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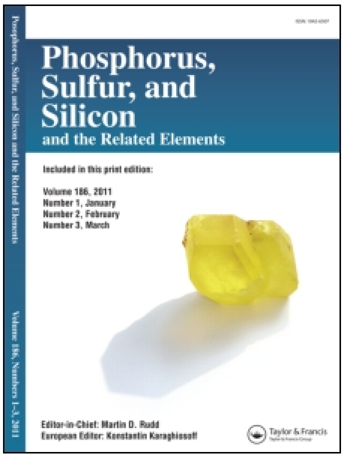

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DERIVATIVES OF 4-CHLORO-3,5-DINITROBENZOTRIFLUORIDE V. SYNTHESIS OF 4,6-DINITRO-2,8-BIS(TRIFLUOROMETHYL) PHENOTHIAZINE (1), ISOPROPYL 2,6-DINITRO-4-TRIFLUOROMETHYLPHENYL SULFIDE (2) AND BIS(2,6-DINITRO-4-TRIFLUOROMETHYLPHENYL) DISULFIDE (3)

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DERIVATIVES OF 4-CHLORO-3,5-DINITROBENZOTRIFLUORIDE V. SYNTHESIS OF 4,6-DINITRO-2,8-BIS(TRIFLUOROMETHYL) PHENOTHIAZINE (1), ISOPROPYL 2,6-DINITRO-4-TRIFLUOROMETHYLPHENYL SULFIDE (2) AND BIS(2,6-DINITRO-4-TRIFLUOROMETHYLPHENYL) DISULFIDE (3)[1]

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(*Received January 11, 1979*)

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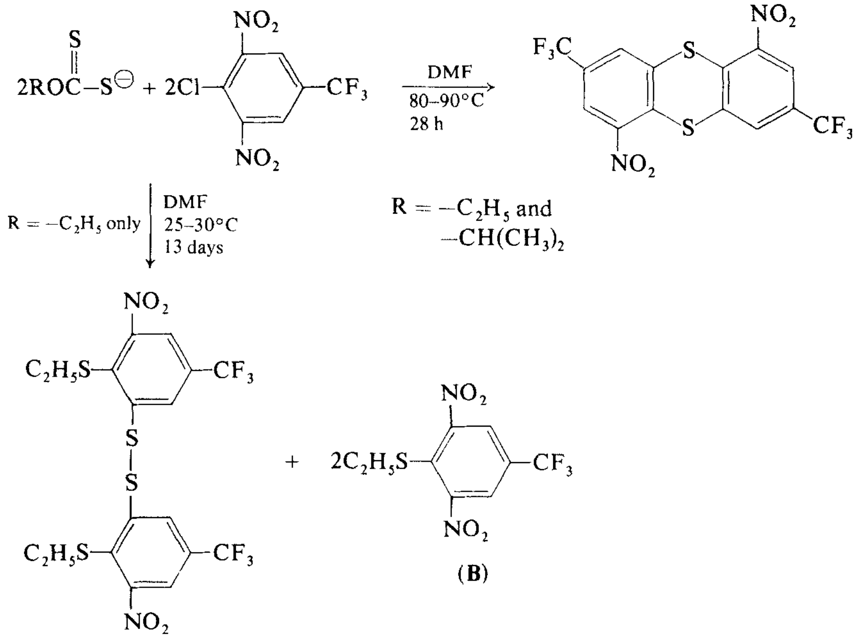
The reaction of potassium isopropyl dithiocarbonate with 4-chloro-3,5-dinitrobenzotrifluoride in dimethylformamide at 25–30°C afforded the titled phenothiazine (1) and sulfide (2). The reaction of *bis*(2,6-dinitro-4-trifluoromethylphenyl)-sulfide or the above halogen compound with sodium hydrosulfide in the same solvent at 80–90°C furnished 1. At 25–30°C the latter reaction afforded the titled disulfide (3). Possible mechanisms and supporting nmr, ir and mass spectral data are discussed.

In a recent communication[2] we reported that the reaction of potassium ethyl or isopropyl dithiocarbonate with 4-chloro-3,5-dinitrobenzotrifluoride in DMF at 80–90°C afforded 1,6-dinitro-3,8-*bis*(trifluoromethyl)-thianthrene. However, when this reaction was repeated using only potassium ethyl dithio-



(A)

(B)

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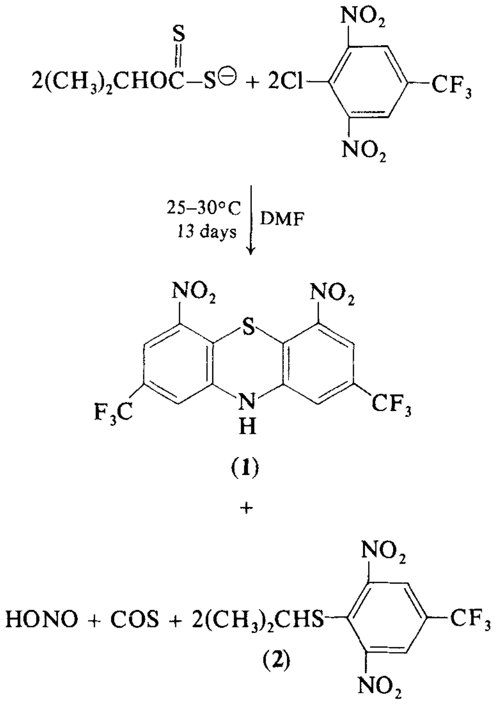
carbonate and the above halogen compound in DMF at 25–30°C, two unexpected (**A**) and (**B**) were obtained.[3]

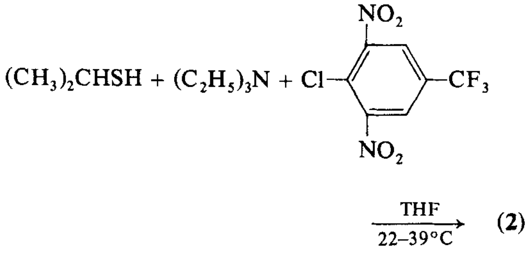
We now wish to report that the reaction of potassium isopropyl dithiocarbonate with the above halogen compound in DMF at 25–30°C afforded two additional unexpected products (**1**) and (**2**) in 29 and 32% yields, respectively.



(1)

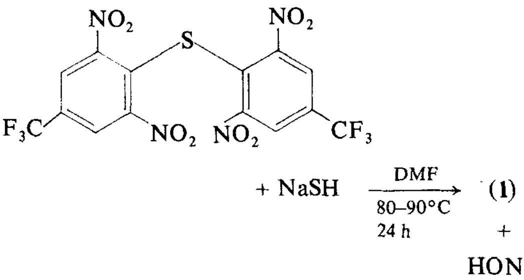
The complete elemental analysis, nmr, ir and mass spectral data are in complete agreement for the proposed structure (**1**). The electron impact mass spectrum of (**1**) furnished the molecular weight data in the form of $M^{+\cdot}$ at *m/e* 425. The presence of a chemical shift at 10.05 ppm (broad singlet) in the nmr and 3460 and 3300 cm^{-1} adsorption bands in the ir spectrum confirmed the presence of the NH moiety in (**1**).

Proof of structure for (**2**) was established by the following conventional reaction (2).



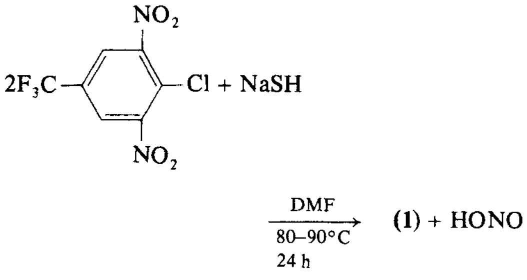
(2)

It was conceived that *bis*(2,6-dinitro-4-trifluoromethylphenyl)sulfide[4] could be the precursor for the formation of (**1**) in reaction (1). Our postulate was substantiated for the reaction of the above sulfide with sodium hydrosulfide in DMF at 80–90°C furnished (**1**) in 47% yield.

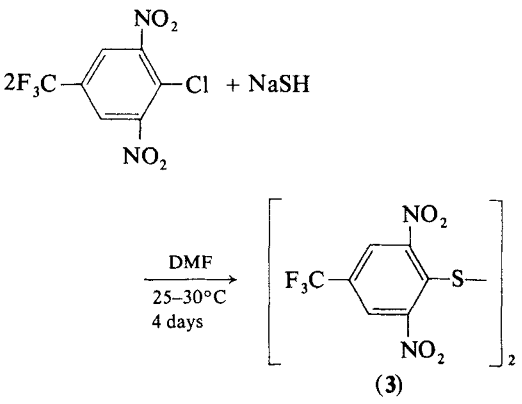


(3)

It was anticipated that the reaction of 4-chloro-3,5-dinitrobenzotrifluoride with sodium hydrosulfide in DMF at 80–90°C would give the above sulfide which then could react with more sodium hydrosulfide to give (**1**). This was actually the case for the above conditions furnished (**1**) in 40% yield (reaction 4). However when reaction (4) was repeated at temperatures of 25–30°C none of (**1**) was formed and the major product, *bis*(2,6-dinitro-4-trifluoromethylphenyl) disulfide (**3**), was obtained in 84% yield.



(4)



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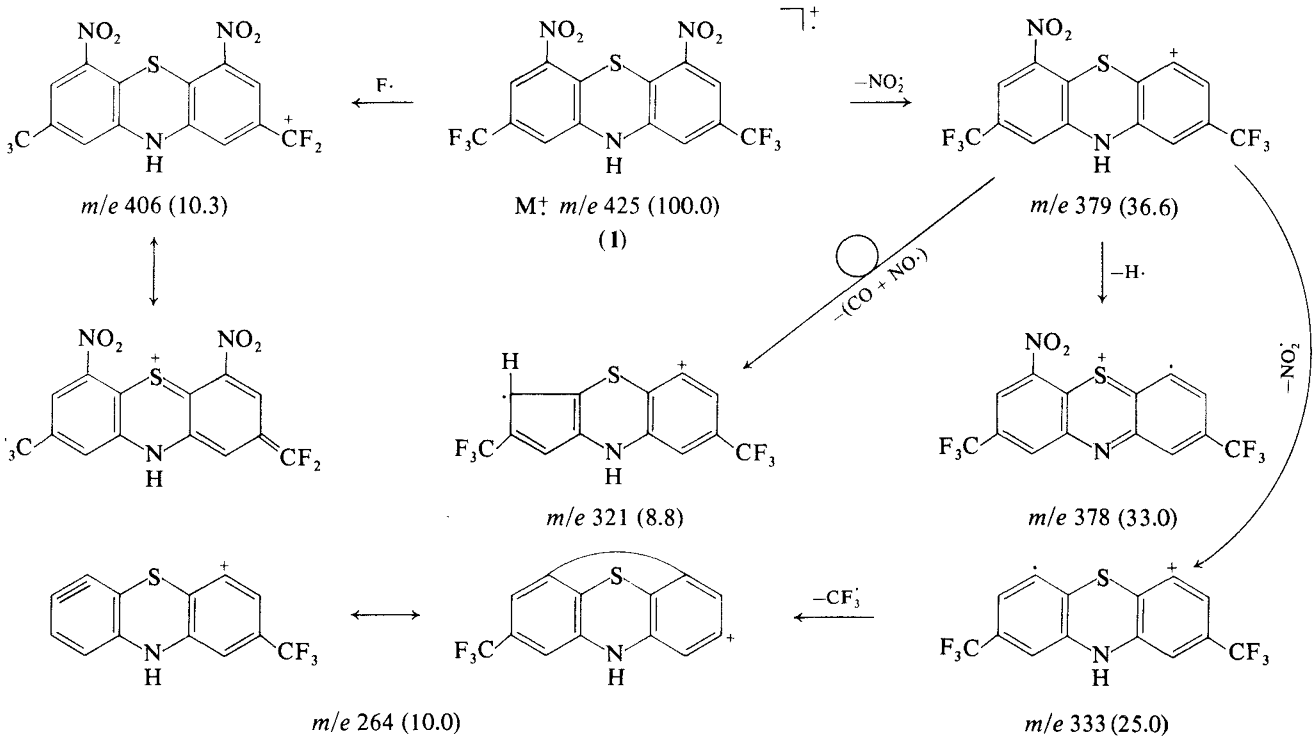
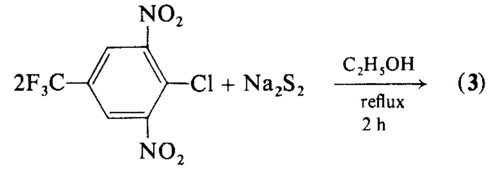
SCHEME 1



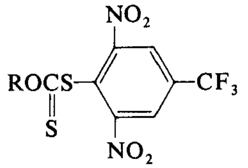
Proof of structure for (**3**) was established by the following conventional reaction:



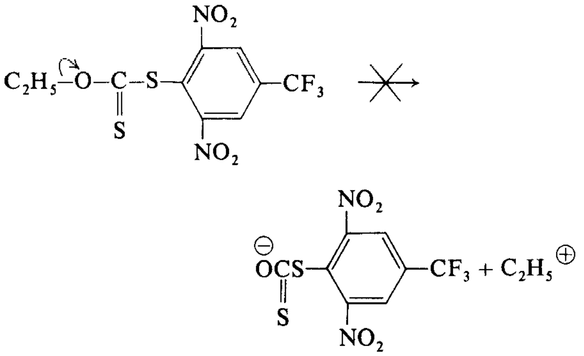
The possible mass spectral fragmentation route for (**1**) is shown in scheme 1.

The proposed mechanisms for reaction (1) and reactions (3) and (4) are depicted in schemes (2) and (3), respectively.

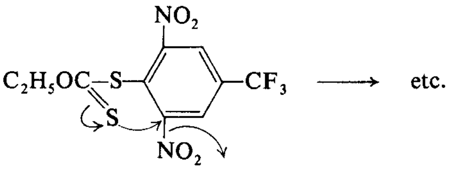
A possible reason why the reaction of potassium isopropyl or ethyl dithiocarbonate with 4-chloro-3,5-dinitrobenzotrifluoride under the same conditions gave two different products, (**1**) and disulfide (**A**) can be explained on the basis of the stability of the intermediate



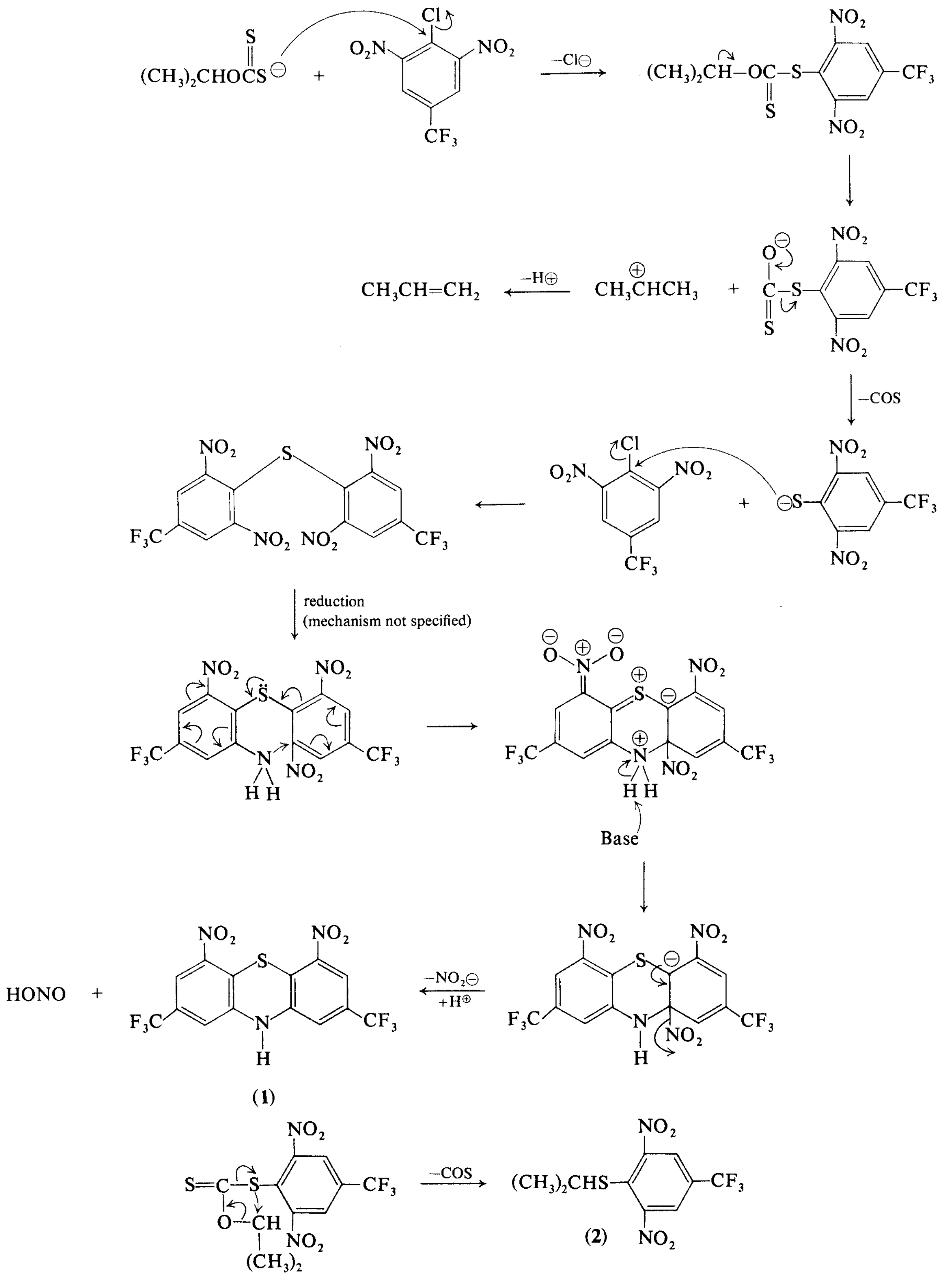
When R is isopropyl, a stable secondary carbonium ion $(CH_2\overset{\oplus}{C}HCH_3)$ can form (see scheme 2). Whereas in the case when R is ethyl, a very unstable primary carbonium ion would form.



Thus the above intermediate would proceed by the pathway depicted in our latest communication.[3]



SCHEME 2



(1)

(2)

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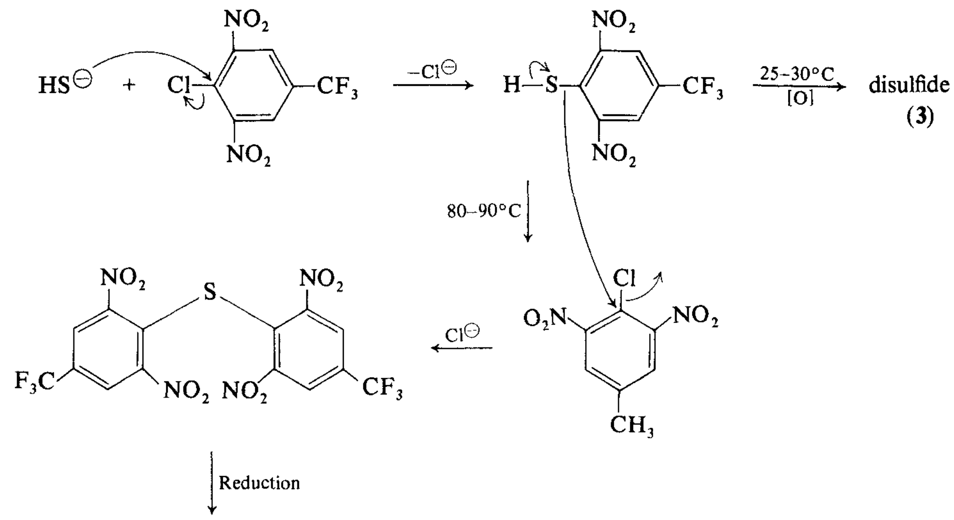
SCHEME 3



The remainder of the pathway
is identical as shown in Scheme 2

EXPERIMENTAL SECTION

Nmr spectra were obtained with a Varian T-60 nmr spectrometer. The chemical shifts are reported in δ, using tetramethylsilane as reference. All melting points were taken upon a Fisher–Johns block and are uncorrected. The electron impact mass spectra of (**1**) was determined with a Varian-MAT CH-7A mass spectrometer operating at an ionizing potential of 70 eV using the direct insertion probe technique with a source temperature of 250°C. The infrared spectra of (**1**) was obtained with a Beckman IR-12 spectrophotometer.

4,6-Dinitro-2,8-bis(trifluoromethyl)-phenothiazine (**1**) (*Method I*) *and isopropyl 2,6-dinitro-4-trifluoromethylphenyl sulfide* (**2**). To a stirred solution containing 138.9 g (0.66 mol) of potassium isopropyl dithiocarbonate dihydrate in 500 ml of dimethylformamide at −20°C, 162 g (0.60 mol) of 4-chloro-3,5-dinitrobenzotrifluoride was added in small portions over a 10 min period while maintaining the temperature below 10°C. The reaction mixture was stirred at 25–30°C for 13 days. During this period COS was liberated and a sample of COS was collected over helium and identified by mass spectrometry. After cooling to 5°C, 650 ml of ethyl ether and 2000 g of ice water were added and stirring continued at 25–30°C for 2 h. The precipitate was collected by filtration, washed with 250 ml of ethyl ether and finally with water until the washings were neutral to litmus and air-dried at 50°C. The crude product (38 g), mp 235–239°C (sinters at 115°C), was slurried with 400 ml of carbon disulfide for 18 h, filtered and air-dried at 50°C. (**1**), mp 246–247°C, was obtained in 29% yield. After recrystallization from ethyl acetate the melting point remained unchanged. The removal of carbon disulfide *in vacuo* gave 1.7 g of sulfur, mp 116–117°C: nmr (Me_2SO-d_6) δ 7.70–8.20 (m, 4, ArH); 10.05 (br s, 1, NH); mass spectrum *m/e* (rel intensity), 425 (100), 408 (5.2), 406 (10.3), 379 (36.6) 378 (33.0), 333 (25.0), 264 (10.0), 212 (4.0) and 69 (7.7). Ir (CsI): 3460 and 3300 (NH), 3110 and 3050 (ArCH), 1628 and 1592 (Ar skeletal ring breathing modes), 1547 (NO_2 asym), 1514 (NH deform), 1451 (Ar skeletal ring breathing mode), 1341 (NO_2 sym), 1313 (CF_3 sym), 1285 (aryl amide CN st), 1172, 1143 and 1122 (CF_3 anti-sym), 910, 890 and 880 (Ar-CH deform) and 700–800 cm^{-1} (CF_3 deform).

Anal. Calcd for $C_{14}H_5F_6N_3O_4S$: C, 39.54; H, 1.19; F. 26.81; N, 9.88; S, 7.54. Found: C, 39.45; H, 1.16; F, 27.01; N, 9.68; S, 7.30.

The ethyl ether of the filtrate was removed *in vacuo*. The filtrate was extracted with four 450 ml portions of chloroform. The combined chloroform extracts were washed with water until neutral to litmus, dried over sodium sulfate and the chloroform removed *in vacuo* on a rotary evaporator at a maximum temperature of 90°C at 1–2 mm. The residue (128.5 g) was slurried with 300 ml of chloroform and filtered to remove 0.5 g of impurities. The filtrate was diluted with chloroform to a volume of 400 ml. One sixth (66.6 ml) of this solution was slurried with 75 g of silica gel and the solvent removed *in vacuo* at maximum temperature of 90°C at 1–2 mm. This mixture was added to a column containing 525 g of silica gel in 60/40 mixture of cyclohexane/chloroform. Elution with 60/40 mixture of cyclohexane/chloroform gave 10 g (32%) of (**2**), mp 64–65°C. After recrystallization from heptane, (**2**) melted at 68–69°C. Nmr ($CDCl_3$) δ 1.23 [d, 6, CH(CH_3)$_2$], 3.53 (h, 1, CH), 8.10 (s, 2, ArH).

Anal. Calcd for $C_{10}H_9F_3N_2O_4S$: C, 38.71; h, 2.92; F, 18.37; N, 9.03; S, 10.33. Found: C, 38.54; H, 2.78; F, 18.53; N, 8.97; S, 10.39.

(**2**) (*Conventional method*). To a stirred solution containing 7.6 g (0.1 mol) of isopropyl mercaptan, 10.3 g (0.1 mol) of triethylamine and 100 ml of tetrahydrofuran, 27 g (0.1 mol) of 4-chloro-3,5-dinitrobenzotrifluoride was added in one portion. An exothermic reaction set in causing a temperature rise from 22 to 39°C. The reaction mixture was stirred at 25–30°C for 1 day. After the addition of 800 g ice water stirring was continued at 0–10°C for 1 h. The solid was collected by filtration, washed with cold water until the washings were neutral to litmus and air-dried at 25–30°C. The crude product (**2**), mp 67–68°C, was obtained in 97% yield. After recrystallization from heptane (**2**),

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melted at 68–69°C. A mixture melting point with the product obtained from the former method was not depressed and the nmr spectra of the two were identical.

Anal. Calcd for $C_{10}H_9F_3N_2O_4S$: C, 38.71; H, 2.92; N, 9.03; S, 10.33. Found: C, 38.71; H, 2.95; N, 9.10; S, 10.38.

(**1**) (*Method II*). To a stirred solution containing 75.4 G (0.15 mol) of *bis*(2,6-dinitro-4-trifluoromethylphenyl)sulfide[4] in 200 ml of dimethylformamide at −20°C, 11.4 g (0.12 mol) of sodium hydrosulfide dihydrate was added in one portion. Cooling was removed and an exothermic reaction set in causing a temperature rise from −20°C to 73°C over a 15 min period. After the exothermic reaction had subsided, the stirred reaction mixture was heated at 80–90°C for 24 h and then at 25–30°C for 24 h. During the exothermic reaction and the heating period a brown yellow gas (HONO) was liberated. After cooling to 5°C, 500 ml of ethyl ether and 1500 g of ice water were added and stirring continued at 25–30°C for 2 h. The precipitate was collected by filtration, washed successively with water until neutral to litmus, then with 250 ml of ethyl ether and air-dried at 50°C. The crude product (30 g), mp 245–246°C, was slurried with 200 ml of carbon disulfide for 2 h, filtered and air-dried at 50°C. (**1**), mp 245–246°C, was obtained in 47% yield. The removal of carbon disulfide *in vacuo* gave no sulfur. After recrystallization from ethyl acetate (**1**) melted at 246–247°C. A mixture melting point with the product obtained by method I was not depressed and the nmr spectra of the two were identical.

Anal. Calcd for $C_{14}H_{15}F_6N_3O_4S$: C, 39.54; H, 1.19; F, 26.81; N, 9.88; S, 7.54. Found: C, 39.40: H, 1.21; F, 26.60; N, 9.69; S, 7.69.

The ethyl ether of the filtrate was removed *in vacuo*. The residue was extracted with four 450 ml portions of chloroform. The combined chloroform extracts were washed with water until the washings were neutral to litmus, dried over sodium sulfate and the chloroform removed *in vacuo* on a rotary evaporator at a maximum temperature of 90–95°C at 1–2 mm. The residue (28.5 g) was slurried with 300 ml of chloroform and filtered to remove 0.1 g of impurities. The filtrate was diluted with chloroform to a volume of 400 ml. Seventy per cent (280 ml) of this solution was slurried with 75 g of silica gel and the solvent removed *in vacuo* at maximum temperature of 90°C at 1–2 mm. This mixture was added to a column containing 525 g of silica gel in 60/40 mixture of cyclohexane/chloroform. Elution with 60/40 mixture of cyclohexane/chloroform gave seven unidentifiable fractions.

(**1**) (*Method III*). To a stirred slurry at 60°C containing 28.2 g (0.31 mol) of sodium hydrosulfide dihydrate and 200 ml of dimethylformamide, a solution containing 108 g (0.4 mol) of 4-chloro-3,5-dinitrobenzotrifluoride in 150 ml of dimethylformamide was added dropwise at 60°C to 84°C over a 1.5 h period. During the addition period a brown-yellow gas (HONO) was liberated. The stirred reaction was heated at 80–90°C for 24 h. After cooling to 5°C, 500 ml of ethyl ether and 1500 g of ice water were added and stirring continued at 25–30°C for 2 h. The precipitate was collected by filtration, washed successively with water until neutral to litmus, then with 250 ml of ethyl ether and air-dried at 50°C. Crude (**1**) (34 g), mp 238–239°C, was slurried with 200 ml of carbon disulfide for 2 h, filtered and air-dried at 50°C. (**1**), mp 238–239°C, was obtained in 40% yield. The removal of carbon disulfide *in vacuo* gave no sulfur. After recrystallization from ethyl acetate (**1**) melted at 246–247°C. A mixture melting with products obtained by method I or II was not depressed and their nmr spectra were identical.

Anal. Calcd for $C_{14}H_{15}F_6N_3O_4S$: C, 39.54; H, 1.19; F, 26.81; N, 9.88; S, 7.54. Found: C, 39.55; H, 1.17; F, 27.04; N, 9.92; S, 7.40.

The ethyl ether of the filtrate was removed *in vacuo*. The residue was extracted with four 450 ml portions of chloroform. The combined chloroform extracts were washed with water until the washings were neutral to litmus, dried over sodium sulfate and the chloroform removed *in vacuo* on a rotary evaporator at maximum temperature of 90°C at 1–2 mm. The residue (107 g) was slurried with 300 ml of chloroform and filtered to remove 1 g of impurities. The filtrate was diluted with chloroform to a volume of 400 ml. One-fifth of this solution was chromatograohed over 600 g of silica gel. Elution with 60/40 mixture of cyclohexane/chloroform gave six unidentifiable fractions.

Bis(2,6-Dinitro-4-trifluoromethylphenyl)disulfide (**3**) (*Method I*). To a stirred slurry at 0°C containing 14.1 g (0.155 mol) of sodium hydrosulfide dihydrate and 100 ml of dimethylformamide, a solution containing 54 g (0.2 mmol) of 4-chloro-3,5-dinitrobenzotrifluoride in 50 ml of dimethylformamide was added dropwise at 0–25°C over a 2 h period. The reaction mixture was stirred at 25–30°C for 4 days. During this period no brown-yellow gas was liberated. After cooling to 5°C, 1000 g of ice water was added and stirring continued at 25–30°C for 2 h. The solid was collected by filtration, washed with water until neutral to litmus and air-dried at 25–30°C. The crude (**3**), mp 135–140°C, was obtained in 84% yield. After recrystallization from isopropyl alcohol and ethyl acetate (10:1), (**3**) melted at 194–195°C. Nmr (Me_2SO-d_6) δ 8.85 (s, 4, ArH).

Anal. Calcd for $C_{14}H_4F_6N_4O_8S_2$: C, 31.47; H, 0.75; F, 21.33; N, 10.49; S, 12.00; M.wt. 534.3. Found: C, 31.65; H, 1.12; F, 21.03; N, 10.30; S, 11.70: M.wt. 530 (C_6H_6).

(**3**) (*Conventional method*). To a stirred solution containing 72 g (0.30 mol) of sodium sulfide nonohydrate in 300 ml of 95% ethyl alcohol, 9.6 g of sulfur was added and heated at reflux for 1 h. This solution was added dropwise over a 30 min period to a stirred slurry containing 108 g (0.4 mol) of 4-chloro-3,5-dinitrobenzotrifluoride and 100 ml of ethyl alcohol. During this addition the temperature rose from 24 to 70°C. The stirred reaction mixture was heated at reflux for 2 h. After cooling to −10°C, the solid was collected by filtration, washed with 100 ml of heptane and air-dried at 25–30°C. The crude product (73.5 g) which contains sodium chloride was slurried with 500 ml of water for 30 min, filtered, washed with water until free of chloride ion and air-dried at 25–30°C. (**3**), mp 191–193°C, was obtained in 45% yield. After recrystallization from isopropyl alcohol–ethyl acetate (10:1), (**3**) melted at 194–195°C. A mixture melting point with the product obtained from method I was not depressed and the nmr spectra of the two were identical.

Anal. Calcd for $C_{14}H_4F_6N_4O_8S_2$: C, 31.47; H, 0.75; F, 21.33; N, 10.49; S, 12.00. Found: C, 31.21; H, 0.81; F, 21.59; N. 10.30; S, 12.20.

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