pyrimidine sulfate (Compound 11). The acetimidate ester (20 g.; 0.8 mole) was added in portions to a stirred solution of 7 g. (0.08 mole) of *N*-methyl-1,3-diaminopropane in 100 ml. of ethanol at 5°. The mixture was stirred at 5° for 1 hr. and at 25° for 1 hr., after which it was vacuum-distilled to an oil. The oil was dissolved in a small volume of dilute hydrochloric acid, clarified by an ether extraction, and made alkaline. The base was extracted with ether, the ether solution was dried and stripped to an oil which solidified; yield, 11 g. (57%); m.p. 69–70° after recrystallization from heptane. The sulfate salt melted at 183–184° after recrystallization from isopropyl alcohol.

2-(p-Chloro-α-hydroxybenzyl)-2-imidazoline hydrochloride (Compound 10). This compound was prepared by essentially the same procedure used for compound 11, using ethylene diamine in place of *N*-methyl-1,3-diaminopropane.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE ORGANIC CHEMICALS DIVISION, MONSANTO CHEMICAL CO.]

The Synthesis of Organic Trithiocarbonates[1]

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Because of the interest of organic trithiocarbonates as biological toxicants and also as oil additives, fifty-five compounds of this class were synthesized which included symmetrical and unsymmetrical dialkyl, symmetrical diaryl, aryl alkyl, and aralkyl alkyl trithiocarbonates. Various synthetic routes for the preparation of these compounds were investigated.

Several members of the class of organic trithiocarbonates, particularly the symmetrical types, have been known for many years and various synthetic routes have been employed for their synthesis; however, no concentrated preparative study has been reported in the literature. Because of this fact and because of certain indications of biological activity[2-4] as well as utility as oil additives,[5] this work was undertaken.

Four methods for the preparation of trithiocarbonates were investigated. A synthetic route, which proved to be of great utility, involved the reaction of an aryl- or alkylthiol in the presence of base with an alkyl (Method A1) or aryl chlorodithioformate (Method A2). Forty-seven compounds were prepared by this general method. Thirty-five

$$\text{Method A } R_1SH + ClCSSR_2 \xrightarrow{NaOH} R_1SCSSR_2$$

$$\text{Method B } R_2SH + CS_2 \xrightarrow{KOH} KSCSSR_2 \xrightarrow{R,Br} R_1SCSSR_2$$

$$\text{Method C } 2RSH + CSCl_2 \xrightarrow{NaOH} RSCSSR$$

$$\text{Method D } R_1N_2^+Cl^- + KSCSSR_2 \longrightarrow R_1SCSSR_2$$

aryl alkyl trithiocarbonates, two aralkyl alkyl trithiocarbonates, and four unsymmetrical dialkyl trithiocarbonates were made by Method A1, and six aryl alkyl trithiocarbonates were made by Method A2.

Another route, which gave very good results, was the reaction of an alkylthiol with carbon disulfide in the presence of potassium hydroxide to form the potassium alkyl trithiocarbonate which subsequently reacted with an alkyl or aralkyl bromide to form the desired trithiocarbonate (Method B). Three aralkyl alkyl trithiocarbonates and two symmetrical dialkyl trithiocarbonates were prepared in this manner. In the case of diethyl trithiocarbonate (Table I, No. 13), the latter method gave a higher yield than when Method A1 was employed (75%, compared to 50%).

Three symmetrical diaryl trithiocarbonates were prepared by the reaction of thiophosgene with an aryl thiol (Method C) in the presence of base.

Only six of the trithiocarbonates reported in this paper have been previously described. Only diphenyl trithiocarbonate was prepared by the same method indicated in the literature. The dimethyl, diethyl, dibutyl, and diallyl trithiocarbonates were previously prepared by reaction of sodium trithiocarbonate, potassium trithiocarbonate or ammonium trithiocarbonate with an appropriate alkyl halide.

In an attempt to prepare ethyl *o*-nitrophenyl trithiocarbonate from *o*-nitrochlorobenzene and potassium ethyl trithiocarbonate by Method B, only bis(*o*-nitrophenyl) disulfide was obtained as determined by infrared analysis and melting point. Also an attempt was made to prepare methyl *p*-nitrophenyl trithiocarbonate by Method A1 using *p* - nitrobenzenethiol and methyl chlorodithioformate. Only bis(*p*-nitrophenyl) disulfide could

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(1) Presented at the Frederick F. Blicke Symposium of the Division of Medicinal Chemistry at the 138th National Meeting of the American Chemical Society, New York, N. Y., September, 1960.

(2) J. T. Bashour, U. S. Patent, **2,676,129** (1954); *Chem. Abstr.* **48**, 8472i (1954); Symmetrical dialkyl trithiocarbonates as nematocides.

(3) J. T. Bashour, U. S. Patent, **2,731,487** (1956); *Chem. Abstr.* **50**, 15583h (1956); Asymmetrical *t*-alkyl trithiocarbonates as insecticides and miticides.

(4) H. J. Renner, G. Schneider, and J. Weissflog, East Ger. Patent **15,431** (1958); *Chem. Abstr.* **54**, 2650f (1960). Symmetrical alkyl- or arylthiomethyl trithiocarbonates as insecticides.

(5) E. S. Blake, U. S. Patent, **2,396,487** (1946); *Chem. Abstr.* **40**, 2974[4] (1946).

TABLE I

TRITHIOCARBONATES

R_1SCSSR_2

No.	R_1	R_2	Empirical Formula	Yield, %	B.P.°, Mm. [M.P.°]	n_D^{25}	Method	Sulfur, % Calcd.	Sulfur, % Found	Chlorine, % Calcd.	Chlorine, % Found
1	*m*-Tolyl	Ethyl	$C_{10}H_{12}S_3$	50	135–139 (0.8)	1.6616	A1	42.1	42.9		
2	*m*-Tolyl	Methyl	$C_9H_{10}S_3$	73	124–127 (0.7)	1.6824	A1	44.9	44.5		
3	*o*-Tolyl	Ethyl	$C_{10}H_{12}S_3$	59	137–139 (0.74)	1.6662	A1	42.1	42.5		
4	*p*-Tolyl	Ethyl	$C_{10}H_{12}S_3$	65	169–173 (2.7)	1.6644	A1	42.1	41.7		
5	*p*-Chlorophenyl	Ethyl	$C_9H_9ClS_3$	58	149–150 (0.67)	1.6823	A1			14.3	15.0
6	Pentachlorophenyl	Ethyl	$C_9H_5Cl_5S_3$	46	[112–115][a]	—	A1	24.88	24.32	45.9	44.7
7	*o*-Chlorophenyl	Ethyl	$C_9H_9ClS_3$	54	150–153 (0.7)	1.6838	A1			14.3	15.0
8	*m*-Chlorophenyl	Ethyl	$C_9H_9ClS_3$	58	150–153 (0.85)	1.6808	A1			14.3	14.6
9	*t*-Butyl	Ethyl	$C_7H_{14}S_3$	27	82–84 (0.57)	1.5988	A1	49.5	51.0		
10	1-Naphthyl	Ethyl	$C_{13}H_{12}S_3$	93	[75–77][b]	—	A1	36.4	36.7		
11	1-Naphthyl	Methyl	$C_{12}H_{10}S_3$	90	[40–41][c]	—	A1	38.4	38.0		
12	2-Naphthyl	Ethyl	$C_{13}H_{12}S_3$	100	Not distilled	—	A1	36.4	36.1		
13[d]	Ethyl	Ethyl	$C_6H_{10}S_3$	77	90.5 (2.6)	1.6233	B[e]	—	—		
14	Ethyl	Methyl	$C_4H_8S_3$	58	92–94 (5.0)	1.6465	A1	63.2	63.9		
15[f]	Methyl	Methyl	$C_3H_6S_3$	71	86–88 (5.4)	1.6760	A1	—	—		
16	Phenyl	Ethyl	$C_9H_{10}S_3$	58	129–130 (0.6)	1.6790	A1	44.9	44.7		
17	*p*-Tolyl	Methyl	$C_9H_{10}S_3$	75	128.5–129 (0.31)	1.6870	A1	44.9	44.6		
18	*p*-Chlorophenyl	Methyl	$C_8H_7ClS_3$	80	137–140 (0.5)	—	A1			15.1	15.1
19	Phenyl	Methyl	C_8HlS_3	68	118–120 (0.4); [37.5][g]	—	A1	48.0	48.2		
20	*o*-Tolyl	Methyl	$C_9H_{10}S_3$	85	125–126 (0.45); [48][g]	—	A1	44.9	45.3		
21	*p*-Methoxyphenyl	Ethyl	$C_{10}H_{12}OS_3$	36	149–153 (0.24)	1.6704	A1	39.4	40.3		
22	*p*-Methoxyphenyl	Methyl	$C_9H_{10}OS_3$	62	[77.5–8][h]	—	A1	41.8	42.5		
23	Butyl	*m*-Tolyl	$C_{12}H_{16}S_3$	28	139–142 (0.18)	1.6219	A2	37.5	36.5		
24	Isopropyl	*m*-Tolyl	$C_{11}H_{14}S_3$	19	134–137 (0.2)	1.6337	A2	39.7	38.5		
25	*t*-Butyl	*m*-Tolyl	$C_{12}H_{16}S_3$	7	[107.5–108.5][g]	—	A2	37.5	37.0		
26	Butyl	*p*-Tolyl	$C_{12}H_{16}S_3$	31	157–159 (0.65)	1.6320	A2	37.5	36.2		
27	Pentyl	*p*-Tolyl	$C_{13}H_{18}S_3$	41	161–163 (0.82)	1.6091	A2	35.6	34.5		
28	*p*-Ethoxyphenyl	Ethyl	$C_{11}H_{14}OS_3$	51	[56.5–57.5][g]	—	A1	37.2	37.5		
29	Benzyl	Ethyl	$C_{10}H_{12}S_3$	61	150–152 (0.95)	1.6579	A1	42.1	41.8		
30[j]	Phenyl	Phenyl	$C_{13}H_{10}S_3$	39	[83–85][i]	—	C	—	—		
31	*p*-Ethoxyphenyl	Methyl	$C_{12}H_{12}OS_3$	71	[65–66][i]	—	A1	39.4	39.3		
32[k]	Benzyl	Methyl	$C_9H_{10}S_3$	69	139–141 (0.66)	—	A1	—	—		
33	*m*-Methoxyphenyl	Methyl	$C_9H_{10}OS_3$	82	[59.5–60.5][i]	—	A1	41.8	42.2		
34	*m*-Methoxyphenyl	Ethyl	$C_{10}H_{12}OS_3$	48	[63–64][i]	—	A1	39.4	39.9		
35	*m*-Ethoxyphenyl	Methyl	$C_{10}H_{12}OS_3$	63	[34–35][i]	—	A1	39.4	39.3		
36	*m*-Ethoxyphenyl	Ethyl	$C_{11}H_{14}OS_3$	66	157–160 (0.7)	1.6417	A1	37.2	36.5		
37	Pentyl	*m*-Tolyl	$C_{13}H_{18}S_3$	33	147–149 (0.55)	1.6327	A2	35.6	34.1		
38	Pentachlorophenyl	Methyl	$C_8H_3Cl_5S_3$	78	[133–134][b]	—	A1			47.6	47.4
39[l]	Butyl	Butyl	$C_9H_{18}S_3$	78	105.5 (0.32)	1.5723	B	—	—		
40	2,5-Xylyl	Ethyl	$C_{11}H_{14}S_3$	62	134–135 (0.64)	1.6532	A1	39.7	38.9		
41	3,4-Xylyl	Ethyl	$C_{11}H_{14}S_3$	70	139–141 (0.43)	1.6622	A1	39.7	40.4		
42	2,4-Xylyl	Ethyl	$C_{11}H_{14}S_3$	58	134–135 (0.55)	1.6557	A1	39.7	39.8		
43	*m*-Methylbenzyl	Ethyl	$C_{11}H_{14}S_3$	70	132 (0.31)	1.6485	B	39.7	40.7		

TABLE I (*Continued*)

No.	R_1	R_2	Empirical Formula	Yield, %	B.P.°, Mm. [M.P.°]	n_D^{25}	Method	Sulfur, % Calcd.	Sulfur, % Found	Chlorine, % Calcd.	Chlorine, % Found
44	3,4-Xylyl	Methyl	$C_{10}H_{12}S_3$	73	134.5–135 (0.4)	1.6804	A1	42.1	42.1		
45	2,3-Xylyl	Ethyl	$C_{11}H_{14}S_3$	66	136.5 (0.68)	1.6603	A1	39.7	39.0		
46	2,6-Xylyl	Ethyl	$C_{11}H_{14}S_3$	53	134–135 (0.73)	1.6518	A1	39.7	39.8		
47	2,5-Xylyl	Methyl	$C_{10}H_{12}S_3$	53	126–127.5 (0.57)	1.6732	A1	42.1	42.8		
48	2,3-Xylyl	Methyl	$C_{10}H_{12}S_3$	65	133 (0.56)	1.6807	A1	42.1	42.2		
49	2,6-Xylyl	Methyl	$C_{10}H_{12}S_3$	54	127 (0.57)	1.6732	A1	42.1	41.3		
50	2,4-Xylyl	Methyl	$C_{10}H_{12}S_3$	61	133–134 (0.55)	1.6755	A1	42.1	42.8		
51	*p*-Chlorobenzyl	Ethyl	$C_{10}H_{11}ClS_3$	62	146.5–148 (0.45)	1.6618	B			13.5	12.4
52	*m*-Chlorobenzyl	Ethyl	$C_{10}H_{11}ClS_3$	34	145 (0.45)	1.6523	B			13.5	11.6
53[m]	Allyl	Allyl	$C_7H_{10}S_3$	60	77–78 (0.3)	1.6360	B	—	—		
54	*p*-Chlorophenyl	*p*-Chlorophenyl	$C_{13}H_8Cl_2S_3$	63	[128–132][n]	—	C	29.0	28.2		
55	*m*-Tolyl	*m*-Tolyl	$C_{15}H_{14}S_3$	60	[69–71][n]	—	C	33.1	33.3		

[a] Recrystallized from acetone. [b] Recrystallized from ethyl acetate. [c] Recrystallized from petroleum ether (b.p. 60–70°). [d] E. Wertheim, *J. Am. Chem. Soc.*, **48**, 828 (1926); b.p. 102–104° (7.0). [e] Method A1 gave a 50% yield. [f] Ref. d; b.p. 110–111° (18.0). [g] Recrystallized from *n*-hexane. [h] Recrystallized from methanol. [i] Recrystallized from petroleum ether (36.5–51.5°). [j] W. Autenrieth and H. Hefner, *Ber.*, **58**, 2154 (1925); m.p. 95° out of alcohol. [k] E. S. Blake and J. R. Durland, U. S. Patent 2,547,150 (1951); *Chem. Abstr.*, **45**, 6422b (1951). No physical properties given [l] H. Hasegawa, *J. Chem. Soc. Japan*, **73**, 728 (1952); *Chem. Abstr.* **48**, 1964g (1953); b.p. 125–127° (4.0). [m] A. Husemann, *Ann.*, **126**, 297 (1863); b.p. 170–175°. [n] Recrystallized from petroleum ether (b.p. 86–100°).

be isolated as a reaction product. In the above two experiments air was not excluded from the reaction.

To attempt the preparation of ethyl *m*-nitrophenyl trithiocarbonate, a solution of *m*-nitrophenyldiazonium chloride reacted with potassium ethyl trithiocarbonate (Method D). A dark red undistillable oil of undetermined structure was obtained which gave a sulfur analysis equivalent to one-half of theory. (Calcd: S, 37.1. Found, 18.7). Infrared analyses did not aid in assigning a structure for the product.

The synthesis of ethyl *m*-tolyl trithiocarbonate, which was prepared by Method A1, was attempted by two alternate methods for comparative purposes. Reaction of ethyl bromide with a solution of potassium *m*-tolyl trithiocarbonate generated from *m*-toluenethiol, carbon disulfide, and potassium hydroxide did not give the product. The reaction of a solution of *m*-tolyldiazonium chloride and sodium ethyl trithiocarbonate (Method D) gave a low yield (23.6%) of impure product as determined by boiling point (132–137° at 0.38 mm.; by Method A1, 135–139° at 0.8 mm.), refractive index (n_D^{25} 1.6462; by Method A1, 1.6616), and infrared analysis.

The sulfur analyses on several of these trithiocarbonates are not in close agreement with the theoretical values; however, the infrared spectra appear to indicate the materials to be essentially pure. Simple acyclic trithiocarbonates are reported to show absorption at 9.45 to 9.50 μ, which is attributed to the C=S stretching frequency.[6] Cyclic trithiocarbonates appear to show the C=S stretching band in the range of 9.25 to 9.35 μ.[7-9] All of our trithiocarbonates exhibited multiple high-intensity maxima in and near these regions. Representative examples are given in the following table. Compounds 1,8,13,21,39,47, and 53 were run as capillary films. Compounds 19,20,28, and 38 were run as 5% carbon disulfide solutions.

No.	Trithiocarbonate	ν_{max} (microns)
13	Diethyl	9.28, 9.57, 9.80
39	Dibutyl	9.24, 9.58
53	Diallyl	9.45
19	Phenyl methyl	9.34, 9.55, 9.81
20	*o*-Tolyl methyl	9.30, 9.57
47	2,5-Xylyl methyl	9.28, 9.60
38	Pentachlorophenyl methyl	9.27, 9.46
1	*m*-Tolyl ethyl	9.26, 9.33, 9.45, 9.79
8	*m*-Chlorophenyl ethyl	9.28, 9.42, 9.76
21	*p*-Methoxyphenyl ethyl	9.32, 9.58
28	*p*-Ethoxyphenyl ethyl	9.31, 9.45, 9.62, 9.80

(6) R. Mecke, R. Mecke, and A. Luttringhaus, *Z. Naturforsch.*, **10b**, 367 (1955).

(7) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3871 (1955).

(8) J. I. Jones, W. Kynaston, and J. L. Hales, *J. Chem. Soc.*, 614 (1957).

(9) S. M. Iqbal and L. N. Owen, *J. Chem. Soc.*, 1030 (1960).

TABLE II

AROMATIC THIOLS

No.	Name	Empirical Formula	Yield, %	B.P.°	(Mm.)
1	*o*-Chlorobenzenethiol[a]	C_6H_5ClS	62	82–4	(9.2)
2	*m*-Chlorobenzenethiol[b]	C_6H_5ClS	54	61–4	(2.4)
3	1-Naphthalenethiol[c]	$C_{10}H_8S$	41	85–8	(0.27)
4	*p*-Ethoxybenzenethiol[d]	$C_8H_{10}OS$	68	77–8	(1.0)
5	*m*-Methoxybenzenethiol[e]	C_7H_8OS	29	74.5	(2.0)
6	*m*-Ethoxybenzenethiol[f]	$C_8H_{10}OS$	21	87.5	(3.5)
7	2,5-Xylenethiol[g]	$C_8H_{10}S$	52	48–9	(0.62)
8	3,4-Xylenethiol	$C_8H_{10}S$	63	76.5–7	(3.6)
9	2,4-Xylenethiol[h]	$C_8H_{10}S$	72	80.5	(9.0)
10	2,3-Xylenethiol	$C_8H_{10}S$	41	121–22.5	(38)
11	2,6-Xylenethiol	$C_8H_{10}S$	33	104	(29)

[a] P. Friedlander and F. Mauthner, *Chem. Zentr.* II, 1176 (1904); b.p. 205–206°. [b] G. Daccomo, *Jahresbericht uber die Fortschritte der Chemie*, 1375 (1891); *Beilstein*, **6**, 326 (1923); b.p. 205–207. [c] E. Bourgeois, *Rec. trav. chim.* **18**, 444 (1899); b.p. 161° (20 mm.) [d] G. Lagai, *Ber.* **25**, 1838 (1892); b.p. 232.5°. [e] K. Fries and E. Engelbertz, *Ann.* **407**, 211 (1915); b.p. 112–114° (20 mm.). [f] A. Delisle and G. Lagai, *Ber.* **23**, 3394 (1890); b.p. 238–239°. [g] L. Gattermann, *Ber.*, **32**, 1147 (1899); b.p. 205–206°. [h] Ref. *g.*; b.p. 207–208°.

Eleven of the intermediate arylthiols were synthesized from their corresponding aniline through the diazonium chloride and corresponding ethylxanthate (Method E) by modifications of a known procedure.[10] Many of these compounds are known: but have been previously prepared by reduction of their corresponding sulfonyl chlorides. The infrared analyses of these intermediate thiols indicated that they were essentially pure materials.

The preparations of the intermediate chlorodithioformates were accomplished by modifications of procedures described in the literature.[11,12] These involve the reaction of methane- or ethanethiol with thiophosgene (Method F) or the reaction of the sodium salt of an arylthiol with thiophosgene (Method G).

EXPERIMENTAL

Preparation of trithiocarbonates. Method A1. The alkyl-, aryl-, or aralkylthiol (0.2 mole) was dissolved in 200 ml. of benzene or ether and a solution of 8.0 g. (0.2 mole) of sodium hydroxide in 8 ml. of water was added at 25°. After stirring for 2 hr., methyl or ethyl chlorodithioformate (0.2 mole) was then added dropwise to the above mixture at 25–30° over a period of 0.5 hr. The reaction mixture was stirred 16 hr. Water (100 ml.) was added to dissolve the precipitated salt; and the ether or benzene layer was separated, washed twice with 100 ml. of water, and dried over magnesium sulfate. After removal of the solvent, the product was fractionated under reduced pressure or recrystallized from an appropriate solvent.

Method A2. The same procedure was employed as described in Method A1 except the sodium salt of an alkylthiol reacted with *M*-tolyl or *p*-tolyl chlorodithioformate.

Method B. To a solution of 16.8 g. (0.3 mole) of potassium hydroxide in 200 ml. of absolute ethanol, the thiol (0.3 mole) was added dropwise over 0.5 hr. with stirring and cooling at 15–20°. After stirring for an additional 0.5 hr., carbon disulfide (22.8 g., 0.3 mole) was then added maintaining the temperature at 15–20°. Subsequently, the reaction mixture was stirred for 3 hr. at 25°. A small crystal of iodine and the alkyl or aralkyl bromide was added dropwise over a period of 2.5 hr. allowing the temperature to rise. The reaction mixture was then refluxed for 8 hr., cooled to 25° and poured into 1 l. of ice water. The aqueous mixture was extracted twice with 200 ml. of ether. The combined ether extracts were washed with 150 ml. of water and dried over magnesium sulfate. After the solvent was removed, the product was distilled.

Method C. The arylthiol (0.4 mole) was dissolved in 200 ml. of benzene and a solution of 16 g. (0.4 mole) of sodium hydroxide in 16 ml. of water was added at 25°. After stirring for 2 hr., thiophosgene (23 g., 0.2 mole) was added dropwise to the mixture at 40–45° and then stirred for 2 hr. at 25°. The workup procedure was the same as described in Method A1.

Method D. The procedure for preparation of the substituted aromatic diazonium chloride solution was the same as given in the preparation of the aromatic thiols (Method E). A solution of potassium or sodium ethyl trithiocarbonate was generated as indicated in Method B. The cold diazonium chloride solution was added slowly over a 3-hr. period to the solution of potassium or sodium ethyl trithiocarbonate (10% excess) in water at 40–45°. After the addition was complete, the mixture was stirred for an additional 0.5 hr. The oily layer was separated, and the aqueous layer extracted with ether. The combined oil and ether extracts were washed with water. The ether solution was dried over magnesium sulfate, and the solvent removed. The product was distilled or recrystallized as was found appropriate.

Preparation of aromatic thiols. Method E. The substituted aniline (1.0 mole) was added slowly to 200 g. of crushed ice and 200 g. of concd. hydrochloric acid. The resulting mixture was cooled to 0° and a cold solution of sodium nitrite (73.3 g., 1.06 moles) in 167 ml. of water was slowly added keeping the temperature below 4°. This cold diazonium solution was then added slowly over a 3-hr. period to a solution of potassium ethylxanthate (186.6 g., 1.17 moles) in 240 ml. of water warmed to 40–45°. After the addition was complete, the reaction mixture was stirred for an additional 0.5 hr. The red oily layer was separated, and the aqueous layer extracted twice with 200 ml. of ether. The combined oil and extracts were washed twice with 200 ml. of water. The ether solution was then dried over calcium chloride and the solvent was removed leaving a red-brown liquid product which was the xanthate.

The resulting xanthate and 600 ml. of 95% ethanol was stirred and heated to reflux and then maintained at reflux by the slow addition of 233 g. (4.0 moles) of potassium hydroxide

(10) D. S. Tarbell and D. K. Fukushima, *Org. Syntheses*, **27**, 81 (1947).

(11) F. Arndt, E. Milde, and G. Eckert, *Ber.*, **56**, 1976 (1923).

(12) J. Houben and K. M. L. Schultz, *Ber.*, **44**, 3232 (1911).

pellets. After the addition was complete, the reaction mixture was stirred at reflux for an additional 10 hr. and then cooled to 25°. The mixture was poured very slowly into a beaker containing 420 g. of concd. hydrochloric acid and 600 g. of ice. The resulting solution was extracted three times with 200 ml. of benzene, the combined benzene extracts dried over magnesium sulfate, and the solvent removed. The product was then fractionated.

Preparation of chlorodithioformates. Method F. A solution of the alkylthiol (0.5 mole) in 75 ml. of benzene at 10° was added dropwise to a stirred solution of thiophosgene (62.1 g., 0.54 mole) in 75 ml. of benzene maintaining the temperature at 10°. After all of the thiol solution was added, the reaction mixture was stirred 16 hr. in an ice bath. The solvent was removed and the product fractionated.

Ethyl chlorodithioformate: b.p., 63° (5.8 mm.), yield, 65%. Lit.,[12] b.p. 74–75° (15 mm.)

Methyl chlorodithioformate: b.p., 156–159°, yield, 66%. Lit.,[11] b.p. 50–52° (15 min.)

Method G. The substituted arylthiol (0.8 mole) was added to a stirred solution of 32 g. (0.8 mole) of sodium hydroxide in 32 ml. of water. Thiophosgene (94.9 g., 0.84 mol.) was dissolved in 200 ml. of benzene. The sodium thiophenolate slurry was slowly added to the thiophosgene solution which was stirred and maintained at 10–15°. After the addition was complete, the reaction mixture was allowed to rise to 25° and stirred for 3 hr. The salt was filtered and the benzene filtrate was washed twice with 150 ml. of water and then dried over magnesium sulfate. The solvent was removed and the product fractionated.

m-Tolyl chlorodithioformate: b.p. 93° (0.5 mm.), yield, 74%.

Anal. Calcd. for $C_8H_7ClS_2$: Cl, 17.5. Found: Cl, 18.4.

p-Tolyl chlorodithioformate: b.p. 102–104° (1.0 mm.), yield, 62%.

Anal. Calcd. for $C_8H_7ClS_2$: Cl, 17.5. Found: 18.2.

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[CONTRIBUTION FROM THE ORGANIC CHEMICAL RESEARCH SECTION, LEDERLE LABORATORIES DIVISION, AMERICAN CYANAMID CO.]

The Rearrangement and Cyclization of Ethyl *N*-(Methylaminoalkyl)carbanilates and 1,1-Dimethyl-3-methylaminoalkyl-3-phenylureas[1]

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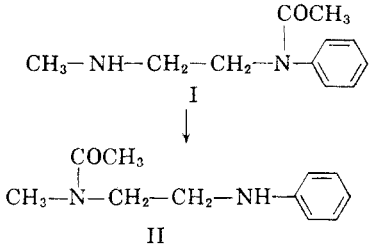
When ethyl *N*-(2-methylaminoethyl)carbanilates and 1,1-dimethyl-3-(2-methylaminoethyl)-3-phenylureas are heated, 1-methyl-3-phenyl-2-imidazolidinones are obtained as the major product. Molecular rearrangement also occurs, and ethyl *N*-methyl-*N*-(2-anilinoethyl)carbamates and 1-anilinoethyl-1,3,3-trimethylureas may be isolated in low yield. Related reactions are discussed.

We have recently described[2] intramolecular *N* → *N'* acyl migrations within a series of *N*-[2-(and 3) *sec*-aminoalkyl]anilides. For example, *N*-(2-methylaminoethyl)acetanilide (I) rearranges slowly on standing at room temperature and rapidly on heating to *N*-(2-anilinoethyl)-*N*-methylacetamide (II).



These observations prompted us to determine if the carbethoxy and dimethylcarbamoyl moieties in a series of related compounds would also migrate.

Ethyl *N*-(methylaminoalkyl)carbanilates and 1,1-dimethyl-3-(methylaminoalkyl)-3-phenylureas were prepared by the catalytic debenzylation of the appropriate *tert*-benzylamines. Samples of these bases were heated and the course of the reaction was followed by frequent determinations of the refractive indices and infrared absorption spectra, and by isolation of the products.

When ethyl *N*-(2-methylaminoethyl)carbanilate (IIIa) was heated for eight hours at 160–165°, both rearrangement and cyclization occurred. Crystalline 1-methyl-3-phenyl-2-imidazolidinone (IV) was isolated in 59% yield and ethyl *N*-(2-anilinoethyl)-*N*-methylcarbamate (Va) was obtained in 25% yield. A second sample heated at 130–135° for two and a half hours resulted in a 39% yield of IV, and examination of the mother liquor indicated that the reaction was incomplete. The index of refraction and infrared spectrum of Va were identical to those of the product prepared by the reaction of ethyl chloroformate with *N*-methyl-*N'*-phenylethylenediamine (VI).

Other carbanilates having a two carbon chain between the nitrogen atoms behaved similarly. When ethyl *m*-methoxy-*N*-(2-methylaminoethyl)-carbanilate was heated for five hours at 200–205°, 1-

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(2) W. B. Wright, Jr., H. J. Brabander, and R. A. Hardy, Jr., *J. Org. Chem.*, **26**, 2120 (1961).