Di(phthalimidomethyl) ethylenebisdithiocarbamate was prepared from disodium ethylenebisdithiocarbamate; crude yield 92.5% (m.p. 188–191°).[20]

Anal. Calcd. for $C_{22}H_{18}N_4O_4S_4$: N, 10.56; S, 24.17. Found[18]: N, 10.20; S, 24.20.

Phthalimidomethyl dithiocarbamate was prepared from ammonium dithiocarbamate; crude yield 93%; m.p. 182-185°.[21]

Anal. Calcd. for $C_{10}H_8N_2O_2S_2$: N, 11.11; S, 25.42. Found: N, 10.71; S, 24.52.

Phthalimidomethyl p-toluenethiolsulfonate was prepared from sodium *p*-toluenethiolsulfonate; yield 56%; m.p. 158.5–160°.[17]

Anal. Calcd. for $C_{16}H_{13}NO_4S$: N, 4.03; S, 18.46. Found: N, 3.96; S, 18.56.

Ethyl phthalimidomethylmercaptoacetate was prepared from ethyl mercaptoacetate; yield 71%; m.p. 106–109°.[17]

Anal. Calcd. for $C_{13}H_{13}NO_4S$: N, 5.02; S, 11.48. Found: N, 5.08; S, 11.36.

N-(p-Chlorophenylthiomethyl)phthalimide was prepared from *p*-chlorobenzenethiol; yield 57%; m.p. 99–101°.[17]

Anal. Calcd. for $C_{15}H_{10}ClNO_2S$: N, 4.61; S, 10.46. Found: N, 4.55; S, 10.45.

2-Phthalimidomethylmercaptobenzothiazole was prepared from 2-mercaptobenzothiazole; yield 86%, m.p. 139–140°.[17]

Anal. Calcd. for $C_{16}H_{10}N_2O_2S_2$: N, 8.64; S, 19.77 Found: 8.46; S, 19.65.

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[20] Attempts to recrystallize this product resulted in excessive decomposition.

[21] Recrystallized from acetone and then from ethanol. Further recrystallization from ethanol yielded a product m.p. 184–186°, of lower sulfur analysis (Found: N, 10.70; S, 23.85).

β-(2-Thioxo-1-imidazolidyl)ethyl Isothiocyanate and Related Compounds

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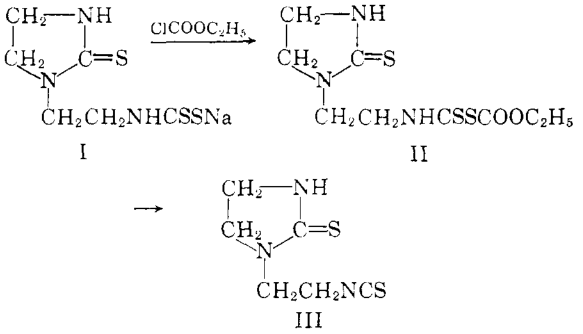
In the general method of preparation of isothiocyanates from monosubstituted dithiocarbamates and alkyl chlorocarbonates,[1-3] the intermediate alkoxycarbonyl dithiocarbamates[4] were not isolated because of their instability. The alkoxycarbonyl derivatives of alkylenebisdithiocarbamic acids, $(CH_2)_n(NHCSSCOOR)_2$ (type A), appear to be more stable than those of the alkyldithiocarbamic acids, R′NHCSSCOOR (type B). Most alkoxycarbonyl monosubstituted dithiocarbamates reported belong to the type A[5-7] and few of the type B have ever been isolated in pure state and characterized.[8] This paper reports the isolation of a solid ethoxycarbonyl β-(2-thioxo-1-imidazolidyl)ethyldithiocarbamate (II) and its conversion to β-(2-thioxo-1-imidazolidyl)ethyl isothiocyanate (III).



When sodium β-(2-thioxo-1-imidazolidyl)ethyldithiocarbamate (I) was allowed to react with ethyl chlorocarbonate in the cold, compound II was isolated as a crystalline solid. Decomposition of II in boiling ethanol yielded III and carbon oxysulfide which was identified by the formation of cyclohexylammonium cyclohexylthiocarbamate. Reaction of I with other chlorocarbonates such as 2-chloroethyl, isopropy *n*-butyl chlorocarbonate, at room temperature yielded III directly. The isothiocyanate III is a stable solid which can be recrystallized from alcohol. It reacts normally with amines to form the expected thioureas. The thiourea IV obtained from III and aniline is identical with that formed by the reaction of phenyl isothiocyanate and 1-β-aminoethyl-2-imidazolidinethione (V). Reaction of III with dimethylamine yielded 1-[β-(2-thioxo-1-imidazolidyl)ethyl]-3,3-dimethyl-2-thiourea (VI).

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(1) For a general discussion and early references, see Houben-Weyl, *Methoden der organischen Chemie*, vol. 9, p. 870, George Theime Verlag. Stuttgart, 1955.

(2) For a general procedure, see M. L. Moore and F. S. Crossley, *Org. Syntheses*, **Coll. Vol. III,** 599 (1955).

(3) For more recent work, see (a) M. G. Ettlinger and J. E. Hodgkins, *J. Am. Chem. Soc.*, **77,** 1831 (1955); (b) M. G. Ettlinger and J. E. Hodgkins, *J. Org. Chem.*, **21,** 204; 404 (1956); (c) N. M. Bortnick, L. S. Luskin, M. D. Hurwitz, and A. W. Rytina, *J. Am. Chem. Soc.*, **78,** 4358 (1956); (d) G. J. O'Neill and F. L. M. Pattison, *J. Am. Chem. Soc.*, **79,** 1956 (1957); (e) A. F. McKay, D. L. Garmaise, R. Gandry, H. A. Baker, G. Y. Paris, R. W. Kay, G. E. Just, and R. Schwartz, *J. Am. Chem. Soc.*, **81,** 4328 (1959); (f) G. D. Thorn and B. Huston, *Can. J. Chem.*, **37,** 2099 (1959).

(4) The alkoxycarbonyl dithiocarbamates have the general structure of $NH_2CSSCOOR$. According to Chemical Abstracts nomenclature these compounds should be named as the thioanhydrides of dithiocarbamic acid and monoalkylcarbonic acid.

(5) A. Y. Yakubovich and V. A. Klimova, *J. Gen. Chem. (U.S.S.R.)*, **9,** 1777 (1939).

(6) O. F. Williams, O. H. Johnson, and J. R. Graham, U. S. Pat. **2,796,376** (1957).

(7) C. P. Lo and W. E. Craig, U. S. Pat. **2,841,519** (1958).

(8) For example: (a) methoxycarbonyl β-hydroxyethyldithiocarbamate was reported by P. G. Sergeev and S. N. Ivanova, *J. Gen. Chem. (U.S.S.R.)*, **7,** 1495 (1937) [*Chem. Abstr.*, **32,** 2534 (1938)]; (b) ethoxycarbonyl phenyldithiocarbamate by O. E. Schultz and E. Barthold, *Arch. Pharm.*, **285,** 267 (1952) [*Chem. Abstr.*, **48,** 5129 (1954)].

Attempts to prepare VI by the reaction of dimethylthiocarbamoyl chloride with V failed to give the desired product, tetramethylthiuram monosulfide being formed instead.

β-(2-Thioxo-1-imidazolidyl)ethyl isothiocyanate (III) is a potent fungicide.[9] It has ED_{90} values of less than 5 ppm. when tested against *Monilinia fructicola* and *Stemphylium sarcinaeforme* by the slide-germination method.[10] It also shows excellent activity in controlling bean rust (*Uromyces appendiculatus*) and tomato late blight (*Phytophthora infestans*) in the greenhouse. The ethoxycarbonyl β-(2-thioxo-1-imidazolidyl)ethyldithiocarbamate also exhibits excellent *in vitro* fungitoxicity[11] but its instability prevents its practical application.

EXPERIMENTAL[12]

Sodium β-(2-thioxo-1-imidazolidyl)ethyldithiocarbamate trihydrate (I) was prepared from 1-β-aminoethyl-2-imidazolidinethione[13,14] according to Croxall and Lo.[14]

Ethoxycarbonyl β-(2-thioxo-1-imidazolidyl)ethyldithiocarbamate (II). A solution of I (38.5 g.) in water (50 ml.) was slowly added to a solution of ethyl chlorocarbonate (13 g.) in ethanol (100 ml.), the temperature being kept at 5–10°. After the addition was completed the mixture was stirred at room temperature for several hours. The white solid formed was collected, washed with water and then with ether. The air dried II weighed 16.5 g. (47%) and melted at 74–75°.

Anal. Calcd. for $C_9H_{15}N_3O_2S_3$: N, 14.3; S, 32.8. Found: N, 14.1; S, 32.5.

β-(2-Thioxo-1-imidazolidyl)ethyl isothiocyanate (III). (A) A mixture of II (10 g.), ethanol (50 ml.), and water (25 ml.) was heated under reflux on a steam bath. The gas evolved was identified as carbon oxysulfide as follows: The gas was passed into a solution of cyclohexylamine (10 g.) in acetone (100 ml.). The white solid formed was collected, washed with acetone and air dried. It weighed 1.2 g. and melted at 213–214°. A mixture of this and an authentic sample of cyclohexylammonium cyclohexylthiocarbamate (see below) melted at 214-215°.

After 2 hr. of refluxing the reaction solution was cooled in an ice bath. The solid which separated was worked up in the usual manner to give 4.6 g. (72%) of III melting at 131.5–133.5°. After recrystallization from aqueous ethanol it had a m.p. of 132–134°.

Anal. Calcd. for $C_6H_9N_3S_2$: N, 22.4; S, 34.2. Found: N, 22.0; S, 34.2.

(B) 2-Chloroethyl chlorocarbonate (28.6 g.) was slowly added to a suspension of I (48.6 g.) in acetone (250 ml.) with stirring. The mixture was stirred at room temperature overnight. The solution was filtered from the sodium chloride and concentrated under reduced pressure. The solid residue was recrystallized from chloroform to give 27 g. (72%) of III, m.p. and mixture m.p. with above, 132–134°.

Similar results were obtained when isopropyl and *n*-butyl chlorocarbonate were used in the above reaction.

1-[β-2-Thioxo-1-imidazolidyl)ethyl]-3-phenyl-2-thiourea (IV). (A) A mixture of III (4.5 g.), aniline (3 g.), and butanol-1 (15 ml.) was heated on a steam bath. The solid which separated was collected and recrystallized from butanol-1. The colorless IV had a m.p. of 176.5–177.5° and weighed 4.8 g. (71%).

Anal. Calcd. for $C_{12}H_{16}N_4S_2$: N, 20.0; S, 22.8 . Found: N. 19.9; S, 22.5.

(B) A mixture of phenyl isothiocyanate (13.5 g.), 1-(β-aminoethyl)-2-imidazolidinethione (14.5 g.), and water (200 ml.) was stirred at room temperature for 24 hr. There was obtained 26 g. (93%) of IV, m.p. and mixture m.p. with above 176–177°. Recrystallization from butanol-1 did not raise its m.p.

1-[β-(2-Thioxo-1-imidazolidyl)ethyl]-3,3-dimethyl-2-thiourea (VI). A mixture of III (5 g.), 40% dimethylamine solution (10 ml.), and water (10 ml.) was heated under reflux on a steam bath for 2 hr. The solid formed was collected and recrystallized from aqueous acetone (1:1) to give 5.8 g. (93%) of VI, m.p. 160–161°. Recrystallization from ethanol did not change the melting point.

Anal. Calcd. for $C_8H_{16}N_4S_2$: N, 24.2; S, 27.6. Found: N, 24.1; S, 27.3.

Reaction of dimethylthiocarbamoyl chloride with 1-(β-aminoethyl)-2-imidazolidinethione (V). A solution of V (35 g.) in water (100 ml.) was slowly added to a solution of dimethylthiocarbamoyl chloride (12.4 g.) in carbon tetrachloride (100 ml.). The mixture was stirred at room temperature for 4 hr. The carbon tetrachloride layer was separated and concentrated under reduced pressure. The residue was recrystallized from butanol-1 to give 11.5 g. of a yellow solid, m.p. 107–109°.[15] This was identified as tetramethylthiuram monosulfide by analysis and mixture m.p. with an authentic sample.

Anal. Calcd. for $C_6H_{12}N_2S_3$: N, 13.4; S, 46.2. Found: N, 13.3; S, 46.3.

Cyclohexylammonium cyclohexylthiocarbamate. Carbon oxysulfide from a cylinder[16] was passed into a cooled and stirred solution containing cyclohexylamine (99 g.) and acetone (800 ml.) until no precipitate was formed (about 1 hr.). The solid was collected, washed with acetone and air dried. The cyclohexylammonium cyclohexylthiocarbamate thus obtained weighed 116 g. (90%) and had a m.p. of 214–215°.[17]

Anal. Calcd. for $C_{13}H_{26}N_2OS$: N, 10.8; S, 12.4. Found: N, 10 7; S, 12.1.

Cyclohexylammonium cyclohexyldithiocarbamate. Replacement of carbon oxysulfide by carbon disulfide (76 ml.) in the above reaction gave a quantitative yield (137 g.) of cyclohexylammonium cyclohexyldithiocarbamate, m.p. 173–174°.[18] (The product melted at 139–140° when the bath was preheated to 120°.)

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(10) Published by the American Phytopathological Society, *Phytopathology*, **33**, 627 (1943).

(11) ED_{90} value 5–10 p.p.m. against both *M. fructicola* *S. sarcinaeforme*.

(12) All melting points are uncorrected.

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(14) W. J. Croxall and C. P. Lo, U. S. Pat. **2,577,700** (1951).

(15) The m.p. of tetramethylthiuram monosulfide was reported as 104°, J. von Braun and F. Stechele, *Ber.*, **36**, 2275 (1903).

(16) Obtained from Matheson Co., Inc.

(17) J. Parrod, *Compt. rend.*, **234**, 1062 (1952) reported this compound but gave no m.p.

(18) A. Skita and H. Rolfes, *Ber.*, **53**, 1242 (1920) reported a m.p. of 160°. We have observed that the melting point of cyclohexylammonium cyclohexyldithiocarbamate varied with the rate of heating. This indicates that it might have converted during the slow heating into 1,3-dicyclohexyl-2-thiourea which had a m.p. of 180–181°.