Thermal Decompositions of Dinitropyridyl and Dinitrothienyl Dithiocarbamates and *t*-Butyl Trithiocarbonates

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The title compounds on heating cyclized to yield 7-nitro-1,3-dithiolo[4,5-*c*]pyridin-2-one (III), 6-nitro-1,3-dithiolo[2,3-*c*]pyridin-2-one (VIIa), 6-nitrothieno[2,3-*d*]-1,3-dithiol-2-one (XIVa) and 6-nitrothieno[2,3-*d*]-1,3-dithiole-2-thione (XIVb).

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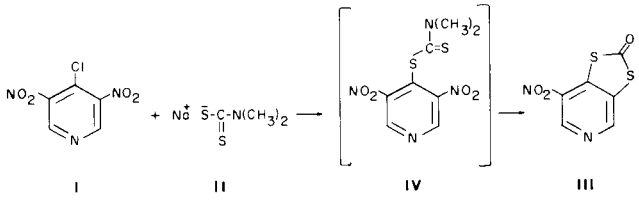
We have already reported that dinitrophenyl dimethyldithiocarbamates and dinitrophenyl *t*-butyl trithiocarbonates on heating cyclize to yield nitro-1,3-benzodithiol-2-ones (1,2) and nitro-1,3-benzodithiole-2-thiones (3), respectively. The extension of these studies to the pyridine and thiophene systems forms the subject of this study.

Decomposition of Dinitropyridine Derivatives.

Reaction of 4-chloro-3,5-dinitropyridine (I) and sodium dimethyldithiocarbamate (II) in dry acetone at 10-20° produced the novel 7-nitro-1,3-dithiolo[4,5-*c*]pyridin-2-one (III) in 45% yield. The intermediate dithiocarbamate IV cyclized to III at room temperature (Equation 1); the

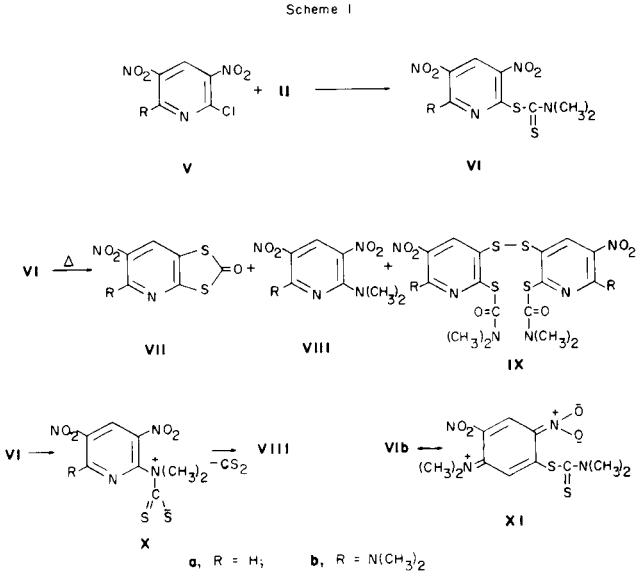
Equation 1



I II IV III

mechanism of this transformation is assumed to be similar to that outlined earlier (2). Reaction of 2-chloro-3,5-dinitropyridine (Va) and II gave dithiocarbamate VIa (82%) as a stable crystalline material. When VIa was refluxed in acetone, three products, 6-nitro-1,3-dithiolo[2,3-*c*]pyridin-2-one (VIIa, 7%), 2-dimethylamino-3,5-dinitropyridine (VIIIa, 3%) and pyridine disulfide (IXa, 24%) were isolated. The structural assignments for these products are based on elemental analyses and nmr spectra. Further support for structure IXa was obtained from its cyclization to VIIa using sodium hydrosulfide in DMSO. This cyclization reaction has already been demonstrated to be quite general (4). Structure VIIIa was confirmed by identity with the product resulting from the reaction of Va with dimethylamine. Compound VIIIa arises either by attack of dimethylamine, produced by reaction of trace amounts of water on VIa or *via* an intramolecular attack of nitrogen of the dimethyldithiocarbamate moiety through the intermediacy of zwitterion Xa (Scheme 1). In order to prevent this side reaction we synthesized 6-dimethylamino-3,5-dinitropyridyl-2-dimethyldithiocarbamate (VIb), expecting the presence of the electron donating dimethylamine group to render attack at the α-position of pyridine less favourable. However, the decomposition of VIb in DMSO produced 2,6-bis(dimethylamino)-3,5-dinitropyridine (VIIIb, 68%) as the sole product. Decomposition of VIb as a dry powder under anhydrous conditions also gave VIIIb (60%). The facile formation of VIIIb is best understood in terms of a significant contribution of the resonance structure XI which makes displacement of the adjacent nitro group to form VIIb energetically unfavourable.

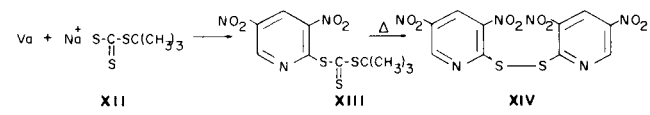
Scheme I



V VI VII VIII IX X XI

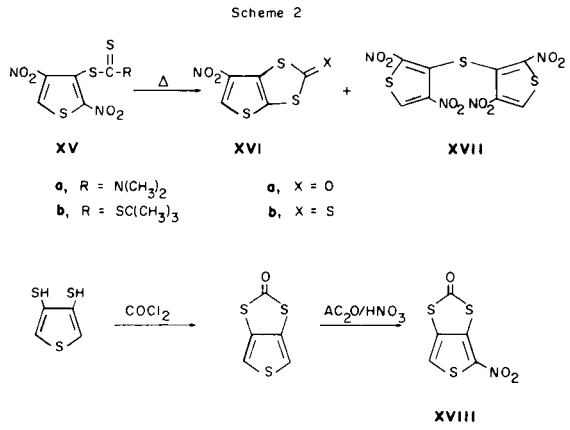
a, R = H; b, R = $N(CH_3)_2$

Equation 2



XII XIII XIV

Scheme 2



Reaction of Va with sodium *t*-butyl trithiocarbonate (XII) (3) in acetone produced XIII (90%). On heating XIII in DMSO at 115-120° disulfide XIV (31%) was isolated (equation 2). There was no evidence for the formation of the thio analog of VIIa.

Decomposition of Dinitrothiophene Derivatives.

Three dithiocarbamates, namely 2,5-dinitrothienyl-2-dimethyldithiocarbamate, 3,4-dinitrothienyl-2-dimethyldithiocarbamate and 2,4-dinitrothienyl-3-dimethyldithiocarbamate (XVa), were prepared by reaction of the appropriate dinitrobromothiophene and II in acetone. These were decomposed by heating in glacial acetic acid at 110-120°. Complex reaction mixtures were obtained in all cases (tlc). Only in the case of XVa were we able to isolate 6-nitrothieno[2,3-*d*]-1,3-dithiol-2-one (XVIa) in very low yield (6%) by careful chromatography of the crude reaction mixture on silica gel. Structure XVIa is based on its nmr spectrum (singlet at 8.52 ppm), mass spectrum and elemental analyses. This unequivocal structural assignment is based on an independent synthesis of the alternate structure XVIII (nmr: singlet at 7.70 ppm).

Reaction of 2,4-dinitro-2-bromothiophene with XII in acetone gave trithiocarbonate XVb (75%). Decomposition of XVb in glacial acetic acid at 110-115° yielded 6-nitrothieno[2,3-*d*]-1,3-dithiole-2-thione (XVIb, 16%) and 2,4-dinitrothienyl-2-sulfide (XVII, 15%). Both of these structures are supported by nmr and mass spectral data. On the basis of the considerable chemical shift differences of the protons in isomeric structures XVIa and XVIII, the

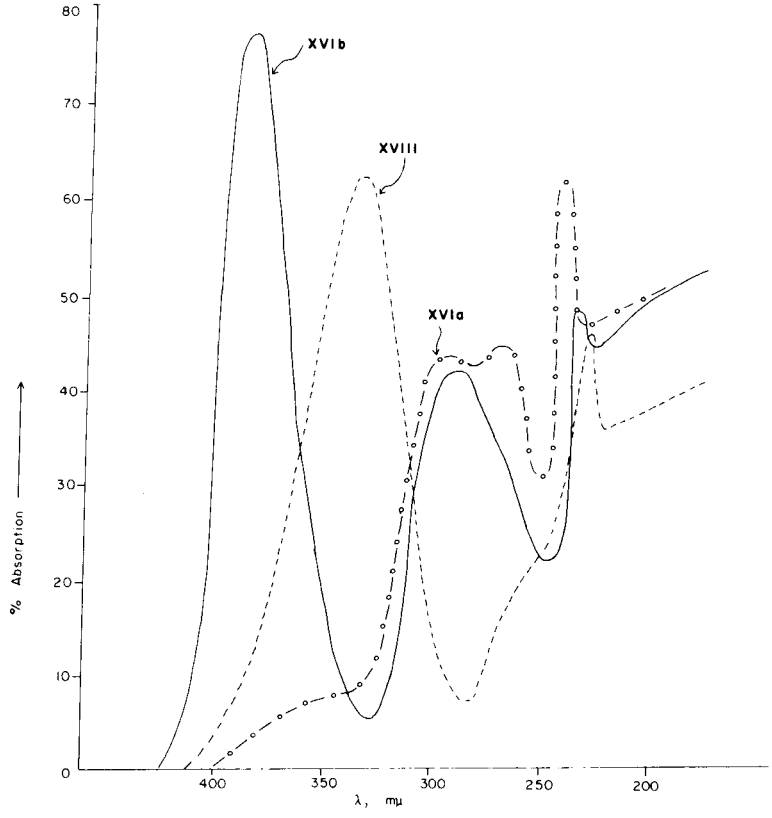


Figure 1. Uv spectra of 6-nitrothieno[2,3-*d*]-1,3-dithol-2-one (XVIa) o-o-o-o- (1.4×10^{-4} moles liter^{-1}); 1-nitrothieno[3,4-*d*]-1,3-dithiol-2-one (XVIII)---- (1.0×10^{-4} moles liter^{-1}) and 6-nitrothieno[2,3-*d*]-1,3-dithiol-2-thione (XVIb)—— (9.1×10^{-5} moles liter^{-1}) in acetonitrile.

nmr spectrum of XVIb with a singlet at 8.65 ppm proves unequivocally the direction of cyclization, ruling out the alternative structure corresponding to the thio analog of XVIII. Nmr spectra of XVa, XVIa and XVIII were all determined in deuterioacetone. Uv spectra for XVIa, XVIb and XVIII are shown in Figure 1.

We conclude that the cyclization reactions in the pyridine and thiophene systems are not as general as those reported in our earlier work for the benzene series (1,2). In isolated cases such as III and XVIb, however, this procedure represents an alternative route to one employing a multistep synthetic sequence.

EXPERIMENTAL

Melting points were determined in open capillaries and are uncorrected. Nmr spectra were recorded on Varian Associates T-60 model spectrometer using TMS as an internal standard. Uv spectra were recorded on Coleman model 124 double beam spectrometer. Elemental analyses were carried out on a Hewlett-Packard Analyzer, model 185, by our Analytical Section and by Spang Microanalytical Laboratory, Ann Arbor, Michigan. Silica used for chromatography was Mallincrodt brand Silicar CC-7.

7-Nitro-1,3-dithiolo[4,5-*c*]pyridin-2-one (III).

To a stirred and ice-cooled solution of 11.2 g (55.2 mmoles) of 4-chloro-3,5-dinitropyridine (I) (5) in dry acetone (110 ml) was added in portions 9.9 g(55.2 mmoles) of sodium dimethyldithiocarbamic acid (II) at 2-10°. On allowing to stir (1 hour), cooling was removed and the mixture stirred overnight at room temperature. After refluxing (2.5 hours) the solvent was removed in vacuum, the residue dissolved in chloroform (200 ml) and the chloroform extract washed with water (3 × 500 ml). After drying over sodium sulfate and filtering silica gel (10 g) was added to the filtrate and the solvent removed in vacuum. The residual powder was chromatographed over silica gel (200 g). Elution with benzene gave a fraction (500 ml) which on evaporation to dryness in vacuum yielded 5.0 g (45%) of III, mp 118-120°. Recrystallization from acetone gave an analytically pure sample, mp 123-125°; uv (acetonitrile) 324 mμ (ε 6.03 × 10^2), 287 (ε 1.41 × 10^3), 252 (ε 3.35 × 10^3), 237 (ε 5.09 × 10^3); nmr (DMSO-d_6): δ 9.48 (s, 1H), 9.40 (s, 1H).

Anal. Calcd. for $C_6H_2N_2O_3S_2$: C, 33.63; H, 0.93; N, 13.08. Found: C, 33.75; H, 1.05; N, 12.86.

3,5-Dinitropyridyl-2-dimethyldithiocarbamate (VIa).

A mixture of 18.4 g (90.6 mmoles) of 2-chloro-3,5-dinitropyridine (Va) (6) and 16.3 g (91 mmoles) of II was allowed to stir in acetone (180 ml) at room temperature overnight. Acetone was removed in vacuum and the resulting solid was washed well with water and finally with ethanol. After drying in vacuum over calcium chloride, 22.7 g (82%) of VIa, mp 109-110° dec was obtained. Recrystallization from ethanol-acetone gave pure VIa, mp 127-128° dec; nmr (deuteriochloroform): δ 9.66 (d, 1H), 9.36 (d, 1H), 3.78 (s, 3H), 3.70 (s, 3H).

Anal. Calcd. for $C_8H_8N_4O_4S_2$: C, 33.33; H, 2.78; N, 19.44. Found: C, 33.49; H, 2.89; H, 19.27.

S,S'-[2,2'-Dithiobis(nitropyridyl)]bis(*N,N*-dimethylcarbamothioate) (IXa).

A solution of 11.5 g (39.9 mmoles) of pyridine dithiocarbamate VIa was refluxed (55 hours) in dry acetone (40 ml). After distillation of acetone in vacuum the residue was extracted with chloroform (100 ml) and the chloroform insoluble solid suction filtered. Recrystallization of the solid from DMSO gave 2.2 g (23.5%) of IXa, mp 176-177°; nmr (DMSO-d_6): δ 9.71 (s), 9.28 (s), 4.01 (s), 3.91 (s) (7).

Anal. Calcd. for $C_{18}H_{22}N_6O_7S_5$: C, 36.36; H, 3.70; N, 14.14. Found: C, 36.49; H, 3.79; N, 14.11.

6-Nitro-1,3-dithiolo[2,3-*c*]pyridin-2-one (VIIa).

The chloroform extract was distilled to dryness in vacuum and the residue chromatographed over silica gel (200 g). The benzene eluate (200 ml) on distilling to dryness in vacuum gave a crystalline residue which was recrystallized from acetone. There was obtained 0.6 g (7%) of VIIa, mp, 178-180°; uv (acetonitrile): 322 mμ (ε 1.96 × 10^3), 240 (ε 9.63 × 10^3); nmr (DMSO-d_6): δ 9.31 (d, 1H), 9.26 (d, 1H).

Anal. Calcd. for $C_6H_2N_2O_3S_2$: C, 33.63; H, 0.93; N, 13.08. Found: C, 33.69; H, 0.94; N, 13.07.

2-Dimethylamino-3,5-dinitropyridine (VIIIa).

A second benzene eluate (200 ml) on removal of solvent yielded a solid which was dissolved in hot ethanol, filtered from insoluble material and allowed to crystallize. There were obtained 0.27 g (3%) of VIIIa, mp 117-119°. This material was identical (mixture mp, nmr, tlc) with the product obtained from the reaction of Va and dimethylamine.

Reaction of Pyridinedisulfide IXa with Sodium Hydrosulfide.

To a stirred and tap-water cooled suspension of 1.55 g (3 mmoles) of IXa in DMSO (25 ml) under nitrogen was added dropwise a solution of 0.5 g (6 mmoles) of sodium hydrosulfide in DMSO (16 ml). The resulting red mixture was allowed to stir (5 hours) at room temperature, poured into water (250 ml), acidified with 2*N* hydrochloric acid and extracted with chloroform (3 × 40 ml). The chloroform extract was washed with water (2 × 100 ml), dried over sodium sulfate and filtered. After addition of silica gel (5 g) to the filtered solution the solvent was distilled in vacuum and the residue chromatographed over silica gel (50 g). Elution with 1:1 hexane-benzene (500 ml) gave a fraction containing elemental sulfur. Further elution with chloroform (250 ml) and removal of solvent yielded 0.35 g (31%) of a solid, mp 179-182°. Recrystallization from ethanol-acetone gave a sample, mp 180-181°, which was identical with VIIa (mixture mp, nmr, tlc). Elution with ethanol (150 ml) and removal of solvent followed by recrystallization of the residue from DMSO gave 0.18 g (11.5%) of starting material, mp 176-178° (mixture mp).

6-Chloro-2-dimethylamino-3,5-dinitropyridine (Vb).

To 70% nitric acid (25 ml) was added 8.2 g (40.7 mmoles) of 6-chloro-2-dimethylamino-3-nitropyridine (8) and a few crystals of sodium nitrite. After stirring at room temperature (10 minutes) the solution was heated to 45° (5 minutes) when a strongly exothermic reaction caused the temperature to rise to 90°. The cooled mixture was poured into water (250 ml) and the insoluble crystalline material suction filtered and chromatographed over silica gel (75 g). Hexane-benzene (1:1) eluted 5.6 g of solid which on recrystallization from ethanol gave 5.3 g (35%) of Vb, mp 100.5-101.5°; nmr (DMSO-d_6): δ 8.91 (s, 1H), 3.11 (s, 6H).

Anal. Calcd. for $C_7H_7ClN_4O_4$: C, 34.08; H, 2.84; N, 22.72. Found: C, 34.31; H, 2.94; N, 22.53.

6-Dimethylamino-3,5-dinitropyridyl-2-dimethyldithiocarbamate (VIb).

To a stirred solution of 2.46 g (10 mmoles) of Vb in acetone (20 ml) at 5-10° was added 1.79 g (10 mmoles) of II. After stirring at room temperature (60 minutes) the mixture was poured into water (150 ml) and the yellow solids obtained suction filtered, washed with water and dried at 60°. Obtained 3.0 g (90%) of VIb, mp 201-203° dec. Recrystallization from acetone yielded analytically pure VIb, mp 202-202.5° dec.

Anal. Calcd. for $C_{10}H_{13}N_5O_4S_2$: C, 36.24; H, 3.93; N, 21.14. Found: C, 36.56; H, 4.06; N, 21.32.

Decomposition of VIb in DMSO.

A solution of 1.5 g (4.5 mmoles) of VIb in dry DMSO (10 ml) was heated to 150-160° (1.5 hours), allowed to cool to room temperature and poured into water (150 ml). The mixture was extracted with methylene chloride (3 × 50 ml), the combined methylene chloride extracts washed with water (3 × 300 ml), dried over sodium sulfate and the solvent removed in vacuum. The residual solid was recrystallized from acetone and gave 0.78 g (68%) of VIIIb, mp 226-227°; nmr (deuteriochloroform): δ 9.09 (s, 1H), 3.16 (s, 12H).

Anal. Calcd. for $C_9H_{13}N_5O_4$:C, 42.35; H, 5.10; N, 27.45. Found: C, 42.36; H, 5.30; N, 27.41.

3,5-Dinitropyridyl-2-*t*-butyl Trithiocarbonate (XIII).

To a stirred and ice-cooled solution of 17.2 g (84.7 mmoles) of 2-chloro-3,5-dinitropyridine (Va) in dry acetone (100 ml) was added dropwise a solution of 21.7 g (115.4 mmoles) of 77% sodium *t*-butyl trithiocarbonate (XII) in dry acetone (175 ml) at 0-5°. After allowing the mixture to stir at 15° (3 hours), acetone was removed by distillation in vacuum, water (100 ml) was added to the residue and extracted with methylene chloride (2 × 100 ml). The organic phase was washed with water (3 × 100 ml), dried over sodium sulfate and solvent distilled in vacuum at 30°. The residual oil on standing crystallized. It was triturated with cold ethanol (50 ml), the solid suction filtered and air dried. Obtained 26 g (92%) of XIII as a brick red solid, mp 76-80°; nmr (deuteriochloroform): δ 10.16 (d, 1H), 9.42 (d, 1H), J = 2 Hz.

Anal. Calcd. for $C_{10}H_{11}N_3O_4S_3$: C, 36.04; H, 3.30; N, 12.61. Found: C, 36.36; H, 3.57; N, 12.40.

3,5-Dinitropyridine-2-disulfide (XIV).

Twenty g (60 mmoles) of XIII was dissolved in glacial acetic acid (180 ml) and the solution heated at 110-115° (3 hours). The mixture was allowed to cool to room temperature and the insoluble solid was suction filtered and dried. This yielded 3.8 g (31%) of XIV, mp 249-251°. One recrystallization from hot DMSO gave XIV, mp 253-255° dec; nmr (DMSO-d_6): δ 9.46 (d, 1H), 9.21 (d, 1H), J = 2 Hz; ms: m/e 400.

Anal. Calcd. for $C_{10}H_4N_6O_8S_2$: C, 30.00; H, 1.00; N, 21.00. Found: C, 30.22; H, 1.21; N, 20.86.

2,4-Dinitrothienyl-3-dimethyldithiocarbamate (XVa).

Prepared from 3-bromo-2,4-dinitrothiophene (0.07 mole) (9) and II (0.073 mole) in acetone (200 ml) at 0-5° as described for VIa. There was obtained 18 g (87%) of XVa, mp 106-108° dec; nmr (deuteriochloroform): δ 8.58 (s, 1H), 3.63 (s, 6H).

Anal. Calcd. for $C_7H_7N_3O_4S_3$: C, 28.67; H, 2.39; N, 14.33. Found: C, 28.98; H, 2.66; N, 14.08.

2,4-Dinitrothienyl-3-*t*-butyl Trithiocarbonate (XVb).

This product was prepared in a manner similar to that described for XIII. Reaction of 25.3 g (0.1 mole) of 3-bromo-2,4-dinitrothiophene and 25.6 g (0.11 mole) of XII on workup gave 25.0 g (75%) of XVb, mp 89-90° dec; nmr (deuteriochloroform): δ 8.59 (s, 1H), 1.73 (s, 9H).

Anal. Calcd. for $C_9H_{10}N_2O_4S_4$: C, 31.95; H, 2.96; N, 8.28. Found: C, 32.16; H, 2.79; N, 8.43.

6-Nitrothieno[2,3-*d*]-1,3-dithiol-2-one (XVIa).

A mixture of 17.2 g (58.5 mmoles) of XVa and glacial acetic acid (200 ml) was heated to 115-120° (evolution of nitrogen oxides). After completion of reaction (1.7 hours) was indicated by tlc, the mixture was cooled to room temperature and poured into water (500 ml). It was worked up as described for III. The chloroform extract was distilled to dryness and the residue chromatographed over silica gel (200 g) by eluting with 50% benzene in hexane. The first fraction containing impurities (750 ml) was discarded. The second fraction (~1200 ml) was concentrated to dryness and gave 0.77 g (6%) of crude XVIa. Recrystallization from hot ethanol gave 0.5 g of analytically pure XVIa, mp 157-159°. For uv spectrum see Figure 1; nmr (acetone-d_6): δ 8.52 (s); ms: m/e = 219.

Anal. Calcd. for $C_5HNO_3S_3$: C, 27.39; H, 0.45; N, 6.39. Found: C, 27.69; H, 0.58; N, 6.22.

6-Nitrothieno[2,3-*d*]-1,3-dithiol-2-thione (XVIb).

A solution of 24.0 g (70 mmoles) of XVb was heated in glacial acetic acid (280 ml) at 110-113° (20 minutes) which resulted in copious evolution of nitrogen oxide fumes. The dark reaction mixture was cooled to room temperature, poured into water (600 ml) and extracted with methylene chloride (2 × 150 ml). The organic extract was washed with water (3 × 600 ml), dried over sodium sulfate and filtered into a flask containing silica gel (20 g). The mixture was distilled to dryness and the residual powder chromatographed overs silica gel (200 g) and eluted with 50% benzene in hexane. The first fraction (1500 ml) eluted was discarded. The second fraction (1900 ml) was distilled to dryness in vacuum and the residual solid obtained was recrystallized from ethanol. This yielded 2.6 g (16%) of XVIb, mp 154-155°; nmr (acetone-d_6): δ 8.63 (s); ms: m/e 235.

Anal. Calcd. for $C_5HNO_2S_4$: C, 25.53; H, 0.43; S, 54.47. Found: C, 25.62; H, 0.53; S, 54.58.

3,3'-Thiobis(2,4-dinitrothiophene) (XVII).

Further elution with benzene gave a fraction (1250 ml) which was distilled to dryness in vacuum. The residual solid was recrystallized from ethanol-acetone mixture and yielded 1.2 g of XVII, mp >250°. Concentration of the mother liquor gave an additional 0.9 g of XVII, mp >250°, total yield of XVII (2.1 g 15%); nmr (DMSO-d_6): δ 9.10 (s); ms: m/e 378.

Anal. Calcd. for $C_8H_2N_4O_8S_3$: C, 25.40; H, 0.53; N, 14.81; S, 25.40. Found: C, 25.53; H, 0.60; N, 14.72; S, 25.46.

1-Nitrothieno[3,4-*d*]-1,3-dithiol-2-one (XVIII).

To a stirred and cooled (ice-bath) solution of 1.5 g (10.1 mmoles) of 3,4-thiophenedithiol (10) in 2*N* sodium hydroxide (15 ml) under nitrogen was added a 12.5% solution of phosgene in benzene (9.5 g, 12 mmoles). The mixture was stirred overnight, benzene (50 ml) added and the mixture shaken in a separatory funnel. The benzene extract was washed with water (2 × 25 ml), dried over sodium sulfate and the solvent distilled to dryness in vacuum. There was obtained 0.7 g (40%) of thieno[3,4-*d*]-1,3-dithiol-2-one, mp 100-102°; nmr (deuteriochloroform): δ 7.36 (s). To a stirred and cooled (ice-bath) solution of 0.55 g (3.16 mmoles) of thieno-[3,4-*d*]-1,3-dithiol-2-one in acetic anhydride (3 ml) was added dropwise an ice-cooled solution of 0.53 g (7.5 mmoles) of 90% nitric acid in acetic anhydride (2 ml). After allowing to stir in an ice-bath (1 hour) and at room temperature (2 hours), the mixture was poured into water (50 ml). The precipitated yellow solid was extracted with chloroform (40 ml), the chloroform extract washed with water (2 × 50 ml), dried over sodium sulfate and filtered. The solid obtained on removal of solvent in vacuuum was recrystallized from ethanol. There was obtained 0.29 g (42%) of XVIII, mp 137-139°. A mixture mp with XVIa gave a depression (118-120°). For uv spectrum of XVIII, see Figure 1; nmr (acetone-d_6): δ 7.70 (s).

Anal. Calcd. for $C_5HNO_3S_3$: C, 27.39; H, 0.45; N, 6.39. Found: C, 27.65; H, 0.56; N, 6.61.

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(5) This compound was prepared by adding 3,5-dinitro-4-pyridone (16 mmoles) to a mixture of phosphoryl chloride (53 mmoles) and dimethylformamide (41 mmoles) and heating to 95-100° (2 hours). To the cooled mixture was added chloroform (30 ml) and the solution obtained washed with ice-water (3 × 50 ml). After drying over sodium sulfate the solvent was removed in vacuum and the residual solid washed with hexane (15 ml). This yielded I in 70% yield. See also C. O. Okafor, *J. Org. Chem.*, **32**, 2007 (1967).

(6) This compound was prepared by adding 3,5-dinitro-2-pyridone (146 mmoles) to a mixture of phosphoryl chloride (520 mmoles) and dimethylformamide (410 mmoles), heating to 90-100° (4 hours). The cooled mixture was dissolved in chloroform (200 ml) and the chloroform solu-

tion washed with ice-water (3 × 200 ml). After drying over sodium sulfate, the solvent was removed in vacuum yielding 2-chloro-3,5-dinitropyridine (95%), mp 56-58°.

(7) Disulfide IXa crystallizes with 1 mole of DMSO. Owing to its poor solubility the nmr spectrum of IXa was recorded in hot DMSO-d_6. The chemical shifts reported are therefore not accurate. The spectrum was not integrated since IXa begins to crystallize from solution as the sample cools.

(8) The product, mp 62-63°, was obtained by treating 2,6-dichloro-3-nitropyridine with 40% aqueous dimethylamine in ethanol.

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