Reactions of Ethylene Di- and Trithiocarbonates with Acetylenes. Anomalous Reaction with Bromocyanoacetylene to Give a Thioacyl Bromide

BRIAN R. O'CONNOR AND FRANK N. JONES

Contribution No. 1613 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Received October 9, 1969

Most acetylenes having electron-withdrawing substituents react with O,S-ethylene dithiocarbonates or ethylene trithiocarbonates to give olefin and O,S-vinylene dithiocarbonates or vinylene trithiocarbonates. Bromocyanoacetylene does not eliminate ethylene from ethylene trithiocarbonate, but gives intensely colored, resonance-stabilized α-cyano-1,3-dithiolane-$\Delta^{2,\alpha}$-thioacetyl bromide (**9**); **9** reacts with alcohols and amines to give thiono esters and thioamides.

In 1965, Easton and Leaver reported that dimethyl acetylenedicarboxylate reacts with ethylene trithiocarbonate (**1**) at 140° to give ethylene and 1,3-dithiole-2-thione (1,3-trithione) derivative **2a**.[1] Other five-membered-ring heterocycles which give cycloaddition–ring-opening reactions with acetylenes include 1,2-trithiones,[1-5] aza 1,2- and 1,3-trithiones,[6-8] and sydnones.[9] A similar reaction of N-sulfinylanilines with ethylene carbonate was reported.[10]

This paper describes further studies of the reactions of ethylene di- and trithiocarbonates with acetylenes.

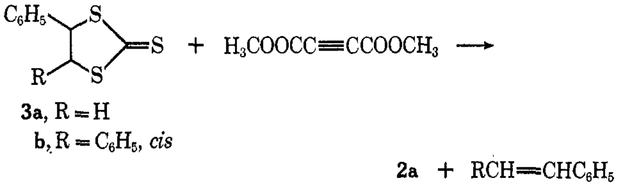
Normal Reaction of Ethylene Trithiocarbonate (1).—Several acetylenes having electron-withdrawing groups reacted smoothly with **1** to give substituted 1,3-dithiole-2-thiones **2a–c**. The reactions proceeded at useful rates at 110–145°; yields were good. However, acetylene reacted with **1** only under forcing conditions to give **2d** in 2–5% yield; the product was grossly contaminated with tar. **1** did not react with methyl-, phenyl-, or diphenylacetylenes at 130–150°. At higher temperatures (180–190°) tar was formed, and no ethylene was detected. Thus, the scope of the reaction appears to be limited to negatively substituted acetylenes, with acetylene as a limiting case.

1

2a, R, R′ = $COOCH_3$
b, R, R′ = CF_3
c, R = CN; R′ = H
d, R, R′ = H

The structures of compounds **2b** and **2d** were established by comparison with published data and were further substantiated by single-line ^1H or ^{19}F nmr spectra, which virtually eliminate the isomeric 1,2-dithiolane-3-thione structures as possibilities. The structure of **2c** was assigned by analogy and was substantiated by spectral similarities to **2b** and **2d**.

Normal Reactions of Phenyl- and *cis*-Diphenylethylene Trithiocarbonates (3a and 3b).—In nmr-tube experiments, **3a**[11] was shown to react smoothly with dimethyl acetylenedicarboxylate at 88–90° to give **2a** and styrene. The reaction appeared to follow second-order kinetics in $CDCl_3$ solution. It was about 40% complete in 55 min and 72% complete in 220 min using equimolar quantities. A small solvent effect was detected; in $(CD_3)_2SO$ solution at 89–90°, the reaction was about 35% complete in 27 min and 88% complete in 220 min.



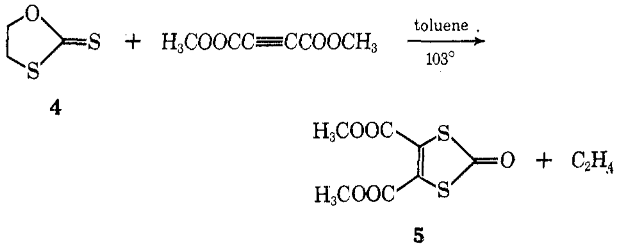
3a, R = H
b, R = C_6H_5, *cis*

cis and *trans*

Similarly, **3b**[12] reacted with dimethyl acetylenedicarboxylate, the reaction being 31% complete in 1.0 hr at 78°. The products were **2a** and an apparent mixture of *cis*- and *trans*-stilbenes.

These results indicate that substitution of phenyl for H in **1** promotes the cycloaddition–ring-opening reaction moderately. However, the effect is apparently insufficient to enlarge the scope of the reaction appreciably. Neither **3a** nor **3b** reacted detectably with phenylacetylene at temperatures up to 160°.

Treatment of Dithiocarbonates with Acetylenes.—O,S-Ethylene dithiocarbonate[13] (**4**) reacted slowly with dimethyl acetylenedicarboxylate at 100° to give known compound **5**, whose structure was established by its spectra and by comparison with published data.[14]



4

5

However, S,S′-ethylene dithiocarbonate (**6**) did not react with dimethyl acetylenedicarboxylate at 110° or 160°, and O,O′-ethylene thiocarbonate[13] (**7**) did not

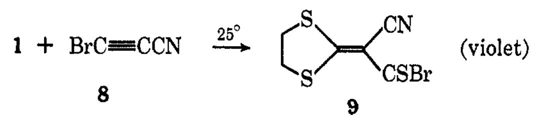
---

[1] D. B. J. Easton and D. Leaver, *Chem. Commun.*, 585 (1965).
[2] H. Behringer and R. Widenmann, *Tetrahedron Lett.*, 3705 (1965).
[3] H. Behringer, J. Kilger, and R. Widenmann, *ibid.*, 1185 (1968).
[4] J. Vialle, *et al.*, *Bull. Soc. Chem. Fr.*, 1150, 3187 (1966).
[5] R. Mayer, H. J. Hartmann, and J. Jentzsch, *J. Prakt. Chem.*, **31**, 312 (1966).
[6] H. Behringer and D. Deichmann, *Tetrahedron Lett.*, 1013 (1967).
[7] D. Noel and J. Vialle, *Bull. Soc. Chim. Fr.*, 2239 (1966).
[8] H. Behringer, D. Bender, J. Falkenberg, and R. Widenmann, *Chem. Ber.*, **101**, 1428 (1968).
[9] R. Huisgen, German Patent 1,261,124 (1968), to Farbwerke Hoechst Aktiengesellschaft.
[10] O. Tsuge, M. Tashiro, and F. Mashiba, *Bull. Chem. Soc. Jap.*, **40**, 2709 (1967).
[11] H. A. Stansbury, J. A. Durden, Jr., and W. H. Catlett, Canadian Patent 682,545 (1964), example 5.
[12] C. G. Overberger and A. Drucker, *J. Org. Chem.*, **29**, 360 (1964).
[13] F. N. Jones and S. Andreades, *ibid.*, **34**, 3011 (1969).
[14] R. Mayer and B. Gebhardt, *Chem. Ber.*, **97**, 1298 (1964).

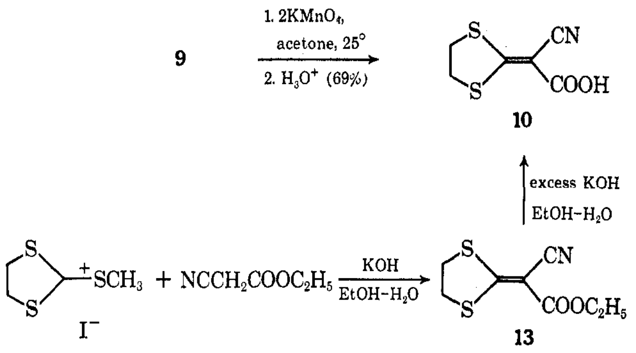
react at 80°, its upper limit of stability. Evidently, this reaction is characteristic of substrates having the -C(=S)S- configuration.

Part of the driving force for the reaction of **4** is probably the conversion of a thionocarbonate to a thiolcarbonate. Bond energy data indicate that this process is exothermic by 24 kcal/mol in simple systems.[15]

Anomalous Reaction of 1 with Bromocyanoacetylene (8).—When **1** and **8**[16] were mixed in benzene, a mildly exothermic reaction occurred and, after a few hours, a good yield of 1:1 adduct was obtained as brilliant violet crystals. No ethylene was evolved. The adduct fumed in a humid atmosphere, but it could be handled in dry air.

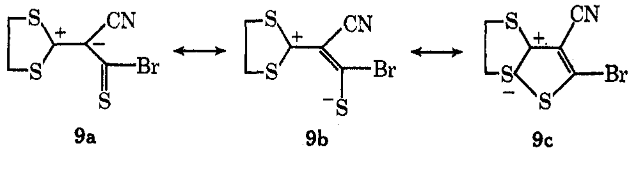


This adduct was assigned structure **9**, α-cyano-1,3-dithiolane-$\Delta^{2,\alpha}$-thioacetyl bromide, primarily on the basis of its conversion to derivative **10** which was prepared independently by an established route.[17]



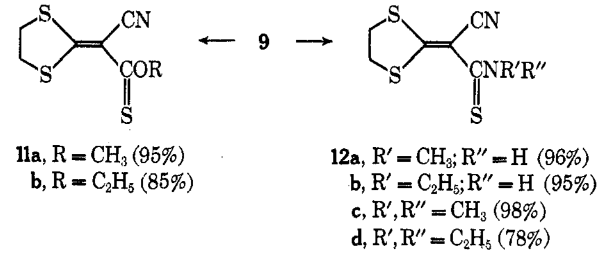
The structure of **9** was substantiated by spectral data. The nmr spectrum in CH_2Cl_2 appeared as a symmetrical pentuplet centered at δ 3.68. The infrared spectrum had a nitrile band at 2200 cm^{-1} and very strong bands at 1355 and 1325 cm^{-1}.

The absence of absorption in the normal double-bond region of the infrared spectrum of **9** and the presence of very strong bonds at 1355 and 1325 cm^{-1} suggest that resonance structures **9a**, **9b**, and **9c** may contribute significantly to the resonance hybrid. The intense color also suggests a resonance hybrid with charge separation.

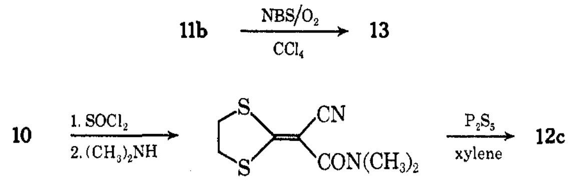


Compound **9** is believed to be the first example of a stable thioacyl bromide, although thioacyl fluorides and chlorides are well known. Its stability probably results from the unusual degree of electron delocalization.

Compound **9** reacts readily with amines and alcohols to form yellow thiono esters **11a** and **b** and thioamides **12a–d**.

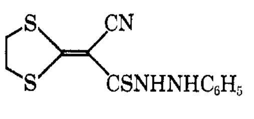


The structures of **11** and **12** were established by conversion of thiono ester **11b** to known ester **13** by treatment with N-bromosuccinimide in air and by independent synthesis of thioamide **12c**.

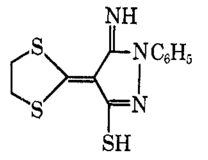


Spectral data also supported the assigned structures. The nmr spectrum of ethanol adduct **11b** in $CDCl_3$ had, in addition to the triplet–quartet pattern of the ethyl protons, a broadened singlet at δ 3.63 (4 H) which at higher resolution appeared as a symmetrical pentuplet. The infrared spectrum had a nitrile band at 2200 cm^{-1} and a strong band at 1445 cm^{-1}. The absence of a strong peak assignable to C=O showed that the ester had the less stable thiocarbonyl structure. The electronic spectrum in CH_3CN had maxima at 246 mμ (ε 12,000), 278 (4350), 300 (5400), and 360 (18,400). Spectra of **11a** and of **12a–d** (see Experimental Section) were consistent with the assigned structures.

Phenylhydrazine reacted with **9** at 25° to give a red-brown solid, mp 235–236° dec, which had no nitrile absorption in the infrared spectrum. Probably the product is not **14** but some product of further reaction such as **15**.



14



15

Thioacetyl bromide (**9**) reacted with potassium fluoride in refluxing acetonitrile to give the corresponding thioacyl fluoride, **16**, similar in color to **9**. The structure was strongly supported by analytical and spectral data. The ^{19}F nmr spectrum had a sharp singlet at −110.2 ppm from $Cl_2FCCFCl_2$; thioacyl fluorides are reported to have resonances between −107 and −162 ppm from $Cl_2FCCFCl_2$.[18]

Treatment of phenylethylene trithiocarbonate (**3a**) with **8** at 25° also gave a red-violet solid for which ana-

---

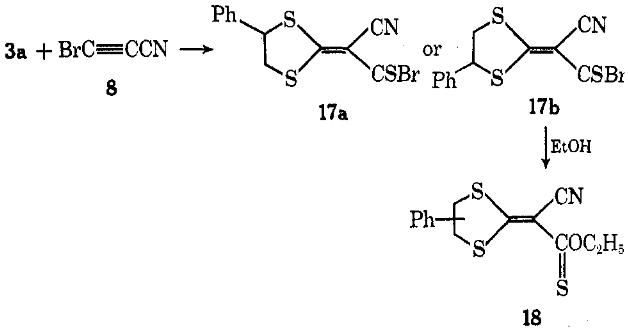
[15] E. S. Kooyman in "Organosulfur Chemistry," M. J. Janssen, Ed., Interscience Publishers, Inc., New York, N. Y., 1967, Chapter 1.

[16] E. Kloster-Jensen, *Acta Chem. Scand.*, **17**, 1859 (1963); **17**, 1862 (1963); **18**, 1629 (1964).

[17] R. Mayer and K. Schafer, *J. Prakt. Chem.*, **26**, 279 (1964).

[18] W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Org. Chem.*, **30**, 1375 (1965).

lytical and spectral data support structure **17a** or **17b**. This thioacetyl bromide was converted into the ethyl thiono ester **18**.



The mechanisms of these reactions have not been studied in detail. The fact that dithionocarbonate **4** reacts to give **5** and that **6** and **7** do not react strongly suggests that the exocyclic sulfur of ethylene trithiocarbonates becomes endocyclic during the normal reaction. Mechanisms in which the two ring sulfur atoms are incorporated in the ring of the final product seem to be eliminated. The anomalous reaction of bromocyanoacetylene (**8**) occurs at lower temperatures, indicating that a lower energy pathway available to **1** and **8** supersedes the normal reaction.

Experimental Section[19]

Dimethyl 2-Thiono-1,3-dithiole-4,5-dicarboxylate (2a).—A mixture of 27.4 g (0.20 mol) of ethylene trithiocarbonate (1), 28.5 g (0.20 mol) of dimethyl acetylenedicarboxylate, and 100 ml of toluene was heated at reflux for 4 hr. Pentane was slowly added to precipitate **2a**. Recrystallization from toluene–pentane gave 26.3 g (53%) of yellow dithiolane **2a**: mp 72–72.5°; ir (KBr) 1721, 1742 cm^{-1}; nmr (CDCl$_3$) δ 3.88. Use of refluxing xylene as solvent gave dark colored **2a**, mp 69–70.5°, in 33% yield.

Anal. Calcd for $C_7H_6O_4S_3$: C, 33.59; H, 2.42; S, 38.51. Found: C, 33.99; H, 2.53; S, 38.70.

4,5-Bis(trifluoromethyl)-1,3-dithiole-2-thione (2b).—A mixture of 34 g (0.25 mol) of **1**, 49 g (0.3 mol) of hexafluoro-2-butyne, and 60 g of toluene was heated in a steel pressure tube at 120° for 3 hr and at 160° for 3 hr. Fractionation through a spinning-band column gave 51 g (76%) of pale orange **2b**, bp 186–187°; the product was identical with the material obtained from hexafluoro-2-butyne, sulfur, and CS$_2$:[20] ir (neat) 1555, 1270, 1250, 1170, 925, 895 cm^{-1}.

2-Thiono-1,3-dithiole-4-carbonitrile (2c).—A solution of 5.9 g (0.043 mol) of **1** and 2.5 g (0.05 mol) of cyanoacetylene in 100 ml of xylene was stirred at 25° for several hours; no gas was evolved. The solution was refluxed for 20 hr, the temperature rose gradually from 120 to 135°, and 0.5 l. of water-insoluble gas evolved. The mixture was cooled and 3.0 g (0.06 mol) of cyanoacetylene was added. After 10 hr of further refluxing, the temperature was 130°, 1.75 l. (*ca.* 0.07 mol) of gas had evolved, and the rate of gas evolution was very slow. The dark red reaction mixture was concentrated under nitrogen, and the semisolid residue was extracted with three 200-ml portions of hot hexane–benzene (98:2). Cooling the extracts gave 2.1 g (33%) of yellow-bronze **2c**, mp 92.5–96°. Recrystallization followed by sublimation at 90° (0.2 mm) gave yellow **2c**: mp 100–101.5°; ir (CHCl$_3$) 3080 (w), 2980 (w), 2210 (m), 1100 (m), 1070 (vs), 872 (m), 840 (m) cm^{-1}; nmr (CDCl$_3$) δ 7.78 (s).

Anal. Calcd for C_4HNS_3: C, 30.16; H, 0.63; N, 8.80. Found: C, 30.04; H, 0.59; N, 8.63.

1,3-Dithiole-2-thione (2d).—A mixture of 34.1 g (0.25 mol) of **1**, 80 g of acetone, and 26 g (1 mol) of acetylene was agitated in a 240-ml stainless steel tube (barricade) at 150° for 4 hr and then at 200° for 4 hr. The resulting red solution was concentrated to give 33.8 g of red oil which was estimated by nmr analysis to contain 5–6% **2d** and much unreacted **1**. Repeated extraction with pentane gave 0.4 g of residual **2d**, an impure oil having all the ir and nmr [δ 7.18 (CDCl$_3$)] peaks of **2d** independently synthesized by the method of Mayer.[14]

Reactions of Phenyl and *cis*-Diphenyl Trithiocarbonates with Dimethyl Acetylenedicarboxylate.—These reactions were effected by immersing solutions of reagents in nmr tubes in a thermostatically controlled oil bath. After the indicated time, the tubes were quickly cooled. The compositions of the resulting solutions were estimated by comparison of their nmr spectra with those of starting materials and products.

Dimethyl 2-Oxo-1,3-dithiole-4,5-dicarboxylate (5).—A solution of 3.6 g (0.03 mol) of yellow O,S-ethylene dithiocarbonate[18] (4) and 4.2 g (0.03 mol) of dimethyl acetylenedicarboxylate in 30 ml of toluene was heated at 103° in the dark for 6 hr and kept at 25° for 3 days. The red solution was concentrated to give 6.9 g of oil whose ir spectrum showed substantial amounts of unreacted starting materials. Fractional recrystallization from methylene chloride and from methanol followed by sublimation gave 2.4 g (34%) of colorless **5**, mp 66–67° and 65.5–67° (lit.[14] mp 70°).

Anal. Calcd for $C_7H_6O_5S_2$: C, 35.89; H, 2.58; S, 27.37. Found: C, 36.02; H, 2.71; S, 27.23.

α-Cyano-1,3-dithiolane-$\Delta^{2,\alpha}$-thioacetyl Bromide (9).—A solution of 25 g (0.19 mol) of bromocyanoacetylene[16] and 27 g (0.20 mol) of ethylene trithiocarbonate (1) in 400 ml of benzene was stirred at 25–30° for 24 hr; 43 g (83%) of purple-red **9**, mp 120–124° dec, was collected. Recrystallization of 1.0 g from 25 ml of benzene yielded 0.5 g of brilliant purple needles: mp 126° dec; ir (KBr) 3000 (w), 2200 (m), 1355, 1325 (s), 1275 (m), 1245 (m), 1155 (m), 1045 (w), 953 (m), 930 (w), 840 (w) cm^{-1}; nmr (CH$_2$Cl$_2$) δ 3.68 (broadened singlet) (at 50-cps sweep width the spectrum appeared to be a symmetrical quintet centered at δ 3.68 with a 7.6-Hz separation between the weak outer wings); uv–vis (CH$_3$CN) λ_{max} 242 mμ (ϵ 20,000), 266 (6400), 294 (3300), 330 (3860), 400 (19,200), 520 (130).

Anal. Calcd for $C_6H_4BrNS_3$: C, 27.07; H, 1.52; N, 5.27; Br, 30.02; S, 36.13; mol wt, 266. Found: C, 27.16; H, 1.43; N, 5.27; Br, 30.10; S, 35.51; mol wt, 284 (cryoscopic, C$_6$H$_6$), 284 (vapor pressure osmometer, CHCl$_3$), 284 (ebullioscopic, CH$_2$Cl$_2$).

α-Cyano-1,3-dithiolane-$\Delta^{2,\alpha}$-acetic Acid (10).—A solution of 12 g (0.0076 mol) of potassium permanganate in 1400 ml of acetone was added rapidly to a slurry of 8 g (0.03 mol) of **9** in 100 ml of acetone. The brown precipitate was collected and extracted thoroughly with dilute aqueous potassium hydroxide. Acidification with dilute sulfuric acid precipitated 3.8 g (67%) of **10**, mp 240–250° dec. Recrystallizations from 400 ml of acetonitrile (Darco) and from acetic acid gave pale yellow **10**: mp 228.5–230° (lit.[17] mp 248–249°); ir (KBr) 3300–2400 (br), 2205 (m), 1670 (s), 1455 (s), 1295–1280 (s), 1180 (m), 930 (w), 900 (w), 725 cm^{-1}; nmr (CD$_3$SOCD$_3$) δ 10.0 (s, 1), 3.77 (s, 4). These spectra were identical with those of acid **10** synthesized independently substantially as described.[17]

Anal. Calcd for $C_6H_5NO_2S_2$: C, 38.48; H, 2.70; N, 7.48; S, 34.25. Found: C, 38.26; H, 2.73; N, 7.49; S, 33.92.

O-Methyl α-Cyano-1,3-dithiolane-$\Delta^{2,\alpha}$-thioacetate (11a).—A slurry of 2.6 g (0.01 mol) of **9** in 75 ml of methanol was stirred for 12 hr at 25°. Thionoester **11a** was collected as 2.1 g (95%) of light brown solid, mp 133–135° dec. Recrystallization from 70:30 benzene–hexane gave yellow **11a**, mp 135–138° dec.

Anal. Calcd for $C_7H_7NS_3O$: C, 38.68; H, 3.25; N, 6.45. Found: C, 38.38; H, 3.15; N, 6.46.

O-Ethyl α-Cyano-1,3-dithiolane-$\Delta^{2,\alpha}$-thioacetate (11b).—This thiono ester, mp 133–134° dec, was prepared similarly, in 85% yield, from **9** and ethanol.

Anal. Calcd for $C_8H_9NOS_3$: C, 41.52; H, 3.93; N, 6.06; S, 41.57. Found: C, 41.42; H, 3.94; N, 6.13; S, 41.88.

Conversion of 11b into Ethyl-α-cyano-1,3-dithiolane-$\Delta^{2,\alpha}$-acetate (13).—A mixture of 9.2 g (0.04 mol) of thiono ester **11b** and 7.2 g (0.04 mol) of N-bromosuccinimide in 120 ml of carbon tetrachloride was refluxed in air for 20 hr. When filtered and cooled, the filtrate yielded 2.85 g (25%) of a yellow solid, mp 97–99°. Recrystallization of 1 g from 25 ml of 60:40 benzene–hexane (Darco) yielded 0.5 g of **13**: mp 102–103° (lit.[17] mp 104.5–105°); ir (KBr) 1700 cm^{-1}. This material was identical with **13** independently prepared by a known method.

---

[19] Melting points and boiling points are uncorrected. Infrared spectra were recorded linear in wavelength using a Perkin-Elmer Model 21 device. Nmr spectra were produced on Varian A-60, HR-100, and A-56/60 devices. Uv-visible spectra were recorded on a Cary Model 14 spectrophotometer.

[20] C. G. Krespan and D. C. England, *J. Org. Chem.*, **33**, 1850 (1968).

Anal. Calcd for $C_8H_9NS_2O_2$: C, 44.63; H, 4.21; N, 6.51; S, 29.79. Found: C, 44.75; H, 4.17; N, 6.54; S, 30.03.

N-Methyl-α-cyano-1,3-dithiolane-$\Delta^{2,\alpha}$-thioacetamide (12a).—Anhydrous methylamine was bubbled through a stirred solution of 5.3 g (0.02 mol) of **9** in 125 ml of tetrahydrofuran until the red color discharged. The precipitate was collected (3.82 g). Extraction with 40 ml of distilled water left 1.63 g of yellow, insoluble **12a**, mp 218–220°. The tetrahydrofuran solution was concentrated to give 2.6 g of **12a**, mp 198–212°. Recrystallization from benzene (110 ml/g) gave yellow **12a**: mp 219–221°; ir (KBr) 3300 (m), sharp, 2910 (w), 2200 (m), 1535 (m), 1480 (s), 1425 (m), 1345 (m), 1275 (m), 1245 (m), 1058 (m), 990 (w), 920 (w), 790 (w), 683 (w), cm^{-1}; nmr (CD_3SOCD_3) δ 8.45 (br, 1), 3.72 (s, 4), 3.12 (d, 3, J = 4.5 Hz).

Anal. Calcd for $C_7H_8N_2S_3$: C, 38.84; H, 3.73; N, 12.94; S, 44.46, mol wt, 216. Found: C, 38.76; H, 3.92; N, 12.97; S, 44.54; mol wt, 209 (cryoscopic, Me_2SO).

N-Phenyl-α-cyano-1,3-dithiolane-$\Delta^{2,\alpha}$-thioacetamide (12b).—A mixture of 5.3 g (0.02 mol) of **9**, 5.5 g (0.061 mol) of aniline, and 100 ml of tetrahydrofuran was stirred for several hours. Aniline hydrobromide (3.4 g, mp 260–280° dec) was filtered. The filtrate was concentrated under nitrogen to yield 5.5 g (95%) of **12b**, mp 153–160°. Two recrystallizations from benzene (*ca.* 1 g/50 ml of benzene) yielded bright yellow **12b**: mp 172.5–174.5°; uv–vis (CH_3CN) λ_{max} 243 mμ (ϵ 17,250), 292 (8400), 342 (17,400), 435 (sh) (550); ir and nmr comparable with those of **12a**.

Anal. Calcd for $C_{12}H_{10}N_2S_3$: C, 51.77; H, 3.63; N, 10.05. Found: C, 51.93; H, 3.47; N, 10.07.

N,N-Dimethyl-α-cyano-1,3-dithiolane-$\Delta^{2,\alpha}$-thioacetamide(12c).—Tetrahydrofuran-soluble thioamide **12c** was prepared essentially as described for the preparation of **12a** and isolated in 98% yield as described for **12b**. Recrystallization from 70:30 benzene–hexane yielded bright yellow needles of **12c**, mp 146–148°; spectra were comparable with those of **12a** and **12b**.

Anal. Calcd for $C_8H_{10}N_2S_3$: C, 41.66; H, 4.37; N, 12.16; S, 41.75; mol wt, 230. Found: C, 41.51; H, 4.54; N, 12.17; S, 41.81; mol wt, 233 (cryoscopic, Me_2SO).

Independent Synthesis of 12b from 10.—**10** (4.7 g, 0.025 mol) was treated with excess thionyl chloride at reflux for 2 hr. After removal of volatiles, the crude acid chloride was treated with dimethylamine in tetrahydrofuran. The amide was isolated as described above for **12b**. Recrystallization from 60:40 hexane–benzene gave N,N-dimethyl-α-cyano-1,3-dithiolane-$\Delta^{2,\alpha}$-acetamide, mp 69–70°.

Anal. Calcd for $C_8H_{10}N_2OS_2$: C, 44.85; H, 4.71; N, 13.07. Found: C, 44.80; H, 4.45; N, 12.95.

A mixture of 1.0 g (0.0047 mol) of this amide, 0.9 g (0.004 mol) of phosphorus pentasulfide, and 25 ml of xylene was heated on a steam bath for 4 hr. The xylene solution was decanted, and the oily residue was extracted with hot xylene. The xylene solution and extract were concentrated under nitrogen to yield 0.5 g of a yellow-orange solid, mp 60–140°. Crystallization from 50:50 hexane–benzene gave 0.025 g (25%) of bright yellow **12c**, mp 144.5–146.5°. The mixture melting point with **12c** obtained from **9** and dimethylamine was 144.5–146.5°. Ir spectra were identical.

N,N-Diethyl-α-cyano-1,3-dithiolane-$\Delta^{2,\alpha}$-thioacetamide (12d).—This thioamide, mp 65–69°, was prepared essentially as described for **12b**. Recrystallization of 2.0 g from 100 ml of 50:50 ether–benzene (Darco treatment) yielded 0.6 g of an analytical sample, mp 66–68°. Spectra were comparable with those of **12a–c**.

Anal. Calcd for $C_{10}H_{14}N_2S_3$: C, 46.47; H, 5.46; N, 10.84. Found: C, 46.33; H, 5.40; N, 10.91.

Reaction of 9 with Phenylhydrazine.—The reaction was effected as described for preparation of **12b**, and the product, sparingly soluble in tetrahydrofuran, was isolated as described for **12a**. The maroon solid had mp 230–250° dec and 213–222° dec. Recrystallization of 1.0 g of the crude product from 100 ml of acetonitrile yielded 0.7 g of shiny red-brown plates tentatively assigned structure **16**: mp 235–236° dec; ir (KBr) 3300 (w), 3180 (w), 2315 (vw), 1640 (m), 1600 (w), 1560 (m), 1480 (s), 1435 (m), 1362, 1285 (m), 1245 (m), 918 (m), 782 (m), 763 (s), 695 (m) cm^{-1}; nmr (CD_3SOCD_3) δ 8.12 (m, 2), 7.51 (m, 3), 6.05 (br s, 2), 3.79 (q, 4, resolved only at 100 MHz); uv–vis (CH_3CN) λ_{max} 230 mμ (ϵ 18,750), 285 (15,100), 326 (20,200), 485 (3100).

Anal. Calcd for $C_{12}H_{11}N_3S_3$: C, 49.12; H, 3.78; N, 14.32; S, 32.83; mol wt, 293. Found: C, 49.23; H, 3.71; N, 14.27; S, 33.00; mol wt, 283 (cryoscopic Me_2SO).

α-Cyano-1,3-dithiolane-$\Delta^{2,\alpha}$-thioacetyl Fluoride (15).—A mixture of 10.5 g (0.04 mol) of **9**, 25 g (0.40 mol) of anhydrous potassium fluoride, and 200 ml of acetonitrile was refluxed under nitrogen for 12 hr. The solids were filtered and washed with acetonitrile. The solutions were concentrated to give 6.9 g of crude **15**, mp 85–101°. Sublimation at 90° (0.05 mm) gave **15**: mp 105.5–107°; ir (KBr) 2995 (w), 2205 (m), 1775 (w), 1420 (s), 1355 (s), 1290 (m), 1248 (m), 1155 (m), 1120 (s), 1048 (m), 1000 (w), 968 (w), and 825 (s) cm^{-1}; uv–vis (CH_3CN), λ_{max} 219 mμ (ϵ 9300), 241 (11,600), 260 (sh) (4750), 317 (5550), 383 (18,200).

Anal. Calcd for $C_6H_4NS_3F$: C, 35.10; H, 1.97; N, 6.82; F, 9.25. Found: C, 35.16; H, 2.04; N, 7.02; F, 9.35.

cis- **or** *trans*-**α-Cyano-4-phenyl-1,3-dithiolane-$\Delta^{2,\alpha}$-thioacetyl Bromide (17a or 17b).**—This product was prepared from **3a** and bromocyanoacetylene as described for preparation of **9**. The initial precipitate (60% yield, mp 125–126° dec) was recrystallized from 50:50 hexane–benzene to give red-violet **17a** or **17b**: mp 125–126°; ir (KBr) 3000 (w), 2205 (m), 1390 (s), 1308 (s), 950 (m), 735 (m), 695 (m), cm^{-1}; nmr ($CDCl_3$) δ 8.5 (s, 5), 5.38 (t, 1), 3.81–4.05 (m, 2); uv–vis (CH_3CN) λ_{max} 244 mμ (ϵ 24,700), 265 (sh), 295 (3750), 334 (3860), 408 (20,150), 522 mμ (126).

Anal. Calcd for $C_{12}H_8NS_3Br$: C, 42.10; H, 2.36; N, 4.09; Br, 23.35; S, 28.11; mol wt, 342. Found: C, 42.16; H, 2.21; N, 3.85; Br, 23.32; S, 28.20; mol wt, 347 (freezing point, C_6H_6).

cis- **or** *trans*-**O-Ethyl-α-cyano-4-phenyl-1,3-dithiolane-$\Delta^{2,\alpha}$-thioacetate.**—A slurry of 1.0 g (2.9 mol) of **17a** or **17b** in 30 ml of ethanol was stirred overnight at 25° to give 0.6 g (60%) of the thiono ester: mp 133–134° without purification; ir (KBr) 3000 (w), 2202 (m), 1455 (s), 1305 (s), 1240 (s), 1108 (m), 1035 (m), 970 (m), 768 (m), 695 (m), cm^{-1}; nmr ($CDCl_3$) δ 8.42, (br, s, 5), 5.18 (t, 1, J = 8.5 Hz), 4.57 (q, 4, J = 7 Hz); uv–vis (CH_3CN) λ_{max} 247 mμ (ϵ 16,300), 305 (5500), 363 (19,000).

Anal. Calcd for $C_{14}H_{13}NOS_3$: C, 54.66; H, 4.26; N, 4.56; S, 31.28. Found: C, 54.82; H, 3.94; N, 4.51; S, 31.64.

Registry No.—**2a**, 7396-41-0; **2b**, 16005-62-2; **2c**, 24058-51-3; **9**, 24058-52-4; **10**, 2080-63-9; **11a**, 24058-54-6; **11b**, 24058-55-7; **12a**, 24058-56-8; **12b**, 24118-55-6; **12c**, 24058-57-9; **12d**, 24058-58-0; **15**, 24118-56-7; **16**, 24058-59-1; **17a**, 24058-34-2; **17b**, 24058-35-3; N,N-dimethyl-α-cyano-1,3-dithiolane-$\Delta^{2,\alpha}$-acetamide, 24058-60-4; *cis*-O-ethyl-α-cyano-4-phenyl-1,3-dithiolane-$\Delta^{2,\alpha}$-thioacetate, 24058-36-4; *trans*-O-ethyl-α-cyano-4-phenyl-1,3-dithiolane-$\Delta^{2,\alpha}$-thioacetate, 24058-37-5; bromocyanoacetylene, 3114-46-3.