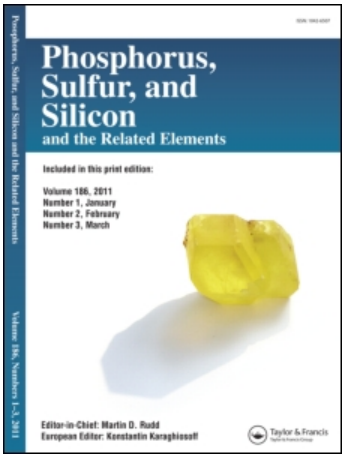

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REACTIONS OF α-OXYGEN SUBSTITUTED METHYLENE ACTIVE DITHIOCARBONATES, THIOCARBAMATES, AND CARBAMATES WITH HETEROCUMULENES

Wolfgang Dölling[a]; Thomas Gildenast[a]
[a] Institut für Organische Chemie, Fachbereich Chemie der Martin-Luther-Universität Halle-Wittenberg, Halle/Saale, Bundesrepublik Deutschland

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REACTIONS OF α-OXYGEN SUBSTITUTED METHYLENE ACTIVE DITHIOCARBONATES, THIOCARBAMATES, AND CARBAMATES WITH HETEROCUMULENES

WOLFGANG DÖLLING,* and THOMAS GILDENAST

Institut für Organische Chemie, Fachbereich Chemie der Martin-Luther-Universität Halle-Wittenberg, Postfach 8, D-O-4010 Halle/Saale, Bundesrepublik Deutschland

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The new compounds ethyl 4-methylthio-2-thioxo-1,3-oxathiole-5-carboxylate **2**, ethyl 4-methylthio-3-phenyl-2-thioxo-1,3-oxazoline-5-carboxylate **3**, O-1-Cyano-2,2-bis(methylthio)vinyl N,N-dimethyl thiocarbamate **7**, and 1-Cyano-2,2-bis(methylthio)vinyl N,N-dimethyl carbamate **9** are prepared by dithiocarboxylation or thiocarbamoylation of S-ethyl O-(ethoxycarbonylmethyl) dithiocarbonate **1**, N,N-Dimethylthiocarbamoyl-glycolonitrile **6**, and N,N-Dimethylcarbamoyl-glycolonitrile **8**, respectively.

Key words: 1,3-Oxathiole-2-thione; dithiocarboxylation; carbon disulfide; dithiocarbonate; thiocarbamate; carbamate; ketene dithioacetals.

INTRODUCTION

The cyclocondensation of xanthates containing active methylene groups with carbon disulfide allows the synthesis of 4-alkylthio-1,3-dithiole-2-thione derivatives.[1–4] In the process of our investigations of such cyclocondensations we have examined the reactions of S-alkyl O-(alkoxycarbonylmethyl)-dithiocarbonate with carbon disulfide or phenyl isothiocyanate in the presence of potassium tert.-butoxide.

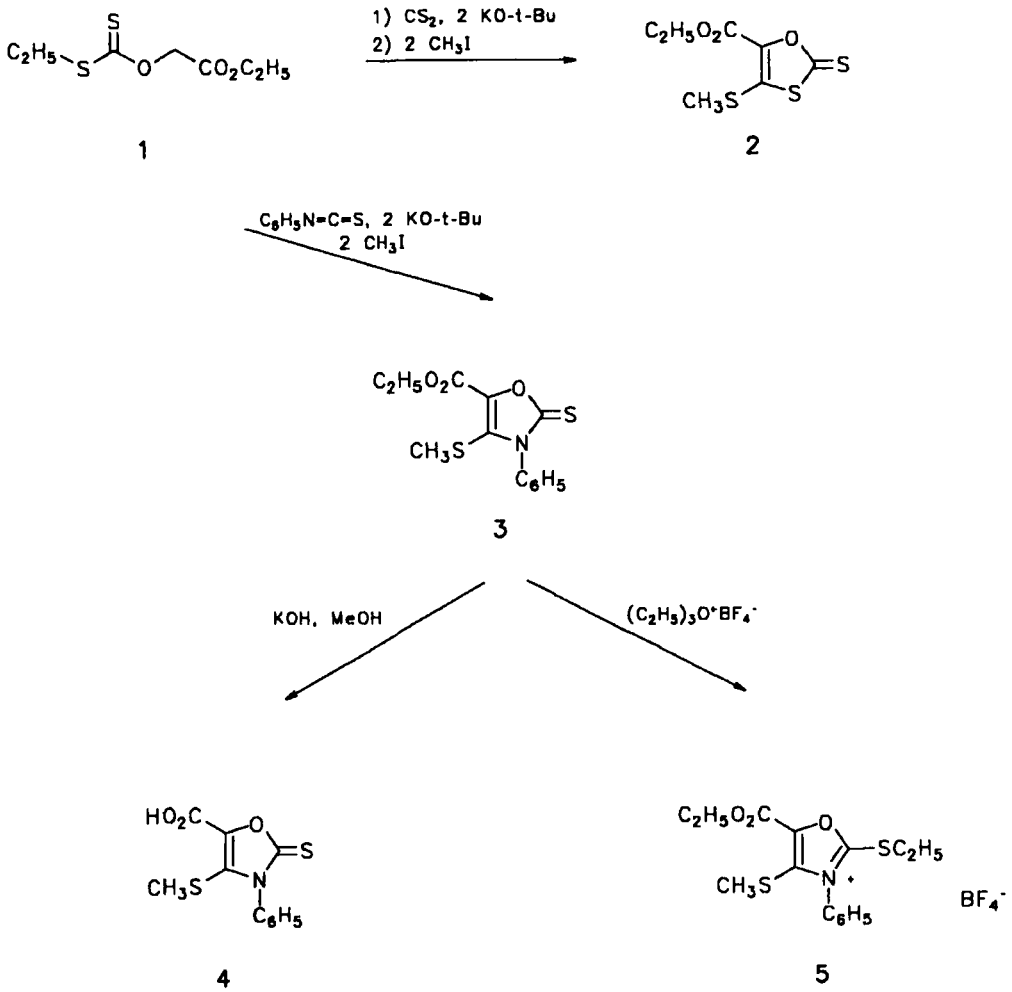
The starting S-ethyl O-(ethoxycarbonylmethyl) dithiocarbonate **1** is obtained by esterification of ethylthio-(thiocarbonyloxy)-acetic acid being prepared according to the procedure of Gotthardt *et al.*[5]

RESULTS AND DISCUSSION

This ester reacts with carbon disulfide in dry THF in the presence of potassium tert.-butoxide at −78°C followed by methylation with methyl iodide to ethyl 4-methylthio-2-thioxo-1,3-oxathiole-5-carboxylate **2**. Using phenyl isothiocyanate the corresponding 2-thioxo-1,3-oxazoline derivative **3** is obtained. This is in analogy to a reported procedure.[6]

The new efficient procedure for the preparation of 1,3-oxathiole and 1,3-oxazoline derivatives, respectively, consists of the reaction of the heterocumulene with the α-oxygen substituted carbanion.

There are only a few reports about the synthesis of 1,3-oxathiole-2-thiones.[7–9] Thus, 1,3-oxathiole-2-thiones are obtained by photochemical reaction of zwitter-

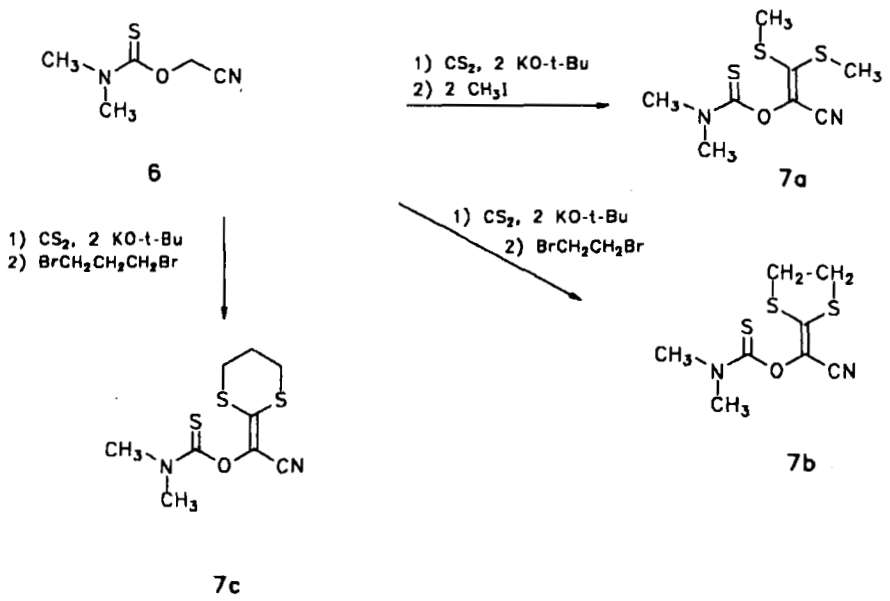


SCHEME 1

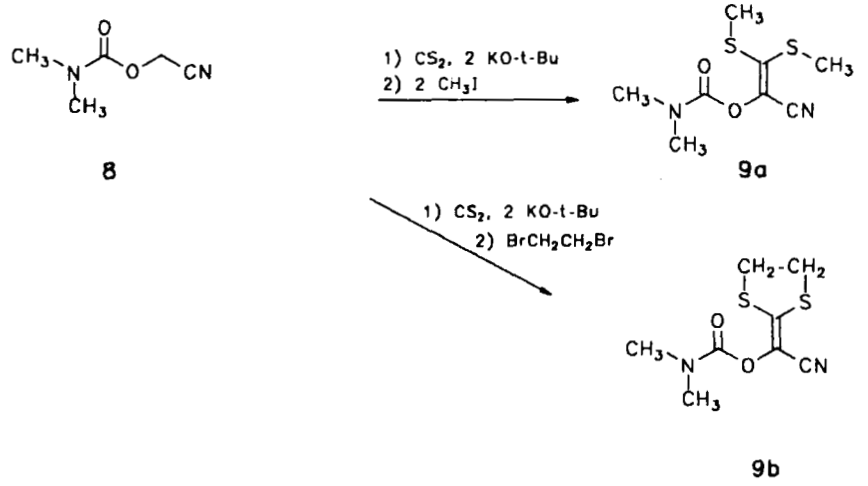
ionic iodonium compounds with carbon disulfide,[9] and in good yields by the rhodium(II) acetate-catalyzed decomposition of α-diazocarbonyl compounds such as substituted α-diazoacetophenones, cyclic diazoketones, cyclic diazodiketones, and α-diazo-β-ketoesters in carbon disulfide.[8]

Conversion of 1,3-oxazoline-2-thiones **3** to the corresponding 4-methylthio-3-phenyl-2-thioxo-1,3-oxazoline-5-carboxylic acid **4** and to the 2-(alkylthio)-1,3-oxazolium salt **5** was carried out by analogy with procedures employed in the 1,3-dithiole series.[10] The corresponding 2-(alkylthio)-1,3-thiazolium salt was used for the synthesis of the first noncondensed crystalline bis(thiazolinylidene) by Tormos, Neilands, and Cava.[11]

The dithiocarboxylation of the novel thiocarbamate **6** and carbamate **8** containing the methylene active group at the oxygen atom leads to the new ketene dithioacetals **7a–c** and **9a–b**. According to previously published results no cyclization took place if the reaction was carried out in the presence of potassium-tert.-butoxide with carbon disulfide.[12] Compounds **6** and **8** were synthesized by reaction of glycolo-



SCHEME 2



SCHEME 3

nitrile with N,N-dimethyl-thiocarbamoyl-chloride or N,N-dimethyl-carbamoyl-chloride, respectively.

EXPERIMENTAL

Melting points were determined using Kofler melting point microscope and are uncorrected. NMR spectra were recorded either at 60 MHz on a BRUKER AC 80 spectrometer or at 200 MHz on a BRUKER WP 200 spectrometer, using either $CDCl_3$ or DMSO-d_6 as solvent. IR spectral were recorded using KBr discs or in nujol on a Carl Zeiss Jena Specord 75/R. Mass spectra were recorded with an AMD 402 of AMD INTECTRA. The solvents were purified and dried by usual procedures.

S-ethyl O-(ethoxycarbonylmethyl)dithiocarbonate **1**. Ethylthio-(thiocarbonyloxy)-acetic acid (23.25 g, 0.13 mol), ethanol (10.5 g, 0.23 mol) and a catalytic amount of conc. sulfuric acid were refluxed in

tetrachloromethane (100 ml) using a trap for azeotroping water. The cooled mixture was washed with water, $NaHCO_3$-solution and water. The solvent was removed in vacuo and the residue was distilled in vacuo to afford 22.1 g (82%) of a yellow liquid b.p. (0.6 mm) = 97–100°C (bath temperature 140°C).

$C_7H_{12}O_3S_2$	calc.	C 40.36	H 5.81	S 30.78
(208.29)	found	40.86	5.88	30.85

IR (Nujol): $\tilde{\nu}$ = 1765 (C=O) cm^{-1}.
^1H NMR ($CDCl_3$): δ = 1.21 (t, 3H, CH_3), 1.3 (t, 3H, CH_3), 3.09 (q, 2H, SCH_2), 4.16 (q, 2H, OCH_2), 5.07 (s, 2H, OCH_2) ppm.
^{13}C NMR ($CDCl_3$): δ = 214.7 (C=S), 166.4 (C=O), 67.4 (OCH_2), 61.5 (OCH_2), 30.6 (SCH_2), 14.1 (CH_3), 13.3 (CH_3) ppm.
MS (%): m/z = 208 (M^+, 57), 163 (26), 147 (12), 105 (100), 45 (63).

Ethyl 4-methylthio-2-thioxo-1,3-oxathiole-5-carboxylate **2**. S-Ethyl O-(ethoxycarbonylmethyl) dithiocarbonate **1** (2.08 g, 10 mmol) and carbon disulfide (0.76 g, 10 mmol) were dissolved in dry THF (30 ml). The mixture was cooled (−78°C) and under nitrogen and magnetically stirring potassium tert.-butoxide (2.24 g, 20 mmol) was added in portions. Stirring was continued at that temperature for 3 h and then MeI (2.84 g, 20 mmol) was added dropwise. After 1 h at −78°C the mixture was allowed to warm up to r.t., and then it was poured onto ice (150 g). The crude product was obtained by filtration. Recrystallization from ethanol gave the pure sample; yield: 0.4 g (17%); m.p. 106–108°C (yellow needles).

$C_7H_8O_3S_3$	calc.	C 35.58	H 3.41	S 40.71
(236.30)	found	36.21	3.49	40.78

IR (KBr): $\tilde{\nu}$ = 1692 (C=O), 1220, 1161 (C—O—C), 1060, 1026 (OSC=S) cm^{-1}.
^1H NMR (DMSO-d_6): δ = 1.29 (t, 3H, CH_3), 2.56 (s, 3H, SCH_3), 4.29 (q, 2H, OCH_2) ppm.
^{13}C NMR (DMSO-d_6): δ = 198.48 (C=S), 155.4 (C=O), 140.2 (C=C), 136.5 (C=C), 61.8 (OCH_2), 17.5 (SCH_3), 13.4 (CH_3) ppm.
MS (%): m/z = 236 (M^+, 100), 191 (2.3), 162 (4).

Ethyl 4-methylthio-3-phenyl-2-thioxo-1,3-oxazoline-5-carboxylate **3**. S-Ethyl O-(ethoxycarbonylmethyl) dithiocarbonate (2.08 g, 10 mmol) and phenyl isothiocyanate (1.35 g, 10 mmol) were dissolved in dry THF (30 ml). The mixture was cooled (−78°C) and under nitrogen and magnetically stirring potassium tert.-butoxide (2.24 g, 20 mmol) was added in portions. Stirring was continued at that temperature for 3 h and then MeI (2.84 g, 20 mmol) was added dropwise. After 1 h at −78°C the mixture was allowed to warm up to r.t., and then it was poured onto ice (150 g). The crude product was obtained by filtration. Recrystallization from ethanol gave the pure sample; yield: 0.65 g (22%); m.p. 121–123°C (colorless needles).

$C_{13}H_{13}NO_3S_2$	calc.	C 52.85	H 4.43	N 4.74	S 21.70
(295.4)	found	52.83	4.59	4.60	21.46

IR (KBr): $\tilde{\nu}$ = 1700 (C=O), 1000, 1035 (NOC=S) cm^{-1}.
^1H NMR ($CDCl_3$); δ = 1.4 (t, 3H, CH_3), 2.25 (s, 3H, SCH_3), 4.42 (q, 2H, OCH_2), 7.29–7.61 (m, 5H, arom.) ppm.
^{13}C NMR ($CDCl_3$): δ = 178.4 (C=S), 156.0 (C=O), 137.9, 135.4 (C=C), 134.3, 130.1, 129.6, 128.0 (C-arom.), 61.9 (OCH_2), 17.8 (SCH_3), 14.1 (CH_3) ppm.
MS (%): m/z = 295 (M^+, 100), 280 (13), 222 (16), 135 (15), 91 (51), 77 (33), 45 (10).

4-Methylthio-3-phenyl-2-thioxo-1,3-oxazoline-5-carboxylic acid **4**. Potassium hydroxide (0.14 g, 2.5 mmol), ethyl 4-methylthio-3-phenyl-2-thioxo-1,3-oxazoline-5-carboxylate **3** (0.74 g, 2.5 mmol), and dry methanol (20 ml) were refluxed for 3 h. Water (40 ml) was added to the cooled mixture. After filtration and addition of conc. HCl the crude acid was obtained. The product was dissolved in half concentrated aqueous ammonia and precipitated by addition of HCl to give colorless crystals, yield: 0.4 g (67%); m.p. 176–179°C.

$C_{11}H_9NO_3S_2$	calc.	C 49.42	H 3.39	N 5.24	S 23.98
(267.32)	found	49.67	3.29	5.01	23.87

IR (KBr): $\tilde{\nu}$ = 1670 (C=O), 3100 (OH), 1020, 1065 (NOC=S) cm^{-1}.
^1H NMR (DMSO-d_6): δ = 2.23 (s, 3H, SCH_3), 7.46–7.59 (m, 5H, arom.) ppm.
^{13}C NMR (DMSO-d_6): δ = 177.6 (C=S), 157.0 (C=O), 138.6, 134.8, 134.6, 129.8, 129.3, 128.4 (C=C), 17.6 (SCH_3) ppm.
MS (%): m/z = 267 (M^+, 100), 252 (10), 223 (89), 150 (15), 135 (37), 91 (70), 77 (86).

5-Carbethoxy-2-ethylthio-4-methylthio-3-phenyl-1,3-oxazolium tetrafluoroborat **5**. Ethyl 4-methylthio-3-phenyl-2-thioxo-1,3-oxazoline-5-carboxylate **3** (0.74 g, 2.5 mmol), dry 1,2-dichloro-ethane (30 ml), and triethyloxonium tetrafluoroborate (0.48 g, 2.5 mmol) were refluxed under nitrogen atmosphere 10 h. The cooled reaction mixture was treated with dry Et_2O (25 ml) to precipitate the salt formed. It was purified by dissolving in a small volume of dry acetone and precipitation with ether, yield: 0.4 g (39%); m.p. 130–133°C (decomp.).

$C_{15}H_{18}BF_4NO_3S_2$	calc.	C 43.92	H 4.42	N 3.41	S 15.63
(410.20)	found	42.73	4.42	3.12	15.44

IR (KBr): $\tilde{\nu}$ = 1720 (C=O), 1040 (BF_4^-) cm^{-1}.
^1H NMR ($CDCl_3$): δ = 1.40 (t, 3H, CH_3), 1.52 (t, 3H, CH_3), 2.43 (s, 3H, SCH_3), 3.56 (q, 2H, SCH_2), 4.46 (q, 2H, OCH_2), 7.63 (s, 5H, arom.) ppm.
^{13}C NMR ($CDCl_3$): δ = 169.6 (OSC=N), 154.7 (C=O), 145.0 (C=C), 138.7 (C=C), 132.3, 130.5, 129.9, 127.3 (C-arom.), 62.9 (CH_2), 28.2 (SCH_2), 18.0 (SCH_3), 14.0 (CH_3), 13.6 (CH_3) ppm.
MS (%): m/z = 343 (3), 324 (9), 295 (100), 280 (25), 150 (21), 135 (13), 91 (52), 77 (32).

N,N-Dimethylthiocarbamoyl-glycolonitrile **6**. To a solution of potassium cyanide (32.6 g, 0.5 mol) in water (100 ml) was added dropwise under cooling with ice and stirring a 35% solution of formaldehyde (42.9 ml, 0.5 mol) within 10 min. Then a solution of N,N-dimethylthiocarbamoylchloride (61.8 g, 0.5 mol) in dry THF (50 ml) was added with cooling and stirring. The cooled mixture was stirred for 2 h and then 2 h at room temperature. The organic layer was separated, the water layer several times extracted with ether. The combined phases were dried with anhydrous sodium sulfate, and the solvents removed in vacuo. The residue was distilled to afford the product; yield: 27.4 g (38%); bp (2.5–3 Torr): 110–115°C (yellow liquid).

$C_5H_8N_2OS$	calc.	C 41.64	H 5.59	N 19.43	S 22.23
(144.20)	found	42.43	5.65	19.08	22.86

IR (KBr): $\tilde{\nu}$ = 2235 (C≡N) cm^{-1}.
^1H NMR ($CDCl_3$): δ = 3.00 (s, 3H, NCH_3), 3.20 (s, 3H, NCH_3), 5.00 (s, 2H, CH_2) ppm.
^{13}C NMR ($CDCl_3$): δ = 185.4 (C=S), 114.6 (CN), 53.8 (OCH_2), 38.4, 43.3 (NCH_3) ppm.
MS (%): m/z = 144 (M^+, 100), 104 (30), 88 (49), 44 (68).

O-(1-Cyano-2,2-bis(methylthio)vinyl)-N,N-dimethyl thiocarbamate **7a**. N,N-Dimethylthiocarbamoyl-glycolonitrile **6** (1.44 g, 10 mmol) and carbon disulfide (0.76 g, 10 mmol) were dissolved in dry THF (30 ml). The mixture was cooled (−78°C) and under nitrogen and magnetically stirring potassium tert.-butoxide (2.24 g, 20 mmol) was added in portions. Stirring was continued at that temperature for 3 h and then MeI (2.84 g, 20 mmol) was added dropwise. After 1 h at −78°C the mixture was allowed to warm up to r.t., and then it was poured onto ice (150 g). The crude product was obtained by filtration. Recrystallization from ethanol gave the pure sample; yield: 0.95 g (38%); m.p. 92–94°C (colorless needles).

$C_8H_{12}N_2OS_3$	calc.	C 38.68	H 4.87	N 11.28	S 38.73
(248.4)	found	38.79	4.82	11.21	38.65

IR (KBr): $\tilde{\nu}$ = 2200 (C≡N) cm^{-1}.
^1H NMR ($CDCl_3$): δ = 2.41 (s, 3H, SCH_3), 2.47 (s, 3H, SCH_3), 3.23 (s, 3H, NCH_3), 3.37 (s, 3H, NCH_3) ppm.
^{13}C NMR ($CDCl_3$): δ = 183.5 (C=S), 143.0 (C=C), 122.4 (C=C), 113.6 (CN), 43.5 (NCH_3), 38.7 (NCH_3), 18.3 (SCH_3), 16.0 (SCH_3) ppm.
MS (%): m/z = 248 (M^+, 25), 201 (92), 160 (6), 188 (99), 72 (100), 56 (28).

α-(N,N-Dimethylaminothiocarbonyl)-α-(1,3-dithiolane-2-ylidene)-glycolonitrile **7b**. N,N-Dimethyl-thiocarbamoyl-glycolonitrile **6** (1.44 g, 10 mmol) and carbon disulfide (0.76 g, 10 mmol) were dissolved in dry THF (30 ml). The mixture was cooled (−78°C) and under nitrogen and magnetically stirring potassium tert.-butoxide (2.24 g, 20 mmol) was added in portions. Stirring was continued at that temperature for 3 h and then 1,2-dibromo-ethane (1.87 g, 10 mmol) was added dropwise. After 1 h at −78°C the mixture was allowed to warm up to r.t., and then it was poured onto ice (150 g). The crude product was obtained by filtration. Recrystallization from ethanol gave the pure sample; yield: (16%); m.p. 117–119°C (beige needles).

$C_8H_{10}N_2OS_3$	calc.	C 38.99	H 4.09	N 11.37	S 39.04
(246.37)	found	38.94	4.38	10.77	38.95

IR (KBr): $\tilde{\nu}$ = 2185 (C≡N) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 3.21 (s, 3H, NCH_3), 3.37 (s, 3H, NCH_3), 3.45–3.61 (m, 4H, SCH_2CH_2S) ppm.
^{13}C NMR ($CDCl_3$): δ = 184.1 (C=S), 154.7 (C=C), 110.9 (C=C), 114.3 (CN), 43.8 (NCH_3), 38.8 (NCH_3), 39.2 (SCH_2), 39.3 (SCH_2) ppm.
MS (%): m/z = 246 (M^+, 19), 158 (9), 88 (99), 72 (100), 56 (8).

α-(N,N-Dimethylaminothiocarbonyl)-α-(1,3-dithiane-2-ylidene)-glycolonitrile **7c**. N,N-Dimethylthiocarbamoyl-glycolonitrile **6** (1.44 g, 10 mmol) and carbon disulfide (0.76 g, 10 mmol) were dissolved in dry THF (30 ml). The mixture was cooled (−78°C) and under nitrogen and magnetically stirring potassium tert.-butoxide (2.24 g, 20 mmol) was added in portions. Stirring was continued at that temperature for 3 h and then 1,3-dibromo-propane (2.02 g, 10 mmol) was added dropwise. After 1 h at −78°C the mixture was allowed to warm up to r.t., and then it was poured onto ice (150 g). The crude product was obtained by filtration. Recrystallization from ethanol gave the pure sample; yield: 0.2 g (8%); m.p. 90–92°C (yellow needles).

$C_9H_{12}N_2OS_3$	calc.	C 41.51	H 4.65	N 10.76	S 36.94
(260.40)	found	41.66	4.64	10.69	37.33

IR (KBr): $\tilde{\nu}$ = 2185 (C≡N) cm^{-1}.
^{1}H NMR ($CDCl_3$): δ = 2.20 (s, 2H, CH_2), 3.00 (m, 4H, 2 SCH_2), 3.22 (s, 3H, NCH_3), 3.38 (s, 3H, NCH_3) ppm.
^{13}C NMR ($CDCl_3$): δ = 183.9 (C=S), 148.12 (C=C), 116.6 (C=C), 113.4 (CN), 43.1 (NCH_3), 38.6 (NCH_3), 28.2, 27.8, 23.4 (CH_2) ppm.
MS (%): m/z = 260 (M^+, 9), 88 (100), 72 (55), 56 (2).

N,N-Dimethylcarbamoyl-glycolonitrile **8**. To a solution of potassium cyanide (30 g, 0.46 mol) in water (90 ml) was added dropwise under cooling with ice and stirring a 35% solution of formaldehyde (40 ml, 0.46 mol) within 10 min. Then a solution of N,N-dimethylcarbamoylchloride (49.47 g, 0.46 mol) in dry THF (60 ml) was added with cooling and stirring. The cooled mixture was stirred for 2 h and then 2 h at room temperature. The organic layer was separated, the water layer several times extracted with ether. The combined phases were dried with anhydrous sodium sulfate, and the solvents removed in vacuo. The residue was distilled to afford the product; yield: 21.8 g (37%); bp (1.5 Torr): 78–80°C (colorless liquid).

$C_5H_2N_2O_2$	calc.	C 46.87	H 6.29	N 21.87
(128.13)	found	45.15	6.20	20.45

IR (KBr): $\tilde{\nu}$ = 2240 (C≡N), 1720 (C=O) cm^{-1}.
^{1}H NMR ($CDCl_3$): δ = 2.72 (s, 6H, 2 NCH_3), 4.54 (s, 2H, OCH_2) ppm.
^{13}C NMR ($CDCl_3$): δ = 154.3 (C=O), 115.4 (CN), 49.6 (OCH_2), 36.7, 35.9 (NCH_3) ppm.
MS (%): m/z = 128.2 (M^+, 63), 88 (49), 72 (100), 44 (91).

Dithiocarboxylation of N,N-Dimethylcarbamoyl-glycolonitrile **9**. *General procedure*. N,N-Dimethylcarbamoyl-glycolonitrile **8** (1.28 g, 10 mmol) and carbon disulfide (0.76 g, 10 mmol) were dissolved in dry THF (30 ml). The mixture was cooled (−78°C) and under nitrogen and magnetically stirring potassium tert.-butoxide (2.24 g, 20 mmol) was added in portions. Stirring was continued at that temperature for 3 h and then the alkylating agent (equimolar amount) was added dropwise. After 1 h at −78°C the mixture was allowed to warm up to r.t., and then it was poured onto ice (150 g). The crude product was obtained by filtration. Recrystallization from ethanol gave the pure sample.

1-Cyano-2,2-bis(methylthio)vinyl N,N-dimethyl carbamate **9a**. Yield: 0.4 g (17%); m.p. 47–48°C (colorless needles).

$C_8H_{12}N_2O_2S_2$	calc.	C 41.72	H 5.21	N 12.06	S 27.60
(232.30)	found	41.85	5.40	11.84	27.82

IR (Nujol): $\tilde{\nu}$ = 2195 (C≡N), 1720 (C=O) cm^{-1}.
^{1}H NMR ($CDCl_3$): δ = 2.40 (s, 3H, SCH_3), 2.41 (s, 3H, SCH_3), 2.96 (s, 3H, NCH_3), 2.99 (s, 3H, NCH_3) ppm.
^{13}C NMR ($CDCl_3$): δ = 151.9 (C=O), 147.2 (C=C), 120.4 (C=C), 113.6 (CN), 37.0 (NCH_3), 36.4 (NCH_3), 18.4, 16.1 (2 SCH_3) ppm.
MS (%): m/z = 232 (M^+, 5), 72 (100), 56 (2).

α-(N,N-Dimethylaminocarbonyl)-α-(1,3-dithiolane-2-ylidene)-glycolonitrile **9b**. Yield: 0.45 g (20%); m.p. 86–88°C (colorless needles).

$C_8H_{10}N_2O_2S_2$	calc.	C 41.36	H 5.21	N 12.06	S 27.60
(230.30)	found	41.29	5.40	11.84	27.82

IR (Nujol): $\tilde{\nu}$ = 2185 (C≡N), 1720 (C=O) cm^{-1}.
^1H NMR ($CDCl_3$): δ = 2.75 (s, 3H, NCH_3), 2.77 (s, 3H, NCH_3), 3.51 (m, 4H, SCH_2CH_2S) ppm.
^{13}C NMR ($CDCl_3$): δ = 153.9 (C=O), 152.4 (C=C), 114.5 (CN), 108.1 (C=C), 36.4 (NCH_3), 37.0 (NCH_3), 39.1, 39.2 (2 SCH_2) ppm.
MS (%): m/z = 230 (M^+, 8), 72 (100), 44 (9).

REFERENCES

1. W. Dölling, K. Friedemann, F. Heinemann and H. Hartung, *Z. Naturforsch., Teil b*, **46b,** 1251–1257 (1991).
2. W. Dölling, A. Vogt and M. Augustin, *Monatsh. Chem.*, **120**, 879–889 (1989).
3. M. Augustin and W. Dölling, *Z. Chem.*, **30,** 395–403 (1990).
4. M. Augustin, W. Dölling and A. Vogt, *Z. Chem.*, **23,** 333 (1983).
5. H. Gotthardt, U. Feist and S. Schoy-Tribbensee, *Chem. Ber.*, **118,** 774–84 (1985).
6. G. V. Tormos, V. Yu. Khodorkovsky, O. Ya. Neilands and S. V. Belyakov, *Tetrahedron*, **48,** 6863–6874 (1992).
7. R. A. Aitken, *Five-Membered Ring Systems: With O & S (Se, Te) Atoms*, in: *Progr. Heterocycl. Chem.*, Bd. 2, Kap. 4.6, S. 134–145 (1990).
8. T. Ibata and H. Nakano, *Bull. Chem. Soc., Jpn.*, **63,** 3096–3102 (1990).
9. M. Papadopoulou, S. Spyroudis and A. Varvoglis, *J. Org. Chem.*, **50**, 1509–1511 (1985).
10. W. Dölling, A. Vogt and M. Augustin, *Z. Naturforsch. Teil b*, **46b**, 133–138 (1991).
11. G. V. Tormos, O. J. Neilands and M. P. Cava, *J. Org. Chem.*, **57,** 1008–1009 (1992).
12. W. Dölling, K. Sperk and M. Augustin, *J. Prakt. Chem.*, **332,** 671–678 (1990).