858. *Acyl* iso*Thiocyanates. Part I. The Synthesis of Esters of* N*-Acyldithiocarbamic Acids.*

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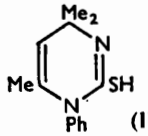
Esters of *N*-acyldithiocarbamic acids (I), which were required for the stepwise degradation of peptides from the end bearing a free amino-group,[1] have been synthesised by the interaction of acyl *iso*thiocyanates and thiols. Side-reactions, which occurred in some cases, have been elucidated.

During an investigation of a new method of stepwise degradation of peptides from the end bearing a free amino-group,[1] it became necessary to synthesise a number of *N*-acyldithiocarbamic esters (I). The only methods previously reported are due to Delépine [2] and Wheeler and Merriam.[3] The former method, which has been used in isolated cases only, involves the treatment of alkyl dithiocarbamates or dialkyl iminodithiocarbonate hydriodides with acid anhydrides at 100°. In the second method, thio-acids, which are of limited accessibility in spite of improved methods of synthesis recently described,[4] are caused to react with alkyl thiocyanates in refluxing benzene. A number of *N*-acyldithiocarbamic esters cannot be prepared by this route, since some thiocyanic esters are either too unstable to be isolated or would isomerise to *iso*thiocyanates under the conditions of the reaction with thio-acids.

Dixon and Doran [5] showed that acyl *iso*thiocyanates with alcohols readily give *N*-acylthioncarbamic esters (II), and it seemed probable that thiols would behave similarly to

(I) R·CO·NH·CS_2R′

(II) R·CO·NH·CS·OR′



(III)

give the desired *N*-acyldithiocarbamates. Although alcohols generally react additively with acyl *iso*thiocyanates, stronger nucleophilic agents such as amines [5,6] and hydrazines [7] show a marked proclivity for substitution, with liberation of thiocyanic acid. The two

[1] Elmore and Toseland, *J.*, 1954, 4533.
[2] Delépine, *Bull. Soc. chim. France*, 1903, **29**, 48, 53.
[3] Wheeler and Merriam, *J. Amer. Chem. Soc.*, 1901, **23**, 283.
[4] Cronyn and Jiu, *ibid.*, 1952, **74**, 4726; Sheehan and Johnson, *ibid.*, p. 4726.
[5] (*a*) Dixon, *J.*, 1895, **67**, 1041; 1899, **75**, 375, 388; 1906, **89**, 892; Dixon and Doran, *J.*, 1895, **67**, 565; Doran, *J.*, 1896, **69**, 324; (*b*) 1901, **79**, 906.
[6] (*a*) Dixon, *J.*, 1889, **55**, 300, 618; 1891, **59**, 551; 1896, **69**, 855, 1593; 1897, **71**, 617; 1904, **85**, 807; Cook, Downer, and Heilbron, *J.*, 1948, 1262; Cook, Heilbron, and Smith, *J.*, 1949, 1440; (*b*) Dixon and Doran, *J.*, 1905, **87**, 331; Dixon and Hawthorne, *J.*, 1905, **87**, 468; Hawthorne, *J.*, 1906, **89**, 556; (*c*) Dixon and Taylor, *J.*, 1908, **93**, 684.
[7] Hoggarth, *J.*, 1949, 1161.

mechanisms often operate competitively and the factors which influence the course of the reaction are not yet clear, although in several cases temperature has an important effect.[6b] Further, it appears that aroyl *iso*thiocyanates react additively in the majority of cases.

In the present work, it has been observed that alkanethiols react smoothly with acyl *iso*thiocyanates to give *N*-acyldithiocarbamic esters in good yield; there was no evidence for the formation of *S*-alkyl thioesters. Acyl *iso*thiocyanates have commonly been prepared by the interaction of lead thiocyanate and acyl chlorides in dry boiling benzene. We have found it more convenient in general to use potassium thiocyanate and dry acetonitrile in which the reactants were soluble. In many cases dry acetone proved to be a satisfactory alternative solvent,[6c] although in one instance its use led to a side-reaction which is discussed below. Production of most aliphatic acyl *iso*thiocyanates was complete in 15 minutes at room temperature or in 1—2 minutes at the boiling point. Aroyl *iso*thiocyanates were formed more slowly and the reaction mixture was heated under reflux for about 15 minutes. The instability of chloroacetyl *iso*thiocyanate required reaction at 0°. It was not necessary to isolate the pure acyl *iso*thiocyanates: an excess of alkanethiol was added to the mixture containing the *iso*thiocyanate, and reaction was conducted at room temperature, usually for about 12 hours.

Reaction of acetyl chloride and potassium thiocyanate in acetone followed by addition of methanethiol afforded a minute yield of methyl *N*-acetyldithiocarbamate (I; R = R′ = Me). The bulk of the product was a foul-smelling, undistillable oil. With aniline this did not give the expected acetanilide or *N*-acetyl-*N*′-phenylthiourea but, instead, 1 : 4-dihydro-2-mercapto-4 : 4 : 6-trimethyl-1-phenylpyrimidine (III), which had previously been synthesised by Mathes, Stewart, and Swedish [8] by brief heating of mesityl oxide with ammonium thiocyanate, aniline, and hydrochloric acid. It is apparent that some of the acetone used as solvent was converted into mesityl oxide by the action of acetyl chloride during the synthesis of methyl *N*-acetyldithiocarbamate. The above oil afforded no identifiable product with *cyclo*hexylamine, an observation which is consonant with the results of Mathes *et al.*[8] It was shown that methyl *N*-acetyldithiocarbamate and *cyclo*hexylamine afforded *N*-acetyl-*N*′-*cyclo*hexylthiourea in high yield; thus the low yield of methyl *N*-acetyldithiocarbamate from acetyl chloride, potassium thiocyanate, and methanethiol in acetone was not due to inadequate isolation. Reaction in acetonitrile gave the desired product in good yield.

A further difficulty was encountered in the synthesis of phenyl *N*-benzoyldithiocarbamate (I; R = R′ = Ph). When the reaction mixture from benzoyl *iso*thiocyanate and thiophenol was poured into water benzamide was the only identifiable product. It is not clear whether this arose by the action of water on benzoyl *iso*thiocyanate [6c] or by hydrolysis of phenyl *N*-benzoyldithiocarbamate. By avoiding the use of water during the isolation, however, the desired compound was isolated, albeit in poor yield.

Synthesis of methyl and benzyl *N*-benzyloxycarbonyldithiocarbamate (I; R = $Ph{\cdot}CH_2{\cdot}O$, R′ = Me or $Ph{\cdot}CH_2$) proved extremely troublesome. A single preparation of each from benzyl chloroformate and potassium thiocyanate in acetonitrile followed by addition of either methanethiol or toluene-ω-thiol gave good yields of these compounds, but could not be reproduced. Many variations of the procedure always gave benzyl thiocyanate as the major product, and carbon dioxide was evolved. It is almost certain that these resulted from the nucleophilic attack by thiocyanate anion on either benzyl chloroformate or benzyloxycarbonyl *iso*thiocyanate, a reaction comparable with the dealkylation of esters of phosphoric acids by anions and tertiary bases.[9] It was not possible to decide between these two alternatives, but the isolation of benzyl thiocyanate in >50% yields eliminates the possibility of debenzylation of the *N*-benzyloxycarbonyldithiocarbamate esters as a major reaction. We therefore reluctantly used a less polar solvent for the formation of the acyl *iso*thiocyanate in order to keep the ionic strength of thiocyanate at a minimum. Doran [5b] reported that reaction of alkyl chloroformates and sodium thiocyanate in benzene at room temperature was extremely slow. We confirm this, since

[8] Mathes, Stewart, and Swedish, *J. Amer. Chem. Soc.*, 1948, **70**, 1452.
[9] Baddiley, Clark, Michalski, and Todd, *J.*, 1949, 815; Clark and Todd, *J.*, 1950, 2023, 2030; Miyano, *J. Amer. Chem. Soc.*, 1955, **77**, 3524; Zervas and Dilaris, *ibid.*, p. 5354.

after reaction of benzyl chloroformate and excess of finely ground potassium thiocyanate in benzene at room temperature for periods of up to two weeks, addition of thiols in general gave poor yields of *N*-benzyloxycarbonyldithiocarbamates, whereas addition of excess of aniline afforded high yields of benzyl carbanilate and aniline hydrochloride. These could only have arisen from unchanged benzyl chloroformate. Reaction between benzyl chloroformate and potassium thiocyanate in toluene or benzene containing 10—20% of acetonitrile, however, proceeded at a convenient rate with no sign of concomitant debenzylation. Addition of methane- or toluene-ω-thiol to the resultant solution of benzyloxycarbonyl *iso*thiocyanate gave the desired compounds, although a week at room temperature was required to obtain optimal yields. As a final refinement, solvent was removed under reduced pressure below 40° after the first step and replaced by acetonitrile, in which the subsequent addition of thiol proceeded in at most two days.

The insolubility of *N*-acyldithiocarbamate esters in water so far used for the stepwise degradation of peptides, has required the use of aqueous ethanol or aqueous dioxan as solvent,[1] in which many peptides and proteins are rather insoluble. To provide a reagent which would be water-soluble at the pH value at which condensation with peptides occurs, synthesis of carboxymethyl *N*-acyldithiocarbamates (I; R′ = $CH_2 \cdot CO_2H$) was attempted. Benzoyl *iso*thiocyanate and thioglycollic acid in acetone gave a good yield of carboxymethyl *N*-benzoyldithiocarbamate (I; R = Ph, R′ = $CH_2 \cdot CO_2H$), but 2 : 4-dichlorobenzoyl *iso*thiocyanate gave an impure product. Attempted purification of the latter by recrystallisation afforded ethyl *N*-2 : 4-dichlorobenzoylthioncarbamate (II; R = $C_6H_3Cl_2$, R′ = Et) identical with a synthetic sample. The most probable explanation for the formation of this compound is that the reaction between 2 : 4-dichlorobenzoyl *iso*thiocyanate and thioglycollic acid was incomplete at the time of working up, and that addition subsequently occurred between the former and ethanol present in the chloroform which was employed as the solvent for recrystallisation. Prolonged reaction between 2 : 4-dichlorobenzoyl *iso*thiocyanate and thioglycollic acid at 37° afforded a small yield of carboxymethyl *N*-2 : 4-dichlorobenzoyldithiocarbamate (I; R = $C_6H_3Cl_2$, R′ = $CH_2 \cdot CO_2H$). Numerous attempts to synthesise carboxymethyl *N*-acetyldithiocarbamate (I; R = Me, R′ = $CH_2 \cdot CO_2H$) were unsuccessful. Occasionally, a high-melting, yellow, amorphous solid, probably a polymer, was obtained which could not be purified. Attempts to isolate carboxymethyl *N*-acetyldithiocarbamate as its *cyclo*hexylammonium salt failed; the only identifiable product was di(*cyclo*hexylammonium) dithiodiglycollate, identical with a synthetic sample. The yield and behaviour of this material during successive recrystallisations suggested that the oxidation of thioglycollate to dithiodiglycollate occurred during this process: a synthetic sample of *cyclo*hexylammonium thioglycollate, however, was stable during recrystallisation under the same conditions.

Although carboxymethyl *N*-acyldithiocarbamates are soluble in aqueous solution at slightly alkaline pH values, their suitability as reagents for the stepwise degradation of peptides remains to be ascertained. It has recently been shown that carboxymethyl *N*-aryldithiocarbamates are unstable at neutral pH in presence of Zn^{2+} ions,[10] and, if the mechanism postulated for this decomposition is correct, the degradation of carboxymethyl *N*-acyldithiocarbamates would probably be even more rapid. As zinc occurs in proteins such as insulin and carboxypeptidase, carboxymethyl *N*-acyldithiocarbamates may find only a limited use in stepwise degradation studies on peptides and proteins.

Experimental

For most experiments potassium thiocyanate was dried overnight at 100°/0·1 mm. over phosphoric oxide. Acetonitrile and acetone were shaken successively with calcium chloride and anhydrous calcium sulphate, distilled, and stored over anhydrous calcium sulphate.

Methyl N-*Benzoyldithiocarbamate* (I; R = Ph, R′ = Me).—Benzoyl chloride (14 g.) and potassium thiocyanate (9·8 g.) were allowed to react in refluxing acetonitrile (50 c.c.) for 15 min., then the mixture was cooled to 0°, treated with methanethiol (5 g.), kept overnight at room temperature with exclusion of moisture, and was poured into water (750 c.c.). The product

[10] Van der Kerk, Pluygers, and de Vries, *Rec. Trav. chim.*, 1955, **74**, 1262.

(17·5 g.) separated as a yellow solid and, after recrystallisation from ethanol, had m. p. 134° (Wheeler and Merriam [3] report m. p. 135°).

Methyl N-2 : 4-*Dichlorobenzoyldithiocarbamate* (I; R = 2 : 4-$Cl_2C_6H_3$, R′ = Me).—In a similar manner, 2 : 4-dichlorobenzoyl chloride (14 g.), potassium thiocyanate (7 g.), and methanethiol (5 g.) gave *methyl* N-2 : 4-*dichlorobenzoyldithiocarbamate* (17 g.) as pale yellow needles [from ethyl acetate–light petroleum (b. p. 40—60°)], m. p. 126—127° (Found : C, 38·8; H, 2·9; N, 5·0; S, 22·9; Cl, 25·2. $C_9H_7ONS_2Cl_2$ requires C, 38·6; H, 2·5; N, 5·0; S, 22·9; Cl, 25·3%).

Methyl N-p-*Nitrobenzoyldithiocarbamate* (I; R = *p*-NO_2·C_6H_4, R′ = Me).—This *ester* (65% yield) was prepared by the foregoing method from *p*-nitrobenzoyl chloride. Recrystallised from aqueous ethanol, it had m. p. 101—104° depending on the rate of heating (Found : C, 42·4; H, 3·4; N, 10·9; S, 25·2. $C_9H_8O_3N_2S_2$ requires C, 42·2; H, 3·1; N, 10·9; S, 25·0%).

Methyl N-3 : 5-*dinitrobenzoyldithiocarbamate* [I; R = 3 : 5-$(NO_2)_2C_6H_3$, R′ = Me) was afforded in 64% yield, but was initially rather gummy. It was recrystallised three times from ethanol, then having m. p. 171—173° after softening at 163° (Found: C, 36·2; H, 2·4; N, 14·3. $C_9H_7O_5N_3S_2$ requires C, 35·9; H, 2·3; N, 14·0%).

Methyl N-*Acetyldithiocarbamate* (I; R = R′ = Me).—A mixture of acetyl chloride (7·7 g.) and potassium thiocyanate (9·7 g.) in acetonitrile (50 c.c.) was shaken for 1 hr. at room temperature, cooled to 0°, and treated with methanethiol (5 g.). The product (11·7 g.), which crystallised overnight, was isolated by pouring the mixture into water; recrystallised from chloroform–light petroleum (b. p. 40—60°), it had m. p. 117—118°. Wheeler and Merriam [3] report m. p. 119°.

Several attempts to carry out this reaction in acetone afforded only minute yields of the required compound together with a foul-smelling, undistillable, yellow oil. Addition of a solution of aniline in ethanol gave after 2 weeks at room temperature good yields of 1 : 4-dihydro-2-mercapto-4 : 4 : 6-trimethyl-1-phenylpyrimidine (III), m. p. 200—201° after recrystallisation from dioxan. Mathes *et al.*[8] report m. p. 192—193°. A sample prepared by their method had m. p. 200—201° alone or mixed with our material; the infrared spectra of the two samples were indistinguishable (Found : C, 67·1; H, 6·7; N, 11·7; S, 13·9. Calc. for $C_{13}H_{16}N_2S$: C, 67·2; H, 6·9; N, 12·1; S, 13·8%). Both specimens were converted into their S-*mercury derivatives* by mercuric oxide in ethanol under reflux, and were isolated by filtration through Hyflo-Supercel and addition of water to the filtrate; they had m. p. 183—184° alone or in admixture, and identical infrared spectra (Found : C, 46·9; H, 4·6; N, 8·3; S, 9·4. $C_{26}H_{30}N_4S_2Hg$ requires C, 47·1; H, 4·6; N, 8·4; S, 9·7%).

N-*Acetyl*-N′-cyclo*hexylthiourea*.—A solution of methyl *N*-acetyldithiocarbamate (6 g.) and *cyclo*hexylamine (5 g.) in benzene (30 c.c.) was kept for 3 weeks. Removal of solvent afforded the crystalline *urea* (5·4 g.), which after recrystallisation from ethyl acetate–light petroleum (b. p. 40—60°) and then from ethanol, had m. p. 104—105° (Found : C, 54·0; H, 8·5; N, 14·1; S, 16·2. $C_9H_{16}ON_2S$ requires C, 54·0; H, 8·1; N, 14·0; S, 16·0%).

Methyl N-*Propionyldithiocarbamate* (I; R = Et, R′ = Me).—This *compound* (80%) was prepared by allowing propionyl chloride and potassium thiocyanate to react at room temperature in acetonitrile. After the mixture had stood with methanethiol overnight, potassium chloride was removed and the filtrate was evaporated under reduced pressure. The product, crystallised from ethanol, had m. p. 106—108° (Found : C, 36·5; H, 5·7; N, 8·9. $C_5H_9ONS_2$ requires C, 36·8; H, 5·6; N, 8·6%).

Methyl N-*Dichloroacetyldithiocarbamate* (I; R = $CHCl_2$, R′ = Me).—The method described for the *N*-propionyl derivative afforded this *dithiocarbamate* (71%) as a brown solid, m. p. 123° (from moist ethanol) (Found : C, 22·1; H, 2·1; N, 6·1; Cl, 33·0. $C_4H_5ONS_2Cl_2$ requires C, 22·0; H, 2·3; N, 6·4; Cl, 32·5%).

Methyl N-*Chloroacetyldithiocarbamate* (I; R = CH_2Cl, R′ = Me).—At room temperature chloroacetyl chloride and potassium thiocyanate reacted vigorously and gave tars. Consequently, the acyl chloride (11·3 g.) in acetonitrile (50 c.c.) was shaken at 0° and powdered potassium thiocyanate (9·7 g.) was added portionwise during 90 min. After a further 30 min., methanethiol (5 g.) was added and the mixture was allowed to warm to room temperature and left overnight. The *product* (11·9 g.), isolated in the usual way, recrystallised from ethanol as light yellow plates, m. p. 114—115° with effervescence. It decomposed rapidly in hot aqueous ethanol and soon became coloured in air (Found : C, 25·9; H, 3·5; S, 34·4. $C_4H_6ONS_2Cl$ requires C, 26·2; H, 3·3; S, 34·9%).

Phenyl N-*Benzoyldithiocarbamate* (I; R = R′ = Ph).—Addition of thiophenol to benzoyl *iso*thiocyanate in acetonitrile proceeded slowly and the mixture was kept 11 days at room temperature under nitrogen. The solution was filtered and evaporated under reduced pressure

to an oil which was extracted with benzene. Addition of light petroleum (b. p. 40—60°) caused a yellow oil to separate, which partially crystallised at 0°. Three recrystallisations of the solid fraction from carbon tetrachloride gave *phenyl* N-*benzoyldithiocarbamate* (7%), m. p. 98—99° (Found: C, 61·2; H, 4·2; N, 5·6; S, 23·2. $C_{14}H_{11}ONS_2$ requires C, 61·5; H, 4·1; N, 5·1; S, 23·5%). Attempts to isolate the dithiocarbamate by pouring the reaction mixture into water gave benzamide as the only crystalline product.

Methyl N-*Benzyloxycarbonyldithiocarbamate* (I; R = Ph·CH_2O, R′ = Me).—For the following reactions, which were conducted in heterogeneous media, potassium thiocyanate was obtained in a finely divided state by pouring an ice-cold, saturated, ethanolic solution with stirring into 4 volumes of ether at 0°.

(*a*) Benzyl chloroformate (8·5 g.), potassium thiocyanate (24·5 g.), and some glass beads were shaken in a mixture of toluene (400 c.c.) and acetonitrile (100 c.c.) at room temperature for 2 days. Potassium salts were removed and washed with toluene, and the combined filtrates were allowed to react with methanethiol (5 g.) at room temperature for a week. The solution was concentrated under reduced pressure, then kept at 0°; the *product* (8·1 g.), when collected and recrystallised from aqueous ethanol, had m. p. 133·5—134·5°. A further quantity (1·3 g.) was obtained from the mother-liquors by concentration and addition of light petroleum (b. p. 40—60°) (Found: C, 50·2; H, 4·6; N, 5·9. $C_{10}H_{11}O_2NS_2$ requires C, 49·8; H, 4·6; N, 5·8%).

(*b*) A solution of benzyloxycarbonyl *iso*thiocyanate, prepared as above in benzene (400 c.c.) and acetonitrile (100 c.c.), was concentrated under reduced pressure below 40° and with a nitrogen leak, to approximately 100 c.c. Acetonitrile (100 c.c.) and methanethiol (5 g.) were added and the solution was kept at room temperature during 2 days. The product (6·2 g.), isolated as described above and recrystallised, had m. p. 133·5—134·5°.

When pure acetonitrile was used as solvent, the major product as a rule was benzyl thiocyanate, whilst in pure benzene reaction between benzyl chloroformate and potassium thiocyanate (10 molar excess) was so slow that after 2 weeks addition of aniline to the filtered reaction mixture afforded high yields of benzyl carbanilate and aniline hydrochloride (cf. Doran [5b]).

Benzyl N-*Benzyloxycarbonyldithiocarbamate* (I; R = Ph·CH_2O, R′ = Ph·CH_2).—This *compound* (50—70%) was prepared by the two methods given for the methyl ester, except that only 1 molar quantity of toluene-ω-thiol was employed. It was almost colourless after recrystallisation from aqueous ethanol and had m. p. 113—114° (Found: C, 60·4; H, 4·7; N, 4·8. $C_{16}H_{15}O_2NS_2$ requires C, 60·5; H, 4·8; N, 4·4%).

Carboxymethyl N-*Benzoyldithiocarbamate* (I; R = Ph, R′ = CH_2·CO_2H).—Equivalent quantities of benzoyl *iso*thiocyanate and thioglycollic acid were kept in acetone solution for 36 hr. at room temperature. Pouring the mixture into water gave the *ester* (60%) as an oil which rapidly crystallised. Recrystallised from ethyl acetate, it had m. p. 156° after softening at 130° and varying with the rate of heating (Found: C, 47·3; H, 3·6; N, 5·3. $C_{10}H_9O_3NS_2$ requires C, 47·0; H, 3·6; N, 5·5%).

Carboxymethyl N-2 : 4-*Dichlorobenzoyldithiocarbamate* (I; R = 2 : 4-$Cl_2C_6H_3$, R′ = CH_2·CO_2H).—A mixture of 2 : 4-dichlorobenzoyl *iso*thiocyanate and thioglycollic acid in acetonitrile was kept at 38° during 10 days. The oily *dithiocarbamate*, which separated in water, solidified at 0° (m. p. 149—155°). After two recrystallisations from chloroform–ethanol (9 : 1) and one from ethanol, it had m. p. 162—163° after darkening above 155° (Found: C, 37·5; H, 2·6; N, 4·3; S, 19·2; Cl, 21·2. $C_{10}H_7O_3NS_2Cl_2$ requires C, 37·0; H, 2·2; N, 4·3; S, 19·8; Cl, 21·9%). In an earlier attempt to synthesise this compound, the reactants were kept in acetone at room temperature during 12 hr. The gummy solid, which separated when the mixture was poured into water, was repeatedly recrystallised from chloroform–light petroleum (b. p. 40—60°). It proved to be *ethyl* N-2 : 4-*dichlorobenzoylthioncarbamate* (II; R = 2 : 4-$Cl_2C_6H_3$, R′ = Et), m. p. 99—100°, undepressed on admixture with an authentic sample. The two samples had identical infrared spectra (Found: C, 42·8; H, 3·5; N, 4·7; S, 11·4; Cl, 25·5. $C_{10}H_9O_2NSCl_2$ requires C, 43·2; H, 3·3; N, 5·0; S, 11·5; Cl, 25·5%).

Ethyl N-2 : 4-*Dichlorobenzoylthioncarbamate.*—A solution of 2 : 4-dichlorobenzoyl *iso*thiocyanate (0·025 mole) in acetonitrile (50 c.c.) and ethanol (5 c.c.) was kept at room temperature during 48 hr. and was then poured into water. The resulting yellow oil (6 g.) solidified at 0° and was recrystallised from aqueous ethanol (charcoal) and then from chloroform–light petroleum (b. p. 40—60°); the *ester* had m. p. 99—100° (Found: C, 43·2; H, 3·5; N, 5·1%).

Attempted Addition of Thioglycollic Acid to Acetyl iso*Thiocyanate.*—Numerous attempts to bring about this reaction failed to give a crystalline product. On two occasions, a yellow, amorphous solid was formed which did not melt below 310°. From its physical properties it

appeared to be a polymer, but no consistent analyses could be obtained. An attempt to isolate the required dithiocarbamate as its *cyclo*hexylammonium salt gave only *di*(cyclo*hexylammonium*) *dithiodiglycollate*. After several recrystallisations from ethanol–ether, this had m. p. 169—170°, undepressed on admixture with an authentic sample and having an identical infrared spectrum (Found: C, 50·2; H, 8·2; N, 6·8; S, 16·4. $C_{16}H_{32}O_4N_2S_2$ requires C, 50·5; H, 8·5; N, 7·4; S, 16·8%).

The authentic sample was obtained in quantitative yield from dithiodiglycollic acid and *cyclo*hexylamine in ethanol (m. p. 169·0—169·5°) (Found: C, 50·3; H, 8·4; N, 7·0; S, 16·6%).

cyclo*Hexylammonium Thioglycollate*.—This *salt*, obtained in quantitative yield from *cyclo*hexylamine and thioglycollic acid in benzene, had m. p. 119—120° after recrystallisation from ethanol–ether (Found: C, 50·0; H, 8·8; N, 7·2. $C_8H_{17}O_2NS$ requires C, 50·2; H, 9·0; N, 7·3%).

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