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# 1,2-Dithiole-3-thione and 1,2,4-Trithiole from α-Cyanodithiocarboxylate

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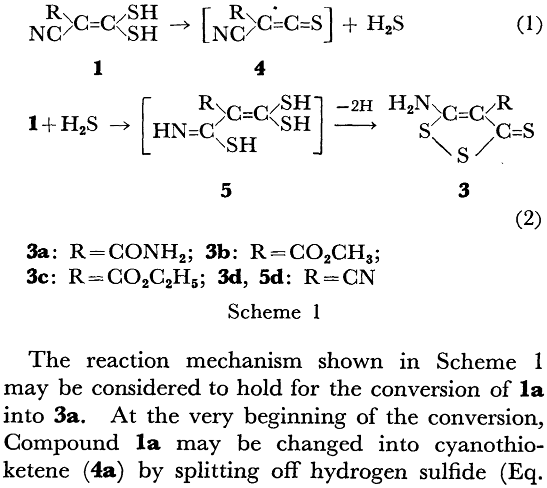
1,2-Dithiole-3-thiones and 1,2,4-trithioles were synthesized by the reaction of α-cyanodithiocarboxylate, hydrogen sulfide, and bromine water. The reaction mechanism and the mass spectra of 1,2-dithiole-3-thiones were discussed.

Our attempt to isloate dimercaptomethylenecyanoacetamide (**1a**) from the reaction mixture of di(ammoniomercapto)methylenecyanoacetamide (**2a**) and mineral acid failed. Compound **1a** was unstable, degraded easily along with the evolution of hydrogen sulfide, and changed to 5-amino-4-carbamoyl-1,2-dithiole-3-thione (**3a**).



**3a**: R=$CONH_2$; **3b**: R=$CO_2CH_3$;
**3c**: R=$CO_2C_2H_5$; **3d**, **5d**: R=CN

Scheme 1

The reaction mechanism shown in Scheme 1 may be considered to hold for the conversion of **1a** into **3a**. At the very beginning of the conversion, Compound **1a** may be changed into cyanothioketene (**4a**) by splitting off hydrogen sulfide (Eq. (1)). The hydrogen sulfide thus generated attacks the cyano group of **1a** to give an intermediate, **5a**, from which **3a** is produced by the formation of the 1,2-dithiole ring (Eq. (2)).

Resinous material which was considered to be a polymer of (4) was obtained in the above reaction. However, its identification was not achieved. The ammonium salt of **5d** could be prepared by the reaction of di(ammoniomercapto)methylenemalononitrile (diammonium salt of **1d**) and hydrogen sulfide, and then converted quantitatively into **3d** by the addition of acetic acid. The results suggest that the unstable intermediate, **5**, is easily dehydrogenated because of the formation of a stable 1,2-dithiole-3-thione derivative (**3**).[1]

From the decomposition mechanism, syntheses were undertaken for several 1,2-dithiole-3-thione derivatives by the reaction of α-cyanodithiocarboxylate (**2**), hydrogen sulfide, and acetic acid. Bromine water was used in place of acetic acid because of its moderate reactivity. Di(ammoniomercapto)methylenecyanoacetamide (**2a**), methyl di(sodiomercapto)methylenecyanoacetate (**2b**), ethyl di(sodiomercapto)methylenecyanoacetate (**2c**), and di(sodiomercapto)methylenemalononitrile (**2d**) gave 5-amino-4-carbamoyl-1,2-dithiole-3-thione (**3a**, yield 94%), 5-amino-4-methoxycarbonyl-1,2-dithiole-3-thione (**3b**, yield 81%), 5-amino-4-ethoxycarbonyl-1,2-dithiole-3-thione (**3c**, yield 83%), and 5-amino-4-cyano-1,2-

Table 1. UV spectra in 99% EtOH[a)]

| Compd. | $\lambda_{max}$, mμ (log ε) |
|---|---|
| **3a** | 240.5(3.96), 286(sh, 3.90), 314.5(4.54), 364.3(3.93)<br>229**, 264 sh**, 282**, 309 sh**, 400** |
| **3b** | 249(4.06), 290.5(sh, 4.17), 312(4.26), 376(3.78)<br>248(4.09)***, 292(4.24)***, 311(4.32)***, 374(3.79)*** |
| **3c** | 247.5(4.09), 287.5(sh, 4.17), 311(4.27), 373(3.76)<br>248(4.11)*, 289(sh, 4.17)*, 311(4.26)*, 373(3.88)* |
| **3d** | 233.5(4.06), 283(sh, 3.87), 311(4.09), 369(3.68)<br>235(4.04)*, 280(sh, 3.91)*, 310(4.15)*, 367(3.94)* |
| **6a** | 244.5(2.96), 320.2(3.98), 336.5(3.68) |
| **6b** | 241.5(2.76), 323(sh, 4.23), 335(4.27) |
| **6c** | 238(2.39), 323(sh, 4.28), 335(4.32) |

a) Absorbance measurements were made with a Hitachi EPS-3T type spectrophotometer. *, ** show the UV data reported by Mayer *et al.*;[2] * in EtOH, ** in cyclohexane. *** shows the UV data (in MeOH) reported by Gewald.[3]

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[1] N. Lozac'h and J. Vialle, "Organic Sulfur Compounds," Vol. II, Pergamon Press, Oxford (1966) p. 258.

[2] R. Mayer, P. Rosmus and J. Fabian, *J. Chromatogr.*, **15**, 153 (1964).

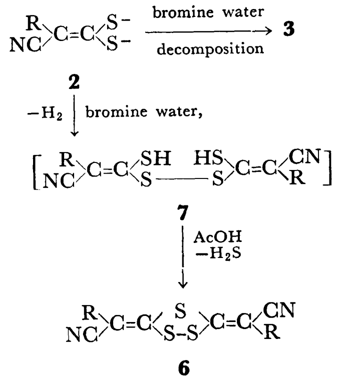
[3] K. Gewald, *J. Prakt. Chem.*, **31**, 214 (1966).

dithiole-3-thione (**3d**, yield 82%) respectively, all in high yields. The UV spectra of **3b**, **3c**, and **3d** coincided with those reported by Mayer and Gewald (see Table 1). This is a new preparative method leading to 1,2-dithiole-3-thione derivatives through the intermediate, **5**. Most of the preparations reported so far have made use of elementary sulfur,[3] phosphorus pentasulfide or a mixture of both.[1]

When the α-cyanodithiocarboxylate (**2**) was mixed with acetic acid, hydrogen sulfide was evolved and **3** was obtained. This reaction was continued until **1** had been degraded completely. On the other hand, bromine water stopped the decomposition of **1** within several hours.

A mixture of α-cyanodithiocarboxylate and bromine water was allowed to stand at room temperature overnight. A small amount of **3** (usually, yield *ca.* 10%) was separated from the reaction mixture. When the filtrate was acidified with acetic acid, hydrogen sulfide was instantly evolved and 1,2,4-trithiole derivative was obtained in a high yield. **2a, 2b**, and **2c** gave 2,5-di(carbamoylcyanomethylene)-1,2,4-trithiole (**6a**, yield 70%), 3,5-di(methoxylcarbonylcyanomethylene)-1,2,4-trithiole (**6b**, yield 74%), and 3,5-di(ethoxylcarbonylcyanomethylene)-1,2,4-trithiole (**6c**, yield 81%), respectively. An attempt to obtain the compound corresponding to **6d** was unsuccessful.

It seems that the conversion of **2** into **6** proceeds through an intermediate, **7**, which is easily changed to a stable compound, **6**, accompanying elimination of hydrogen sulfide on treatment with acetic acid (see Scheme 2). The IR spectrum of **6b** coincided with that of the compound synthesized from **2b** and ammonium peroxydisulfate by Gompper's method.[4] The UV spectra of **3** and **6** showed several characteristic absorptions (see Table 1).



**2a, 6a**: R=$CONH_2$; **2b, 6b**: R=$CO_2CH_3$; **2c, 6c**: R=$CO_2C_2H_5$; **2d**: R=CN

Scheme 2

Kirby has proposed that **6** is presumably planar for the conjugation through the **3d** orbitals of sulfur.[5] The strong bands near 320 mμ and 335 mμ may be explained in terms of the through-conjugation. It was considered that **6** existed in a *trans* form with respect to R groups, because the two R groups were shown to be unequivalent from the results of NMR spectra (see Table 2).

Table 2. Chemical shifts and coupling constants for **6***

| | |
|---|---|
| **6a** | 4.10(br, $NH_2$) |
| **6b** | 3.92(s, $CH_3$), 3.90(s, $CH_3$) |
| **6c** | 4.38(q, $CH_2$, $J$=7 Hz), 4.36(q, $CH_2$, $J$=7 Hz), 1.35(t, $2CH_3$) |

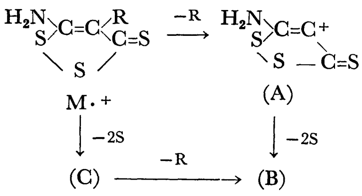
* NMR spectra were recorded with a JNM-C-60 high resolution NMR spectrometer operating at 60 MHz. Chemical shift values were shown in δ downfield from tetramethylsilane as an internal standard in deuteriodimethyl sulfoxide as solvent.

Table 3. Mass spectra for **3***, *m/e* (rel. int. %)

| **3a** | **3c** | **3d** |
|---|---|---|
| 194(23) | 223(13) | 176(7.5) |
| 192(100)M·+ | 221(100)M·+ | 174(100)M·+ |
| 176(7) | 177(57) | 110(99) |
| 148(8.5) | 148(40) | 83(12) |
| 128(45) | 84(73) | 64(8.5) |
| 84(33) | 72(13) | |
| 64(10) | 64(15) | |

* Mass spectra were measured with a Nihon Densi JMS-01 SG mass spectrometer. Ionizing energy was maintained at 75 eV and the total ionizing current 200 μA.

Table 3 shows the mass spectra of **3**. Measurement of the fragments revealed different scissions of two sulfur atoms (see Scheme 3). Compound **3c** was changed into fragment (B) through fragment (A) by the removal of group R and then two sulfur atoms. In the case of **3d**, the separation of two sulfur atoms occurred to give fragment (C) from which group R was then separated to give fragment (B). Compound **3a** showed both types of scission.



Scheme 3

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4) R. Gompper and W. Töpfel, *Chem. Ber.*, **95**, 2861 (1962).

5) A. J. Kirby, *Tetrahedron*, **22**, 3001 (1966).

## Experimental

Compound **2a** was prepared by the reaction of ethyl cyanoacetate and carbon disulfide in aqueous ammonia (28%). Compounds **2b**, **2c**, and **2d** were prepared by Soderback's method.[6)]

**Isolation of Diammonium Salt of 5d.** A mixture of malononitrile (25 g, 0.38 mol), carbon disulfide (57 g, 0.75 mol) and *ca.* 200 m*l* of liquid ammonia was stirred for 30 min under cooling with dry ice-methanol. The reaction mixture was then allowed to stand at room temperature. A yellow solid material was recrystallized from methanol-chloroform to give light yellow plates (65.5 g, di(ammoniomercapto)methylenemalononitrile).[7)] The light yellow material (8 g) was dissolved in 100 m*l* of ethanol and hydrogen sulfide was passed through for 30 min. The whole was shaken for an additional 3 hr. The yellow material was collected, recrystallized from water, washed with ethanol, and dried: yellow plates (0.5 g, diammonium salt of **5d**), mp 136—137°C (dec.) (slow heating), 153—156°C (dec.) (rapid heating). IR (KBr): 3310 (s, $\nu$ NH), 3080, 2960 (s, br, $\nu$ $NH_4^+$), 2180 (s, $\nu$ CN), 1590 (s, $\nu$ C=N), 1505 (m, $\nu$ conj. C=C), 1415 cm$^{-1}$ (s, br, $\delta$ $NH_4^+$). Found: C, 23.23; H, 4.83; N, 26.56; S, 45.36%; mol wt, 214.7 (vapor-pressure osmometer, in acetone). Calcd for $C_4H_{10}N_4S_3$: C, 22.86; H, 4.86; N, 26.66; S, 45.68%; mol wt, 210.15.

The ammonium salt of **5d** was methylated by dimethyl sulfate. Yellow needles (mp 219—220°C) were obtained and from analytical results, and was assigned the structure di(methylmercapto)methylenecyanoacetamide. The NMR spectrum in deuterioacetone revealed signals at $\delta$ 7.40 (br, 1, NH) and $\delta$ 1.80 (s, 1, SH).

**Treatment of Diammonium Salt of 5d with Acetic Acid.** To the diammonium salt of **5d** (2 g) in 100 m*l* of water was added acetic acid (4.5 m*l*). This was allowed to stand for 1 hr at 20°C. The crude product was collected and recrystallized from pyridine-water to give yellow prisms quantitatively. The IR spectrum agreed with that of **3d**.

**Preparation of 3a.** Through the mixture of **2a** (8 g, 0.04 mol) and water (50 m*l*) was passed hydrogen sulfide 30 min at room temperature. The reaction mixture was stirred for 3 hr, and treated under diminishing pressure at 30—40°C in order to remove unchanged hydrogen sulfide. To this was added 50 m*l* of a saturated bromine water and allowed to stand for several hours. The crude yellow material was filtered, washed with water and ether, and recrystallized from pyridine-water: 9.0 g of yellow prisms (**3a**, yield *ca.* 94%), mp 247—248°C. NMR (DMSO-d$_6$): $\delta$ 10.35 (br, $CONH_2$), $\delta$ 8.70 (br, $NH_2$); IR (KBr): 3280, 3260, 3220, 3140, 3020 (w, $\nu$ $NH_2$), 1650 (sh, $\nu$ CO), 1638 (s, $\delta$ $NH_2$), 1550 cm$^{-1}$ (s, $\nu$ C=C). Found: C, 25.31; H, 2.16; N, 14.47; S, 49.95%; mol wt, 183.1 (vapor-pressure osmometer, in acetone). Calcd for $C_4H_4N_2S_3O$: C, 25.01; H, 2.10; N, 14.58; S, 49.95%; mol wt, 192.09.

**Preparation of 3b.** Compound **3b** was prepared by the same method as above. 8.1 g of yellow needles was produced from **2b** (15 g, 0.05 mol) and recrystallized from methanol (yield *ca.* 81%): mp 201—202°C (dec.). NMR (acetone-d$_6$): $\delta$ 9.20 (br, $NH_2$), $\delta$ 3.82 (s, $CH_3$); IR (KBr): 3270, 3150, 3100 (s, $\nu$ $NH_2$), 2950 (m, $\nu$ $CH_3$), 1658 (vs, $\nu$ C=O), 1572 (vs, $\delta$ $NH_2$), 1562 (sh, $\nu$ conj. C=C), 1332 cm$^{-1}$ (vs, $\nu$ C–O–C). Found: C, 29.10; H, 2.62; N, 6.78; S, 46.09%; mol wt, 217.0 (vapor-pressure osmometer, in acetone). Calcd for $C_5H_5NS_3O_2$: C, 28.97; H, 2.44; N, 6.76; S, 46.39%; mol wt, 207.29.

**Preparation of 3c.** Compound **3c** was prepared as in the case of **3a**. Crude material was prepared from 10.6 g (0.03 mol) of **2c** and recrystallized from pyridine-water to give 6 g of yellow needles (**3c**, yield *ca.* 83%), mp 181°C. NMR (DMSO-d$_6$): $\delta$ 9.20 (br, $NH_2$), $\delta$ 4.32 (q, $CH_2$, $J$=6 Hz), $\delta$ 1.32 (t, $CH_3$, $J$=6 Hz); IR (KBr): 3340, 3200 (s, $\nu$ $NH_2$), 2980 (w, $\nu$ $CH_3$), 1652 (s, $\nu$ C=O), 1590 (vs, $\delta$ $NH_2$), 1340 cm$^{-1}$ (s, $\nu$ C–O–C). Found: C, 32.80; H, 3.10; N, 6.49; S, 43.26%; mol wt, 226.4 (vapor-pressure osmometer, in acetone). Calcd for $C_6H_7NS_3O_2$: C, 32.59; H, 3.19; N, 6.34; S, 43.60%; mol wt, 221.12.

**Another Preparative Method of 3b and 3c.** Through the mixture of **2**, water and acetic acid (30 m*l*) was immediately passed hydrogen sulfide. Yellow material was collected and recrystallized. The yield was almost equal to that of the above method.

**Preparation of 3d.** Preparation was the same as for **3a**. Crude product was obtained from **2** (8.5 g, 0.035 mol) and recrystallized from methanol: 5 g of yellow prisms (**3d**, yield 82%), mp $<$300°C. NMR (DMSO-d$_6$): $\delta$ 9.58 (br, $NH_2$); IR (KBr): 3170 (m, br, $\nu$ $NH_2$), 2220 (s, $\nu$ CN), 1615 (vs, $\nu$ C=N), 1505 cm$^{-1}$ (vs, $\nu$ C–C). Found: C, 27.77; H, 0.87; N, 16.35; S, 54.95%; mol wt, 180.0 (vapor-pressure osmometer, in acetone). Calcd for $C_4H_2N_2S_3$: C, 27.60; H, 1.15; N, 16.10; S, 55.00%; mol wt, 174.

**Preparation of 6a.** To the mixture of **2a** (7 g, 0.036 mol) and water (50 m*l*) was added 50 m*l* of the saturated bromine water. The solution was allowed to stand overnight at 20°C and 0.6 g of light yellow material (**3a**) was filtered off. The filtrate was added with 30 m*l* of acetic acid and kept to stand for 3 hr. Crude yellow material was collected and washed with water and a small amount of methanol. Recrystallization from dioxane gave 3.8 g of light yellow needles (**6a**, yield 70%), mp $<$300°C. IR (KBr): 3340, 3180 (s, $\nu$ $NH_2$), 2210 (s, $\nu$ conj. CN), 1670 (sh, $\nu$ C=O), 1655 (vs, $\delta$ $NH_2$), 1450 cm$^{-1}$ (vs, probable ring stretching). Found: C, 33.79; H, 1.31; N, 19.80; S, 34.00%; mol wt, 283.5 (vapor-pressure osmometer, in acetone). Calcd for $C_8H_4N_4S_3O_2$: C, 33.81; H, 1.42; N, 19.72; S, 33.79%; mol wt, 284.14.

**Preparation of 6b.** Preparation was carried out as above. Crude product was obtained from **2b** (7 g, 0.023 mol) and recrystallized from dioxane: 2.5 g of light yellow needles (**6b**, yield 74%), mp 227—228°C (reported mp 225—228°C[4)]). IR (KBr): 2960 (m, $\nu$ $CH_3$), 2220 (s, $\nu$ conj. CN), 1675 (vs, $\nu$ C=O), 1472 (vs, probable ring stretching), 1300 cm$^{-1}$ (vs, $\nu$ C–O–C). Found: C, 38.33; H, 2.05; N, 9.13; S, 30.47%; mol wt, 314 (mass spectrum). Calcd for $C_{10}H_6N_2S_3O_4$: C, 38.22; H, 1.91; N, 8.92; S, 30.63%; mol wt, 314.18.

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6) E. Söderbäck, *Acta Chem. Scand.*, **19**, 554 (1965).

7) T. Takeshima, M. Yokoyama, N. Fukada and M. Akano, *J. Org. Chem.*, July (1970), in press: "The Reaction of Malononitrile with Carbon Disulfide in an Aqueous Alkali Medium."

**Preparation of 6b.** Preparation was carried out as for **6a**. Crude product was obtained from **2c** (7 g, 0.022 mol) and recrystallized from methanol: a light yellow needles (**6c**, 3 g, yield 81%), mp 215—216°C. IR (KBr): 2980 (m, $\nu$ CH), 2220 (s, $\nu$ conj. CN), 1760, 1655 (vs, $\nu$ C=O), 1475 (vs, probable ring stretching), 1305 cm$^{-1}$ (vs, $\nu$ C–O–C). Found: C, 41.91; H, 3.14; N, 8.09; S, 28.13%; mol wt, 342 (mass spectrum). Calcd for $C_{12}H_{10}N_2S_3O_4$: C, 42.11; H, 2.95; N, 8.19; S, 28.05%; mol wt, 342.22.

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