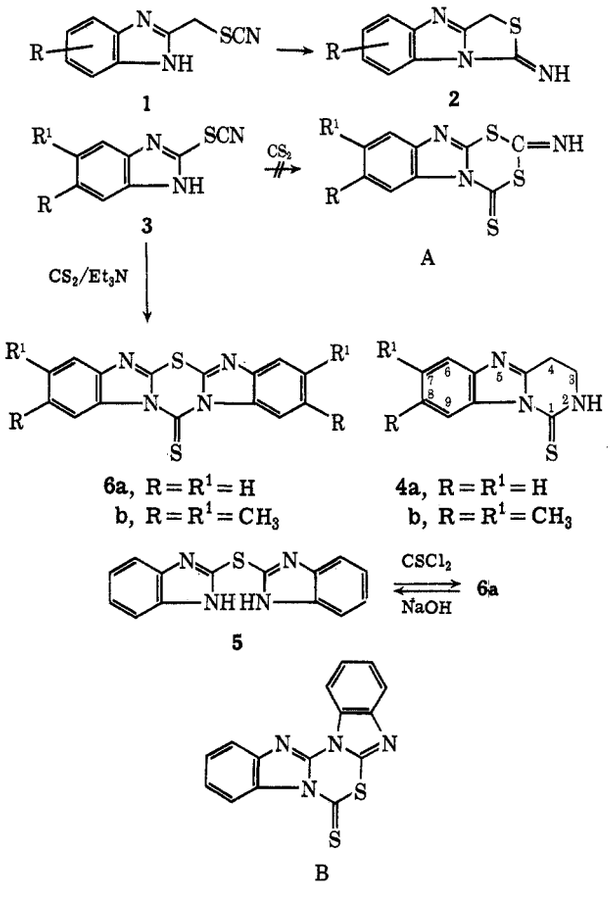
[3,4-*a*]benzimidazole-1(2*H*)-thiones (**4**) the most downfield signal, namely 9-H, being due to the deshielding effect of the thione function. The ir of the product was devoid of NH absorption but showed a band at 1500 cm^{-1} compatible with a S=CN< moiety. Its mass spectrum showed a molecular ion of M^+ 308 consistent with the formula $C_{15}H_8N_4S_2$, suggestive of two benzimidazole rings linked by CS_2 (structure **6a** or B). Whereas oxidative degradation of the reaction product resulted in ill-defined products and acid hydrolysis led to the recovery of starting material, mild base hydrolysis furnished a white solid which was subsequently identified as dibenzimidazol-2-yl sulfide[3] **5**, obtained by the alkylation of 2-mercaptobenzimidazole with 2-chlorobenzimidazole. Based on the above facts, we have assigned the pentacylic structure **6a** to the product. This was confirmed by synthesizing **6a** from **5** by the interaction of the sodium salt of **5** with thiophosgene.

We have extended this facile one-step synthesis of the pentacyclic system to the preparation of the tetramethyl analog **6b**.

Presently, we are investigating the scope of this interesting cyclization.



Experimental Section

Melting points were determined on a Thomas-Hoover "Uni-Melt" apparatus and are uncorrected. Ir spectra were determined in Nujol. Nmr spectra were obtained on a Varian A-60 instrument. Signals are described as singlet (s) or multiplet (m).

13*H*-[1,3,5]Thiadiazino[3,2-*a*:5,6-*a*']bisbenzimidazole-13-thione (6a).—To a solution of 5 g of 2-thiocyanobenzimidazole in 20 ml of dimethyl sulfoxide, there was added at once 5 ml of carbon disulfide and 5 ml of triethylamine. A yellow solid, deposited after 1 min, was filtered off after 1 hr of standing. The solid was washed with ethanol to yield 3.6 g of **6a**. Two crystallizations from benzene–ethyl ether furnished the pure product: mp 184–185°; nmr ($CDCl_3$) δ 7.26–7.84 (m, 6 H, ArH), 8.93–9.09 (m, 2 H, 1-H, 11-H); mass spectrum *m/e* 308.0187 (M^+). *Anal.* Calcd for $C_{15}H_8N_4S_2$: C, 58.42; H, 2.62; N, 18.17; S, 20.80. Found: C, 58.42; H, 2.75; N, 18.50; S, 21.03.

2,3,9,10-Tetramethyl-13*H*-[1,3,5]thiadiazino[3,2-*a*:5,6-*a*']bisbenzimidazole-13-thione (6b).—To a solution of 1.9 g of 2-thiocyano-5,6-dimethylbenzimidazole in 10 ml of dimethyl sulfoxide was added 2 ml of carbon disulfide and 2 ml of triethylamine. The mixture was allowed to stand at room temperature overnight. The yellow crystals were filtered off, washed with methanol, and crystallized from benzene to yield 0.8 g of **6b**. Recrystallization from benzene yielded the pure product, mp 338–340°, mass spectrum *m/e* 364.0856 (M^+). *Anal.* Calcd for $C_{19}H_{16}N_4S_2$: C, 62.61; H, 4.43; N, 15.37. Found: C, 62.74; H, 4.66; N, 15.46.

3,4-Dihydropyrimido[3,4-*a*]benzimidazole-1(2*H*)-thione (4a).—A mixture of 4.6 g of 2-(β-aminoethyl)benzimidazole, 30 ml of dimethyl sulfoxide, 4.6 ml of triethylamine, and 4.6 ml of carbon disulfide was stirred at room temperature for 14 hr. The product that separated upon diluting the reaction mixture with water was crystallized from acetone to yield **4a**: mp 212–213° (lit.[4] mp 216°); nmr (dimethyl sulfoxide-d_6) δ 3.13–3.83 (m, 4 H, $-CH_2-CH_2-$), 7.23–7.92 (m, 3 H, ArH), 8.82–9.02 (m, 1 H, 9-H).

7,8-Dimethyl-3,4-dihydropyrimido[3,4-*a*]benzimidazole-1(2*H*)-thione (4b).—A suspension of 6 g of 2-(β-aminoethyl)-5,6-dimethylbenzimidazole dihydrochloride, 6 ml of triethylamine, 6 ml of carbon disulfide, and 40 ml of dimethyl sulfoxide was stirred at room temperature overnight. Water was added and the crude product was filtered off. Crystallization from diglyme gave 3.5 g of pure **4b**: mp 232°, nmr (dimethyl sulfoxide-d_6) δ 2.34 (s, 6 H, CH_3), 2.98–3.78 (m, 4 H, $-CH_2CH_2-$), 7.38 (s, 1 H, 6-H), 8.57 (s, 1 H, 9-H), 10–10.53 (s, 1 H, NH). *Anal.* Calcd for $C_{12}H_{13}N_3S$: C, 62.30; H, 5.66; N, 18.17. Found: C, 61.95; H, 5.94; N, 18.45.

Hydrolysis of 13*H*-[1,3,5]Thiadiazino[3,2-*a*:5,6-*a*']bisbenzimidazole-13-thione (6a).—A mixture of 0.4 g of **6a**, 8 ml of methanol and 2 ml of 10% NaOH was heated on the steam bath for 1 min. By this time, the compound has dissolved and had lost its yellow color. The cooled mixture was filtered and the filtrate was adjusted to pH 7 with 10% HCl. The precipitate was filtered off and dried to yield 0.35 g of crude sulfide **5**. Crystallization from ethanol yielded the pure product, mp 273–275°, the ir of which was identical with that of an authentic sample prepared by the method of Harrison and Ralph.[3]

Synthesis of 6a.—To a suspension of 0.15 g of the sulfide **5** in 20 ml of glyme, there was added 0.03 g of sodium hydride. After 2 hr of stirring at room temperature 0.05 ml of thiophosgene was added to the suspension and the stirring was continued for 2 hr. The mixture was evaporated and the product was extracted with benzene. Two crystallizations from benzene–ethyl ether furnished 0.05 g of **6a**, mp 180–182°, the ir of which was identical with that of the product obtained by the reaction of 2-thiocyanobenzimidazole with carbon disulfide.

Registry No.—**4b**, 34858-78-1; **5**, 2469-66-1; **6a**, 34858-80-5; **6b**, 34858-81-6.

(3) D. Harrison and J. T. Ralph, *J. Chem. Soc.*, 3132 (1965).

(4) K. Nagarajan, V. Rangh Rao, and A. Venkateswalcu, *Indian J. Chem.*, **8**, 126 (1970).

Quaternary Ammonium Salts and Betaines of Thionocarbamic Esters

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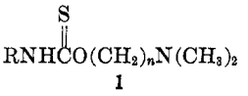
Received February 28, 1972

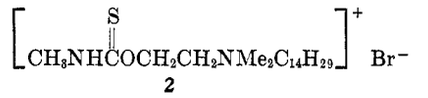
An earlier paper[1] described tertiary aminoalkyl esters of thionocarbamic acids (**1**) and their isomerism due to

(1) R. A. Bauman, *J. Org. Chem.*, **32**, 4129 (1967).



1

restricted rotation about the N–C bond as revealed by nmr spectroscopy. The present paper is concerned with the behavior of quaternary ammonium salts of these tertiary amines. Examples of aliphatic thionocarbamate quaternaries prepared are **2** and **3** and of



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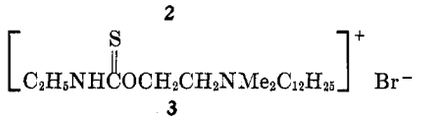

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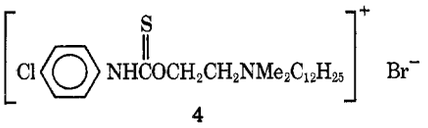
aromatic thionocarbamate quaternaries are **4** and **5**.



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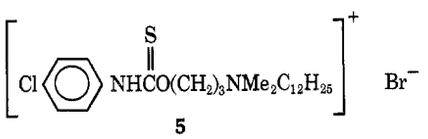

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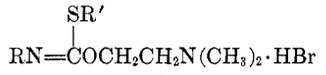
At room temperature an alkyl bromide reacts quantitatively with **1**; the sulfur atom is not attacked. This was shown by comparison of the nmr spectra of these products with those formed from the analogous carbamates where alkylation can occur only on the tertiary nitrogen. In both cases the methyl protons undergo upon quaternization a downfield shift of about 1 ppm and remain a singlet, which would not be the case for the hypothetical product **6** of S-alkylation.



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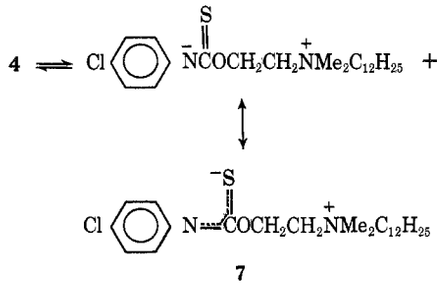
Another feature of the nmr spectra (in chloroform-*d*) was a broadening of the signals, perhaps due to the viscosity of the solutions, which made difficult the detection of cis–trans isomerism, except for **2** where two unequal doublets for the carbamate CH_3 were discernible. The aromatic protons in **4** showed an assymmetric broadening, with the downfield pair being most affected.

The carbamate proton in the quaternary salts showed a downfield shift of 1–2 ppm compared to the starting amines (measured on equimolar solutions at the same temperature). This appears to be due to a marked increase in the acidity of this proton. Indeed, for **4** this increase in acidity was enough to permit titration to a sharp end point with aqueous sodium hydroxide; **5** showed a shallower break at the end point. Why alkylation of the molecule at a position remote from the carbamate proton should affect the acidity might be explained by the preceding equilibrium, with the negative charge being stabilized both by delocalization and by the positive charge on the quaternary nitrogen. Proof for this hypothesis was obtained by the isolation of several betaines of this type.



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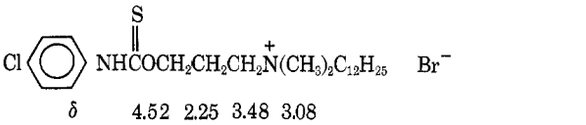
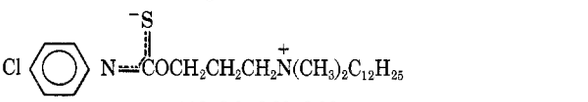
Treatment of compounds **4** and **5** with 1 equiv of methanolic sodium methoxide followed by solvent evaporation at room temperature and crystallization from acetone gave products with the correct elemental analyses, and ir spectra in which the NH absorption had disappeared and a strong characteristic band at 1365 cm^{-1} had been replaced by an equally strong band at about 1080 cm^{-1}. The fingerprint region of the spectrum of the inner salt was completely different from that of the normal quaternary salt.

The nmr spectra of **5** and its betaine **8** were compared in dimethyl sulfoxide. All protons in **8** showed an upfield shift from those in **5**.



δ 4.52 2.25 3.48 3.08

5



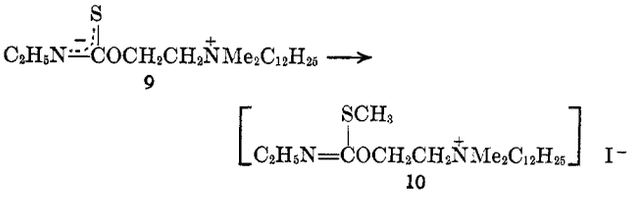
4.12 2.0 3.38 3.02

8

The aliphatic thionocarbamate quaternaries were also readily converted to the inner salts by sodium methoxide; however, these were not stable enough to be recrystallized for analysis. The betaine of **3** was obtained pure by an alternate method of preparation in which an aqueous solution of **3** was passed through a column of Dowex 1-X8 in the hydroxide form. This ordinarily would result in formation of a solution of a quaternary ammonium hydroxide, but here spontaneous crystallization occurred in the eluate to form the inner salt **9**, with an acceptable analysis and an ir spectrum related to that of betaine **7**.

Redissolved in water, **9** gave a strongly basic solution indicating formation of the quaternary hydroxide. Neutralization with 1 equiv of HCl or HBr gave the normal quaternary chloride or bromide. Treatment with HF also gave the quaternary fluoride, as deduced from the ir spectrum of partly dried material, but removal of the water under vacuum also removed HF, and the spectrum reverted to that of the inner salt **9**.

The betaine can be further alkylated at the sulfur atom. For example, **9** when treated with excess methyl iodide gave a single product characterized by elemental analysis, argentimetric titration, ir, and nmr spectroscopy as **10**; no N-alkylation product was found.



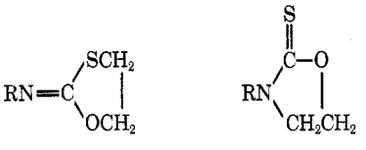
10

With the exception of **8** the betaines prepared are only moderately stable. In a melting point determination the betaine **7** melted sharply to two immiscible liquids. Also when refluxed in benzene for 1 hr it slowly dissolved, and, upon removal of the solvent, two liquid phases remained. The lighter of these was in both cases identified as dimethyldodecylamine. The other phase contained some of the amine as well as two other major products. Separated by their different solubilities in hexane and obtained as pure crystalline compounds, these were isomers of molecular weight 213 (mass spectrometry). The nmr spectrum of each showed a four-proton group typical of the para-substituted benzene ring and two two-proton groups coupled to each other (J = 7 Hz). The two isomers, referred to temporarily as A and B, had different chemical shifts, which are shown in Table I.

TABLE I
CHEMICAL SHIFTS OF THERMAL DEGRADATION PRODUCTS

Isomer	Methylene protons	Benzene protons	*N*-Alkyl protons
A (**11**)	3.38, 4.48	6.90, 7.26	
B (**14**)	4.20, 4.66	7.37, 7.54	
A′ (**12**)	3.40, 4.36		3.01
B′ (**15**)	3.84, 4.52		3.22
A″ (**13**)	3.42, 4.35		1.19, 3.17
B″ (**16**)	3.78, 4.56		1.24, 3.74

The two structures which conform to these spectra are as follows.



11, R = ClC_6H_4 **14**, R = ClC_6H_4
12, R = CH_3 **15**, R = CH_3
13, R = C_2H_5 **16**, R = C_2H_5

Compound A, the less retentive in both gas and thin layer chromatography, shows very strong absorption at 1640 cm^{-1}, which is interpreted as due to the C=N bond.[2] For compound B the 1640-cm^{-1} band is missing, and the principal absorption bands are very close to those reported for 3-phenyl-1,3-oxazolidine-2-thione.[3] The chemical shifts help establish the structures. It has been found[4] that there is a greater difference in chemical shift between the ortho and meta protons of *p*-chlorophenyl isothiocyanate (and isocyanate) than between the corresponding protons of *p*-chlorothionocarbanilic esters; thus one would expect the aromatic protons of structure **11** to have a greater chemical shift difference than those of **14**. Further, from the nmr data reported for related open-chain[1,5] and cyclic[6] compounds, it appears that resonances for methylene groups attached to O, N, and S occur at increasing field in accordance with their relative electronegativities. This, too, confirms the assignment of A as **11** and B as **14**.

Although the isomeric products from the betaines of **2** and **3** (A′ and B′, and A″ and B″, respectively, in Table I) were not separated on a preparative scale, they could be distinguished in an nmr spectrum of the mixture, and similarly identified from the chemical shifts as the 1,3-oxathiolane-2-imines (**12** and **13**) and the 1,3-oxazolidine-2-thiones (**15** and **16**).

The structural assignments in the aliphatic cases can be further verified by the use of benzene-induced shifts. All the protons of B′ show large positive solvent shifts (δ 0.4–0.9 downfield), whereas in A′ the methylene protons have similar large positive shifts (0.6), but the methyl protons a small shift of 0.05. Also, the methyl protons of B″ have a solvent shift of 0.4, whereas in A″ the shift is only 0.01. Past experience[7] with aromatic solvent-induced shifts of protons near double bonds would make it probable that the protons with the very small shift are located in front of a plane passed perpendicularly through the double-bonded carbon. This procedure identifies A′ as **12** and A″ as **13**.

The thermal decomposition products of the betaines probably represent the results of internal S- and N-alkylation, and thus provide justification for formulating the inner salts with a delocalized negative charge. Approximately the same ratio of products—30% oxazolidinethione **14** and 70% oxathiolane **11**—was obtained when the betaine of **4** was decomposed in benzene and in acetonitrile; for the betaine of **2** the proportions were 78% of **15** and 22% of **12**. This reaction did not occur on refluxing the betaine in methyl or ethyl alcohol, presumably because in protic solvents the compound exists as a normal quaternary ammonium hydroxide rather than as a betaine. The homologous quaternary salt **5** formed a betaine **8** which showed no tendency to eliminate dimethyldodecylamine in refluxing benzene, although one might have expected six-membered rings of structures analogous to **11** and **14**.

The stability of the betaines of the various quaternary salts seems to correlate with the shift in position of the strong infrared absorption band found about 1540 cm^{-1} in the spectra of all thionocarbamic esters examined[4] and recorded in Table II.

TABLE II
INFRARED BAND SHIFT[a] ON BETAINE FORMATION

Quaternary salt	Stability	Absorption band, cm^{-1} Bromide	Betaine	Δ
2	low	1546	1598	52
3	low	1530	1580	50
4	moderate	1522	1560	38
5	high	1534	1534	0

[a] Measured on Nujol mulls.

The synthetic implications of this work are interesting because methods for preparing these particular heterocycles are rare and few examples of the compounds themselves have been recorded. For 3-substituted oxazolidine-2-thiones there is the decomposi-

(2) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Wiley, New York, N. Y., 1958, p 267.
(3) T. Mukaiyama, I. Kuwajima, and K. Mizui, *J. Org. Chem.*, **31**, 32 (1966).
(4) R. A. Bauman, *J. Chem. Eng. Data*, **11**, 274 (1966).
(5) R. Radeglia, S. Scheithauer, and R. Mayer, *Z. Naturforsch. B*, **24**, 283 (1969).
(6) (a) J. L. Richards, D. S. Tarbell, and E. H. Hoffmeister, *Tetrahedron*, **24**, 6485 (1968); (b) F. N. Jones and S. Andreades, *J. Org. Chem.*, **34**, 3011 (1969); (c) K. Pihlaja, *Suomen Kemistilehti B*, **43**, 143 (1970); (d) G. E. Wilson, Jr., M. G. Huang, and F. A. Bovey *J. Amer. Chem. Soc.*, **92**, 5907 (1970).
(7) J. D. Connolly and R. McCrindle, *Chem. Ind. (London)*, 379 (1965).

tion of *N*-(2-hydroxyethyl)dithiocarbamate salts,[8,8,9] and for 1,3-oxathiolane-2-ylideneamines there is the reaction of isocyanide dihalides with 2-mercaptoethanol.[10,11] It has been demonstrated here that in the decomposition of thionocarbamate betaines an aryl substituent on the carbamate nitrogen favors S-alkylation, whereas an alkyl substituent favors N-alkylation. We have not studied the possible influence of other solvents or reaction conditions on the product ratio nor the possibility that a preparative method for one or both of these heterocyclic systems might be developed.

Experimental Section

3-Dimethylaminopropyl *p*-Chlorothionocarbanilate.—Two grams of sodium was powdered in 25 ml of xylene. With stirring and warming 8.8 g of 3-dimethylamino-1-propanol was added. When the reaction was over in 3 hr, 13.9 g of *p*-chlorophenyl isothiocyanate was stirred in. After 15 min the stiff paste was diluted with 200 ml of water and acidified with HCl. The precipitate was separated, dried, and crystallized from alcohol (Nuchar) to give 16.5 g (66% of theory) of white crystals. An analytical sample was recrystallized from alcohol, mp 175.5–176°.

Anal. Calcd for $C_{12}H_{18}Cl_2N_2OS$: C, 46.60; H, 5.87; N, 9.06; neut equiv, 309.3. Found: C, 46.44; H, 5.94; N, 8.96; neut equiv, 310.1.

The free base was obtained by neutralization and recrystallization from benzene–hexane, mp 113–115°. The same method was used to prepare the previously reported 2-dimethylaminoethyl esters of methylthionocarbamic,[1] ethylthionocarbamic,[1] and *p*-chlorothionocarbanilic[4] acids.

Quaternary Ammonium Bromides.—Equimolar quantities of an aminoalkyl thionocarbamate and a 1-bromoalkane were mixed neat (for **3**) or in just sufficient acetone or acetonitrile (for **2**, **4**, **5**) for solubility, and were allowed to stand at room temperature for 1 week or longer to obtain substantially quantitative yields. The solidified reaction mixtures were recrystallized from ethyl acetate or acetone. Melting points for the compounds are given in Table III.

TABLE III[a]

MELTING POINTS FOR QUATERNARY AMMONIUM BROMIDES AND BETAINES

Compd	Formula	Mp, °C
2	$C_{20}H_{43}BrN_2OS$	73.5–77.0
3	$C_{19}H_{41}BrN_2OS$	94.0–95.5
4	$C_{28}H_{40}BrClN_2OS$	140.5–142.5
5	$C_{24}H_{42}BrClN_2OS$	150.0–151.0
7	$C_{23}H_{39}ClN_2OS$	116.5–117.0
8	$C_{24}H_{41}ClN_2OS$	157.0–158.0

[a] Satisfactory analytical data (0.4% for C, H, and N) were reported for all compounds. Ed.

Betaines.—The quaternary ammonium bromides **4** and **5** were treated in methanol with 1 equiv of sodium hydroxide or methoxide, and the solvent was removed under vacuum at room temperature. The products, **7** and **8**, were dissolved in acetone with the minimum heating time, filtered from sodium bromide, and allowed to crystallize. Melting points are given in Table III.

2-(Ethylthiocarbamoyloxy)ethyldodecyldimethylammonium Hydroxide Inner Salt (9).—A solution of 12 g of **3** in 200 ml of water was passed through a column packed with 60 g of Dowex 1 X-8 (50–100 mesh) ion exchange resin in OH^- form, collecting 600 ml of eluate at *ca.* 6 ml/min. Crystallization began spontaneously and was completed in the refrigerator. The solid (7 g) was recovered by filtration and washed with ether: mp 118–119° dec; ir (Nujol) 1580 (C=N), 1122, 1054 cm^{-1}.

Anal. Calcd for $C_{19}H_{40}N_2OS$: C, 66.22; H, 11.70; neut equiv, 344.6. Found: C, 66.39; H, 11.75; neut equiv, 344.2.

2-(*N*-Ethyl-*S*-methylisothiocarbamoyloxy)ethyldodecyldimethylammonium Iodide (10).—One gram (2.9 mmol) of **9** was allowed to stand with 1.2 ml (19 mmol) of methyl iodide for 64 hr. At this time the 1577- and 1054-cm^{-1} bands typical of **9** were missing from the infrared spectrum, and there was no absorption at 1545 cm^{-1} as expected of an N-methylated product. The pale yellow liquid solidified in ether to 1.4 g of white solid, which was recrystallized from 6 ml of ethyl acetate: mp 65–69°; ir (Nujol) 1634 (C=N), 1178 cm^{-1}; nmr ($CDCl_3$) δ 2.45 (SCH_3).

Anal. Calcd for $C_{20}H_{43}IN_2OS$: C, 49.37; H, 8.91; I, 26.08. Found: C, 49.11; H, 8.91; I, 26.17.

Thermal Decomposition of 7.—Two grams of the betaine **7** in 25 ml of benzene was refluxed for 1 hr and filtered from a trace of insoluble material. Evaporation of the solvent left two liquid layers, the lighter of which had an infrared spectrum identical with that of dodecyldimethylamine. The heavier liquid, when chromatographed on silica gel (Eastman chromagram plate) with ether, showed two components at R_f 0.6 and 0.8. This liquid was stirred overnight with 100 ml of hexane. The crystals present in the morning were washed with more hexane and dried to 290 mg; this was the component of R_f 0.6. Recrystallization from CCl_4 and benzene–hexane gave colorless prisms: mp 124–125.5°; ir (KBr) 1490, 1468, 1440, 1320, 1291, 1163, 821 cm^{-1}. The ir and nmr data (Table I) lead to assignment of the compound as **3-*p*-chlorophenyl-1,3-oxazolidine-2-thione (14)**.

Anal. Calcd for C_9H_8NOSCl: C, 50.59; H, 3.77. Found: C, 50.53; H, 3.78.

The hexane solution obtained above was evaporated to a viscous oil which was induced to crystallize. Recrystallization from hexane gave 350 mg of white needles: mp 68–69°; ir (KBr) 1640 (broad), 1480, 1113, 1022, 839 cm^{-1}. The spectroscopic data lead to formulation of the compound as **p-chloro-*N*-1,3-oxathiolane-2-ylideneaniline (11)**.[12]

Anal. Calcd for C_9H_8NOSCl: C, 50.59; H, 3.77. Found: C, 50.59; H, 3.91.

Thermal Decomposition of 2-(Methylthiocarbamoyloxy)ethyltetradecyldimethylammonium Hydroxide Inner Salt.—In 25 ml of 0.2 *N* sodium methoxide solution was dissolved 2.2 g (5 mmol) of **2**. The solution was evaporated under vacuum at 30° and the product (admixed with sodium bromide) was characterized as a betaine by its infrared spectrum as compared to that of **9**: ir (Nujol) 1598, 1134, 1075, 1058, 1045, 995, 920 cm^{-1}.

Benzene (25 ml) was added and the mixture was refluxed for 20 min and then filtered hot from sodium bromide. After flash evaporation two liquid phases remained, of which the lighter was tetradecyldimethylamine (ir identification). Sufficient benzene was added to obtain homogeneity, and the solution was then analyzed by gc (4 ft × 0.25 in. column of Apiezon L on Chromosorb W, 178°, thermoconductivity detector). Integration gave a product composition of 78% oxazolidinethione **15** and 22% oxathiolane **12** (nmr identification).

Decomposition of the betaine **9** gave results which were essentially similar, but under the gc conditions used there was a partial overlap of peaks due to dodecyldimethylamine and the oxazolidinethione **16**, so the isomer ratio could not be determined.

Registry No.—**2**, 34524-02-2; **3**, 34523-95-0; **4**, 34916-01-3; **5**, 34916-02-4; **7**, 34916-03-5; **8**, 34916-04-6; **9**, 34916-05-7; **10**, 34934-79-7; **11**, 34916-06-8; **14**, 34916-07-9; 3-dimethylaminopropyl *p*-chlorothiocarbanilate, 34916-08-0; 3-dimethylaminopropyl *p*-chlorothiocarbanilate hydrochloride, 34916-09-1.

Acknowledgments.—The author wishes to thank Messrs. Michael Camara for assistance in the syntheses, Gilbert Suarez for the nmr spectra, Karl Kellenbach for the infrared spectra, and E. Emery for the mass spectra.

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