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HETEROCYCLIC AND RELATED COMPOUNDS DERIVED FROM DIPOTASSIUM 1,1-DIMERCAPTO-2,2-DICYANOETHYLENE AND SODIUM 2-MERCAPTOPYRIDINE N-OXIDE

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HETEROCYCLIC AND RELATED COMPOUNDS DERIVED FROM DIPOTASSIUM 1,1-DIMERCAPTO-2,2-DICYANOETHYLENE AND SODIUM 2-MERCAPTOPYRIDINE N-OXIDE^{1,2}

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J. J. FREEMAN and W. E. DAHL

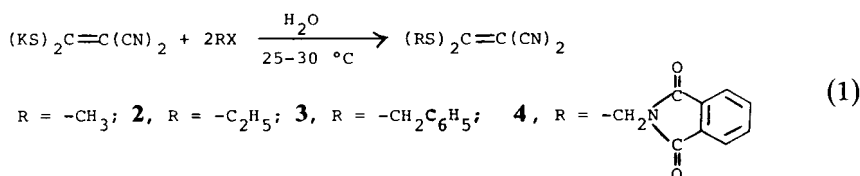
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The reaction of dipotassium 1,1-dimercapto-2,2-dicyanoethylene with certain halogen compounds furnished the expected dialkylolation products (1)–(4). Replacing the halogen compound with 4-chloro-3,5-dinitrobenzotrifluoride afforded a novel heterocycle (5). The reaction of the potassium salt with phenyl or p-chlorophenylchlorothioformate gave 2,2-diphenyl or di-p-chlorophenylthio-2,2-dicyanoethylene (6) and (7). The reaction of 1 or 2 with excess hydrogen peroxide afforded substituted oxiranes (8) and (9). Depending on reaction conditions, the reaction of sodium 2-mercaptopyridine N-oxide with 4-chloro-3,5-dinitrobenzotrifluoride afforded either the expected sulfide (11) or the unexpected heterocycle (12). Possible mechanisms and supporting NMR, Ir and mass spectral data are discussed.

In a previous communication³ we reported that the reaction of dipotassium 1,1-dimercapto-2,2-dicyanoethylene⁴ with 3-bromo-1-propyne, 3-chloro-3-methyl-1-propyne, 3-chloro-2,4-pentanedione, ethyl α-chloroacetoacetate or chloroacetone afforded novel heterocyclic compounds. Thus it appeared desirable to replace the above halogen compounds with other electrophiles.

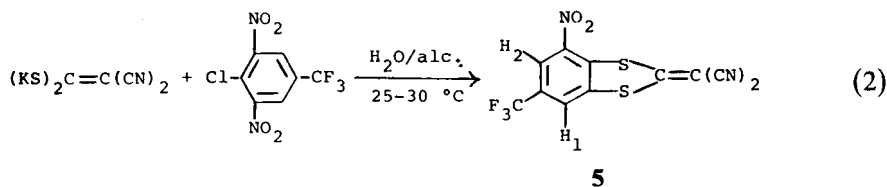
The reaction of an aqueous solution of dipotassium 1,1-dimercapto-2,2-dicyanoethylene⁴ with methyl iodide, ethyl bromide, benzyl bromide and N-(chloromethyl) phthalimide afforded the expected 1,1-dimethylthio-2,2-dicyanoethylene (1), 1,1-diethylthio-2,2-dicyanoethylene (2), 1,1-dibenzylthio-2,2-dicyanoethylene (3) and Bis[(1,3-dihydro-1,3-dioxo-2H-isoindol-2-yl)methyl]thio[methylene]propanedinitrile (4), respectively.



1 and **2** were first prepared in 1950 by Edwards and Tendall.⁵ Their method for the synthesis of **1** and **2** is tedious, inefficient, difficult and uneconomical. However, when the above halogen compounds were replaced with 4-chloro-3,5-dinitrobenzotrifluoride, the expected product was not obtained but instead [4-nitro-6-(tri-

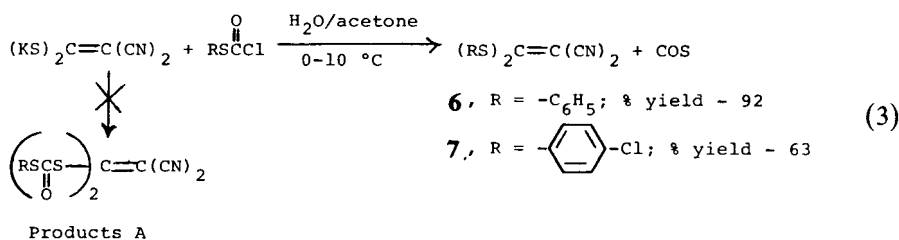
*Author to whom all correspondence should be addressed.

fluoromethyl)-1,3-benzodithiol-2-ylidene]propanedinitrile (**5**) was obtained in 94% yield.

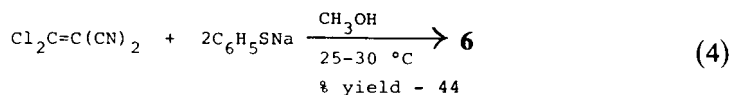


Proof of structure **5** was based on analysis, NMR and mass spectra. The H_1 and H_2 protons appeared as broad singlets 8.90 and 9.16 δ , respectively. Furthermore, the electron impact mass spectrum of **5** furnished the molecular weight data in the form of M^+ 329 (100%). The proposed mechanisms (one electron transfer or stabilized anion) are depicted in Scheme 1.

The reaction of the potassium salt with phenyl or *p*-chlorophenylchlorothioformate did not furnish the expected products **A** but instead afforded 1,1-diphenylthio-2,2-dicyanoethylene (**6**) and 1,1-di-*p*-chlorophenylthio-2,2-dicyanoethylene (**7**), respectively.

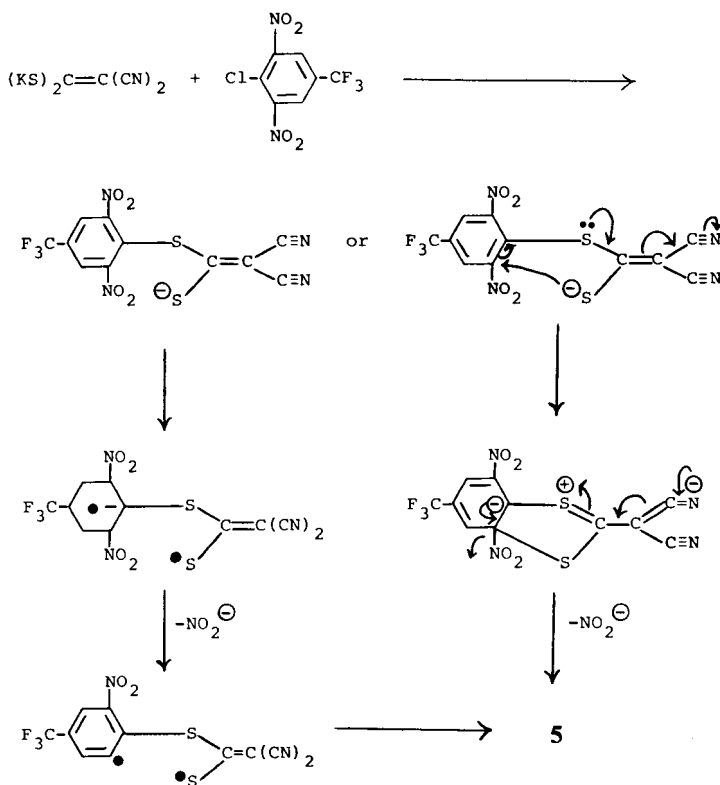


The analysis, NMR and mass spectra data are in complete agreement for the proposed structures **6** and **7**. The synthesis of **6** and **7** by reaction 3 illustrates the use of dipotassium 1,1-dimercapto-2,2-dicyanoethylene as an effective sulfur transfer agent. The proposed mechanism for reaction 3 is depicted in Scheme 2. Preparation of **6** was first reported by Soulen and co-workers⁶ by the reaction of 1,1-dichloro-2,2-dicyanoethylene (powerful irritant to the throat and lungs) with sodium thiophenoxide.

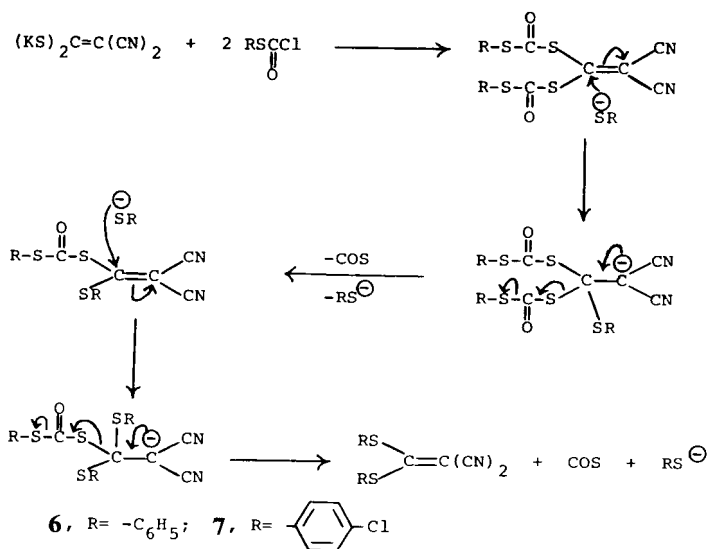


In summary, our new route provides a synthesis of **6** and related derivatives that is fast, efficient, economical and uncomplicated by side reactions. Moreover, the required reactants (reaction 3) are readily available and inexpensive and the yields are superior to the yield obtained by reaction 4.

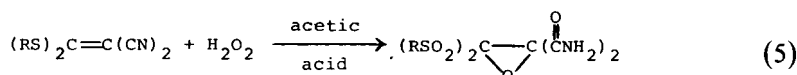
The reaction of **1** and **2** in an acetic acid solution with excess hydrogen peroxide (a very exothermic reaction) afforded 3,3-bis(methylsulfonyl)-2,2-oxiranedicarboxamide (**8**) and 3,3-bis(ethylsulfonyl)-2,2-oxiranedicarboxamide (**9**), respectively.

SNR' or STABILIZED ANION

SCHEME 1

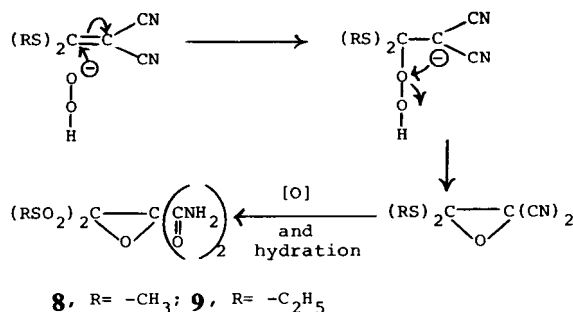
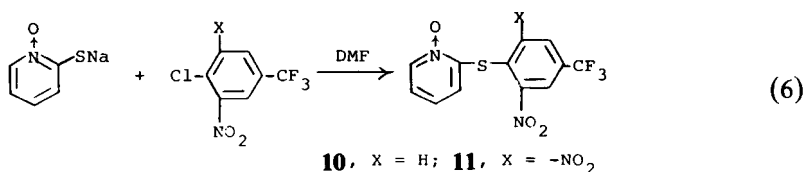


SCHEME 2

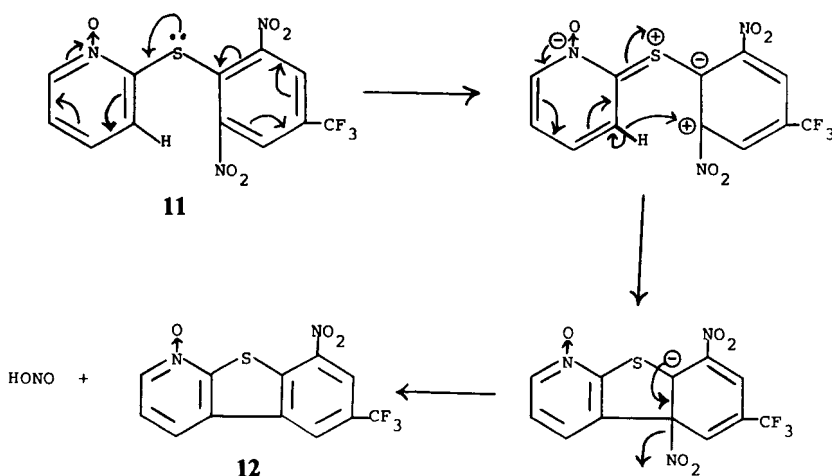


It is noteworthy that in reaction 5 the sulfide, olefin and nitrile groups were converted to the sulfone, epoxide and amido moieties, respectively. Proof of structure for crude **8**, mp 191–193°C dec., and **9**, mp 195–197°C dec., was established by analysis, NMR and Ir. The formation of the epoxide ring in reaction 5 was confirmed by the presence of 1240 and 821 cm⁻¹ for **8** and 1234 and 807 cm⁻¹ for **9** adsorption bands in the Ir spectra. The shelf life stability of **8** and **9** was good. The oxiranes **8** and **9** were insoluble in most organic solvents (ether, acetone, chloroform, benzene, heptane, ethyl acetate and ethanol) but possessed limited solubility in a 95% dimethylformamide-water solution. Attempts were made to recrystallize **8** and **9** from 95% DMF. In each case the recovered yield was very low and the isolated **8** and **9** melted at 140–150°C (dec.) and 130–145°C (dec.), respectively. Moreover, based on the erratic elemental analysis⁷ (C, H, N and S) and NMR spectral data for the recrystallized samples, assignment of structures was not possible and it was concluded that **8** and **9** either reacted with the 95% DMF at 100–110°C or decomposed to give a mixture of unidentifiable products. The limited stability of these compounds prevented the use of more definitive analytical techniques such as electron impact or isobutane chemical ionization mass spectra. The proposed mechanism for reaction 5 is depicted in Scheme 3.

Since reaction 2 furnished the novel heterocycle **5**, we anticipated that by replacing the nucleophile with sodium 2-mercaptopyridine-*N*-oxide would have followed the same pathway as depicted in scheme 1, i.e. the initial formation of the sulfide followed by cyclization and with the loss of the NO₂⁻ anion would have afforded another novel heterocycle. Our postulate was substantiated for the reaction of sodium 2-mercaptopyridine-*N*-oxide with 4-chloro-3-nitrobenzotrifluoride in DMF at 90–100°C or 4-chloro-3,5-dinitrobenzotrifluoride in same solvent at 25–30°C afforded the expected 2-[2-nitro-4-trifluoromethylphenylthio]pyridine *N*-oxide (**10**) and 2-[2,6-dinitro-4-trifluoromethylphenylthio]pyridine *N*-oxide (**11**), respectively.

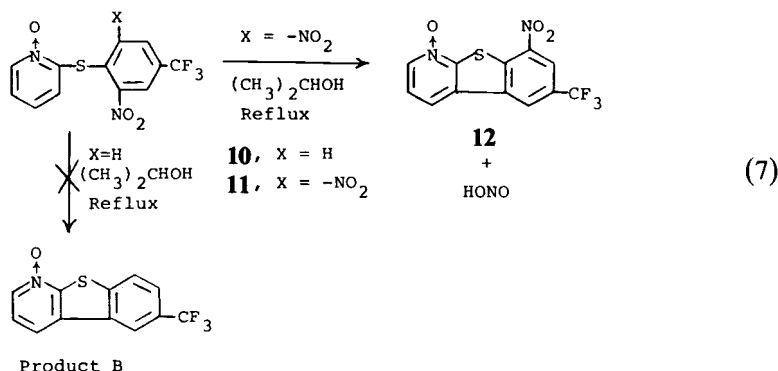


SCHEME 3



SCHEME 4

Moreover, by heating **11** in isopropyl alcohol at reflux for 4 h furnished the cyclic product, 8-nitro-6-trifluoromethyl[1]benzothieno[2.3-b]-pyridine *N*-oxide (**12**). The treatment of **10** under the same conditions did not yield the cyclized product **B** but instead furnished unreacted **10**.



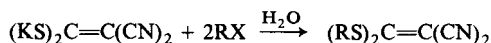
A related cyclization reaction was previously reported by us.⁸ Proof of structure for **12** was established by analysis, NMR and mass spectra data. The proposed mechanism for reaction 6 is depicted in Scheme 4.

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 were 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 spectra⁹ of **8** and **9** were obtained with a Beckman IR-12 spectrophotometer.

1,1-Dimethylthio-2,2-dicyanoethylene (**1**), *1,1-Diethylthio-2,2-dicyanoethylene* (**2**) and *1,1-Dibenzylthio-2,2-dicyanoethylene* (**3**). To a stirred solution comprising 21.9 g (0.1 mol) of dipotassium 1,1-dimercapto-


TABLE I

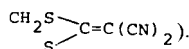


No.	R	Crude % Yield	Mp °C	NMR, δ (ppm) $\text{CDCl}_3\text{—Me}_4\text{Si}$	M ⁺ (Rel. intensity)	Empirical Formula ^d
1	—CH ₃	89	83–84 ^a	2.77 (s, 6(SCH ₃) ₂)	—	C ₆ H ₆ N ₂ S ₂
2	—CH ₂ CH ₃	83	37–88 ^b	1.43 (t, 6, (SCH ₂ CH ₃) ₂) 3.27 (q, H), (SCH ₂ CH ₃) ₂)	—	C ₈ H ₁₀ N ₂ S ₂
3	—CH ₂ C ₆ H ₅	96	85–86 ^c	4.29 (s, 4, (SCH ₂ C ₆ H ₅) ₂) 7.26 (s, 10, (SCH ₂ C ₆ H ₅) ₂)	322(2)	C ₈ H ₁₄ N ₂ S ₂

^a Lit. Ref. 5 mp 80°C.^b Lit. Ref. 5 mp 37°C.^c Recrystallization from ethyl alcohol.^d Satisfactory analytical data ($\pm 0.4\%$) for C, H, N and S were reported.

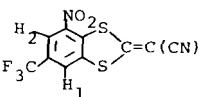
2,2-dicyanoethylene⁴ in 200 mL of water, 0.2 mol of methyl iodide, ethyl bromide or benzyl bromide was added in one portion. The reaction mixture was stirred at 25–30°C for 3 days. For **1** and **3** after cooling to 0°C, the solid was collected by filtration, washed with water until the washings were neutral to litmus and air-dried at 25–30°C. For **2** 400 mL of ethyl ether was added and stirring was continued at 25–30°C for 15 min. The separated ether layer was washed with water until neutral to litmus and dried over sodium sulfate. The ether was removed *in vacuo* at a maximum temperature of 25–30°C at 1–2 mm. The data are summarized in Table I.

[*Bis*[(1,3-dihydro-1,3-dioxo-2H-isoindol-2-yl)methyl]thio]methylene]propanedinitrile (**4**). To a stirred solution containing 26.2 g (0.12 mol) of dipotassium 1,1-dimercapto-2,2-dicyanoethylene⁴ in 150 mL of water and 150 mL of acetone, 39.2 g (0.2 mol) of *N*-(chloromethyl) phthalimide was added in one portion. The reaction mixture was stirred at 25–30°C for 1 day. After the addition of 500 mL of water stirring was continued at 25–30°C for 30 min. The solid was collected by filtration, washed with water until the washings were neutral to litmus and air-dried at 25–30°C. **4**, mp 186–188°C, was obtained in 59% yield. After recrystallization from methyl ethyl ketone **4** melted at 192–193°C. NMR (Me₂SO-*d*₆) δ 5.42 (s, 4, NCH₂S), 7.90 (s, 8, 2ArH); mass spectrum *m/e* (rel intensity), 460(1) (M⁺), 160(100) (M⁺—).



Anal. Calcd for C₂₂H₁₂N₄O₄S₂: C, 57.38; H, 2.63; N, 12.17; S, 13.93. Found: C, 57.31; H, 2.65; N, 12.11; S, 13.87.

[4-Nitro-6-(trifluoromethyl)-1,3-benzodithiol-2-ylidenepropanedinitrile (**5**). To a stirred solution containing 21.9 g (0.1 mol) of dipotassium 1,1-dimercapto-2,2-dicyanoethylene⁴ in 200 mL of water, a solution comprising 27 g (0.1 mol) of 4-chloro-3,5-dinitrobenzotrifluoride in 200 mL of ethyl alcohol was added in one portion. An exothermic reaction set in causing a temperature rise from 23° to 40°C and the formation of a thick precipitate. The reaction mixture was stirred at 25–30°C for 3 days. After the addition of 800 mL of water stirring was continued at 25–30°C for 30 min. The solid was collected by filtration, washed with water until the washings were neutral to litmus and air-dried at 25–30°C. Crude **5**, mp 216–218°C, was obtained in 94% yield. **5** melted at 220–221°C after recrystallization from toluene: NMR (Me₂SO-*d*₆)

δ 8.90 (br s, 1, H₁); 9.16 (br s, 1, H₂) ; mass spectrum *m/e* (rel intensity), 329(100) (M⁺).


Anal. Calcd for C₁₁H₂F₃N₃O₂S₂: C, 40.12; H, 0.61; F, 17.31; N, 12.76; S, 19.47. Found: C, 40.00; H, 0.65; F, 17.22; N, 12.68; S, 19.24.

1,1-Diphenylthio-2,2-dicyanoethylene (**6**) and 1,1-Di-*p*-chlorophenylthio-2,2-dicyanoethylene (**7**). To a stirred solution at 5°C containing 21.9 g (0.1 mol) of dipotassium 1,1-dimercapto-2,2-dicyanoethylene⁴ in 150 mL of acetone and 50 mL of water, 0.2 mol of phenyl chlorothioformate or *p*-chlorophenylchloro-

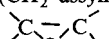
thioformate was added dropwise at 0–10°C in 30 min. The reaction mixture was stirred at 0–10°C for 6 h and at 25–30°C for 18 h. After the addition of 700 mL of water stirring was continued at 25–30°C for 30 min. The solid was collected by filtration, washed with water until neutral to litmus and air-dried at 25–30°C. Crude **6**, mp 105–108°C, and crude **7**, mp 150–152°C, were obtained in 92 and 63% yield, respectively. **6** melted at 112–114°C (lit⁶ mp 111.5–112.5°C) and **7** melted at 158–159°C after recrystallization from ethyl alcohol and ethyl alcohol-ethyl acetate, respectively. **6**, NMR (CDCl₃) δ 6.83–7.46 (m, 10, 2ArH); mass spectrum m/e (rel intensity) 294 (5.89) (M^+). Anal. Calcd for C₁₆H₁₀N₂S₂: C, 65.28; H, 3.42; N, 9.52; S, 21.78. Found: C, 65.06; H, 3.51; N, 9.49; S, 21.67.

7, NMR (CDCl₃) δ 6.88–7.44 (m, 8, 2ArH); mass spectrum m/e (rel intensity) 362 (0.7) (M^+), 143 (100) ($M^+ - Cl - \text{C}_6\text{H}_4 - \text{SC}=\text{C}(\text{CN})_2$).

Anal. Calcd for C₁₆H₈Cl₂N₂S₂: C, 52.90; H, 2.22; Cl, 19.52; N, 7.21; S, 17.65. Found: C, 52.88; H, 2.25; Cl, 19.52; N, 7.70; S, 17.64.

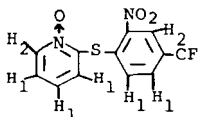
3,3-Bis(methylsulfonyl)-2,2-oxiranedicarboxamide (8) and **3,3-Bis(ethylsulfonyl)-2,2-oxiranedicarboxamide (9)**. To a stirred solution at 70°C comprising 0.3 mol of **1** or **2** in 300 mL of acetic acid, 203 g (1.8 mol) of 30% hydrogen peroxide was added dropwise at 90–100°C over a 1 h period. *The reaction is very exothermic during the addition of 30% hydrogen peroxide and must be cooled intermittently in order to maintain the temperature at 90–100°C.* After the exothermic reaction had subsided the stirred reaction mixture was heated at 90–100°C for 5 h and at 25–30°C for 18 h. After cooling to –20°C stirring was continued at –20 to –15°C for 30 min. The precipitate was collected by filtration (slow), washed with 150 mL of ethyl ether and air-dried at 25–30°C. **8**, mp 191–193°C (dec), and **9**, 195–197°C (dec), were obtained in 34 and 36% yield, respectively. *Attempts made to recrystallize 8 and 9 from DMF resulted in decomposition.* **8**, NMR (Me₂SO-*d*₆) δ 3.32 (s, 6, 2CH₃SO₂); 7.44 and 7.69 (2 br s, 4, 2CONH₂); Ir (KBr): 3448 (free NH), 3407 and 3336 (bonded NH), 2925 and 2853 (CH₃), 1703 (C=O amide I), 1603 (NH₂ deform), 1408 (assym CH₃ deform), 1322 (assym SO₂ + sym CH₃S deform), 1240 (sym , 1156 (sym SO₂), 971 (CH₃S) and 821 cm^{–1} (epoxide ring deform).

Anal. Calcd for C₆H₁₀N₂O₇S₂: C, 25.17; H, 3.52; N, 9.79; O, 39.12; S, 22.40. Found: C, 24.91; H, 3.80; N, 9.60; O, 38.93; S, 22.13.

9, NMR (Me₂SO-*d*₆) δ 1.34 (t, 6, 2CH₃CH₂SO₂); 3.60 (q, 4, 2CH₃CH₂SO₂); 7.54 and 7.70 (2 br s, 4, 2CONH₂); Ir (KBr): 3463 (free NH), 3354 (bonded NH), 1707 (C=O amide I), 1591 (NH₂ deform), 1459 (CH₂ assym deform), 1408 (CH₂ sym + CH₃ deform), 1331 (assym SO₂), 1158 (sym SO₂), 1234 (sym ) and 807 cm^{–1} (epoxide ring deform).

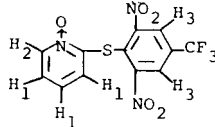
Anal. Calcd for C₈H₁₄N₂O₇S₂: C, 30.57; H, 4.49; N, 8.91; S, 20.40. Found: C, 30.53; H, 4.52; N, 8.89; S, 20.33.

2-[2-Nitro-4-trifluoromethylphenylthio]pyridine N-oxide (10). To a stirred solution containing 34 g (0.2 mol) of 90% sodium 2-mercaptopyridine-*N*-oxide in 200 mL of DMF, 45.2 g (0.2 mol) of 4-chloro-3-nitrobenzotrifluoride was added in one portion. An exothermic reaction set in causing a temperature rise from 22 to 34°C. The stirred reaction mixture was heated at 90–100°C for 24 h. After cooling to 10°C, 800 g of ice water was added and stirring continued at 0–10°C for 30 min. The solid was collected by filtration, washed with water until neutral to litmus and air-dried at 25–30°C. The crude **10**, mp 180–181°C, was obtained in 84% yield. After recrystallization from ethyl acetate **10** melted at 187–188°C;

NMR (CDCl₃) δ 7.05–8.00 (m, 5, H₁), 8.35–8.75 (m, 2, H₂) ; mass spectrum m/e (rel intensity), 316 (2.4) (M^+).

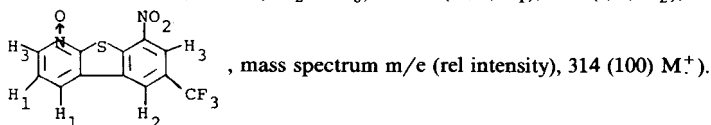
Anal. Calcd for C₁₂H₇F₃N₂O₃S: C, 45.57; H, 2.23; F, 18.02; N, 8.86; S, 10.14. Found: C, 45.87; H, 2.06; F, 17.67; N, 8.86; S, 10.16.

2-[2,6-Dinitro-4-trifluoromethylphenylthio]pyridine N-oxide (11). To a stirred solution comprising 34 g (0.2 mol) of 90% sodium 2-mercaptopyridine-*N*-oxide in 200 mL of DMF, 54 g (0.2 mol) of 4-chloro-3,5-dinitrobenzotrifluoride was added in one portion. An exothermic reaction set in causing a temperature rise from 25 to 43°C. The reaction mixture was stirred at 25–30°C for 3 days. The remainder of the procedure was identical as described for **10**. Crude **11**, mp 114–115°C (dec), was obtained in 86% yield. After recrystallization from isopropyl alcohol **11** melted at 134–135°C (dec); NMR (Me₂SO-*d*₆) δ

6.85–7.60 (m, 3, H₁), 8.20–8.60 (m, 1, H₂), 8.95 (s, 2, H₃) ; mass spectrum m/e (rel intensity), 361 (4.9) (M^+).

Anal. Calcd for $C_{12}H_6F_3N_3O_5S$: C, 39.90; H, 1.67; F, 15.78; N, 11.63; S, 8.88. Found: C, 40.00; H, 1.62; F, 16.02; N, 11.42; S, 9.06.

8-Nitro-6-trifluoromethyl[1]benzothieno[2,3-*b*]pyridine *N*-oxide (12). A stirred slurry containing 36.1 g (0.1 mol) of **11** and 200 mL of isopropyl alcohol was heated at reflux for 4 h. After 80 min at reflux a solution resulted and a brownish yellow gas was liberated. The stirred solution was allowed to cool to 30°C and at 47°C a precipitate resulted. The stirred slurry was cooled to -5°C and stirring was continued at -5 to 0°C for 30 min. The precipitate was collected by filtration and air-dried at 25–30°C. Crude **12**, mp 108–110°C, was obtained in 40% yield. After recrystallization from methyl alcohol **12** melted at 121–2°C; NMR (Me_2SO-d_6) δ 7.38 (m, 2, H_1), 7.79 (s, 1, H_2), 8.24 (m, 2, H_3)



Anal. Calcd for $C_{12}H_5F_3N_2O_3S$: C, 45.87; H, 1.60; F, 18.14; N, 8.91; S, 10.20. Found: C, 45.81; H, 1.59; F, 18.29; N, 8.89; S, 10.07.

Attempted cyclization of 10. A stirred mixture containing 31.7 g (0.1 mol) of **10** and 200 mL of isopropyl alcohol was heated at reflux for 4 h. During this heating period no gas was liberated and **10** was recovered unchanged.

REFERENCES AND NOTES

1. Presented at the 188th National Meeting of the American Chemical Society, Organic Division, Philadelphia, Pa. August (1984).
2. The chemical abstracts preferred name for compounds **4**, **5**, **8** and **9** was kindly furnished by Dr. K. L. Loening of the Chemical Abstracts service.
3. L. A. Suba, P. G. Ruminski and J. J. D'Amico, *Phosphorus and Sulfur*, **20**, 251 (1984).
4. M. Brown, U.S. Patent 3,057,875 dated 10/9/62 (DuPont Co.).
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6. R. L. Soulen, D. B. Clifford, F. F. Crim and J. A. Johnston, *J. Org. Chem.*, **36**, 3386 (1971).
7. Analysis for recrystallized **8**, mp 140–150°C (dec.), and **9**, mp 130–145°C (dec.). For **8** Calcd for $C_6H_{10}N_2O_7S_2$: C, 25.17; H, 3.52; N, 9.79; O, 39.12; S, 22.40. Found: C, 24.57; H, 3.98; N, 8.81; O, 23.76; S, 35.65. For **9** Calcd $C_8H_{14}N_2O_7S_2$: C, 30.57; H, 4.49; N, 8.91; S, 20.40. Found: C, 20.01; H, 4.39; N, 11.30; S, 22.75.
8. J. J. D'Amico, C. C. Tung and W. E. Dahl, *J. Org. Chem.*, **42**, 600 (1977).
9. References used in interpreting the IR data are: (a) "The Infrared Spectra of Complex Molecules", L. J. Bellamy, 3rd edition, John Wiley and Sons, N.Y. (1975); (b) "Introduction to Infrared Spectra and Raman Spectroscopy", N. B. Colthup, L. H. Daly, and S. E. Wiberley, Academic Press, N.Y. (1975); (c) "Physical Methods in Heterocyclic Chemistry" Vol. II, pg. 179, A. R. Katritzky, Ed., Academic Press, N.Y. (1963).