and 1 ml. of water. The resulting crude product (98 mg.) was submitted to chromatography over Florisil; the fractions eluted by 5% acetone in chloroform were crystallized from acetone–pentane and then from methanol to yield 33 mg. of prisms, m.p. 206–209°, $[\alpha]^{20}D$ +31.6° ($CHCl_3$); $\lambda_{max}^{CHCl_3}$ 2.79 and 2.91 (OH), 6.02 and 6.29 μ ($\Delta^{16}$-20-one).

The **acetate IVc** of IVe, which was prepared in the usual manner, crystallized as needles from benzene–pentane, m.p. 181–184°, $[\alpha]^{20}D$ −19.5° ($CHCl_3$); $\lambda_{max}^{Nujol}$ 2.86 (OH), 5.79 (OAc), 6.01 and 6.29 μ($\Delta^{16}$-20-one).

*Anal.* Calcd. for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15. Found: C, 73.57; H, 9.33.

**Allopregnane-3β,9α-diol-20-one Acetate** (Vj).—The aforementioned 16-dehydro derivative (IVc, 36 mg.) was dissolved in 4 ml. of ethyl acetate with 32 mg. of 10% palladium–barium sulfate and hydrogenated at atmospheric pressure. Chromatography of the reduction product over alumina (Woelm neutral, activity II) and elution with benzene and 10% ether in benzene afforded a compound (29 mg.) which crystallized as plates, m.p. 187–191°, $[\alpha]^{20}D$ +58.2° ($CHCl_3$); $\lambda_{max}^{CS_2}$ 2.78 and 2.83 (OH), 5.76 (OAc), 5.85 μ (20-ketone).

The substance was identical in properties (melting point, mixture melting point, and infrared spectrum) with an authentic specimen of Vj prepared from 9α-hydroxysolasodine.[3a]

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# Reactions of Mercaptoamines. II. With Chloroformates and Chlorothiolformates[1]

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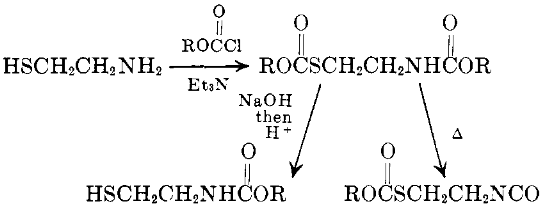
2-Mercaptoethylamine reacted with alkyl chloroformates and chlorothiolformates to give the N,S-disubstituted products, which on basic hydrolysis gave 2-(mercaptoethyl)carbamates in the first case and regenerated 2-mercaptoethylamine in the second. On pyrolysis or treatment with silver nitrate, the S-alkyl N-[2-(alkyldithiolcarbonato)ethyl]thiolcarbamates gave the 2-(alkyldithiolcarbonato)ethyl isocyanates. These reacted with amines to give the corresponding ureas, hydrolyzable to 2-mercaptoethyl ureas.

In continuation of studies of the reaction of mercaptoamines with compounds potentially capable of reacting at both the mercapto and amino functions,[2] the reaction of 2-mercaptoethylamine (MEA) with chloroformates and chlorothiolformates has been examined.

In the presence of triethylamine as an acid acceptor, solutions of 2-mercaptoethylamine in dry acetonitrile reacted with ethyl, *n*-propyl, *n*-butyl, and *n*-hexyl chloroformates to give good yields of the N,S-disubstituted products, the O-alkyl N-[2-(alkylthiolcarbonato)ethyl]carbamates. The ethyl and *n*-propyl compounds could be distilled at reduced pressure, but the higher molecular weight compounds underwent partial pyrolysis when distillation was attempted, giving products with isocyanate absorption in their infrared spectra. The critical temperature for the onset of pyrolysis appeared to be about 150°. All the N,S-disubstituted compounds were hydrolyzed readily at the thiolcarbonato function by sodium hydroxide in aqueous alcohol to give the 2-(mercaptoethyl)carbamates in good yield. The properties of the N,S-disubstituted compounds are reported in Table I and those of the 2-(mercaptoethyl)carbamates in Table II.

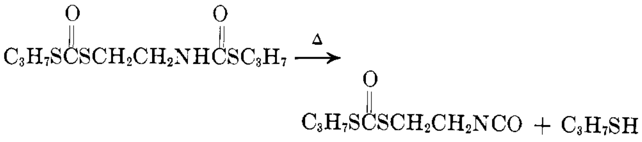


$$\mathrm{HSCH_2CH_2NH_2} \xrightarrow[\mathrm{Et_3N}]{\mathrm{RO\overset{O}{\overset{\|}{C}}Cl}} \mathrm{RO\overset{O}{\overset{\|}{C}}SCH_2CH_2NH\overset{O}{\overset{\|}{C}}OR}$$

$$\mathrm{RO\overset{O}{\overset{\|}{C}}SCH_2CH_2NH\overset{O}{\overset{\|}{C}}OR} \xrightarrow{\mathrm{NaOH\ then\ H^+}} \mathrm{HSCH_2CH_2NH\overset{O}{\overset{\|}{C}}OR}$$

$$\mathrm{RO\overset{O}{\overset{\|}{C}}SCH_2CH_2NH\overset{O}{\overset{\|}{C}}OR} \xrightarrow{\Delta} \mathrm{RO\overset{O}{\overset{\|}{C}}SCH_2CH_2NCO}$$

Alkyl chlorothiolformates reacted with 2-mercaptoethylamine in the same manner as the chloroformates to give N,S-disubstituted products (Table I). The compounds from methyl and ethyl chlorothiolformate were solids which could be purified by recrystallization, but the product from *n*-propyl chlorothiolformate was a liquid. Like the higher molecular weight chloroformate products, it underwent partial pyrolysis when distillation was attempted. Several repetitions of the distillation completed the pyrolysis, and eventually pure 2-(*n*-propyldithiolcarbonato)ethyl isocyanate was obtained in 30% yield. A number of attempts were made to hydrolyze the S-alkyl N-[2-(alkyldithiolcarbonato)ethyl]thiolcarbamates to the corresponding 2-(mercaptoethyl)thiolcarbamates, but hydrolysis occurred as readily at the thiolcarbamate function as at the thiolcarbonato function, and it proved impossible to isolate the half-hydrolyzed products.



$$\mathrm{C_3H_7S\overset{O}{\overset{\|}{C}}SCH_2CH_2NH\overset{O}{\overset{\|}{C}}SC_3H_7} \xrightarrow{\Delta} \mathrm{C_3H_7S\overset{O}{\overset{\|}{C}}SCH_2CH_2NCO} + \mathrm{C_3H_7SH}$$

It is readily apparent that a convenient intermediate for the preparation of 2-mercaptoethylureas would be an S-substituted 2-mercaptoethyl isocyanate wherein the mercapto function was covered by a group easily removed after urea formation. As noted before, pyrolysis of the S-alkyl N-[2-(alkyldithiolcarbonato)ethyl]thiolcarbamates provides one route to such an intermediate. A more convenient route is offered by the metal ion-assisted mercaptan elimination reaction.[3] Treatment of S-methyl N-[2-(methyldithiolcarbonato)ethyl]thiolcarbamate with a solution of silver nitrate in acetonitrile gave a solution of 2-(methyldithiolcarbonato)ethyl isocyanate which reacted with water to give 1,3-bis[2-(methyldithiolcarbonato)ethyl]urea and with amines to give 2-(methyldithiolcarbonato)ethylureas (Table III). Successful reaction was obtained with aniline, *t*-butylamine, *n*-octylamine, morpholine, and diethyl iminodiacetate. All the products from primary amines, including 1,3-bis[2-(methyldithiolcarbonato)ethyl]urea, underwent basis hydrolysis to give the corresponding 2-mercaptoethylureas. The secondary amine products were completely de-

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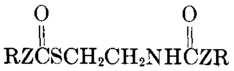
(1) This work was supported by the U. S. Army Medical Research and Development Command, Department of the Army, under Contract No. DA-49-193-MD-2174.

(2) Previous paper in this series: A. F. Ferris and B. A. Schutz, *J. Org. Chem.*, **28**, 3140 (1963).

(3) A. F. Ferris and B. A. Schutz, *ibid.*, **28**, 71 (1963)

TABLE I

ALKYL N-[2-(ALKYLTHIOL- AND DITHIOLCARBONATO)ETHYL]CARBAMATES AND THIOLCARBAMATES



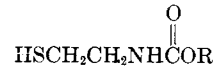
$RZ\overset{O}{\overset{\|}{C}}SCH_2CH_2NH\overset{O}{\overset{\|}{C}}ZR$

| R | Z | Yield, % | M.p. or b.p. (mm.), °C. | Calcd., % C | Calcd., % H | Calcd., % N | Calcd., % S | Found, % C | Found, % H | Found, % N | Found, % S |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_2H_5$ | O | 83 | 109–110 (0.11)<br>30 | 43.42 | 6.83 | 6.33 | 14.49 | 43.21 | 6.91 | 6.46 | 14.32 |
| $n$-$C_3H_7$ | O | 73 | 140–141 (0.21)[a] | 48.17 | 7.68 | 5.62 | 12.86 | 48.27 | 7.49 | 5.76 | 13.04 |
| $CH_3$ | S | 84 | 44–46 | 31.98 | 4.92 | 6.22 | 42.68 | 32.13 | 5.06 | 6.13 | 42.90 |
| $C_2H_5$ | S | 65 | 58–59 | 37.92 | 5.97 | 5.53 | 37.96 | 37.86 | 5.85 | 5.45 | 37.75 |

[a] $n^{27}_D$ 1.4729.

TABLE II

ALKYL N-2-(MERCAPTOETHYL)CARBAMATES



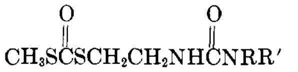
$HSCH_2CH_2NH\overset{O}{\overset{\|}{C}}OR$

| R | Yield, % | B.p. (mm.), °C. | $n^{27}_D$ | Calcd., % C | Calcd., % H | Calcd., % N | Calcd., % S | Found, % C | Found, % H | Found, % N | Found, % S |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_2H_5$[a] | 84 | 75–77 (0.05) | 1.4812 | 40.25 | 7.43 | 9.39 | 21.49 | 40.22 | 7.17 | 9.60 | 21.44 |
| $n$-$C_3H_7$ | 89 | 79–80 (0.18) | 1.4789 | 44.15 | 8.03 | 8.55 | 19.64 | 44.22 | 8.30 | 8.61 | 19.92 |
| $n$-$C_4H_9$ | 83 | 94 (0.21) | 1.4766 | 47.43 | 8.53 | 7.90 | 18.09 | 47.24 | 8.37 | 7.98 | 18.18 |
| $n$-$C_6H_{13}$ | 57 | 105 (0.11) | 1.4748 | 52.65 | 9.33 | 6.82 | 15.62 | 52.50 | 9.37 | 6.92 | 15.77 |

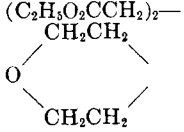
[a] This compound was reported by K. Schimmelschmidt, H. Hoffmann, and E. Mundlos, *Ber.*, **96**, 38 (1963); b.p. 96–98° (0.6 mm.).

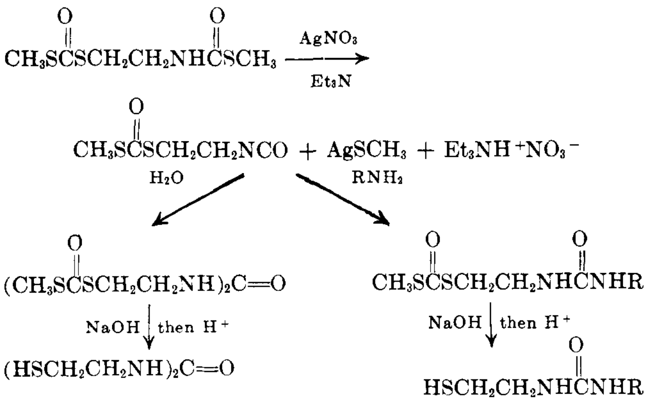
TABLE III

1-ALKYL OR ARYL 3-[2-(METHYLDITHIOLCARBONATO)ETHYL]UREAS



$CH_3S\overset{O}{\overset{\|}{C}}SCH_2CH_2NH\overset{O}{\overset{\|}{C}}NRR'$

| RR' | Yield, % | M.p., °C. | Calcd., % C | Calcd., % H | Calcd., % N | Calcd., % S | Found, % C | Found, % H | Found, % N | Found, % S |
|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3S\overset{O}{\overset{\|}{C}}SCH_2CH_2$—, H | 81 | 94.5–96 | 32.91 | 4.91 | 8.53 | 39.04 | 33.04 | 5.01 | 8.67 | 39.13 |
| $t$-$C_4H_9$—, H | 77 | 115–116 | 43.17 | 7.25 | 11.19 | 25.61 | 43.25 | 7.16 | 11.01 | 25.79 |
| $n$-$C_8H_{17}$—, H | 73 | 76.5–78 | 50.94 | 8.55 | 9.14 | 20.92 | 50.71 | 8.60 | 8.98 | 21.04 |
| $C_6H_5$—, H | 81 | 130.5–132 | 48.86 | 5.22 | 10.36 | 23.72 | 48.99 | 5.31 | 10.56 | 23.91 |
| $(C_2H_5O_2CCH_2)_2$— | 74 | 125–127 | 42.61 | 6.05 | 7.65 | 17.50 | 42.84 | 5.82 | 7.66 | 17.66 |
|  | 60 | 119–120.5 | 40.89 | 6.10 | 10.60 | 24.25 | 41.01 | 6.23 | 10.67 | 24.08 |



composed by aqueous alcoholic sodium hydroxide, and no mercaptoethylureas could be isolated.

Though the literature[4,5] indicates that reaction of isocyanates with carboxylic acids can be used to prepare amides, reaction of 2-(methyldithiolcarbonato)ethyl isocyanate with acids was not in general a useful route to N-(2-mercaptoethyl)amides. Success was achieved only in one case. Phenylacetic acid reacted with the isocyanate to give a liquid product which was hydrolyzed to N-(2-mercaptoethyl)phenylacetamide, a liquid identified as the 2,4-dinitrophenyl sulfide. Over-all yield was 32%. With other acids the isocyanate either failed to react entirely or reacted with adventitous water to give the bisurea.

## Experimental[6]

**O-*n*-Propyl N-[2-(*n*-Propylthiolcarbonato)ethyl]carbamate.**—To a suspension of 11.4 g. (0.10 mole) of 2-mercaptoethylamine hydrochloride in 50 ml. of dry acetonitrile was added 30.4 g. (0.30 mole) of triethylamine. A new solid came out of solution. The resulting suspension was added in portions, with stirring and cooling, to a solution of 24.4 g. (0.20 mole) of *n*-propyl chloroformate. The temperature was kept below 60°, and when the addition was complete, the mixture was allowed to stand for 1 hr. It was then poured into ice-water and an oil separated. The oil was extracted into three 50-ml. portions of ether, and the solution was dried over magnesium sulfate. Evaporation of the ether left 18.2 g. (73%) of crude O-*n*-propyl N-[2-(*n*-propylthiolcarbonato)ethyl]carbamate. Distillation under reduced pressure gave an analytical sample, b.p. 140–141° (0.21 m.), $n^{27}_D$ 1.4729.

*Anal.* Calcd. for $C_{10}H_{19}O_4NS$: C, 48.17; H, 7.68; N, 5.62; S, 12.86. Found: C, 48.27; H, 7.49; N, 5.76; S, 13.04.

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[4] J. von Braun, *Ber.*, **42**, 2743 (1909).

[5] C. L. Agre, G. Dinga, and R. Pflaum, *J. Org. Chem.*, **20**, 695 (1955).

[6] Melting points are corrected and boiling points are uncorrected. Microanalyses by Galbraith Laboratories, Knoxville, Tenn.

**O-*n*-Propyl N-(2-Mercaptoethyl)carbamate.**—To a solution of 16.5 g. (0.07 mole) of O-*n*-propyl N-[2-(*n*-propylthiolcarbonato)-ethyl]carbamate in 50 ml. of 95% ethanol was added a solution of 13.3 g. (0.33 mole) of sodium hydroxide in 50 ml. of water. The temperature rose from 25° to 42°, and the solution was allowed to stand for 2 hr. A white solid had come out of solution, but dissolved upon the addition of another 100 ml. of water. The solution was made just strongly acid with 5 *N* hydrochloric acid. A gas evolved and an oil separated. The oil was extracted into four 50-ml. portions of ether. After drying over magnesium sulfate, the ether was evaporated under reduced pressure leaving 9.6 g. (89%) of crude O-*n*-propyl N-(2-mercaptoethyl)carbamate. Distillation under reduced pressure gave an analytical sample, b.p. 79–80° (0.18 mm.), $n^{27}$D 1.4789.

*Anal.* Calcd. for $C_6H_{13}O_2NS$: C, 44.15; H, 8.03; N, 8.55; S, 19.64. Found: C, 44.22; H, 8.30; N, 8.61; S, 19.92.

**S-Methyl N-[2-(Methyldithiolcarbonato)ethyl]thiolcarbamate.**—To a suspension of 5.7 g. (0.05 mole) of 2-mercaptoethylamine hydrochloride in 50 ml. of acetonitrile was added 15.2 g. (0.15 mole) of triethylamine. A new solid (triethylamine hydrochloride) came out of solution. The suspension was added in portions, with stirring and cooling, to a solution of 11.0 g. (0.10 mole) of methyl chlorothiolformate in 25 ml. of acetonitrile. The mixture was allowed to stand for an hour and then was poured into ice–water. An oil separated and slowly hardened to a solid. After recovery by suction filtration and drying, the S-methyl N-[2-(methyldithiolcarbonato)ethyl]thiolcarbamate amounted to 9.5 g. (84%), m.p. 34–35.5°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60–70°) gave an analytical sample, m.p. 44–46°.

*Anal.* Calcd. for $C_6H_{11}O_2NS_3$: C, 31.98; H, 4.92; N, 6.22; S, 42.68. Found: C, 32.13; H, 5.06; N, 6.13; S, 42.90.

**2-(*n*-Propyldithiolcarbonato)ethyl Isocyanate.**—To a suspension of 11.4 g. (0.10 mole) of 2-mercaptoethylamine hydrochloride in 50 ml. of acetonitrile was added 30.4 g. (0.30 mole) of triethylamine. A new solid precipitated. The resulting suspension was added in portions, with stirring and cooling, to a solution of 27.6 g. (0.20 mole) of *n*-propyl chlorothiolformate in 50 ml. of acetonitrile. When there was no further rise in temperature, the mixture was allowed to stand for 1 hr. and then was poured into ice–water. An oil separated and was extracted into 150 ml. of ether, and the solution was dried over magnesium sulfate. Evaporation of the ether left 24.2 g. of liquid. Three distillations under reduced pressure with accompanying pyrolysis were carried out on a 10.0-g. sample at a pot temperature of 188–197° and at pressure of 0.7 mm. A fourth distillation gave 2.5 g. (30%) of pure 2-(*n*-propyldithiolcarbonato)ethyl isocyanate, b.p. 108–110° (1 mm.), $n^{27}$D 1.5299.

*Anal.* Calcd. for $C_7H_{11}O_2NS_2$: C, 40.95; H, 5.40; N, 6.82; S, 31.23. Found: C, 41.06; H, 5.33; N, 6.72; S, 31.41.

**1-[2-(Methyldithiolcarbonato)ethyl]-3-*n*-octylurea.**—To a solution of 22.5 g. (0.10 mole) of S-methyl 2-(methyldithiolcarbonato)ethylthiolcarbamate and 10.0 g. (0.10 mole) of triethylamine in 50 ml. of dry acetonitrile was added a solution of 17.0 g. of silver nitrate in 25 ml. of dry acetonitrile. A yellow solid formed, and the temperature rose from 25° to 42°. Then 12.9 g. (0.10 mole) of *n*-octylamine was added, and the temperature rose to 70°. The mixture was allowed to stand until it was at room temperature. Another 100 ml. of acetonitrile was added, and the mixture was heated to boiling and filtered hot. The filtrate was poured into ice–water and a cream colored solid separated. There was thus recovered 22.4 g. (73%) of 1-[2-(methyldithiolcarbonato)ethyl]-3-*n*-octylurea. Recrystallization from 95% ethanol gave an analytical sample, m.p. 76.5–78°.

*Anal.* Calcd. for $C_{13}H_{26}O_2N_2S$: C, 50.94; H, 8.55; N, 9.14; S, 20.92. Found: C, 50.71; H, 8.60; N, 8.98; S, 21.04.

**1,3-Bis[2-(methyldithiolcarbonato)ethyl]urea.**—This compound was prepared by the previous procedure through the addition of silver nitrate solution. At this point 20 ml. of water was added. The temperature rose from 40° to 54°. The mixture was allowed to stand until the temperature had dropped back to 25°. Another 100 ml. of acetonitrile was added, the mixture was heated to boiling, and then filtered hot. The filtrate was poured into ice–water, and a white solid formed. The yield of recovered 1,3-bis[2-(methyldithiolcarbonato)ethyl]urea was 13.5 g. (81%). Two recrystallizations from 95% ethanol gave an analytical sample, m.p. 94.5–96°.

*Anal.* Calcd. for $C_9H_{16}O_3N_2S_4$: C, 32.91; H, 4.91; N, 8.53; S, 39.04. Found: C, 33.04; H, 5.01; N, 8.67; S, 39.13.

**1-(2-Mercaptoethyl)-3-*n*-octylurea.**—To a suspension of 15.6 g. (0.05 mole) of 1-(2-methyldithiolcarbonatoethyl)-3-*n*-octylurea in 250 ml. of 95% ethanol was added a solution of 8.0 g. (0.20 mole) of sodium hydroxide in 250 ml. of water. The mixture was stirred vigorously for 2 hr. and then made just strongly acid with 5 *N* hydrochloric acid. A gas evolved and a solid formed. The recovered 1-(2-mercaptoethyl)-3-*n*-octylurea amounted to 10.9 g. (92%). Two recrystallizations from acetonitrile gave an analytical sample, m.p. 80.5–82°.

*Anal.* Calcd. for $C_{11}H_{24}ON_2S$: C, 56.85; H, 10.41; N, 12.06; S, 13.80. Found: C, 57.01; H, 10.24; N, 11.96; S, 13.88.

**1-(2-Mercaptoethyl)-3-*t*-butylurea.**—Similar hydrolysis of 19.5 g. (0.08 mole) of 1-[2-(methyldithiolcarbonato)ethyl]-3-*t*-butylurea gave 10.3 g. (75%) of 1-(2-mercaptoethyl)-3-*t*-butylurea. Three recrystallizations from a mixture of ethanol and water gave an analytical sample, m.p. 115–116.5°.

*Anal.* Calcd. for $C_7H_{18}ON_2S$: C, 47.69; H, 9.15; N, 15.90; S, 18.19. Found: C, 47.86; H, 9.20; N, 15.98; S, 18.29.

**1,3-Bis(2-mercaptoethyl)urea.**—Similar hydrolysis of 22.7 g. (0.07 mole) of 1,3-bis[2-(methyldithiolcarbonato)ethyl]urea gave 8.8 g. (71%) of 1,3-bis(2-mercaptoethyl)urea. Two recrystallizations from 95% ethanol gave an analytical sample, m.p. 121.5–122°.

*Anal.* Calcd. for $C_5H_{12}ON_2S_2$: C, 33.51; H, 6.71; N, 15.54; S, 35.57. Found: C, 33.28; H, 6.63; N, 15.55; S, 35.66.

**1-(2-Mercaptoethyl)-3-phenylurea.**—Similar hydrolysis of 2.7 g. (0.01 mole) of 1-[2-methyldithiolcarbonato)ethyl]-3-phenylurea gave 1.7 g. (87%) of 1-(2-mercaptoethyl)-3-phenylurea, m.p. 140.5–141.5°. The infrared spectrum of this material was identical with that of an authentic sample of 1-(2-mercaptoethyl)-3-phenylurea.[2]

**N-[2-(Mercaptoethyl)]phenylacetamide.**—To a solution of 22.5 g. (0.10 mole) of S-methyl N-[2-(methyldithiolcarbonato)-ethyl]thiolcarbamate and 10.1 g. (0.10 mole) of triethylamine in 50 ml. of dry acetonitrile was added a solution of 17.0 g. (0.10 mole) of silver nitrate in 25 ml. of acetonitrile. The temperature rose from 20° to 39°, and a yellow solid formed. To this mixture was added a solution of 13.6 g. (0.10 mole) of phenylacetic acid in 20 ml. of dry acetonitrile. When the mixture was heated to 60° a gas evolved vigorously.

The mixture was heated until there was no further evolution of gas and then allowed to cool to room temperature. The yellow solid was filtered out, and the filtrate was poured into ice–water. A yellow semisolid separated and was extracted into two 50-ml. portions of ether, and the solution was dried over magnesium sulfate. Evaporation of the ether left 14.3 g. (53%) of a yellow semisolid which gave an infrared spectrum consistent with that expected for N-[2-(methyldithiolcarbonato)ethyl]phenylacetamide. The semisolid was taken up in 25 ml. of 95% ethanol, and to this solution was added a solution of 8.0 g. (0.20 mole) of sodium hydroxide in 25 ml. of water. The temperature rose from 25° to 47°. The solution was allowed to cool to room temperature. A solid had formed, but dissolved upon adding another 100 ml. of water. This solution was made just strongly acid with hydrochloric acid. A gas evolved and an oil separated. It was extracted with two 50-ml. portions of ether. After drying over magnesium sulfate, the ether was evaporated under reduced pressure. A yellow liquid amounting to 6.5 g. (62%) remained. It gave an infrared spectrum consistent with that expected for N-[2-(mercaptoethyl)]phenylacetamide. A dinitrophenyl sulfide derivative of this product was prepared by dissolving 1.9 g. (0.01 mole) of the product in 25 ml. of 95% ethanol and adding 4 ml. of 10% sodium hydroxide solution (0.01 mole) and a solution of 2.0 g. (0.01 mole) of 1-chloro-2,4-dinitrobenzene in 30 ml. of warm 95% ethanol. The resulting solution was heated to boiling, filtered hot, and the filtrate chilled. A yellow solid formed. The solid was recovered, and a second crop of solid was recovered from the filtrate. The total yield of solid was 2.2 g. (61%). Two recrystallizations from absolute ethanol gave an analytical sample, m.p. 134–137°.

*Anal.* Calcd. for $C_{16}H_{15}O_5N_3S$: C, 53.18; H, 4.18; N, 11.63; S, 8.87. Found: C, 52.95; H, 3.99; N, 11.77, S, 8.97.