Alkyl or Aryl [*N*-(2-Substitutedthiol or dithiolcarbonato)ethyl]carbamates

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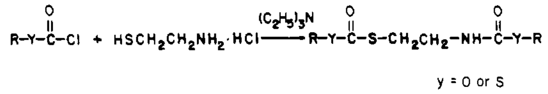
Phenyl, methyl, and *n*-butyl *N*-substituted carbamate and thiolcarbamate compounds and complex ureas derived from *n*-propyl and *n*-butyl *N*-substituted thiolcarbamates were synthesized and characterized. Yields, melting or boiling points, elemental analyses, and infrared data are reported.

IN A RESEARCH program designed to develop compounds with potential herbicidal activity, a series of complex carbamates and thiolcarbamates was synthesized by a published procedure (*1*).



n-Butyl and *n*-propyl *N*-substituted thiolcarbamates were treated further with silver nitrate and an amine to yield complex ureas (*1*).

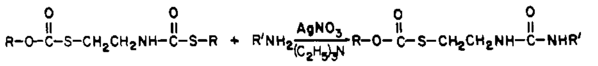


Table I shows the yields, melting or boiling points, and elemental analyses of compounds prepared. Characteristic infrared spectral data are recorded in Table II. The infrared spectrum of each compound was consistent with the desired structure.

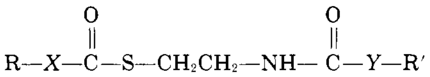
EXPERIMENTAL

Reactants for the carbamates and thiolcarbamates were obtained commercially and used without further purification. Melting points were taken on a Hershberg melting point apparatus and are uncorrected. Distillations were performed using conventional vacuum distillation techniques and equipment. Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer in a potassium bromide matrix for solids and between sodium chloride prisms for liquids.

PROCEDURE FOR PREPARATION OF COMPOUNDS 1, 2, AND 3

The procedure of Ferris and Schutz was used (*1*). To a suspension of 2-mercaptoethylamine hydrochloride (22.8 grams, 0.201 mole) in dry acetonitrile (100 ml.) was added triethylamine (60.8 grams, 0.603 mole). The mixture was added in portions, with stirring and cooling, to a solution of methyl, *n*-butyl, or phenyl chloroformate (0.40 mole) in dry acetonitrile (100 ml.), maintaining the temperature below 60° C. After the addition was complete, the mixture was allowed to stand for 1 hour; then it was poured into

Table I. Alkyl or Aryl N-[2-(Alkyl or Arylthiol and Dithiolcarbonato)ethyl] Carbamates and Thiolcarbamates and Ureas



$$R-X-\overset{O}{\overset{\|}{C}}-S-CH_2CH_2-NH-\overset{O}{\overset{\|}{C}}-Y-R'$$

Compounds	R	R′	*X*	*Y*	% Yield	B.P. or M.P., ° C.	Analyses[a] Calcd. Found %C	%H	%S
1 Methyl *N*-[2-(methylthiolcarbonato)ethyl]carbamate	CH_3-	CH_3-	O	O	31[b]	106–107/ 0.3 mm.	37.2 37.2	5.7 5.7	16.6 16.9
2 Phenyl *N*-[2-(phenylthiolcarbonato)ethyl]carbamate	C_6H_5-	C_6H_5-	O	O	48[c]	74–76	60.5 60.6	4.8 4.7	10.1 10.0
3 *n*-Butyl *N*-[2-(*n*-butyldithiolcarbonato)ethyl]thiolcarbamate	C_4H_9-	C_4H_9-	S	S	77[d]	Oil	46.6 47.1	7.5 7.8	31.1 31.1
4 1,3-Bis[2-(*n*-butyldithiolcarbonato)ethyl]urea	C_4H_9-	$C_4H_9S\overset{O}{\overset{\|}{C}}-SCH_2CH_2-$	S	N	17[c]	71.5–73.5	43.6 43.5	6.8 6.8	31.0 31.2
5 1-Allyl-3-[2-(*n*-butyldithiolcarbonato)ethyl]urea	C_4H_9-	$CH_2=CH-CH_2-$	S	N	13[e]	50–54	47.8 47.5	7.3 7.2	23.2 23.0
6 2-(Piperidinocarboxamido)ethylpropyldithiocarbonate	C_3H_7-		S	N	44	Oil[d,f]	49.6 49.9	7.6 7.8	22.0 22.2

[a] Analyses performed by Carol K. Fitz, Needham Heights, Mass. [b] n_D^{27} 1.4711. [c] Recrystallized from 95% ethanol. [d] Compound decomposed on attempted distillation. [e] Recrystallized from ether. [f] n_D^{29} 1.5301.

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Table II. Characteristic Infrared Absorption Bands of Carbamates, Thiolcarbamates, and Ureas

Compound No.	Alphatic C—H Stretch, Cm.$^{-1}$	C=O Stretch, Cm.$^{-1}$	C—O Stretch, Cm.$^{-1}$	Secondary Amide, Cm.$^{-1}$	N—H Stretch, Cm.$^{-1}$
1[a]	2810– 2900	1710	1150 (str) 1260 (str) 1190 (str)	1530[b]	3290
2[c]	2810–[d] 2860	1750	1155 (str) 1250 (str)	1525[b]	3290
3[e]	2900– 2810	1640 1740 (w)	1210 (str)	1515[b]	3290
4[c]	2810– 2900	1640 1740 (w)	1250 (str)	1560	3290
5[c]	2810-2900	1625 1750 (w)	1250 (str)	1570[f]	3290
6[a]	2810-2900	1640 1710 (str)	1210 (str) 1180 (str)	1530[b]	3310

[a] Liquid film. [b] A weak band near 1460 cm.$^{-1}$ is also present. [c] Nujul mull. [d] Aromatic C—H stretch at 3030 cm.$^{-1}$ appears also. [e] Cast film from chloroform. [f] A strong band near 1460 cm.$^{-1}$ is also present.

an ice-water mixture. The oil that separated was extracted with ether (3 x 200 ml.) and the combined ether extracts were dried over anhydrous sodium sulfate. Removal of the drying agent by filtration and concentration of the ether solution under diminished pressure yielded a crude product, which was purified as indicated in Table I. Compound 3 was prepared in the same manner from 2-mercaptoethylamine hydrochloride (93.1 grams, 0.825 mole), triethylamine (249 grams, 2.48 moles), and butyl chlorothiolformate (250 grams, 1.65 mole) in dry acetonitrile. It was isolated as a yellow oil. Attempted vacuum distillation of a small portion resulted in decomposition.

1,3-BIS[2-(*n*-BUTYLDITHIOLCARBONATO)ETHYL]UREA (*1*)

To a solution of *n*-butyl *N*-[2-(*n*-butyldithiolcarbonato)-ethyl]thiolcarbamate (30.9 grams, 0.10 mole), prepared as described for compound 1, and triethylamine (10.1 grams, 0.10 mole) in dry acetonitrile (50 ml.) was added a solution of silver nitrate (17.0 grams, 0.10 mole) in dry acetonitrile (25 ml.). Water (20 ml.) was added and the temperature rose from 35° to 55° C. After the reaction cooled to room temperature, acetonitrile (100 ml.) was added and the mixture was heated to boiling, then filtered hot. The filtrate was poured into an ice-water mixture; the solid was removed by filtration and purified as indicated in Table I.

1-ALLYL-3-[2-(*n*-BUTYLDITHIOLCARBONATO)ETHYL]UREA (*1*)

This compound was prepared in the same manner as above, through the silver nitrate addition. At this point, allyl amine (5.7 grams, 0.1 mole) was added and the mixture was allowed to stand until it came to room temperature. Additional acetonitrile (100 ml.) was added, and the mixture was heated to boiling and filtered hot. The filtrate was poured into an ice-water mixture; the solid was removed by filtration and purified as indicated in Table I.

2-(PIPERIDINOCARBOXAMIDO)ETHYL PROPYLDITHIOLCARBONATE (*1*)

This compound was prepared in the same manner as compound 5, from *n*-propyl *N*-[2-(*n*-propyldithiolcarbonato)ethyl]thiolcarbamate (42.2 grams, 0.15 mole, prepared similarly to compound 3), triethylamine (15.2 grams, 0.15 mole), silver nitrate (25.5 grams, 0.15 mole), and piperidine (12.8 grams, 0.15 mole). It was isolated as an orange oil, n_D^{29} 1.5301. Attempted vacuum distillation of a small portion resulted in decomposition.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Ferris, A.F., Schutz, B.A., *J. Org. Chem.* **29**, 201 (1964).

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CORRECTION

In the article "Syntheses and Reactions of Some 2,6-Disubstituted Piperidines" by C. G. Overberger and Siegfried Altscher [J. CHEM. ENG. DATA **14**, 266 (1969)], the following references related to the article were inadvertently omitted.

Henry, R. A., *J. Org. Chem.* **24**, 1363 (1959.)

Johnson, H. E., Crosley, D. G., *Ibid.*, **27**, 1298 (1962).

CORRECTION

In the article "Pressure-Volume-Temperature Behavior of a Mixture of Difluoromethane and Pentafluoromonochloroethane" by W. H. Mears, J. V. Sinka, P. F. Malbrunot, P. A. Meunier, A. G. Dedit, and G. M. Scatena [J. CHEM. ENG. DATA **13**, 344 (1968)], on page 345, in Equation 1, the second constant should read $B = -1247.326$. The minus sign was omitted in the original text.