

The infrared spectra of the ketone mixtures from the *p*-chloro and *p*-methyl azides contained no peaks which were not attributable to one or both of the pure reference compounds, indicating the absence of any appreciable concentrations of absorbing impurities. The spectra of substituted and unsubstituted benzophenones differed sufficiently for accurate analysis only in the region 800–860  $\text{cm}^{-1}$  (*p*-substituted phenyl). Since benzophenone itself was thus determined by difference, non-absorbing impurities could seriously affect the analysis. Consequently the spectrum of the unknown mixture in chloroform solution was determined and known mixtures prepared at such concentrations that the carbonyl absorption (1660–1670  $\text{cm}^{-1}$ ) was essentially the same as that of the unknown. This correction was unnecessary for the products from the *p*-methyl azide, but did considerably improve the precision of the analyses for the products from the *p*-chloro azide.

In two cases (*p*-methoxyl and *p*-nitro), the identities of the anilines from hydrolysis of the anil mixtures were established. The anilines were converted to *N*-arylbenzamidates by the Schotten–Baumann method. The ultraviolet spectra of these mixtures in 95% ethanol were com-

pared with the spectra of authentic samples of the appropriate *m*- and *p*-substituted *N*-arylbenzamidates again using the Dewar<sup>28</sup> procedure. Excellent straight lines were obtained when the mixtures were assumed to consist of *N*-arylbenzamide and *p*-substituted *N*-arylbenzamide, while the fit was completely unsatisfactory when *m*-substituted *N*-arylbenzamide was assumed to be present. One new compound, benz-*m*-anisidate, m.p. 110.5–111.5°, was prepared in the course of this work. *Anal.* Calcd. for  $\text{C}_{14}\text{H}_{13}\text{NO}_2$ : C, 73.99; H, 5.76. Found: C, 73.73; H, 5.74.

**Nitrogen Yields.**—A 100–200-mg. sample of the azide was heated at 186° for 4 hours in a test-tube connected to a mercury-filled gas buret. Readings were taken before the heating was started and after the reaction vessel had cooled to room temperature. Results (assuming one mole of nitrogen per mole of azide) are recorded in Table I and were reproducible to about 1%.

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## Amino Acids. VI. Preparation and Chemistry of $\omega$ -Carbalkoxyalkyl Isothiocyanates

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A series of  $\omega$ -carbalkoxyalkyl isothiocyanates has been prepared from the corresponding amino acid ester hydrochlorides. Addition of the isothiocyanates to amines gave a number of unsymmetrical  $\omega,\omega'$ -disubstituted thioureas. Treatment of disodium  $\epsilon$ -carboxypentylidithiocarbamate with basic lead acetate gave 1,3-di-(5-carboxypentyl)-thiourea as the major product as well as 5-carboxypentyl isothiocyanate. The reaction between 1-phenyl-3-(2-carboxyethyl)-thiourea and acetic anhydride gave a mixture of 3-phenyl-2-thiohydroureil and 1-acetyl-3-phenyl-2-thiohydroureil.

A series of  $\omega$ -carbalkoxyalkyl isothiocyanates were prepared as part of a study of functional derivatives of thiourea. The first two members of the series, namely, carbethoxy isothiocyanate and carbethoxymethyl isothiocyanate, have been known for some time. Carbethoxy isothiocyanate<sup>1,2</sup> was prepared by the reaction of ethyl chloroformate with potassium thiocyanate, while carbethoxymethyl isothiocyanate was prepared by treating ethyl glycinate with thiophosgene<sup>3</sup> and by pyrolysis of the ethyl carbethoxymethylidithiocarbamate.<sup>4</sup>

on the earlier observations of Kaluza.<sup>6</sup> He found that *N*-substituted dithiocarbamates on pyrolysis gave the corresponding isothiocyanates. Recently, Hodgkins and Ettlinger<sup>7</sup> showed that carbethoxydithiocarbamates are decomposed into isothiocyanates readily at room temperature by aqueous alkali or by triethylamine in chloroform solution. They prepared the carbethoxydithiocarbamate in dioxane solution. It has now been found that replacement of the dioxane solvent with chloroform or methylene dichloride prevents the precipitation

TABLE I  
CARBALKOXYALKYL ISOTHIOCYANATES,  $\text{ROOC}(\text{CH}_2)_n\text{NCS}$

R	n	Yield, %	B.p. °C.	Mm.	$n^{\text{20D}}$	$d_4^{20}$	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Sulfur, %	
								Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Methyl	2	81.0	110–112	1.0	1.5036	1.193	$\text{C}_5\text{H}_9\text{NO}_2\text{S}$	41.36	41.76	4.86	5.16	9.65	9.61	22.08	21.74
Ethyl	2	42.4	92–95	0.04	1.4904	1.132	$\text{C}_6\text{H}_9\text{NO}_2\text{S}$	45.27	44.92	5.70	5.92	8.80	8.56	20.12	19.75
Methyl <sup>a</sup>	3	81.2	64–67	.17	1.5059	1.135	$\text{C}_8\text{H}_9\text{NO}_2\text{S}$	45.27	45.06	5.70	5.65	8.80	8.67	20.12	19.95
Methyl	5	36.9	120–122	.30	1.5000	1.101	$\text{C}_8\text{H}_{11}\text{NO}_2\text{S}$	51.30	51.66	7.00	7.06	7.48	7.84	17.13	17.30
Methyl	10	59.8	166–168	.1	1.4879	1.022	$\text{C}_{11}\text{H}_{23}\text{NO}_2\text{S}$	60.65	61.01	9.01	9.07	5.44	5.45	12.46	12.36

<sup>a</sup> Kjaer and Gmelin<sup>5</sup> report b.p. 70° (0.2 mm.),  $n^{\text{20D}}$  1.5066.

Since the completion of the present work, Kjaer and Gmelin<sup>5</sup> have reported the isolation of 3-carbomethoxypropyl isothiocyanate as a component of a naturally occurring glycoside, glucoerypestrin.

The procedure used in preparing the carbalkoxyalkyl isothiocyanates listed in Table I was based

- (1) A. E. Dixon and J. Taylor, *J. Chem. Soc.*, **93**, 697 (1908).
- (2) C. W. Capp, A. H. Cook, J. D. Downer and I. Heilbron, *ibid.*, 1342 (1948).
- (3) T. B. Johnson and E. H. Hemingway, *THIS JOURNAL*, **38**, 1550 (1916).
- (4) T. B. Johnson and A. G. Renfrew, *ibid.*, **47**, 242 (1925).
- (5) A. Kjaer and R. Gmelin, *Acta Chem. Scand.*, **11**, 577 (1957).

of triethylamine hydrochloride which eliminates the filtration step. Moreover, the amine could be used in the form of its hydrochloride if an additional equivalent of triethylamine were used in the reaction. Thus it was not necessary to isolate the reactive free amino acid esters.

5-Carboxypentyl isothiocyanate was prepared by the lead acetate process.<sup>8</sup> The disodium salt of 5-carboxypentylidithiocarbamate on treatment

- (6) (a) L. Kaluza, *Monatsh.*, **30**, 717 (1909); (b) **33**, 364 (1912).
- (7) J. E. Hodgkins and M. G. Ettlinger, *J. Org. Chem.*, **21**, 401 (1956).
- (8) M. Delepine, *Compt. rend.*, **144**, 1125 (1907).

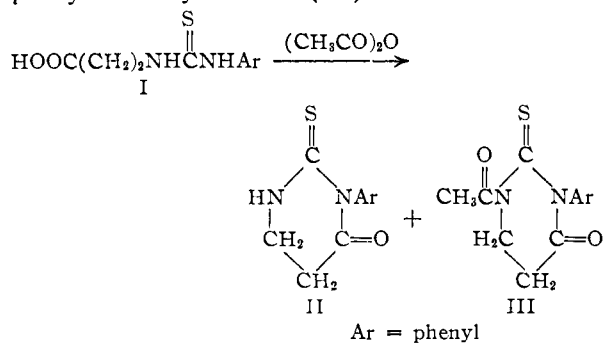
TABLE II

Name	Method, solvent	Yield, %	M.p., °C.	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Sulfur, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1-Carboethoxy-3-(5-carboxypentyl)-thiourea	C	47.0	106-107	C <sub>10</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> S	45.80	46.19	6.91	7.01	10.68	10.44	12.23	12.20
1-Carboethoxy-3-(2-cyanoethyl)-thiourea	A, ether	82.0	101.5-102.5	C <sub>7</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> S	41.78	42.27	5.51	5.50	20.88	20.59	15.94	15.78
N,N'-Di-(carboethoxythiocarbonyl)-ethylenediamine	A, ether	84.5	206.5-207	C <sub>10</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub> S	37.25	37.13	5.63	5.57	17.38	17.73	19.89	20.06
1-(2-Carboethoxyethyl)-3-(2-carboxyethyl)-thiourea	C	45.0	134-135	C <sub>9</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> S	43.53	43.63	6.50	6.41	11.29	11.21	12.91	12.72
1-(2-Carboxyethyl)-3-phenylthiourea <sup>a</sup>		92.0	117.5-118	C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S	53.54	53.84	5.40	5.83	12.49	12.49	14.30	14.91
1-(3-Carboxypropyl)-3-benzylthiourea	B, benzene	48.8	140.5-141	C <sub>12</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> S	57.13	57.07	6.39	6.47	11.11	10.86	12.71	12.66
1-(5-Carboxypentyl)-3-(6-hydroxyhexyl)-thiourea	B, ethanol	76.8	85-86	C <sub>11</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> S	53.76	53.92	9.03	8.97	11.04	11.34	9.65	10.06
5-Carbomethoxy-pentylthiourea	A, ethanol	72.7	77.5-78.5	C <sub>8</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> S	47.01	47.04	7.90	7.90	13.72	13.85	15.70	15.48
1-(5-Carboxypentyl)-3-benzylthiourea	B, benzene	48.8	127-128	C <sub>14</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> S	59.97	60.34	7.19	7.05	10.00	10.14	11.43	11.17
1-(5-Carboxypentyl)-3-(2-cyanoethyl)-thiourea	C	81.2	105.5-106.5	C <sub>10</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub> S	49.36	49.30	7.06	7.20	17.28	17.12	13.18	12.88
10-Carbomethoxydecylthiourea	A, ethanol	100	111.5-112.5	C <sub>11</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> S	56.90	56.84	9.55	9.45	10.21	10.30	11.68	11.66
1-(10-Carbomethoxydecyl)-3-(10-carboxydecyl)-thiourea	C	81.5	87.5-88.5	C <sub>24</sub> H <sub>40</sub> N <sub>2</sub> O <sub>4</sub> S	62.84	62.94	10.12	10.32	6.11	6.55	7.00	6.91
1-(10-Carbomethoxydecyl)-3-benzylthiourea	A, benzene	78.1	69-69.5	C <sub>20</sub> H <sub>26</sub> N <sub>2</sub> O <sub>2</sub> S	65.89	65.65	8.85	8.76	7.69	7.71	8.79	8.62
1-(10-Carbomethoxydecyl)-3-(6-hydroxyhexyl)-thiourea	A, benzene	89.3	63-63.5	C <sub>19</sub> H <sub>28</sub> N <sub>2</sub> O <sub>2</sub> S	60.92	60.79	10.22	9.97	7.48	7.59		
1-(10-Carbomethoxydecyl)-3-(2-cyanoethyl)-thiourea	A, benzene	84.8	81.0-81.5	C <sub>14</sub> H <sub>20</sub> N <sub>3</sub> O <sub>2</sub> S	58.68	58.50	8.93	8.66	12.83	12.77	9.79	9.96
1-(10-Carbomethoxydecyl)-3-(3-cyanopropyl)-thiourea	C	80.0	82.5-83	C <sub>17</sub> H <sub>24</sub> N <sub>3</sub> O <sub>2</sub> S	59.78	59.92	9.15	9.33	12.31	12.31	9.39	9.09
N,N'-Di-(10-carbomethoxydecylthiocarbonyl)-ethylenediamine	A, ethanol	92.2	125-126.5	C <sub>28</sub> H <sub>44</sub> N <sub>4</sub> O <sub>4</sub> S	58.49	57.95	9.47	9.26	9.75	9.82	11.16	11.00

<sup>a</sup> Prepared from phenyl isothiocyanate and  $\beta$ -alanine.

with basic lead acetate solution gave 1,3-di-(5-carboxypentyl)-thiourea<sup>9</sup> as well as the desired 5-carboxypentyl isothiocyanate.

The carbalkoxyalkyl isothiocyanates were added to a number of substituted amines to give the 1,3-disubstituted thioureas listed in Table II. Addition of carboethoxy isothiocyanate to hydrazine hydrate gave a good yield of 1,6-dicarboethoxydithiourea. Cyclization of 1-(2-carboxyethyl)-3-phenylthiourea (I) with acetic anhydride gave a mixture of 3-phenyl-2-thiohydrouacil (II) and 1-acetyl-3-phenyl-2-thiohydrouacil (III).<sup>10</sup>



### Experimental<sup>11</sup>

#### Methyl $\gamma$ -Aminobutyrate Hydrochloride.— $\gamma$ -Amino-

(9) A. F. McKay, E. J. Tarlton, S. I. Petri, P. R. Steyermark and M. A. Mosley, *This Journal*, **80**, 1510 (1958).

(10) The formation of thiohydrouacils from substituted thioureas is discussed fully in Amino Acids. IV, *Can. J. Chem.*, **36**, 496 (1958).

(11) All melting points are uncorrected. Microanalyses were determined by Micro-Tech Laboratories, Skokie, Ill.

butyric acid hydrochloride<sup>12</sup> (27 g., 0.21 mole) in 2.5 N methanolic hydrogen chloride (600 ml.) was allowed to stand at room temperature for 5 days. After the solution was evaporated to dryness, the residue was crystallized from acetone. The crude methyl  $\gamma$ -aminobutyrate hydrochloride melted at 89-104°, yield 18.8 g. (61%). A sample (1 g.) was extracted with hot chloroform (10 ml.) and the chloroform solution was taken to dryness. The residue from the chloroform extract was crystallized from ethanol-ether solution to provide an analytical sample. It melted at 121.5-122.5°, reported<sup>9</sup> m.p. 96-99°.

*Anal.* Calcd. for C<sub>6</sub>H<sub>12</sub>ClNO<sub>2</sub>: C, 39.09; H, 7.88; Cl, 23.08; N, 9.12. Found: C, 39.11; H, 7.92; Cl, 23.25; N, 8.84.

**Methyl  $\epsilon$ -Aminocaproate Hydrochloride.**—A solution of  $\epsilon$ -caprolactam (113 g., 1 mole) in water (150 ml.) containing concentrated hydrochloric acid solution (150 ml.) was refluxed for 3 hours. This solution on dilution with acetone (500 ml.) at room temperature gave 106 g. (64%) of  $\epsilon$ -aminocaproic acid hydrochloride (m.p. 132-133°). The  $\epsilon$ -aminocaproic acid hydrochloride (105 g., 0.62 mole) in 8.6 N methanolic hydrogen chloride (125 ml.) was refluxed for 2 hours. Evaporation of this solution gave a semi-crystalline residue, yield 110 g. (97%). A sample of the product was crystallized from methanol-ether solution to a constant melting point of 121-122.5°.

*Anal.* Calcd. for C<sub>7</sub>H<sub>16</sub>ClNO<sub>2</sub>: C, 46.29; H, 8.88; Cl, 19.52; N, 7.71. Found: C, 46.20; H, 8.73; Cl, 19.41; N, 8.06.

**Methyl 11-Aminoundecanoate Hydrochloride.**—Methyl 11-aminoundecanoate hydrochloride (m.p. 159.5-160.5°) was prepared as previously<sup>13</sup> described.

**2-Carbomethoxyethyl Isothiocyanate.**<sup>14</sup>—Carbon disulfide (57 g., 0.75 mole) in chloroform (200 ml.) was added

(12) E. Abderhalden and K. Kautzsch, *Z. physiol. Chem.*, **81**, 301 (1912).

(13) A. F. McKay, M. Skulski and D. L. Garmaise, *Can. J. Chem.*, **36**, 147 (1958).

(14) Prepared by Dr. P. R. Steyermark.

over a period of 90 minutes to a stirred suspension of  $\beta$ -alanine methyl ester hydrochloride (104 g., 0.75 mole) and triethylamine (151 g., 1.5 moles) in methylene dichloride (500 ml.) at  $-12^\circ$ . The reaction mixture was allowed to warm up to  $10^\circ$  and it was stirred at this temperature for 10 minutes. It was treated dropwise with ethyl chloroformate (81 g., 0.75 mole) in chloroform (60 ml.) at  $0-5^\circ$  over a period of 30 minutes. After the mixture was stirred for a further 25 minutes at room temperature, triethylamine (75.5 g., 0.75 mole) was added dropwise with stirring over a period of 30 minutes at  $0^\circ$ . The stirring was continued for 30 minutes at room temperature and then the solution was washed with water, dilute hydrochloric acid solution, 5% sodium bicarbonate solution and water. The organic phase was dried and the solvent was removed *in vacuo*. Fractional distillation of the residue *in vacuo* gave 87 g. (81%) of product (b.p.  $110-112^\circ$  (1 mm.),  $n_D^{20}$  1.5036,  $d_4^{20}$  1.193).

Similar procedures were used in the preparation of the other  $\omega$ -carbalkoxyalkyl isothiocyanates listed in Table I.

*N*-Carbomethoxyisothiocyanate (b.p.  $65-71^\circ$  (30 mm.)) was prepared by the method of Dixon and Taylor.<sup>1</sup>

**Substituted Thioureas.**—The substituted thioureas described in Table II were prepared by three procedures. The following examples describe details of these procedures.

**Method A.** 1-(10-Carbomethoxydecyl)-3-benzylthiourea.—10-Carbomethoxydecyl isothiocyanate (0.52 g., 0.002 mole) was added to benzylamine (0.21 g., 0.002 mole) in benzene (5 ml.). The reaction mixture was allowed to stand at room temperature for several hours and then the product was recovered by filtration, yield 0.57 g. (78%). Three crystallizations from ether raised the melting point from  $63.5-66.5^\circ$  to  $69-69.5^\circ$ .

**Method B.** 1-(5-Carboxypentyl)-3-(6-hydroxyhexyl)-thiourea.—5-Carbomethoxyethyl isothiocyanate (0.5 g., 0.0027 mole) was added at room temperature to a solution of 6-aminohexanol-1 (0.32 g., 0.0027 mole) in absolute ethanol (2 ml.). After 1 hour the solution was evaporated to dryness and the waxy ester (m.p.  $52-56^\circ$ ) was saponified by heating in 0.95 *N* sodium hydroxide solution (3.0 ml.) at  $100^\circ$  for 30 minutes. Acidification of the solution with hydrochloric acid gave 0.62 g. (77%) of product (m.p.  $78-82^\circ$ ). Three crystallizations from ethyl acetate raised the melting point to  $85-86^\circ$ .

**Method C.** 1-(10-Carbomethoxydecyl)-3-(10-carboxydecyl)-thiourea.—A solution of 10-carbomethoxydecyl isothiocyanate (0.52 g., 0.002 mole) in ethanol (14 ml.) was added to a solution of 11-aminoundecanoic acid (0.4 g., 0.002 mole) in 0.95 *N* sodium hydroxide solution (2.1 ml.). After 1 hour at room temperature, the solution was acidified with hydrochloric acid. The precipitated product was recovered by filtration, yield 0.76 g. (81%). Three crystallizations from ethyl acetate gave a constant melting point of  $87.5-88.5^\circ$ .

**5-Carboxypentyl Isothiocyanate and 1-(5-Carboxypentyl)-3-(2-cyanoethyl)-thiourea.**— $\epsilon$ -Aminocaproic acid (26.2 g., 0.2 mole) was dissolved in 2.36 *N* sodium hydroxide solution (85 ml.) and carbon disulfide (15.2 g., 0.2 mole) and 2.36 *N* sodium hydroxide solution (85 ml.) were added simultaneously with stirring at  $30^\circ$ . The solution was maintained at a pH of 8-9 during the addition period of 3 hours. An aliquot of the solution containing 0.12 mole of sodium  $\epsilon$ -

carboxypentylthiocarbamate was treated with a solution of lead oxide (13.4 g., 0.06 mole) and lead acetate (22.8 g., 0.06 mole) in water (96 ml.) and the resulting suspension was stirred for 30 minutes at  $25-30^\circ$ . The precipitated lead sulfide was removed by filtration and the pH of the filtrate was adjusted to 2 with hydrochloric acid. The filtrate was extracted with chloroform (75 ml.). A precipitate of 1,3-di-(5-carboxypentyl)-thiourea (m.p.  $128-129^\circ$ ) formed and it was recovered by filtration, yield 9.76 g. (50%). The product was identified by a mixed melting point determination with a known sample of 1,3-di-(5-carboxypentyl)-thiourea<sup>9</sup> (m.p.  $128-129^\circ$ ). The chloroform extract was dried and on evaporation gave 3.4 g. (16.4%) of crude 5-carboxypentyl isothiocyanate.

A sample of the crude 5-carboxypentyl isothiocyanate (1.7 g., 0.0096 mole) in 2.36 *N* sodium hydroxide solution (4.07 ml.) was added to  $\beta$ -aminopropionitrile (0.67 g., 0.0096 mole) in water (7 ml.). After 4 hours at room temperature, the solution was acidified. It gave 1.9 g. (81%) of crude 1-(5-carboxypentyl)-3-(2-cyanoethyl)-thiourea melting at  $100-105^\circ$ . Three crystallizations from ethyl acetate raised the melting point to  $105.5-106.5^\circ$ .

**1-(2-Carboxyethyl)-3-phenylthiourea.**—Phenyl isothiocyanate (13.5 g., 0.1 mole) was added to a solution of  $\beta$ -alanine (8.9 g., 0.1 mole) in 0.98 *N* sodium hydroxide solution (103 ml.) and the mixture was shaken at room temperature for 3 days. After the reaction mixture was acidified, the reaction product (m.p.  $117-118^\circ$ ) was obtained in 92% yield (20.6 g.). One crystallization from water raised the melting point to  $117.5-118^\circ$ .

**3-Phenyl-2-thiohydrouracil and 1-Acetyl-3-phenyl-2-thiohydrouracil.**—A solution of 1-(2-carboxyethyl)-3-phenylthiourea (1.62 g., 0.07 mole) in acetic anhydride (10 ml.) was heated at  $100^\circ$  for 15 minutes after which the solution was evaporated to dryness *in vacuo*. The residue was crystallized from ethanol (10 ml.), yield 1.27 g. (71.4%). Several crystallizations from ethanol raised the melting point of the 1-acetyl-3-phenyl-2-thiohydrouracil from  $130-134^\circ$  to a constant value of  $146-147^\circ$ .

*Anal.* Calcd. for  $C_{12}H_{12}N_2O_2S$ : C, 58.04; H, 4.87; N, 11.29; S, 12.91. Found: C, 58.34; H, 4.96; N, 11.59; S, 12.73.

Concentration of the mother liquors from the first and second crystallizations gave colorless crystals of 3-phenyl-2-thiohydrouracil, yield 90 mg. Crystallization from ethanol did not alter the melting point of  $228-229^\circ$ .

*Anal.* Calcd. for  $C_{10}H_{10}N_2OS$ : C, 58.21; H, 4.89; N, 13.59; S, 15.55. Found: C, 58.25; H, 4.88; N, 13.86; S, 15.41.

**1,6-Dicarbonyldithiourea.**—Hydrazine hydrate (0.19 g., 0.004 mole) was added to a solution of carbomethoxy isothiocyanate (0.5 g., 0.004 mole) in ether (10 ml.). The crystals, which separated from the solution at room temperature, did not melt below  $360^\circ$ , yield 0.45 g. (80%). The analytical sample was crystallized from methanol.

*Anal.* Calcd. for  $C_8H_{14}N_4O_4S_2$ : C, 32.63; H, 4.79; N, 19.05; S, 21.78. Found: C, 32.94; H, 5.09; N, 19.10; S, 22.10.

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