap water cooling (3 h), poured into water (500 mL), and extracted with chloroform (4 × 250 mL). The chloroform–water insoluble solid was suction filtered and recrystallized from acetone to yield 6.5 g (18%) of **24**, mp 166–168 °C. Anal. Calcd for $C_{15}H_{10}N_6O_{11}S_2$: C, 35.00; H, 1.94; N, 16.34. Found: C, 35.00; H, 1.93; N, 16.34. NMR (Me_2SO-d_6) δ 9.66 (d, 1 H), 9.09 (d, 1 H), 8.56 (s, 2 H), 3.84 (s, 3 H), 3.78 (s, 3 H).

Sodium Salt of *N*-Methyl-*N*-*tert*-butyldithiocarbamic Acid (18). To a stirred and ice-cooled suspension of 120 g (0.96 mol) of *N*-methyl-*N*-*tert*-butylamine hydrochloride[30] was added 160 g (2 mol) of 50% sodium hydroxide. Sufficient water was added to bring the solid in solution. Carbon disulfide (200 mL) was added to this mixture over 15 min at 5–10 °C. After stirring at 5–10 °C (20 min) the crystalline solid was suction filtered and purified by extracting with hot acetone. The acetone extract was concentrated to half its volume and allowed to crystallize. This yielded 90 g (39%) of the dithiocarbamic acid sodium salt as the trihydrate: NMR (Me_2SO-d_6) δ 3.52 (s, N-CH_3), 3.55 (s, H_2O), 1.70 (s, N-C(CH_3)$_3$). The product sinters at 140 °C and does not melt till 240 °C.

***S,S'*-[2,2'-Dithiobis(6-nitro-α,α,α-trifluoro-*p*-tolyl)] Bis(*N*-methyl-*N*-*tert*-butylcarbamothioate) (20).** To a stirred and cooled (ice–salt bath) solution of 5.8 g (21.6 mmol) of benzotrifluoride **1a** in DMF (25 mL) at −9 °C was added dropwise a solution of 5.26 g (22 mmol) of the sodium salt of *N*-methyl-*N*-*tert*-butyldithiocarbamic acid (**18**) in DMF (30 mL), keeping the temperature of the reaction mixture below 0 °C during addition. After being stirred at 0–5 °C (2 h), the mixture was stirred at ambient temperature overnight. It was poured into water (250 mL) and extracted with chloroform (2 × 60 mL), and the organic extract was washed with water (2 × 200 mL) and dried (Na_2SO_4). To the chloroform filtrate was added silica gel (10 g) and the solvent was removed in vacuum. The residual powder was chromatographed over silica gel (200 g) and eluted with 20% benzene in hexane (500 mL). Further elution with 30% benzene in hexane (450 mL) and distillation of the eluate to dryness gave a crystalline residue (140 mg), mp 108–110 °C, which was identical with 1,3-benzodithiol-2-one **4a** (mmp). Elution was continued with 50% benzene in hexane, which eluted a red fraction (450 mL). This fraction on evaporation of solvent gave a red crystalline material, which on recrystallization from ethanol yielded 0.2 g, mp 232–233 °C. Further elution with 50% benzene in hexane (3 L) gave a fraction which was distilled to dryness in vacuum and the residual solid was recrystallized from acetone–ethanol. This yielded 2.95 g (37%) of disulfide **20**, mp 194–195 °C. Anal. Calcd for $C_{26}H_{28}F_6N_4O_6S_4$: C, 42.50; H, 3.81; N, 7.63. Found: C, 42.46; H, 3.79; N, 7.65. NMR ($CDCl_3$) δ 8.23 (m, 1 H), 8.03 (m, 1 H), 1.55 (s, 9 H).

***S,S'*-[2,2'-Dithiobis(3-(dimethylamino)-4-nitro-α,α,α-trifluoro-*o*-tolyl)] Bis(*N*-methyl-*N*-*tert*-butylcarbamothioate) (23).** To a stirred and cooled (ice–salt bath) solution of 12.54 g (0.04 mol) of 2-chloro-3-5-dinitro-4-(dimethylamino)benzotrifluoride (**6c**) in acetone (130 mL) at −7 °C was added 8.84 g (0.04 mol) of the sodium salt of *N*-methyl-*N*-*tert*-butyldithiocarbamic acid (**18**) as a solid in portions. The mixture was allowed to warm from −6 to 10 °C (3.5 h) and stirred at room temperature overnight. Acetone was removed by distillation in vacuum, water (150 mL) was added, and the mixture was extracted with methylene chloride (2 × 75 mL). The methylene chloride extract was washed with water (2 × 200 mL), dried (Na_2SO_4), and filtered and the residue obtained after removal of solvent was chromatographed over silica gel (200 g). Elution with 30% benzene in hexane gave a fraction (300 mL) which contained traces of oil. The orange-yellow fraction was eluted as the next fraction (800 mL). Removal of solvent and recrystallization of the residue from ethanol gave 1.8 g (14%) of starting material, mp 92–93 °C (mmp). Benzene (1250 mL) eluted an orange-red band. Removal of solvent gave 10 g of solid which was recrystallized by dissolving in hot acetone (150 mL), concentrating to 40 mL, and crystallizing. There was obtained 2.7 g (fraction 1) of orange-red crystals, mp 218–219 °C. The filtrate was diluted to 100 mL with ethanol and allowed to crystallize, yielding 1.3 g (fraction 2) of solid, mp 219–220 °C. The filtrate from fraction 2 was diluted with ethanol to 500 mL and allowed to crystallize overnight and yielded 0.65 g (Fraction 3), mp 169–171 °C. This last filtrate when concentrated to 10 mL gave 2.3 g (Fraction 4) of product, mp 165–167 °C. A mixture of fractions 2 and 3 melted at 167–200 °C. When 0.5 g of fraction 4 was recrystallized from hot ethanol, there was obtained 0.3 g of crystalline material consisting of large crystals, mp 175–180 °C, and smaller crystals mp 209–216 °C. It appears that this material crystallizes in different crystal forms. Fraction 2 was recrystallized from ethanol–acetone to give disulfide **23**, mp 220–221 °C. Anal. Calcd for $C_{30}H_{38}F_6N_6O_6S_4$: C, 43.90; H, 4.63; N, 10.24. Found: C, 43.96; H, 4.69; N, 10.25. NMR ($CDCl_3$) δ 8.10 (m, 1 H), 3.10 (m, 6 H), 3.0 (s, 3 H), 1.42 (d, 9 H).

7-Chloro-4-nitro-6-(trifluoromethyl)- (26) and 7-(*N,N*-Dimethyldithiocarbamyl)-4-nitro-6-(trifluoromethyl)-1,3-benzodithiol-2-one (27). To a stirred mixture of 47.8 g (0.15 mol) of 2,4-dichloro-3,5-dinitrobenzotrifluoride (**25**) in Me_2SO (150 mL) at 10 °C (ice–water bath) was added dropwise a solution of 26.9 g (0.15 mol) of **2** in Me_2SO (150 mL) within 15 min. Nitrogen oxides were evolved and by the end of addition the temperature had risen to 22 °C. The reaction mixture was allowed to stir at 10–15 °C (75 min) and at room temperature overnight. It was poured into water (600 mL) and extracted with chloroform (3 × 150 mL). After washing with water (3 × 800 mL), drying (Na_2SO_4), and filtering, silica gel (40 g) was added to the filtrate and the solvent was removed in vacuum. The residual powder was chromatographed over silica gel (450 g) and eluted with hexane–benzene (1:1). Distillation of the eluate to dryness in vacuum gave 19.2 g (40.6%) of **26.** Recrystallization from ethanol gave pure **26**, mp 87–89 °C. Anal. Calcd for $C_8HClF_3NO_3S_2$: C, 30.42; H, 0.31; N, 4.43. Found: C, 30.30; H, 0.36; N, 4.36. NMR ($CDCl_3$) δ 8.82 (s, 1 H). Elution with chloroform (250 mL), distillation of the eluate to dryness, and recrystallization of the residual solid from ethanol–acetone yielded a product, mp 194–195 °C. This was identical with that obtained after the residue from chloroform–ethanol (1:1) eluate (250 mL) was recrystallized from ethanol–acetone. A total of 4.5 g (7.5%) of sulfide **28**, mp 194–195 °C, was obtained. Anal. Calcd for $C_{17}H_8Cl_2F_6N_4O_7S_2$: C, 32.43; H, 1.27; N, 8.90. Found: C, 32.44; H, 1.22; N, 8.76. NMR (acetone-d_6) δ 8.78 (s, 1 H), 8.65 (s, 1 H), 3.23 (s, 6 H). The ethanol–acetone mother liquor from recrystallization of the chloroform eluate was evaporated to dryness and the residue was triturated with hot ethanol and suction filtered. Recrystallization from ethanol gave 2.0 g (3.3%) of **27**, mp 138–140 °C. Anal. Calcd for $C_{11}H_7F_3N_2O_3S_4$: C, 33.00; H, 1.75; N, 7.00. Found: C, 32.96; H, 1.68; N, 6.93.

Bis[2,6-dinitro-4-(trifluoromethyl)phenyl] Sulfide (32). A solution of 2.9 g (20 mmol) of *N*-methyldithiocarbamic acid sodium salt in Me_2SO (20 mL) was added to a stirred solution of 5.4 g (20 mmol) of **1a** in Me_2SO (20 mL). The resulting deep red solution was allowed to stir (4 h) and the mixture was made acidic with 2 N HCl, poured into water (400 mL), and extracted with chloroform (3 × 75 mL). After two water washings and drying (Na_2SO_4), the solvent was removed in vacuum and the solid residue on recrystallization from ethanol gave 1.2 g (24%) of **32**, mp 191–193 °C. Anal. Calcd for $C_{14}H_4F_6N_4O_8S$: C, 33.46; H, 0.79; N, 11.15. Found: C, 33.26; H, 0.70; N, 10.97. NMR (Me_2SO-d_6) δ 8.93 (s).

4-(Dipropylamino)-5-nitro-7-(trifluoromethyl)-1,3-benzodithiol-2-one (39). To a solution of 23.2 g (64 mmol) of 2-chloro-3,5-dinitro-4-(dipropylamino)benzotrifluoride in acetone (130 mL) at −5 °C (ice–salt bath) was added 11.3 g (63 mmol) of **2** as a solid in portions. After being stirred (2 h) at 0–5 °C and room temperature (2 h) the mixture was refluxed overnight. After removal of acetone in vacuum, the residue was chromatographed over silica gel (200 g) and eluted with hexane (2 L). Removal of solvent from the hexane eluate yielded 18.6 g (78%) of **39**, mp 58–60 °C. Recrystallization from hot ethanol yielded 14.0 g of analytically pure **39**, mp 60–61 °C.

5-Nitro-4-(*n*-propylthio)-7-(trifluoromethyl)-1,3-benzodithiol-2-one (59). To a stirred and cooled (water bath) solution of 12.2 g (35.5 mmol) of 2-chloro-3,5-dinitro-4-(*n*-propylthio)benzotrifluoride in acetone (100 mL) was added 8.0 g (50 mmol) of **2** as a solid. After being stirred with water-bath cooling (40 min) the mixture was refluxed (5.5 h). Acetone was removed in vacuum, and the residue was dissolved in chloroform (100 mL) and washed with water (3 × 50 mL).

After drying (Na_2SO_4), the solvent was removed in vacuum and the residue was chromatographed over silica gel (150 g). Elution with hexane–benzene (1:1) gave 10 g of solid, which on recrystallization from ethanol gave 8.6 g (68%) of **59**, mp 87–88 °C. Anal. Calcd for $C_{11}H_8F_3NO_3S_3$: C, 37.18; H, 2.25; N, 3.94. Found: C, 36.87; H, 2.14; N, 3.81. NMR ($CDCl_3$) δ 8.1 (s, 1 H), 3.1 (t, 2 H), 1.6 (m, 2 H), 1.05 (t, 3 H).

***N,N*-Dimethyl-2-[2,6-dinitro-4-(trifluoromethyl)thiophenyl]-3-methylbut-3-enethioamide (34).** To a stirred solution of 17.3 g (64 mmol) of benzotrifluoride **1a** in dry methanol (75 mL) at −3 to −5 °C (ice–salt bath) was added dropwise a solution of 12.6 g (64 mmol) of mercaptothioamide sodium salt (**33**)[14] in dry methanol (75 mL). The mixture was stirred at 0 °C (2 h) and at room temperature (2 h), poured into water (1200 mL), and extracted with chloroform (2 × 150 mL). The chloroform extract was washed with water (3 × 1000 mL), dried (Na_2SO_4), and filtered into a flask containing silica gel (20 g). The solvent was removed in vacuum, and the residual powder was chromatographed over silica gel (150 g) and eluted with 50% benzene in hexane. The first fraction (950 mL) was discarded. The following fraction (500 mL) was distilled to dryness in vacuum and yielded 12 g (46%) of **34**, mp 113–115 °C. Anal. Calcd for $C_{14}H_{14}F_3N_3O_4S_2$: C, 40.97; H, 3.41; N, 10.24. Found: C, 41.04; H, 3.49; N, 10.05. NMR ($CDCl_3$) δ 8.23 (s, 2 H), 5.38 (s, 1 H), 5.03 (m, 1 H), 4.59 (m, 1 H), 3.59 (s, 3 H), 3.44 (s, 3 H), 1.91 (s, 3 H).

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Registry No.—**1a**, 393-75-9; **1b**, 88-88-0; **1c**, 1930-72-9; **1d**, 62558-39-8; **1f**, 5264-65-3; **2**, 128-04-1; **6c**, 59431-66-2; **17**, 68151-96-2; **18**, 68151-97-3; **20**, 68151-98-4; **23**, 68151-99-5; **24**, 68152-00-1; **25**, 29091-09-6; **26**, 63417-86-7; **27**, 63417-85-6; **28**, 68152-01-2; **32**, 59983-53-8; **33**, 68152-02-3; **34**, 68152-03-4; 2,6-dinitro-4-fluorophenol, 364-32-9; 1,4-dichloro-2,6-dinitrobenzene, 2213-82-3; 2,6-dinitro-4-chlorophenol, 88-87-9; 3,6-dichloro-2,4-dinitrotoluene, 40319-44-6; 4-chloro-2,6-dinitro-3-methylphenol, 15968-57-7; 4-chloro-3,5-dinitrobenzamide, 20731-63-9; 2-chloro-3,5-dinitro-4-(*n*-propylthio)benzotrifluoride, 63418-02-0; 2-chloro-3,5-dinitro-4-(isopropylthio)benzotrifluoride, 63418-03-1; *N*-methyl-*N*-*tert*-butylamine hydrochloride, 22675-79-2; carbon disulfide, 75-15-0; *N*-methyldithiocarbamic acid sodium salt, 137-42-8; 2-chloro-3,5-dinitro-4-(dipropylamino)benzotrifluoride, 29091-20-1.

Supplementary Material Available: Analytical data on 1,3-benzodithiol-2-ones and disulfides (3 pages). Ordering information is given on any current masthead page.

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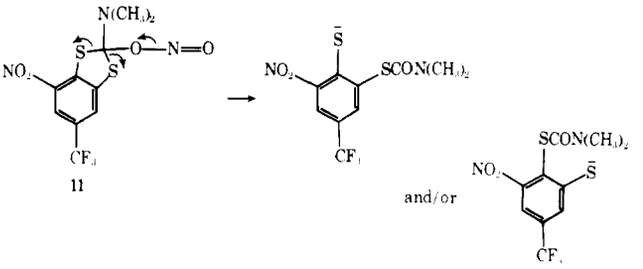

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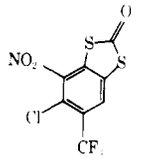
(13) We have no experimental evidence to rule out the following alternative structure for dithiolone **26**. This also applies to dithiolones **27** and **66** (Table I). We have arbitrarily favored removal of the more sterically crowded nitro



group. The resulting relief of steric strain from an ortho substituent may be responsible for the exclusive formation of only one isomer. We plan work to distinguish between these two possible structures.
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