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Thiolcarbamates. Preparation and Molar Refractions[1]

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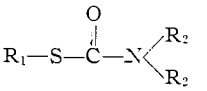
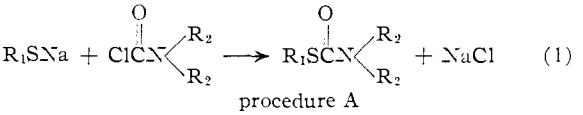
The synthesis of 265 thiolcarbamates is described and the physical data of the compounds are tabulated. An improved method for the preparation of pure anhydrous sodium alkylmercaptides is also presented. Bond refractions have been assigned to allyl, methallyl, crotyl, 2-propynyl, cyanomethyl, halogenoallyl, 3-chloro-2-butenyl, 3-chloropropyl, methoxymethyl, ethoxyethyl, methylmercaptomethyl, morpholinyl, piperidyl, 2-methylpiperidyl, pyrrolidyl and cyclohexyl groups. These values give much better agreement with the observed molar refractions of thiolcarbamates than the bond refractions which are presently available. Some observations on the effect of structure on molar refraction have been made with the aid of structural isomers. A *t*-butyl group attached to the sulfur atom of the thiolcarbamate molecule increases the average molar refraction by 0.25 cc. in comparison to the other butyl isomers. A *trans*-3-chloroallyl group increases the average molar refraction by 0.5 cc. over a 2-chloroallyl group when it is attached to the sulfur atom, but an average increase of only 0.3 cc. is observed when this group is attached to the nitrogen atom. A similar, but smaller effect, is noted when a crotyl group is compared to a methallyl group.

Ethyl di-*n*-propylthiolcarbamate has been shown to have outstanding effectiveness and selectivity for the control of annual grasses and many broadleaved weeds. To extend our knowledge on the herbicidal activity of the thiolcarbamates, we synthesized several hundred analogs. The methods of synthesis and properties of some of these thiolcarbamates and their intermediates are presented here.

The synthetic routes which were employed depended on the availability of the starting material and the structure of the desired thiolcarbamate. When R_1 and R_2 were saturated alkyl, an anhydrous

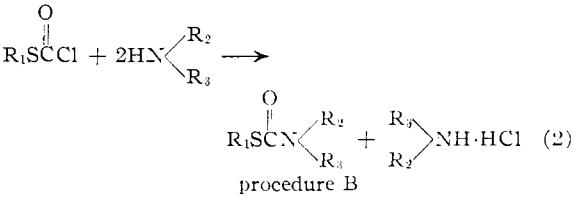


alkoxide-free sodium alkylmercaptide was treated with the appropriate dialkylcarbamoyl chloride in refluxing xylene, forming the thiolcarbamate in yields of 30–90% (eq. 1). Table I summarizes the yields and properties of the thiolcarbamates prepared by procedure A.



procedure A (1)

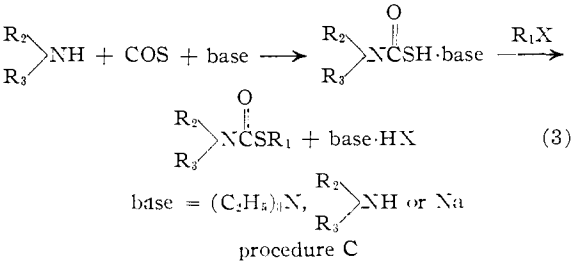
When R_1 was saturated alkyl or chloroalkyl, R_2 was hydrogen, saturated or unsaturated alkyl and R_3 was saturated or unsaturated alkyl, the procedure of Riemschneider and Lorenz[2] was followed (eq. 2).



procedure B (2)

In this procedure, the amine was treated with an alkyl chlorothiolformate in ether. The yields obtained by this method were in the range of 53–84%. Table II summarizes the properties and yields of the thiolcarbamates prepared by procedure B.

When R_1 was an allyl, methallyl, crotyl, 2-propynyl, cyanomethyl, 3-chloro-2-butenyl, halogenoallyl, alkoxyalkyl or methylmercaptomethyl group and R_2 and R_3 were saturated alkyl or any of the R_1 groups, the following procedure was used: Carbonyl sulfide was passed into a solution of the secondary amine in the presence of a base and the thiolcarbamate salt which was formed was then caused to react with the R_1 halide to yield the thiolcarbamate as shown in equation 3.

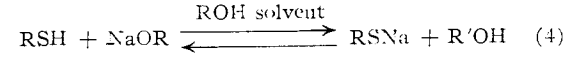


procedure C (3)

Although the yields of procedure C (13–84% range) were inferior to the yields obtained in procedures A and B, the ready accessibility of the R_1 halides made this method the most attractive for this group of thiolcarbamates. Table III summarizes the properties and yields of the thiolcarbamates prepared by procedure C. Dialkylammonium thiolcarbamates have been synthesized by several workers,[3] but they did not react these salts further to form thiolcarbamate esters. Batty, Jackson and Jeffers have reported the formation of thiolcarbamate esters from sodium thiolcarbamates prepared from primary amines.[4]

In Table IV are listed the yields and properties of thiolcarbamates prepared from heterocyclic amines such as pyrrolidine, piperidine, 2-methylpiperidine and morpholine. Procedures A and C were used for the preparation of these compounds.

The usual method of preparing an anhydrous sodium alkylmercaptide is to treat the mercaptan in anhydrous alcohol with the corresponding sodium alkoxide[5] (eq. 4). However, this is an equilibrium



(4)

(1) Presented in part before the Agriculture and Food Chemistry Division of the American Chemical Society at San Francisco, Calif., April 13–18, 1958.

(2) R. Riemschneider and O. Lorenz, *Monatsh. Chem.*, **84**, 518 (1953).

(3) C. Hagellock, *Chem. Ber.*, **83**, 258 (1956); H. L. Klopping and G. J. M. van der Kerk, *Rec. trav. chim.*, **70**, 917 (1951); J. Parrod, *Compt. rend.*, **234**, 1062 (1952).

(4) J. W. Batty, H. E. Jackson and F. G. Jeffers, British Patent 599,178 (1948).

(5) H. Gilman, "Organic Chemistry, An Advanced Treatise," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 846; D. C. Noller and H. W. Post, *J. Org. Chem.*, **17**, 1393 (1952).

reaction and depending on the acidity of the mercaptan relative to the alcohol, there is always more or less sodium alkoxide together with the sodium mercaptide. This equilibrium can be shifted to the right by removal of the alcohol, but if the mercaptan boils lower than the alcohol, the equilibrium is shifted toward the left during distillation. Hence, during the preparation of thiolcarbamates by procedure A, the yields of desired product are lowered by the formation of carbamates when low boiling mercaptans are employed.

Plieninger[6] prepared sodium methylmercaptide by this procedure and stated that the final filtered salt still contained methanol. When the sodium alkoxide procedure was used in this Laboratory for the preparation of ethyl di-*n*-propylthiolcarbamate, compound 18, by procedure A in which methanol was the alcohol and xylene was the inert solvent, a 24% yield of methyl di-*n*-propylcarbamate was obtained in addition to a 76% yield of the desired thiolcarbamate. This by-product most probably resulted from reaction of the di-*n*-propylcarbamoyl chloride with sodium methoxide or methanol entrapped in the sodium ethylmercaptide crystals.

In order to eliminate the tedious procedure and by-products encountered in the above method, it would be desirable to treat the alkyl mercaptan with metallic sodium in an inert solvent. If a small lump of clean sodium is added to a primary alkyl mercaptan in anhydrous xylene at 30°, there is hardly any evidence of reaction. On the other hand, it has been found that sodium dispersion in xylene containing particles of sodium in the range of 20–200 μ reacts almost instantaneously at 30–35° with most primary alkyl mercaptans except methyl mercaptan. The reaction with this mercaptan proceeds *via* an induction period and might become violent if too much mercaptan is added to the dispersion before reaction commences. The difference between the reactivities of lump sodium and dispersed sodium is emphasized when a tertiary alkyl mercaptan is used. If a small piece of clean sodium is added to *t*-butyl mercaptan in anhydrous xylene at room temperature and the mixture is gradually heated to 90°, there is hardly any evidence of reaction throughout the whole temperature range. A few minutes after addition of the sodium to the mercaptan solution, the initial reaction indicated by slow evolution of hydrogen decreases still further as the surface of the sodium probably becomes coated with insoluble mercaptide. On the other hand, sodium dispersion reacts smoothly and rapidly with *t*-butyl mercaptan at 50–60°.

From the large number of sodium alkylmercaptides that have been prepared in this work, it has been possible to qualitatively classify the alkyl mercaptans into three classes of reactivity toward sodium dispersion.

The most reactive mercaptans are ethyl, *n*-propyl, *n*-butyl and *n*-amyl mercaptans. These mercaptans can be added to the sodium dispersion at a temperature as low as 30° and reaction commences immediately. *sec*-Butyl, *t*-butyl, *i*-amyl and *t*-amyl mercaptans react slower than the primary mercaptans and require an initial temperature of 50–60° for smooth, rapid reaction. *i*-Butyl and *i*-propyl mercaptans are the least reactive and require an initial temperature of 105–115° for satisfactory reaction.

The dialkylcarbamoyl chlorides were prepared by a slightly modified procedure of Irwin.[7]

The alkyl chlorothiolformates required as intermediates for method B were prepared according to the procedures of Riemschneider and Lorenz.[2] Table V summarizes the yields and properties of the alkyl chlorothiolformates.

Table VI presents the properties and yields of some of the secondary amines which were prepared for method C.

A modified procedure of Weston, Ruddy and Suter[8] was followed for the synthesis of these amines.

Crotyl bromide is reported to be an equilibrium mixture containing approximately 87% 3-methylallyl bromide and 13% 1-methylallyl bromide[9] and the possibility of an allylic rearrangement taking place during the reaction of crotyl bromide could not be overlooked. Since the crotyl thiolcarbamates, compounds 187–203, were prepared by the reaction of crotyl bromide with the appropriate thiolcarbamate salt (method C), it was necessary to determine whether the products obtained were the 3-methylallyl thiolcarbamates or the 1-methylallyl thiolcarbamates. The latter compounds would be formed if extensive rearrangement took place. Since all of the compounds under consideration were carefully fractionated through a Podbielniak distillation column rated at 90 theoretical plates and gas chromatographic analyses of representative compounds showed minimum purities of 99 mole per cent., it was assumed that we were dealing with pure compounds and not mixtures. It was indeed interesting that during the fractional distillation of compounds 187–203 we encountered much larger fore fractions and more difficult separation of the fore fraction from the main fraction, than in any of the other 101 compounds prepared by method C which were distilled. Boiling point data showed that the impurities boiled about 10–15° below the main fraction. Since there was no interest in the prefractions at the time they were obtained, they were discarded without attempting to identify them. It was to be expected that the 1-methylallyl thiolcarbamates which contained a branched chain should boil somewhat lower than the straight chain 3-methylallyl thiolcarbamates. This view was supported by comparing the boiling point of *sec*-butyl diethylthiolcarbamate, compound 13, with the boiling point of *n*-butyl diethylthiolcarbamate, compound 11. In this case, the branched chain isomer boiled 11° lower than the straight chain isomer. The amount of pot residue left in the still-pot after the distillation of compounds 187–203 was negligible.

The above data indicate that the main fractions which were collected are the 3-methylallyl thiolcarbamates, if it is assumed that the lower boiling fractions were the 1-methylallyl thiolcarbamates.

(6) H. Plieninger, *Ber.*, **83**, 265 (1950).

(7) C. F. Irwin, U. S. Patent 2,644,007 (1953).

(8) A. W. Weston, A. W. Ruddy and C. M. Suter, THIS JOURNAL, **65**, 674 (1943).

(9) S. Winstein and W. G. Young, *ibid.*, **58**, 104 (1936).

TABLE I

THIOLCARBAMATES PREPARED BY PROCEDURE A $R_1SC(=O)N(R_2)R_2$

No.	R_1	R_2	Yield, %	B.p. °C.	B.p. Mm.	$n^{20}D$	d^{20}_4	MR_D Calcd.	MR_D Found	Mol. wt.	Nitrogen, % Calcd.	Nitrogen, % Found
1	Methyl[a]	Methyl	36	115.0–116.0[c]	88.5	1.4932	1.0717	32.37	32.33	119.2	11.75	11.44
2	Ethyl[a]	Methyl	26	124.0–124.5	88.5	1.4872	1.0330	37.29	37.10	133.2	10.51	10.49
3	*n*-Butyl[b]	Methyl	56	114.0–115.0[d]	18	1.4823	0.9883	46.58	46.54	161.3	8.69	8.53
4	*i*-Butyl[b]	Methyl	48	108.0–109.0	18	1.4800	.9844	46.61	46.54	161.3	8.69	8.42
5	*sec*-Butyl	Methyl	68	104.0–105.0	17	1.4820	.9860	46.60	46.63	161.3	8.69	8.60
6	*t*-Butyl	Methyl	58	93.0– 93.5	17	1.4810	.9807	46.91	46.80	161.3	8.69	8.59
7	*t*-Amyl	Methyl	35	113.0–114.0	20	1.4858	.9786	51.41	51.41	175.3	7.99	7.97
8	Methyl[b]	Ethyl	35	132.5–133.0	87	1.4833	1.0098	41.67	41.66	147.2	9.51	9.59
9	Ethyl[b]	Ethyl	53	141.5–142.0	87	1.4774	0.9791	46.59	46.57	161.3	8.69	8.88
10	*n*-Propyl	Ethyl	88	115.6–116.6	18	1.4776	.9664	51.26	51.32	175.3	7.99	8.07
11	*n*-Butyl[b]	Ethyl	51	129.0–131.0[e]	18	1.4766	.9573	55.88	55.84	189.3	7.40	7.42
12	*i*-Butyl	Ethyl	70	124.0–125.0	19	1.4741	.9525	55.91	55.87	189.3	7.40	7.39
13	*sec*-Butyl	Ethyl	74	119.5–120.0	18	1.4753	.9538	55.90	55.92	189.3	7.40	7.34
14	*t*-Butyl	Ethyl	67	108.0–109.0	19	1.4739	.9469	56.21	56.18	189.3	7.40	7.45
15	*n*-Amyl	Ethyl	82	154.5–155.0	30	1.4760	.9484	60.54	60.48	203.4	6.89	6.85
16	*t*-Amyl	Ethyl	43	126.0–127.0	20	1.4780	.9482	60.71	60.71	203.4	6.89	7.05
17	Methyl[b]	*n*-Propyl	62	128.5–129.5	30	1.4783	.9760	51.01	50.87	175.3	7.99	7.86
18	Ethyl[h]	*n*-Propyl	90[f]	137.0–138.0	30	1.4750	.9546	55.93	55.84	189.3	7.40	7.17
19	*n*-Propyl[i]	*n*-Propyl	86[g]	149.0–150.0	30	1.4736	.9440	60.60	60.49	203.4	6.89	7.01
20	*n*-Butyl	*n*-Propyl	76	151.0–151.5	19	1.4734	.9370	65.22	65.13	217.4	6.44	6.40
21	*i*-Butyl	*n*-Propyl	77	144.0–145.0	18	1.4716	.9327	65.25	65.21	217.4	6.44	6.60
22	*sec*-Butyl	*n*-Propyl	81	141.5–142.0	18.5	1.4728	.9343	65.24	65.24	217.4	6.44	6.35
23	*t*-Butyl	*n*-Propyl	62	129.5–130.0	18	1.4717	.9292	65.55	65.47	217.4	6.44	6.44
24	*n*-Amyl	*n*-Propyl	64	159.0–160.0	20	1.4729	.9289	69.88	69.87	231.4	6.05	6.09
25	*i*-Amyl	*n*-Propyl	73	159.0–160.0	20	1.4721	.9267	70.02	69.94	231.4	6.05	6.23
26	*t*-Amyl	*n*-Propyl	30	134.5–135.0	11.4	1.4741	.9288	70.05	70.03	231.4	6.05	6.11
27	Ethyl	*i*-Propyl	56	113.0–114.0	21.5	1.4751	.9556	55.95	55.79	189.3	7.40	7.30
28	*n*-Propyl	*i*-Propyl	71	126.5–127.5	20.6	1.4745	.9449	60.62	60.54	203.4	6.89	6.81
29	*n*-Butyl	*i*-Propyl	69	142.0–143.5	22	1.4738	.9370	65.24	65.18	217.4	6.44	6.37
30	*sec*-Butyl	*i*-Propyl	86	128.0–129.0	18	1.4722	.9343	65.26	65.18	217.4	6.44	6.48
31	*n*-Amyl	*i*-Propyl	68	148.0–149.0	22	1.4724	.9281	69.90	69.87	231.4	6.05	6.18
32	Methyl[b]	*n*-Butyl	69	144.5–146.0	20	1.4761	.9511	60.25	60.31	203.4	6.89	6.79
33	Ethyl[b]	*n*-Butyl	77	154.0–154.2	22	1.4729	.9355	65.17	65.17	217.4	6.44	6.31
34	*n*-Propyl	*n*-Butyl	88	158.0–159.0	15	1.4724	.9279	69.84	69.89	231.4	6.05	6.02
35	*i*-Propyl	*n*-Butyl	74	155.0–155.5	20	1.4702	.9227	70.04	70.00	231.4	6.05	6.08
36	*n*-Butyl	*n*-Butyl	88	161.0–162.0	10.4	1.4722	.9227	74.46	74.51	245.4	5.71	5.75
37	*i*-Butyl	*n*-Butyl	77	152.5–153.0	10	1.4705	.9193	74.49	74.55	245.4	5.71	5.83
38	*sec*-Butyl	*n*-Butyl	88	155.0–157.0	10.4	1.4714	.9210	74.48	74.54	245.4	5.71	5.69
39	*t*-Butyl	*n*-Butyl	56	142.5–144.0	10	1.4707	.9156	74.79	74.88	245.4	5.71	5.48
40	*n*-Amyl	*n*-Butyl	71	166.0–167.0	10	1.4717	.9176	79.12	79.14	259.5	5.40	5.39
41	Ethyl	*i*-Butyl	73	137.5–138.0	21.5	1.4701	.9296	65.23	65.25	217.4	6.44	6.24
42	*n*-Propyl	*i*-Butyl	68	150.0–150.5	21.5	1.4698	.9227	69.90	69.95	231.4	6.05	6.13
43	*i*-Propyl	*i*-Butyl	77	142.0–142.5	21.5	1.4673	.9164	70.10	70.11	231.4	6.05	5.95
44	*n*-Butyl	*i*-Butyl	77	163.0–163.5	21.5	1.4698	.9176	74.52	74.60	245.4	5.71	5.79
45	*i*-Butyl	*i*-Butyl	70	167.0–168.0	32.8	1.4682	.9154	74.55	74.56	245.4	5.71	5.66
46	*sec*-Butyl	*i*-Butyl	73	162.0–163.0	30.5	1.4688	.9156	74.54	74.62	245.4	5.71	5.78
47	*t*-Butyl	*i*-Butyl	58	150.6–151.0	29.5	1.4670	.9088	74.85	74.93	245.4	5.71	5.65
48	*n*-Amyl	*i*-Butyl	68	179.2–183.5	34.8	1.4691	.9120	79.18	79.24	259.5	5.40	5.45
49	*i*-Amyl	*i*-Butyl	73	182.5–183.5	34.5	1.4684	.9097	79.32	79.34	259.5	5.40	5.55
50	*t*-Amyl	*i*-Butyl	49	152.0–154.0	20	1.4704	.9128	79.35	79.36	259.5	5.40	5.28
51	Ethyl	*n*-Amyl	66	185.5–187.5	30.8	1.4723	.9230	74.49	74.50	245.4	5.71	5.46
52	*n*-Propyl	*n*-Amyl	76	183.0–185.0	20	1.4722	.9185	79.16	79.13	259.5	5.40	5.15
53	*i*-Propyl	*n*-Amyl	63	175.0–177.0	20	1.4698	.9123	79.36	79.32	259.5	5.40	5.30
54	*n*-Butyl	*n*-Amyl	83	199.0–199.5	20	1.4723	.9134	83.78	83.89	273.5	5.12	5.23
55	*i*-Butyl	*n*-Amyl	66	193.5–194.5	20	1.4700	.9108	83.81	83.78	273.5	5.12	5.15
56	*sec*-Butyl	*n*-Amyl	82	189.0–191.0	20	1.4708	.9111	84.00	83.87	273.5	5.12	4.84
57	*t*-Butyl	*n*-Amyl	72	179.0–180.0	20	1.4697	.9058	84.11	84.19	273.5	5.12	5.06
58	*i*-Amyl	*n*-Amyl	85	200.0–202.0	20	1.4706	.9068	88.58	88.56	287.5	4.87	4.79
59	Methyl	*i*-Amyl	79	156.6–157.8	20	1.4713	.9317	69.47	69.46	231.4	6.05	5.82
60	Ethyl	*i*-Amyl	87	163.7–165.0	20	1.4694	.9183	74.59	74.48	245.4	5.71	5.55

61	*n*-Propyl	*i*-Amyl	80	175.5–176.5	20	1.4692	.9123	79.26	79.23	259.5	5.40	5.52
62	*i*-Propyl	*i*-Amyl	78	168.5–169.0	20	1.4683	.9081	79.56	79.47	259.5	5.40	5.36
63	*n*-Butyl	*i*-Amyl	80	185.0–187.0	20	1.4690	.9078	83.88	83.90	273.5	5.12	5.09
64	*i*-Butyl	*i*-Amyl	71	180.5–180.6	20	1.4675	.9048	83.91	83.95	273.5	5.12	5.30
65	*sec*-Butyl	*i*-Amyl	72	176.0–177.5	20	1.4683	.9056	84.00	84.00	273.5	5.12	5.11
66	*t*-Butyl	*i*-Amyl	63	166.0–167.8	20	1.4671	.9000	84.20	84.33	273.5	5.12	5.06
67	*n*-Amyl	*i*-Amyl	85	195.0–197.0	20	1.4691	.9037	88.54	88.62	287.5	4.87	4.67
68	*i*-Amyl	*i*-Amyl	81	192.5–194.0	20	1.4694	.9017	88.78	88.86	287.5	4.87	4.71
69	*t*-Amyl	*i*-Amyl	57	179.0–180.0	20	1.4696	.9018	88.91	88.89	287.5	4.87	4.96
70	Allyl[b]	Methyl	39	102.5–103.0	17	1.5054	1.0369	41.69	41.57	145.2	9.64	9.72
71	Allyl[b]	Ethyl	41	116.5–117.0	17	1.4942	0.9922	50.99	50.86	173.3	8.08	8.06
72	Allyl	*n*-Propyl	53	139.0–140.0	19	1.4888	0.9628	60.33	60.33	201.3	6.96	6.90

[a] Prepared by the reaction of the dialkylcarbamoyl chloride with the alkyl mercaptan in the presence of a molar equivalent of pyridine. This procedure was dropped in favor of the sodium alkylmercaptide method. [b] The sodium alkylmercaptide was prepared by the sodium alkoxide method. [c] Délepine and Schwing, *Bull. soc. chim. France*, [4] **7**, 902 (1864), report b.p. 180°, $n^{21}D$ 1.5056, d^{21}_4 1.0904. [d] Riemschneider (ref. 2) reports b.p. 112° (17 mm.). [e] Riemschneider (ref. 2) reports b.p. 145° (16 mm.). [f] A yield of 76% was obtained using the sodium alkoxide method. [g] A yield of 61% was obtained using the sodium alkoxide method. [h] *Anal.* Calcd. for $C_9H_{19}NOS$: C, 57.10; H, 10.12; S, 16.94; mol. wt., 189. Found: C, 57.41; H, 10.26; S, 16.71; mol. wt. (Rast), 185. [i] *Anal.* Calcd. for $C_{10}H_{21}NOS$: C, 59.06; H, 10.41; S, 15.77. Found: C, 59.22; H, 10.41; S, 15.77.

TABLE II

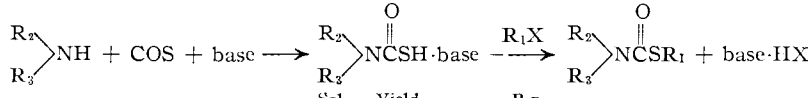
THIOLCARBAMATES PREPARED BY PROCEDURE B $R_1SC(=O)N(R_2)R_3$

No.	R_1	R_2	R_3	Yield, %	B.p. °C.	B.p. Mm.	$n^{30}D$	d^{30}_4	MRD Calcd.	MRD Found	Mol. wt.	Nitrogen, % Calcd.	Nitrogen, % Found
73	*n*-Propyl	Methyl	Hydrogen	73	121.0–121.5	15	1.4922	1.0392	37.38	37.20	133.2	10.51	10.53
74	*n*-Propyl	Ethyl	Hydrogen	71	122.0–122.5	15	1.4878	1.0085	42.03	42.05	147.2	9.51	9.48
75	Ethyl[a]	*n*-Propyl	Hydrogen	75	120.5–120.7	15	1.4876	1.0092	42.03	42.01	147.2	9.51	9.72
76	*n*-Propyl	*n*-Propyl	Hydrogen	74	127.0–128.0	10	1.4850	0.9902	46.70	46.68	161.3	8.69	8.55
77	Ethyl	*n*-Butyl	Hydrogen	74	125.0–125.5	10	1.4848	.9904	46.70	46.65	161.3	8.69	8.42
78	*n*-Propyl	*n*-Butyl	Hydrogen	75	121.0–122.0	5	1.4832	.9748	51.32	51.38	175.3	7.99	7.94
79	*n*-Propyl	*i*-Butyl	Hydrogen	65	120.5–121.0	5	1.4808	.9694	51.32	51.44	175.3	7.99	7.90
80	Ethyl	*n*-Amyl	Hydrogen	72	125.0–127.0	4.6	1.4829	.9770	51.32	51.24	175.3	7.99	7.98
81	Ethyl	*n*-Hexyl	Hydrogen	78	134.5–135.8	4.6	1.4811	.9623	55.92	56.00	189.3	7.40	7.14
82	Ethyl	Allyl	Hydrogen	71	101.0–103.0	5	1.5047	1.0405	41.42	41.38	145.2	9.64	9.36
83	*n*-Propyl	Allyl	Hydrogen	78	115.0–115.5	5	1.4999	1.0159	46.09	46.10	159.3	8.80	8.74
84	*n*-Butyl	Allyl	Hydrogen	78	126.5–127.0	5	1.4962	0.9975	50.71	50.76	173.3	8.08	8.02
85	Ethyl	Allyl	Allyl	83	135.0–136.5	30	1.4992	.9914	54.95	54.91	185.3	7.56	7.47
86	*n*-Propyl[b]	Allyl	Allyl	77	132.0–132.2	15	1.4959	.9771	59.62	59.58	199.3	7.03	6.88
87	*n*-Butyl	Allyl	Allyl	84	136.5–138.0	10	1.4934	.9658	64.24	64.24	213.4	6.57	6.58
88	Ethyl	*n*-Propyl	Allyl	82	137.0–138.0	30	1.4872	.9719	55.44	55.45	187.3	7.48	7.60
89	Ethyl	Ethyl	Methallyl	62	119.0–119.5	15	1.4877	.9740	55.44	55.38	187.3	7.48	7.34
90	*n*-Propyl	Ethyl	Methallyl	67	130.0–130.5	15	1.4863	.9626	60.07	60.08	201.3	6.96	6.65
91	*i*-Propyl	Ethyl	Methallyl	61	119.5–120.0	15	1.4830	.9529	60.27	60.34	201.3	6.96	6.88
92	*n*-Butyl	Ethyl	Methallyl	77	141.0–141.5	15	1.4849	.9523	64.69	64.80	215.4	6.50	6.33
93	*i*-Butyl	Ethyl	Methallyl	76	135.0–135.1	15	1.4826	.9482	64.72	64.82	215.4	6.50	6.38
94	Ethyl	*n*-Propyl	Methallyl	64	135.5–136.0	15	1.4858	.9613	60.07	60.11	201.3	6.96	6.94
95	*n*-Propyl	*n*-Propyl	Methallyl	68	151.0–151.5	15	1.4840	.9514	64.74	64.76	215.4	6.50	6.71
96	Ethyl	Ethyl	*n*-Propyl	75	125.0–125.1	30	1.4770	.9669	51.26	51.23	175.3	7.99	8.01
97	*n*-Propyl	Ethyl	*n*-Propyl	75	138.0–138.5	30	1.4758	.9547	55.93	55.91	189.3	7.40	7.41
98	Ethyl	*n*-Propyl	*n*-Butyl	81	148.0–148.5	30	1.4748	.9463	60.55	60.48	203.4	6.89	6.84
99	2-Chloroethyl	Ethyl	Ethyl	72	144.5–145.0	20	1.5011	1.1199	...	51.50	195.7	7.16	7.05
												18.12[c]	18.06[c]
100	3-Chloropropyl	Ethyl	Ethyl	71	142.5–142.8	10	1.4989	1.0994	55.97	56.01	209.8	6.68	6.66
												16.90[c]	17.01[c]
101	3-Chloropropyl	*n*-Propyl	*n*-Propyl	54	158.5–159.0	10	1.4925	1.0570	65.31	65.33	237.8	5.89	5.78
												14.91[c]	15.12[c]
102	3-Chloropropyl	Allyl	Allyl	76	159.0–159.5	10	1.5147	1.0966	64.33	64.25	233.8	5.99	5.85
												15.17[c]	15.08[c]
103	3-Chloropropyl	Ethyl	*n*-Butyl	63	161.5–162.0	10	1.4929	1.0588	65.26	65.26	237.8	5.89	5.81
												14.91[c]	14.91[c]
104	3-Chloropropyl	Allyl	*n*-Propyl	72	159.5–160.0	10	1.5037	1.0768	64.82	64.80	235.8	5.94	5.96
												15.04[c]	15.13[c]
105	3-Chloropropyl	Methallyl	*n*-Propyl	79	164.0–164.1	10	1.5013	1.0593	69.45	69.51	249.8	5.61	5.53
												14.19[c]	13.94[c]
106	3-Chloropropyl	Methallyl	Allyl	72	163.5–164.0	10	1.5113	1.0773	68.96	68.94	247.8	5.65	5.69
												14.31[c]	14.51[c]
107	3-Chloropropyl	*n*-Propyl	2-Propynyl	53	167.0–167.5	10	1.5117	1.1121	63.08	63.04	233.8	5.99	5.83
												15.17[c]	15.31[c]
108	Ethyl	*n*-Propyl	2-Propynyl	73	145.0–145.5	30	1.4965	1.0095	53.70	53.66	185.3	7.55	7.55
109	*n*-Propyl	*n*-Propyl	2-Propynyl	72	156.0–156.5	30	1.4935	0.9932	58.37	58.37	199.3	7.03	6.75
110	*n*-Butyl	*n*-Propyl	2-Propynyl	76	168.5–169.0	30	1.4911	0.9800	62.99	63.06	213.4	6.56	6.54

[a] *Anal.* Calcd. for $C_6H_{13}NOS$: C, 48.94; H, 8.90; S, 21.78; mol. wt., 147. Found: C, 49.11; H, 8.87; S, 21.51; mol. wt. (Rast), 155. [b] *Anal.* Calcd. for $C_{10}H_{17}NOS$: C, 60.26; H, 8.60; S, 16.09; mol. wt., 199. Found: C, 60.30; H, 8.44; S, 15.98; mol. wt. (Rast), 210. [c] Halogen, %.

TABLE III

THIOCARBAMATES PREPARED BY PROCEDURE C



No.	R_1	R_2	R_3	X	Base[a]	Solvent[b]	Yield, %	B.p. °C.	B.p. Mm.	$n^{30}D$	d^{30}_4	MRD Calcd.	MRD Found	Mol. wt.	Nitrogen, % Calcd.	Nitrogen, % Found	Halogen, % Calcd.	Halogen, % Found
111	$CH_2{=}CHCH_2$	CH_3	n-C_4H_9	Br	S	T	84	131.0–132.0	15	1.4923	0.9761	55.63	55.70	187.3	7.48	7.27		
112	$CH_2{=}CHCH_2$	C_2H_5	n-C_4H_9	Br	S	T	54	136.0–136.2	15	1.4885	0.9629	60.28	60.30	201.3	6.96	6.84		
113	$CH_2{=}CHCH_2$	C_6H_{11}[c]	C_2H_5	Br	TEA	TBA	58	141.5–142.5	4.5	1.5158	1.0196	67.36	67.33	227.4	6.16	6.00		
114	$CH_2{=}CHCH_2$	$CH_2{=}CHCH_2$	$CH_2{=}CHCH_2$	Cl	S	B	45	133.0–134.0	15	1.5113	0.9959	59.35	59.38	197.3	7.10	6.89		
115	$CH_2{=}CHCH_2$	$CH_2{=}CHCH_2$	C_2H_5	Br	S	T	31	140.5–140.7	30	1.5038	.9953	55.17	55.13	185.4	7.56	7.37		
116	$CH_2{=}CHCH_2$	$CH_2{=}CHCH_2$	n-C_3H_7	Br	S	EGDE	69	151.0–151.2	30	1.4995	.9804	59.84	59.74	199.3	7.03	6.81		
117	$CH_2{=}CHCH_2$	n-C_3H_7	$ClCH{=}CHCH_2$[f]	Br	TEA	TBA	63	138.0–140.0	4.5	1.5178	1.0941	...	64.73	233.8	5.99	6.01	15.17	15.20
118	$CH_2{=}CHCH_2$	$CH_2{=}CHCH_2$	$ClCH{=}CHCH_2$[f]	Br	TEA	TBA	71	164.0–166.0	15	1.5294	1.1157	...	64.10	231.8	6.01	5.79	15.30	15.40
119	$CH_2{=}CHCH_2$	$CH_2{=}C(CH_3)CH_2$	C_2H_5	Br	TEA	TBA	72	130.0–130.5	15	1.5012	0.9819	59.80	59.82	199.3	7.03	7.00		
120	$CH_2{=}CHCH_2$	$CH_2{=}C(CH_3)CH_2$	n-C_3H_7	Br	TEA	TBA	76	139.0–140.0	15	1.4975	.9689	64.47	64.49	213.4	6.56	6.55		
121	$CH_2{=}CHCH_2$	$CH_2{=}C(CH_3)CH_2$	$CH_2{=}CHCH_2$	Br	TEA	TBA	69	139.0–139.5	15	1.5080	.9849	63.98	63.96	211.3	6.63	6.38		
122	CH_3OCH_2	C_2H_5	C_2H_5	Cl	DAA	TBA	49	136.5–138.0	30	1.4845	1.0474	48.41	48.46	177.3	7.90	7.80		
123	CH_3OCH_2	n-C_3H_7	n-C_3H_7	Cl	DAA	TBA	54	155.0–156.0	30	1.4788	1.0059	57.75	57.86	205.3	6.82	6.71		
124	CH_3OCH_2	CH_3	n-C_4H_9	Cl	TEA	PE	58	155.0–156.0	30	1.4828	1.0296	53.05	53.04	191.3	7.32	7.21		
125	CH_3OCH_2	C_2H_5	n-C_4H_9	Cl	TEA	PE	48	144.0–144.2	15	1.4795	1.0088	57.70	57.77	205.3	6.82	6.74		
126	CH_3OCH_2	n-C_4H_9	n-C_4H_9	Cl	DAA	PE	74	135.5–136.5	4.6	1.4762	0.9840	66.99	66.92	233.4	6.00	5.83		
127	CH_3OCH_2	i-C_4H_9	i-C_4H_9	Cl	TEA	PE	38	122.0–123.0	4.6	1.4730	0.9750	67.05	67.15	233.4	6.00	5.87		
128	CH_3OCH_2	$CH_2{=}CHCH_2$	$CH_2{=}CHCH_2$	Cl	S	EGDE	69	114.0–115.0	4.5	1.5040	1.0511	56.77	56.70	201.3	6.96	6.85		
129	CH_3OCH_2	$CH_2{=}CHCH_2$	C_2H_5	Cl	S	EGDE	67	149.0–149.2	30	1.4951	1.0528	52.59	52.44	189.3	7.40	7.34		
130	CH_3OCH_2	$CH_2{=}CHCH_2$	n-C_3H_7	Cl	TEA	PE	70	114.5–115.0	4.5	1.4912	1.0317	57.26	57.09	203.3	6.89	6.72		
131	CH_3OCH_2	C_2H_5	$CH_2{=}C(CH_3)CH_2$	Cl	TEA	TBA	61	137.5–137.6	15	1.4930	1.0342	57.22	57.13	203.3	6.89	6.67		
132	CH_3OCH_2	n-C_3H_7	$CH_2{=}C(CH_3)CH_2$	Cl	TEA	TBA	61	146.0–146.5	15	1.4898	1.0163	61.89	61.80	217.3	6.45	6.53		
133	CH_3OCH_2	$CH_2{=}CHCH_2$	$CH_2{=}C(CH_3)CH_2$	Cl	TEA	TBA	66	146.0–146.5	15	1.5007	1.0348	61.40	61.27	215.3	6.51	6.21		
134	CH_3SCH_2	C_2H_5	C_2H_5	Cl	TEA	PE	43	140.0–141.5	10	1.5265	1.0895	54.49	54.51	193.3	7.25	7.17		
135	CH_3SCH_2	n-C_3H_7	n-C_3H_7	Cl	TEA	PE	71	136.0–137.5	4.5	1.5157	1.0469	63.83	63.84	221.4	6.33	6.20		
136	CH_3SCH_2	CH_3	n-C_4H_9	Cl	TEA	PE	72	136.5–137.0	4.5	1.5212	1.0687	59.13	59.10	207.4	6.76	6.79		
137	CH_3SCH_2	C_2H_5	n-C_4H_9	Cl	TEA	PE	64	140.0–140.5	4.5	1.5155	1.0476	63.78	63.78	221.4	6.33	6.23		
138	CH_3SCH_2	n-C_4H_9	n-C_4H_9	Cl	TEA	PE	71	157.5–158.5	4.5	1.5078	1.0163	73.07	73.14	249.4	5.62	5.41		
139	CH_3SCH_2	i-C_4H_9	i-C_4H_9	Cl	TEA	PE	78	144.5–145.0	4.5	1.5059	1.0118	73.13	73.23	249.4	5.62	5.54		
140	CH_3SCH_2	$CH_2{=}CHCH_2$	$CH_2{=}CHCH_2$	Cl	TEA	PE	61	139.0–139.5	4.5	1.5405	1.0878	62.85	62.74	217.4	6.44	6.26		
141	CH_3SCH_2	$CH_2{=}CHCH_2$	C_2H_5	Cl	TEA	PE	49	131.0–132.0	4.5	1.5344	1.0896	58.67	58.62	205.4	6.82	6.60		
142	CH_3SCH_2	$CH_2{=}CHCH_2$	n-C_3H_7	Cl	TEA	PE	39	140.5–141.0	4.5	1.5280	1.0673	63.34	63.29	219.4	6.38	6.28		
143	CH_3SCH_2	$CH_2{=}CHCH_2$	i-C_3H_7	Cl	TEA	PE	13	135.0–136.0	4.5	1.5301	1.0745	63.35	63.08	219.4	6.38	6.60		
144	CH_3SCH_2	$CH_2{=}CHCH_2$	n-C_4H_9	Cl	TEA	PE	47	150.0–150.5	4.5	1.5227	1.0185	67.96	67.97	233.4	6.00	6.01		
145	CH_3SCH_2	$CH_2{=}CHCH_2$	i-C_4H_9	Cl	TEA	PE	37	144.0–145.0	4.5	1.5215	1.0463	67.99	67.98	233.4	6.00	5.85		
146	CH_3SCH_2	C_2H_5	$CH_2{=}C(CH_3)CH_2$	Cl	TEA	PE	44	136.0–137.0	4.5	1.5298	1.0692	63.30	63.36	219.4	6.38	6.23		
147	CH_3SCH_2	n-C_3H_7	$CH_2{=}C(CH_3)CH_2$	Cl	TEA	PE	39	144.0–144.5	4.5	1.5239	1.0497	67.97	68.02	233.4	6.00	5.95		
148	CH_3SCH_2	$CH_2{=}CHCH_2$	$CH_2{=}C(CH_3)CH_2$	Cl	TEA	TBA	74	144.5–145.5	4.5	1.5353	1.0684	67.48	67.46	231.4	6.05	5.84		
149	CH_3SCH_2	C_2H_5	$ClCH{=}CHCH_2$[f]	Cl	TEA	TBA	61	164.8–168.0	4.5	1.5505	1.2027	...	63.56	239.8	5.84	5.82	14.79	14.66
150	CH_3SCH_2	n-C_3H_7	$CH_2{=}C(Cl)CH_2$	Cl	TEA	TBA	72	158.5–160.5	4.5	1.5383	1.1668	68.04	68.08	253.8	5.52	5.46	13.97	14.20
151	CH_3SCH_2	n-C_3H_7	*trans*-$ClCH{=}CHCH_2$	Cl	TEA	TBA	44	190.0–190.5	10	1.5443	1.1719	68.30	68.41	253.8	5.52	5.30	13.97	14.10
152	CH_3SCH_2	$CH_2{=}CHCH_2$	$CH_2{=}C(Cl)CH_2$	Cl	TEA	TBA	68	159.0–160.0	4.5	1.5503	1.1903	67.55	67.42	251.8	5.56	5.38	14.08	13.87
153	CH_3SCH_2	$CH_2{=}CHCH_2$	*trans*-$ClCH{=}CHCH_2$	Cl	TEA	TBA	59	189.5–190.0	10	1.5560	1.1948	67.81	67.74	251.8	5.56	5.52	14.08	14.07
154	$CH_2{=}C(CH_3)CH_2$	C_2H_5	C_2H_5	Cl	TEA	TBA	58	139.8–140.5	30	1.4928	.9794	55.57	55.56	187.3	7.48	7.29		
155	$CH_2{=}C(CH_3)CH_2$	n-C_3H_7	n-C_3H_7	Cl	TEA	TBA	63	134.0–135.0	10	1.4878	.9556	64.91	64.91	215.4	6.50	6.32		
156	$CH_2{=}C(CH_3)CH_2$	CH_3	n-C_4H_9	Cl	TEA	TBA	49	157.5–158.5	30	1.4913	.9690	60.21	60.21	201.3	6.96	6.80		
157	$CH_2{=}C(CH_3)CH_2$	C_2H_5	n-C_4H_9	Cl	TEA	TBA	59	138.5–139.0	10	1.4882	.9565	64.86	64.89	215.4	6.50	6.32		
158	$CH_2{=}C(CH_3)CH_2$	C_6H_{11}[c]	C_2H_5	Cl	TEA	TBA	34	153.0–154.0	5.0	1.5130	1.0079	71.94	71.99	241.4	5.80	5.66		

TABLE III (*Continued*)

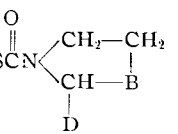
No.	R_1	R_2	R_3	X	Base[a]	Solvent[b]	Yield, %	B.p. °C.	B.p. Mm.	$n^{20}D$	d^{20}_4	MR_D Calcd.	MR_D Found	Mol. wt.	Nitrogen, % Calcd.	Nitrogen, % Found	Halogen, % Calcd.	Halogen, % Found
159	$CH_2{=}C(CH_3)CH_2$	$CH_2{=}CHCH_2$	$CH_2{=}CHCH_2$	Cl	TEA	TBA	52	133.5–134.0	10	1.5094	0.9872	64.15	63.96	211.3	6.63	6.51		
160	$CH_2{=}C(CH_3)CH_2$	n-C_3H_7	$CH_2{=}CHCH_2$	Cl	TEA	TBA	50	135.0–136.0	10	1.4981	.9711	64.42	64.41	213.4	6.56	6.46		
161	$CH_2{=}C(CH_3)CH_2$	i-C_3H_7	$CH_2{=}CHCH_2$	Cl	TEA	TBA	40	131.0–132.0	10	1.5004	.9761	64.43	64.33	213.4	6.56	6.45		
162	$CH_2{=}C(CH_3)CH_2$	n-C_4H_9	$CH_2{=}CHCH_2$	Cl	TEA	TBA	46	147.5–148.0	10	1.4954	.9613	69.04	69.02	227.4	6.16	5.91		
163	$CH_2{=}C(CH_3)CH_2$	i-C_4H_9	$CH_2{=}CHCH_2$	Cl	TEA	TBA	58	144.0–144.5	10	1.4942	.9581	69.07	69.11	227.4	6.16	6.06		
164	$CH_2{=}C(CH_3)CH_2$	$CH_2{=}C(CH_3)CH_2$	Cl	Cl	TEA	TBA	54	130.0–131.0	10	1.4995	.9723	64.38	64.48	213.4	6.56	6.55		
165	$CH_2{=}C(CH_3)CH_2$	$CH_2{=}C(CH_3)CH_2$	n-C_3H_7	Cl	TEA	TBA	58	140.0–140.5	10	1.4965	.9614	69.05	69.14	227.4	6.16	6.28		
166	$CH_2{=}C(CH_3)CH_2$	$CH_2{=}C(CH_3)CH_2$	$CH_2{=}CHCH_2$	Cl	TEA	TBA	59	147.0–147.2	10	1.5058	.9755	68.56	68.61	225.4	6.22	6.16		
167	$CH_2{=}C(CH_3)CH_2$	C_2H_5	$ClCH{=}CHCH_2$[f]	Cl	TEA	TBA	46	137.5–138.0	4.5	1.5192	1.0979	...	64.65	233.8	5.99	5.87	15.17	15.47
168	$CH_2{=}C(CH_3)CH_2$	n-C_3H_7	$CH_2{=}C(Cl)CH_2$	Cl	TEA	TBA	43	134.0–135.0	4.5	1.5098	1.0716	69.12	69.14	247.8	5.65	5.96	14.31	14.19
169	$CH_2{=}C(CH_3)CH_2$	n-C_3H_7	*trans*-$ClCH{=}CHCH_2$	Cl	TEA	TBA	34	164.5–165.0	10	1.5156	1.0777	69.38	69.40	247.8	5.65	5.58	14.31	14.60
170	$CH_2{=}C(CH_3)CH_2$	$CH_2{=}CHCH_2$	$CH_2{=}C(Cl)CH_2$	Cl	TEA	TBA	40	133.0–134.5	4.5	1.5208	1.0892	68.63	68.69	245.8	5.70	5.53	14.43	14.46
171	$CH_2{=}C(CH_3)CH_2$	$CH_2{=}CHCH_2$	*trans*-$ClCH{=}CHCH_2$	Cl	TEA	TBA	50	164.5–165.0	10	1.5261	1.0956	68.89	68.87	245.8	5.70	5.74	14.43	14.43
172	$CH_2{=}C(Cl)CH_2$	C_2H_5	C_2H_5	Cl	DAA	EA	46	129.0–129.5	10	1.5090	1.1179	55.45	55.48	207.7	6.74	6.58	17.07	17.20
173	$CH_2{=}C(Cl)CH_2$	n-C_3H_7	n-C_3H_7	Cl	DAA	B	36	147.0–149.0	10	1.5002	1.0719	64.79	64.72	235.8	5.94	6.13	15.04	15.20
174	$CH_2{=}C(Cl)CH_2$	CH_3	n-C_4H_9	Cl	P	W	20	147.0–147.5	10.5	1.5059	1.0955	60.09	60.13	221.8	6.32	6.08	15.99	16.20
175	$CH_2{=}C(Cl)CH_2$	C_2H_5	n-C_4H_9	Cl	Py	TBA	23	152.0–153.5	10	1.5008	1.0744	64.74	64.63	235.8	5.94		15.04	15.10
176	$CH_2{=}C(Cl)CH_2$	$CH_2{=}CHCH_2$	$CH_2{=}CHCH_2$	Cl	DAA	TBA	41	147.0–150.0	10	1.5230	1.1086	63.81	63.86	231.8	6.04	5.80	15.30	15.40
177	$CH_2{=}C(Cl)CH_2$	n-C_3H_7	$CH_2{=}CHCH_2$	Cl	S	EGDE	48	146.5–147.0	10	1.5115	1.0893	64.30	64.34	233.8	5.99	5.94	15.17	14.90
178	*cis*-$ClCH{=}CHCH_2$	C_2H_5	C_2H_5	Cl	TEA	TBA	69	146.5–147.5	15	1.5141	1.1218	55.77	55.76	207.7	6.74	6.56	17.07	16.70
179	*trans*-$ClCH{=}CHCH_2$	C_2H_5	C_2H_5	Cl	TEA	TBA	65	149.0–149.5	15	1.5159	1.1205	56.00	55.99	207.7	6.74	6.66	17.07	16.68
180	*cis*-$ClCH{=}CHCH_2$	n-C_3H_7	n-C_3H_7	Cl	TEA	TBA	57	154.5–155.0	10	1.5060	1.0750	65.11	65.16	235.8	5.94	5.89	15.04	14.95
181	*trans*-$ClCH{=}CHCH_2$	n-C_3H_7	n-C_3H_7	Cl	TEA	TBA	56	156.0–156.5	10	1.5068	1.0736	65.34	65.33	235.8	5.94	5.98	15.04	14.90
182	*cis*-$ClCH{=}CHCH_2$	$CH_2{=}CHCH_2$	$CH_2{=}CHCH_2$	Cl	TEA	TBA	45	155.5–156.0	10	1.5284	1.1147	64.13	64.06	231.8	6.04	6.02	15.30	15.10
183	*trans*-$ClCH{=}CHCH_2$	$CH_2{=}CHCH_2$	$CH_2{=}CHCH_2$	Cl	TEA	TBA	55	157.0–157.5	10	1.5299	1.1135	64.36	64.28	231.8	6.04	6.00	15.30	15.05
184	*cis*-$ClCH{=}CHCH_2$	$CH_2{=}CHCH_2$	n-C_3H_7	Cl	TEA	TBA	52	156.0–156.5	10	1.5174	1.0946	64.62	64.65	233.8	5.99	6.04	15.17	14.95
185	*trans*-$ClCH{=}CHCH_2$	$CH_2{=}CHCH_2$	n-C_3H_7	Cl	TEA	TBA	34	156.5–157.0	10	1.5190	1.0921	64.85	64.97	233.8	5.99	6.00	15.17	15.00
186	$ClCH{=}CHCH_2$[f]	C_2H_5	$CH_2{=}CHCH_2$	Cl	S	EGDE	53	147.0–148.0	10	1.5234	1.1193	...	60.01	219.7	6.38	6.28	16.14	15.90
187	$CH_3CH{=}CHCH_2$	C_2H_5	C_2H_5	Br	TEA	TBA	60	148.0–148.5	30	1.4978	0.9814	55.91	55.92	187.3	7.48[d]	7.50		
188	$CH_3CH{=}CHCH_2$	n-C_3H_7	n-C_3H_7	Br	TEA	TBA	69	141.0–142.0	10	1.4912	.9572	65.25	65.18	215.4	6.50	6.45		
189	$CH_3CH{=}CHCH_2$	n-C_4H_9	CH_3	Br	TEA	TBA	58	121.0–122.0	4.5	1.4950	.9697	60.55	60.55	201.3	6.96	6.87		
190	$CH_3CH{=}CHCH_2$	n-C_4H_9	C_2H_5	Br	TEA	TBA	66	124.5–125.0	4.5	1.4915	.9575	65.20	65.20	215.4	6.50	6.42		
191	$CH_3CH{=}CHCH_2$	$CH_2{=}CHCH_2$	$CH_2{=}CHCH_2$	Br	TEA	TBA	57	122.5–123.5	4.5	1.5128	.9889	64.27	64.21	211.3	6.63	6.67		
192	$CH_3CH{=}CHCH_2$	C_2H_5	C_6H_{11}[c]	Br	TEA	TBA	59	156.0–156.5	4.5	1.5166	1.0100	72.28	72.26	241.4	5.80	5.85		
193	$CH_3CH{=}CHCH_2$	$CH_2{=}CHCH_2$	n-C_3H_7	Br	TEA	TBA	65	122.0–123.0	4.5	1.5020	0.9723	64.76	64.76	213.4	6.56	6.46		
194	$CH_3CH{=}CHCH_2$	$CH_2{=}CHCH_2$	n-C_4H_9	Br	TEA	TBA	62	133.5–134.5	4.5	1.4990	.9616	69.38	69.43	227.4	6.16	6.21		
195	$CH_3CH{=}CHCH_2$	$CH_2{=}CHCH_2$	i-C_4H_9	Br	TEA	TBA	63	126.0–126.5	4.5	1.4976	.9592	69.41	69.43	227.4	6.16	6.16		
196	$CH_3CH{=}CHCH_2$	n-C_3H_7	$CH_2{=}C(Cl)CH_2$	Br	TEA	TBA	66	141.0–141.5	4.5	1.5128	1.0732	69.46	69.38	247.8	5.65	5.59	14.31	14.21
197	$CH_3CH{=}CHCH_2$	n-C_3H_7	*trans*-$ClCH{=}CHCH_2$	Br	TEA	TBA	61	171.0–172.0	10	1.5188	1.0778	69.72	69.76	247.8	5.65	5.58	14.31	14.30
198	$CH_3CH{=}CHCH_2$	$CH_2{=}CHCH_2$	$CH_2{=}C(Cl)CH_2$	Br	TEA	TBA	63	141.0–141.5	4.5	1.5233	1.0902	68.97	68.90	245.8	5.70	5.63	14.43	14.25
199	$CH_3CH{=}CHCH_2$	$CH_2{=}CHCH_2$	*trans*-$ClCH{=}CHCH_2$	Br	TEA	TBA	64	170.5–171.5	10	1.5292	1.0965	69.23	69.15	245.8	5.70	5.51	14.43	14.66
200	$CH_3CH{=}CHCH_2$	C_2H_5	$ClCH{=}CHCH_2$[f]	Br	TEA	TBA	40	144.5–145.0	4.5	1.5232	1.0982	...	65.05	233.8	5.99	5.72	15.17	15.37
201	$CH_3CH{=}CHCH_2$	C_2H_5	$CH_2{=}C(CH_3)CH_2$	Br	TEA	TBA	58	137.0–137.5	10	1.5033	0.9737	64.72	64.80	213.4	6.56	6.44		
202	$CH_3CH{=}CHCH_2$	n-C_3H_7	$CH_2{=}C(CH_3)CH_2$	Br	TEA	TBA	61	146.0–146.5	10	1.4998	.9626	69.39	69.45	227.4	6.16	5.93		
203	$CH_3CH{=}CHCH_2$	$CH_2{=}CHCH_2$	$CH_2{=}C(CH_3)CH_2$	Br	TEA	TBA	66	145.0–145.5	10	1.5094	.9762	68.90	68.97	225.4	6.22	6.21		
204	$CH_2{=}C(Br)CH_2$	CH_3	CH_3	Cl	TEA	TBA	65	133.5–134.0	10	1.5458	1.4509	48.70	48.90	224.1	6.25	6.04	35.66	36.02
205	$CH_2{=}C(Br)CH_2$	n-C_3H_7	n-C_3H_7	Br	TEA	TBA	31	165.5–166.0	10	1.5172	1.2589	67.34	67.37	280.2	5.00	4.98	28.52	28.74
206	$CH_2{=}C(Br)CH_2$	n-C_4H_9	CH_3	Br	TEA	TBA	60	159.5–160.0	10	1.5229	1.2961	62.64	62.73	266.2	5.26	5.23	30.02	30.01
207	$CH_2{=}C(Br)CH_2$	$CH_2{=}CHCH_2$	$CH_2{=}CHCH_2$	Cl	TEA	TBA	49	159.5–160.0	10	1.5400	1.3049	66.36	66.41	276.2	5.07	5.00	28.94	29.17
208	$CH_2{=}C(Br)CH_2$	C_2H_5	$CH_2{=}C(CH_3)CH_2$	Cl	TEA	TBA	38	157.5–157.6	10	1.5308	1.2895	66.81	66.73	278.2	5.04	4.85	28.73	29.10
209	$CH_2{=}C(Br)CH_2$	n-C_3H_7	$CH_2{=}CHCH_2$	Br	TEA	TBA	68	159.5–160.0	10	1.5283	1.2838	66.85	66.76	278.2	5.04	5.00	28.73	28.91
210	$HC{\equiv}CCH_2$	C_2H_5	C_2H_5	Br	TEA	TBA	66	119.5–120.0	10	1.5070	1.0354	49.20	49.22	171.3	8.19	8.08		
211	$HC{\equiv}CCH_2$	n-C_3H_7	n-C_3H_7	Br	TEA	TBA	71	121.0–121.5	4.6	1.4978	0.9972	58.54	58.57	199.3	7.03	6.71		

TABLE III (*Concluded*)

No.	R_1	R_2	R_3	X	Base[a]	Solvent[b]	Yield, %	B.p., °C.	Mm.	$n^{30}D$	d^{30}_4	MRD Calcd.	MRD Found	Mol. wt.	Nitrogen, % Calcd.	Nitrogen, % Calcd.	Halogen, % Calcd.	Halogen, % Found
212	$HC\equiv CCH_2$	C_2H_5	n-C_4H_9	Br	TEA	TBA	54	138.5–140.0	10	1.4983	0.9981	58.49	58.56	199.3	7.03	6.98		
213	$HC\equiv CCH_2$	$CH_3CH=CHCH_2$	$CH_2=CHCH_2$	Br	TEA	TBA	64	137.0–137.5	10	1.5232	1.0379	57.56	57.50	195.3	7.18	7.26		
214	$HC\equiv CCH_2$	$CH_2=CHCH_2$	n-C_3H_7	Br	TEA	TBA	56	137.5–137.6	10	1.5105	1.0174	58.05	58.04	197.3	7.11	7.08		
215	$HC\equiv CCH_2$	$CH_2=CHCH_2$	$CH_2=C(Cl)CH_2$	Br	TEA	TBA	57	155.5–156.0	10	1.5346	1.1502	62.26	62.15	229.7	6.10	6.19	15.43	15.41
216	$HC\equiv CCH_2$	n-C_3H_7	$CH_2=C(Cl)CH_2$	Br	TEA	TBA	67	155.5–156.0	10	1.5250	1.1268	62.75	63.03	231.8	6.04	6.10	15.30	15.31
217	$HC\equiv CCH_2$	n-C_3H_7	$CH_2=C(CH_3)CH_2$	Br	TEA	TBA	61	141.0–141.5	10	1.5072	1.0025	62.68	62.75	211.3	6.63	6.69		
218	$N\equiv C-CH_2$	C_2H_5	C_2H_5	Cl	TEA	TBA	75	155.5–155.6	10	1.4991	1.0901	46.35	46.40	172.3	16.26	16.10		
219	$N\equiv C-CH_2$	n-C_3H_7	n-C_3H_7	Cl	TEA	TBA	56	156.5–157.0	5.0	1.4920	1.0436	55.69	55.69	200.3	13.98	13.73		
220	$N\equiv C-CH_2$	C_2H_5	n-C_4H_9	Cl	TEA	TBA	78	171.0–171.5	10	1.4921	1.0433	55.64	55.71	209.3	13.98	14.02		
221	$N\equiv C-CH_2$	$CH_2=CHCH_2$	$CH_2=CHCH_2$	Cl	TEA	TBA	71	170.5–171.0	10	1.5191	1.0906	54.71	54.63	196.3	14.27	14.10		
222	$N\equiv C-CH_2$	n-C_3H_7	$CH_2=CHCH_2$	Cl	TEA	TBA	46	168.0–168.5	10	1.5059	1.0667	55.20	55.14	198.3	14.12	14.17		
223	$CH_3C(Cl)=CHCH_2$[e]	C_2H_5	C_2H_5	Cl	TEA	TBA	32	146.5–147.0	10	1.5133	1.0971	60.78	60.78	221.8	6.32	6.28	15.99	15.84
224	$CH_3C(Cl)=CHCH_2$	n-C_3H_7	n-C_3H_7	Cl	TEA	TBA	53	171.0–171.5	10	1.5052	1.0568	70.12	70.13	249.8	5.61	5.55	14.19	13.80
225	$CH_3C(Cl)=CHCH_2$	n-C_4H_9	CH_3	Cl	TEA	TBA	58	172.0–173.5	10	1.5094	1.0769	65.42	65.47	235.8	5.94	5.87	15.04	14.56
226	$CH_3C(Cl)=CHCH_2$	$CH_2=CHCH_2$	$CH_2=CHCH_2$	Cl	TEA	TBA	58	163.5–164.0	10	1.5262	1.0921	69.14	69.10	245.8	5.70	5.52	14.43	14.21
227	$CH_3C(Cl)=CHCH_2$	$CH_2=CHCH_2$	i-C_3H_7	Cl	TEA	TBA	43	161.0–161.2	10	1.5181	1.0809	69.64	69.48	247.8	5.65	5.53	14.31	14.40
228	*cis*-$BrCH=CHCH_2$	n-C_3H_7	n-C_3H_7	Br	TEA	TBA	48	169.5–170.0	10	1.5217	1.2573	67.98	67.95	280.2	5.00	4.85	28.52	28.73
229	*cis*-$BrCH=CHCH_2$	n-C_4H_9	CH_3	Br	TEA	TBA	62	167.0–167.1	10	1.5279	1.2951	63.28	63.29	266.2	5.26	5.30	30.02	30.20
230	*cis*-$BrCH=CHCH_2$	$CH_2=CHCH_2$	$CH_2=CHCH_2$	Br	TEA	TBA	66	167.0–167.5	10	1.5466	1.3066	67.09	67.00	276.2	5.07	5.14	28.94	28.96
231	*cis*-$BrCH=CHCH_2$	$CH_2=CHCH_2$	n-C_3H_7	Br	TEA	TBA	70	166.5–167.0	10	1.5337	1.2898	67.49	67.49	278.2	5.04	4.78	28.73	28.99
232	$CH_3CH_2OCH_2CH_2$	C_2H_5	C_2H_5	Br	TEA	TBA	44	132.5–133.0	10	1.4773	1.0064	57.66	57.67	295.3	6.82	6.68		
233	$CH_3CH_2OCH_2CH_2$	n-C_3H_7	n-C_3H_7	Br	TEA	TBA	55	149.5–150.0	10	1.4734	0.9783	67.00	66.97	233.4	6.00	5.79		
234	$CH_3CH_2OCH_2CH_2$	n-C_4H_9	C_2H_5	Br	TEA	TBA	49	151.5–152.0	10	1.4738	.9791	66.95	66.96	233.4	6.00	6.17		

[a] The abbreviations for the bases are: DAA = dialkylamine, P = potassium carbonate, Py = pyridine, S = sodium dispersion, TEA = triethylamine. [b] The abbreviations for the solvents are: B = benzene, EA = absolute ethanol, EGDA = ethylene glycol dimethyl ether, PE = petroleum ether (b.p. 30–60°), T = toluene, TBA = *t*-butyl alcohol, W = water. [c] Cyclohexyl. [d] *Anal.* Calcd. for $C_9H_{17}NOS$: C, 57.71; H, 9.15; S, 17.12; mol. wt., 187.3. Found: C, 57.88; H, 9.18; S, 17.33; mol. wt. (Rast), 180. [e] The 3-chloro-2-butenyl thiolcarbamates were prepared from the α-isomer of 1,3-dichloro-2-butene, b.p. 127.0–128.5° (760 mm.), $n^{31}D$ 1.4669; L. F. Hatch and S. K. Ballin, THIS JOURNAL, **71,** 1039 (1949), give b.p. 127.9° (745 mm.), $n^{30}D$ 1.4670. It is assumed that the α-configuration is retained in the thiolcarbamate. [f] *cis–trans* compound.

TABLE IV

THIOLCARBAMATES PREPARED FROM HETEROCYCLIC AMINES R_1SCN 

No.	R_1	B	D	X[a]	Base[a]	Solvent[a]	Method	Yield, %	B.p., °C.	Mm.	$n^{30}D$	d^{30}_4	MRD Calcd.	MRD Found	Mol. wt.	Nitrogen, % Calcd.	Nitrogen, % Found	Halogen, % Calcd.	Halogen, % Found
235	CH_3	CH_2CH_2	H				A[b]	61	124.5–125.0	16	1.5209	1.0945	44.27	44.30	159.3	8.79	8.89		
236	C_2H_5	CH_2CH_2	H				A[b]	56	150.5–151.0	31.5	1.5139	1.0631	49.19	49.06	173.3	8.08	8.03		
237	n-C_3H_7	CH_2CH_2	H				A[b]	65	139.5–142.0	11.5	1.5090	1.0387	53.86	53.84	187.3	7.48	7.75		
238	i-C_3H_7	CH_2CH_2	H				A[b]	45	138.0–138.2	17	1.5069	1.0344	53.87	53.88	187.3	7.48	7.80		
239	$CH_2=CHCH_2$	CH_2CH_2	H	Br	TEA		C	65	119.5–120.0	4.5	1.5269	1.0631	53.59	53.57	185.3	7.56	7.39		
240	$CH_2=C(CH_3)CH_2$[e]	CH_2CH_2	H	Cl	TEA	TBA	C	55	148.0–149.0	10	1.5224	1.0445	58.17	58.24	199.3	7.03	7.24		
241	$CH_3CH=CHCH_2$	CH_2CH_2	H	Br	TEA	TBA	C	49	135.0–137.0	4.5	1.5267	1.0466	58.51	58.52	199.3	7.03	6.87		
242	$HC\equiv CCH_2$	CH_2CH_2	H	Br	TEA	TBA	C	28	133.5–134.0	4.5	1.5393	1.1081	51.80	51.84	183.3	7.64	7.49		
243	CH_3OCH_2	CH_2CH_2	H	Cl	TEA	TBA	C	58	126.5–127.0	4.5	1.5168	1.1233	51.01	50.96	189.3	7.40	7.28		
244	CH_3SCH_2	CH_2CH_2	H	Cl	TEA	TBA	C	66	152.5–153.5	4.5	1.5578	1.1585	57.09	57.13	205.4	6.82	7.04		
245	$CH_2=C(Cl)CH_2$	CH_2CH_2	H	Cl	TEA	TBA	C	54	144.7–145.0	4.5	1.5385	1.1829	58.05	58.15	219.7	6.38	6.48	16.14	16.42

246	ClCH=CHCH$_2$[e]	CH_2CH_2	H	Cl	TEA	TBA	C	60	152.5–153.0	4.5	1.5449	1.1869	...	58.53	219.7	6.38	6.41	16.14	15.74	
247	CH_2=C(Br)CH_2	CH_2CH_2	H	Br	TEA	TBA	C	58	176.0–176.8	10	1.5573	1.3959	60.60	60.96	264.2	5.30	5.42	30.25	30.01	
248	CH_2=$CHCH_2$	CH_2CH_2	CH_3	TEA	TBA	C	61	123.5–125.0	4.5	1.5222	1.0470	58.10	58.08	199.3	7.03	6.98				
249	CH_2=C(CH_3)CH_2[d]	CH_2CH_2	CH_3	Cl	TEA	TBA	C	41	152.0–153.0	10	1.5186	1.0300	62.68	62.83	213.4	6.56	6.47			
250	CH_3CH=$ClCH_2$	Cl_2CH_2	CH_3	Br	TEA	TBA	C	49	140.5–141.0	4.5	1.5232	1.0340	63.02	63.05	213.4	6.56	6.83			
251	CH_2OCH_2	CH_2CH_2	CH_3	Cl	TEA	TBA	C	52	130.5–131.0	4.5	1.5123	1.1018	55.52	55.39	203.3	6.89	7.15			
252	CH_3SCH_2	CH_2Cl_2	CH_3	Cl	TEA	TBA	C	57	155.5–156.5	4.5	1.5515	1.1370	61.60	61.61	219.4	6.38	6.59			
253	CH_2=C(Cl)CH_2	CH_2CH_2	CH_3	Cl	TEA	TBA	C	34	149.0–152.0	4.5	1.5331	1.1591	62.56	62.60	233.8	5.99	5.98	15.17	15.33	
254	ClCH=$CHCH_2$[e]	CH_2CH_2	CH_3	Cl	TEA	TBA	C	44	155.5–155.7	4.5	1.5393	1.1640	...	62.94	233.8	5.99	6.00	15.17	14.95	
255	HC≡CCH_2	CH_2CH_2	CH_3	Br	TEA	TBA	C	32	137.5–137.6	4.5	1.5329	1.0862	56.31	56.36	197.3	7.09	7.23			
256	CH_2=$CHCH_2$	CH_2	H	Br	TEA	TBA	C	74	118.0–118.5	4.5	1.5285	1.0837	48.79	48.70	171.3	8.18	8.02			
257	CH_3CH=$CHCH_2$	CH_2	H	Br	TEA	TBA	C	54	134.5–135.0	4.5	1.5280	1.0632	53.71	53.66	185.3	7.56	7.71			
258	HC≡CCH_2	CH_2	H	Br	TEA	TBA	C	53	133.8–134.0	4.5	1.5430	1.1343	47.00	47.03	169.2	8.28	8.48			
259	CH_3OCH_2	CH_2	H	Cl	TEA	TBA	C	33	126.0–126.5	4.5	1.5167	1.1468	46.21	46.21	175.3	7.99	7.78			
260	CH_3SCH_2	CH_2	H	Cl	TEA	TBA	C	66	153.5–154.0	4.5	1.5619	1.1861	52.29	52.30	191.3	7.32	7.42			
261	CH_2=C(Cl)CH_2	CH_2	H	Cl	TEA	TBA	C	53	146.0–146.5	4.6	1.5409	1.2124	53.25	53.31	205.7	6.81	6.90	17.24	17.34	
262	ClCH=$CHCH_2$[e]	CH_2	H	Cl	TEA	TBA	C	70	151.0–153.0	4.5	1.5473	1.2154	...	53.70	205.7	6.81	6.69	17.24	17.20	
263	C_2H_5	CH_2O	H				A[b]	66	156.3–157.0	32	1.5158	1.1443	46.20	46.24	175.3	7.99	8.16			
264	n-C_3H_7	CH_2O	H				A[b]	62	145.0–145.2	11.7	1.5106	1.1152	50.87	50.81	189.3	7.40	7.51			
265	i-C_3H_7	CH_2O	H				A[b]	63	137.0–137.5	11.8	1.5084	1.1090	50.88	50.91	189.3	7.40	7.54			

[a] Applies only to method C; refer to Table III. [b] The sodium alkylmercaptide was prepared by the sodium alkoxide method. [c] *Anal.* Calcd. for $C_{10}H_{17}NOS$: C, 60.26; H, 8.60. Found: C, 60.27; H, 8.75. [d] *Anal.* Calcd. for $C_{11}H_{19}NOS$: C, 61.93; H, 8.98. Found: C, 62.11; H, 9.14. [e] *cis-trans* compound.

TABLE V

ALKYL AND ARYL CHLOROTHIOLFORMATES O ‖ RSCCl

R	Yield, %	B.p. °C.	Mm.	$n^{30}D$	Chlorine, % Calcd.	Found
n-Propyl	60	59.0–60.0	26	1.4750	25.59	24.85
i-Butyl	42	63.0–64.0	19	1.4704	23.24	22.90
2-Chloroethyl[a]	55	77.0–78.0	16	1.5167	44.60	44.60
3-Chloropropyl[a]	57	98.5–99.0	15	1.5118	40.97	41.07

[a] Prepared by the method of F. Arndt, *et al.*, see Experimental.

Further confirmation on the structure of the crotyl thiolcarbamates is obtained from the infrared spectra of these compounds. The crotyl thiolcarbamates, compounds 187, 189 and 190, show a strong band at 10.37 μ, indicative of a symmetrically disubstituted *trans* double bond and no bands at 3.24–3.25, 5.45–5.49, 10.00–10.10 and 10.95–11.00 μ, characteristic of the vinyl group RCH=CH_2.[10] On the other hand, the corresponding allyl thiolcarbamates which contain a terminal vinyl group, compounds 71, 111 and 112, do show a weak band at 3.24 μ, a weak band at 5.42–5.43 μ, a moderate band at 10.09–10.10 μ and a strong band at 10.88–10.92 μ, but no band at 10.37 μ. When we examine the spectra of thiolcarbamates which contain both a terminal vinyl and a crotyl group, such as compounds 193, 194 and 195, all of the bands characteristic of a terminal vinyl and symmetrically disubstituted *trans* double bonds appear, but the 10.09–10.10 and 10.88–10.92 μ bands have been shifted to a shorter wave length; *e.g.*, bands appear at 3.24, 5.42–5.43, 10.03, 10.37 and 10.80 μ. The shift of the 10.09–10.10 and 10.88–10.92 μ band pair to 10.03 and 10.80 μ when the allyl group becomes connected to the nitrogen atom of a thiolcarbamate has also been observed in compounds 85, 86, 87, 88, 102, 104, 140, 141, 142, 143, 144, 145 and 191.

It was observed that this band pair reappeared at 10.1 and 10.9 μ when the allyl group was bonded to an amino nitrogen such as N-ethylallylamine, N-allyl-*n*-propylamine, N-allyl-*i*-propylamine, N-allyl-*n*-butylamine and N-allyl-*i*-butylamine.

Attempts to oxidize crotyl diethylthiolcarbamate, compound 187, to the monocarboxylic acid with both aqueous permanganate and a glacial acetic acid solution of permanganate were unsuccessful. However, the above infrared data demonstrate that the crotyl esters have the 3-methylallyl structure.

Since the possibility existed that the reaction of *cis* and *trans*-1,3-dichloro-1-propenes with thiolcarbamate salts (procedure C) could also lead to rearranged products, it was necessary to examine the chloroallyl thiolcarbamates, compounds 178–186, to determine whether they were 3-chloroallyl thiolcarbamates or 1-chloroallyl thiolcarbamates.

The infrared spectra of the four *cis*-3-chloro-2-propenyl thiolcarbamates, compounds 178, 180, 182 and 184, prepared from *cis*-1,3-dichloro-1-propene are distinctly different from the spectra of the corresponding *trans*-alkenyl thiolcarbamates, compounds 179, 181, 183 and 185, prepared from *trans*-1,3-dichloro-1-propene. If allylic rearrangement

(10) A. Weissberger, "Technique of Organic Chemistry, Vol. IX, Chemical Applications of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 377–384.

TABLE VI

SECONDARY AMINES, $R_1 \diagdown \atop R_2 \diagup$NH

R_1	R_2	Yield, %	B.p. °C.	B.p. Mm.	$n^{30}D$	d^{30}_4	MR_D Calcd.	MR_D Found	Mol. wt.	Nitrogen, % Calcd.	Nitrogen, % Found	Halogen, % Calcd.	Halogen, % Found
CH_2=$CHCH_2$	*i*-C_3H_7	29	97.0–97.5	760	1.4103	0.7406	33.06	33.20	99.2	14.12	14.03	98.0[a]	
CH_2=$CHCH_2$	*i*-C_4H_9	59	123.0–123.5	760	1.4165	.7518	37.70	37.83	113.2	12.38	12.37	110.7[a]	
CH_2=$C(CH_3)CH_2$	C_2H_5	57	104.5–105.0	760	1.4173	.7526	33.01	33.16	99.2	14.12	13.78	98.2[a]	
CH_2=$C(CH_3)CH_2$	*n*-C_3H_7	66	128.2–128.8	760	1.4218	.7606	37.68	37.80	113.2	12.38	12.67	110.4[a]	
CH_2=$C(CH_3)CH_2$	CH_2=$CHCH_2$	63	129.0–129.2	760	1.4383	.7839	37.19	37.26	111.2	12.60	12.78	111.1[a]	
HC≡CCH_2	*n*-C_3H_7	42	123.0–123.2	760	1.4307	.8021	31.48	31.34	97.2	14.41	14.63	9.70[a]	
CH_2=$C(Cl)CH_2$	*n*-C_3H_7	76	73.5–74.0	50	1.4449	.9409	37.75	37.79	133.6	10.49	10.20	26.54 131.1[a]	26.37
CH_2=$C(Cl)CH_2$	CH_2=$CHCH_2$	69	74.0–75.0	50	1.4634	.9740	37.26	37.24	131.6	10.64	10.50	26.94 128.7[a]	26.75
trans-ClCH=$CHCH_2$	*n*-C_3H_7	64	78.0–78.5	30	1.4531	.9496	38.01	38.04	133.6	10.48	10.14	26.53 135.1[a]	26.69
trans-ClCH=$CHCH_2$	CH_2=$CHCH_2$	52	78.0–78.5	30	1.4720	.9820	37.40	37.53	131.6	10.64	10.41	26.94 134.9[a]	26.39

[a] Neutralization equivalent performed by potentiometric titration.

took place during the reaction with both *cis*- and *trans*-1,3-dichloro-1-propenes, the 1-chloroallyl thiolcarbamates which would be formed would be identical, since there could be no *cis–trans* isomerism. However, it is possible that only one stereoisomer might rearrange and hence this would account for the difference in the infrared spectra between the *cis* and *trans* compounds. This possibility is not consistent with the observed boiling points of the *cis* and *trans* isomers. The *cis* isomers boil 0.5–2.0° lower than the corresponding *trans* isomers. It would be expected that the 1-chloroallyl thiolcarbamate, a secondary halide, would boil more than 2° lower than the 3-chloroallyl thiolcarbamate, a primary halide. The secondary halide would be expected to have a similar boiling point to the corresponding 2-chloroallyl thiolcarbamate which is also a secondary halide. On comparing the 2-chloroallyl thiolcarbamates, compounds 172, 173, 176 and 177 with the corresponding *trans*-3-chloroallylthiolcarbamates, compounds 179, 181, 183 and 185, we see that the boiling points of the former compounds are 7.5–18° lower than the latter, which is significantly different from the maximum 2° lowering between the *cis*- and *trans*-3-chloroallylthiolcarbamates. The 10.1, 10.8–10.9 μ band pair characteristic of the vinyl group CH_2=CHR is absent in compounds 178, 179, 180 and 181, but is present in compounds 184 and 185 which contain an allyl group. Although this is not a rigorous proof that rearrangement did not take place, this information together with the well established evidence in the literature that simple allylic halides do not rearrange when treated in absolute alcohol with nucleophilic reagents,[11] make it reasonable to assume that allylic rearrangement did not take place.

Infrared evidence indicates that the 3-chloro-2-butenyl thiolcarbamates, compounds 223–227, are also formed without rearrangement. The 10.1, 10.8–10.9 μ band pair is absent in compounds 223 and 224, but appears in compound 227 which contains an allyl group.

Evidence that the 3-chloroallyl group present in compounds 117, 118, 149, 151, 153, 167, 169, 171, 197, 199 and 200, in which this group is connected to the nitrogen atom of the thiolcarbamate molecules does not rearrange, is on less firm ground. Infrared spectra are inapplicable because of interfering strong broad bands in the 10.1, 10.9 μ region. The comparison of boiling points between the 2-chloroallyl thiolcarbamates and the corresponding *cis–trans* mixture of 3-chloroallyl thiolcarbamates[12] indicates that rearrangement does not take place. The 2-chloroallylthiolcarbamates, compounds 150, 152, 168, 170, 196 and 198, boil from 8.5–11° lower than the corresponding *cis–trans*-3-chloroallylthiolcarbamates and the same arguments apply in this instance as in the case when the 3-chloroallyl groups are connected to the sulfur atom.

Molar Refractions.—The system of atomic, group and bond refractions proposed by various workers[13–15] has become generally accepted as a useful tool for the structural determination and identification of organic compounds. These refraction values are based on the principle of additivity which, unfortunately, is only partially true since the molar refraction of a compound is also a constitutive property and hence, in some cases, is sensitive to the arrangement of the atoms within the molecule. The departure from additivity occurs especially frequently in molecules which contain easily polarizable elements and groups such as sulfur, nitrogen, the halogens and the carbonyl group. Numerous examples of departure from additivity occur in the thiolcarbamates wherein some structural isomers can have molar refractions which differ by as much as 0.6 cc. with one another. Where such large differences can occur within a given class of compounds such as the thiolcarbamates, it is not feasible to use the literature bond constants for the calculation of molar refractions, since these bond constants cannot take into account the structural effects which can influence the molar refraction.

(11) J. D. Roberts, W. G. Young and S. Winstein, THIS JOURNAL, **64**, 2157 (1942); A. G. Catchpole and E. D. Hughes, *J. Chem. Soc.*, 4 (1948); B. D. England, *ibid.*, 1615 (1955).

(12) A number of *cis–trans*-3-chloroallylthiolcarbamates were not included in Table III because the pure *trans* isomers were prepared later on during the synthesis program. The *cis–trans*-3-chloroallylthiolcarbamates were distilled at the same pressure (4.5 mm.) as the 2-chloroallylthiolcarbamates, and since the boiling point difference between the *cis* and *trans* isomers was not greater than 2°, direct comparisons between the boiling points of the 2-chloroallyl and 3-chloroallylthiolcarbamates were possible.

(13) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

(14) A. S. Vogel, W. T. Cresswell, G. H. Jeffery and J. Leicester, *J. Chem. Soc.*, 514 (1952).

(15) A. Weissberger, "Technique of Organic Chemistry, Vol. I, Part II, Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1949, pp. 1162–1177.

Since we had prepared such a large number of closely related thiolcarbamates, we could select the changes in molar refraction which occurred with slight changes in structure and thus could incorporate these effects into the bond refractions of the various groups concerned. On using these new empirical values of the bond constants of the various groups contained in the thiolcarbamates, we obtained very close agreement between calculated and observed molar refractions. It must be emphasized that these values might not apply to other classes of compounds, although satisfactory agreement was found between calculated and observed values in the secondary amines employed in this work.[16]

All of the bond constants derived in this work are based on the bond constants for alkyl groups reported by Vogel, *et al.*[14] When the values of the alkyl groups R_1, R_2 and R_3 are subtracted from the observed values of the molar refractions of the thiolcarbamate compounds 1 — 69, $R_1SCON(R_2)(R_3)$, there is obtained a series of values which incorporate the bond refractions for (SCON) + (CS) + 2(CN). These values range from a low of 17.18 cc. for methyl di-*n*-propylthiolcarbamate, compound 17, to a high of 18.23 cc. for *i*-amyl di-*i*-amylthiolcarbamate, compound 68. When we examine the distribution curve of these values, a definite trend becomes apparent between the average distributions and the structure and arrangement of the respective R groups. This is shown in Table VII.

TABLE VII $R_1SC(=O)N(R_2)(R_2)$

Bond refraction values of (SCON) + (CS) + 2(CN) = R_D

R_1	R_2	R_D, cc.
	Group I	
CH_3	CH_3, C_2H_5 *n*-C_3H_7, *i*-C_3H_7 *n*-C_4H_9, *i*-C_4H_9 *n*-C_5H_{11}, $CH_2(CH_2)_2CH_2$ $CH_2(CH_2)_3CH_2$, $CH(CH_2)_3CH_2$ (CH$_3$ branch)	17.37
	Group II	
C_2H_5, *n*-C_3H_7 *n*-C_4H_9, *i*-C_4H_9 *n*-C_5H_{11}	Same as group I	17.64
	Group III	
i-C_3H_7, *sec*-C_4H_9 *i*-C_5H_{11}	Same as group I	17.83
	Group IV	
C_2H_5, *n*-C_3H_7 *n*-C_4H_9, *i*-C_4H_9 *i*-C_5H_{11}	*i*-C_5H_{11}	17.84
	Group V	
t-C_5H_{11}	Same as group I	17.73
	Group VI	
t-C_4H_9	Same as group I	17.94
	Group VII	
i-C_3H_7, *sec*-C_4H_9 *t*-C_4H_9, *i*-C_5H_{11} *t*-C_5H_{11}	*i*-C_5H_{11}	18.13

If we let R_D equal the bond refraction value of (SCON) + (CS) + 2(CN) as was done in Table VII, we can now derive bond refractions for all of the various groups connected to the SCON moiety in the thiolcarbamate molecule. If the group connected to the nitrogen or sulfur atom contains no α-substituent, the value 17.64 cc. is used for R_D as long as the skeletal structure does not differ appreciably from the primary alkyl groups listed under group II, Table VII. Since none of the compounds prepared in this work with the exception of the saturated alkyl thiolcarbamates have groups differing appreciably from the skeletal structures listed under group II, Table VII, the value of 17.64 cc. is used throughout the derivation of the other bond refractions.

The bond refractions of the different groups were obtained from equation 5

$$X = MR_D - (17.64 + X_1 + X_2) \qquad (5)$$

in which X is the bond refraction to be determined, MR_D is the observed molar refraction and X_1 and X_2 are known bond refractions. The arithmetical average of the values found for each group was obtained and the results are shown in Table VIII.

TABLE VIII

BOND REFRACTIONS

Group	Refraction value, cc.
CH_2=$CHCH_2$ on N	13.83
CH_2=$CHCH_2$ on S	14.05
CH_2=$C(Cl)CH_2$ on N	18.53
CH_2=$C(Cl)CH_2$ on S	18.51
trans-ClCH=$CHCH_2$ on N	18.79
trans-ClCH=$CHCH_2$ on S	19.06
cis-ClCH=$CHCH_2$ on S	18.83
CH_2=$C(CH_3)CH_2$ on N	18.46
CH_2=$C(CH_3)CH_2$ on S	18.63
HC≡CCH_2 on N	12.09
HC≡CCH_2 on S	12.26
CH_3OCH_2 on S	11.47
CH_3SCH_2 on S	17.55
CH_3CH=$CHCH_2$ on S	18.97
$ClCH_2CH_2CH_2$ on S	19.03
CH_2=$C(Br)CH_2$ on S	21.06
cis-BrCH=$CHCH_2$ on S	21.70
N≡CCH_2 on S	9.41
α-$CH_3C(Cl)$=$CHCH_2$ on S	23.84
$CH_2CH_2CH_2CH_2CH_2$ on N	21.90
$CH_2(CH_3)CH_2CH_2CH_2CH_2$ on N	26.41
$CH_2CH_2CH_2CH_2$ on N	17.10
$CH_2CH_2OCH_2CH_2$ on N	18.91
Cyclohexyl on N	26.02
$CH_3CH_2OCH_2CH_2$ on S	20.72

It is interesting to observe in Table VIII that, with the exception of the 2-chloroallyl group, the unsaturated groups connected to the sulfur atom

(16) A more detailed account of the discussion and results obtained in the molar refraction section has been deposited as Document number 5710 with ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting in advance $3.75 for photoprints or $2.00 for 35 mm. microfilm payable to Chief, Photoduplication Service, Library of Congress.

have bond refractions about 0.2 cc. higher than when these groups are connected to the nitrogen atom. It is not known whether this increase in refraction is localized in the unsaturated group or whether it is present in the (SCON) + (CS) + 2(CN) term. It is also conceivable that this increased refraction is distributed throughout the entire molecule. However, for simplicity in calculating molar refractions of the thiolcarbamates it is sufficient to include this increased refraction in the unsaturated group.

For the calculation of the molar refraction of any unknown thiolcarbamate containing any of the groups shown in Table VIII it is only necessary to add the bond refractions to the appropriate R_D value. In the case of thiolcarbamates prepared from primary amines which are shown in Table II, the R_D value used for the calculation of the molar refraction is 18.06 cc. and includes the term (SCON) + (CS) + (CN) + (NH). The bond refractions for alkyl groups can be obtained from Vogel's paper.[14]

Structural Effects on Molar Refraction.—The large number of isomeric thiolcarbamates which have been prepared have revealed some interesting relationships between molar refraction and structure. An examination of the isomeric butyl esters of the dialkylthiolcarbamic acids listed in Table I, for example, compounds 44, 45, 46 and 47, shows that the molar refractions of *n*-butyl, *i*-butyl and *sec*-butyl thiolcarbamates are nearly constant, but the value of the *t*-butyl thiolcarbamate is 0.3 cc. higher. This phenomenon is observed in all of the other butyl thiolcarbamates. West, Webster and Wilkinson[17] have observed a similar exaltation taking place in tetraalkyltin compounds when *n*- and *sec*-butyl groups were replaced by *t*-butyl groups.

When a chlorine substituent is shifted from the β- to the γ-position of an allyl group attached to the sulfur atom there results an average increase of the molar refraction of 0.5 cc., whereas if the chloroallyl group is connected to the nitrogen atom, the average increase amounts to only 0.3 cc. If the substituent is a methyl group, the increase amounts to only 0.3 cc. when the allyl group is connected to the sulfur atom. Specific instances of this effect are observed on comparing compounds 172, 179; 168, 169 and 155, 188. More examples of this phenomenon can be obtained from Tables III and IV.

It is possible that the increase in molar refraction in going from a 2-chloroallyl group to a *trans*-3-chloroallyl group is due to an intrinsically larger refraction of the 3-chloroallyl group itself. However, if this is the case, it would be expected that the exaltations would be the same whether the chloroallyl groups were connected to the sulfur or the nitrogen atom. As shown above, the exaltation is greater when the chloroallyl group is connected to the sulfur atom. The molar refractions of *cis*- and *trans*-1-chloropropene are, respectively, 20.1 and 20.4 cc. and that of 2-chloropropene is 20.5 cc.[18] Since the 1-chloropropenes can be considered as the simplest representatives of the 3-chloroallyl groups and 2-chloropropene as the simplest representative of the 2-chloroallyl group, the intrinsic refraction of the 3-chloroallyl group is lower, not higher, than the 2-chloroallyl group. The increase in refraction in going from a 2-chloroallyl to a 3-chloroallyl group in the thiolcarbamates must then be explained by an interaction of the chlorine and the sulfur atom or carbon–sulfur bond when the chloroallyl group is connected to the sulfur atom and to an interaction of the chlorine and the nitrogen atom or carbon–nitrogen bond when the chloroallyl group is connected to the nitrogen atom. From the fact that the exaltation is greater when the chloroallyl group is attached to the sulfur than when it is attached to the nitrogen, there must be a greater interaction between the chlorine and the sulfur atom or carbon–sulfur bond than between the chlorine and the nitrogen atom or carbon–nitrogen bond. The difference between the molar refractions of the *cis*- and *trans*-3-chloroallyl thiolcarbamates as exemplified by compounds 178, 179; 180, 181; 182, 183 and 184, 185 is about the same order of magnitude (0.2 cc.) as the difference between *cis*-1-chloropropene and *trans*-1-chloropropene (0.3 cc.) and, therefore, it can be assumed that the refraction differences between the *cis*- and *trans*-3-chloroallylthiolcarbamates are due to the intrinsic refractions of the *cis*- and *trans*-3-chloroallyl groups and not to any sort of interaction between these groups and the rest of the thiolcarbamate molecules.

The same type of argument applies to the exaltation observed on changing from a methallyl to a crotyl thiolcarbamate. However, in this case, refraction data are not available for 2-butene and 2-methylpropene, which can be considered as the simplest representatives of the crotyl and methallyl groups, respectively. Refraction data are available for the next higher homologs, *cis* and *trans*-2-pentene and 2-methyl-1-butene, and since the polarizability of the carbon–carbon bond does not differ appreciably from the carbon–hydrogen bond, these three compounds will be used as reference standards to determine whether an interaction is occurring between the methyl group substituted at the γ-position of the allyl group and the sulfur atom or carbon–sulfur bond. The molar refraction of *cis*-2-pentene is 25.06, *trans*-2-pentene is 25.01 and 2-methyl-1-butene is 24.89.[19] Winstein and Young[9] report that crotyl bromide exists as only one identifiable isomer and since the infrared spectra of the crotyl thiolcarbamates show a strong band at 10.37 μ, indicative of a symmetrically disubstituted *trans* double bond, it is assumed that the crotyl group in the thiolcarbamates exists as the *trans* isomer. On comparing the molar refraction of *trans*-2-pentene, which represents the *trans*-crotyl group, with the molar refraction of 2-methyl-1-butene, which represents the methallyl group, it is seen that the value of the *trans*-2-pentene is 0.1 cc. higher than the value of the 2-methyl-1-butene. Hence, the *trans*-crotyl group can be considered to have an intrinsic refraction 0.1 cc. higher than the methallyl group. This is such a small value that its significance is uncertain, but it is safe to assume that the

(17) R. West, M. H. Webster and G. Wilkinson, THIS JOURNAL, **74**, 5794 (1952).

(18) W. T. Rogers, *ibid.*, **69**, 1243 (1947); W. H. King and H. A. Smith, *ibid.*, **72**, 3459 (1950).

(19) G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1939, pp. 176, 177, 179.

interaction of the methyl group substituted at the γ-position of the allyl group with the sulfur atom or carbon–sulfur bond produces an exaltation of 0.2–0.3 cc. This exaltation is about half as large as that observed on replacing the methyl group by a chlorine atom.

The chlorine–nitrogen and chlorine–sulfur interactions have also been observed in compounds other than thiolcarbamates. Table IX shows this effect taking place in secondary amines. The observed exaltation is about the same as in the thiolcarbamates (0.3 cc.). Table X shows the exaltation taking place in some chloroallyl alkyl sulfides. In this case, the observed exaltation is somewhat lower than in the thiolcarbamates, but this may not be significant because only two pair of sulfides were studied. Since the same effect has been observed in three different types of molecules (thiolcarbamates, amines and sulfides) in which the only group in common is the $ClCH{=}CHCH_2S{-}$ or $ClCH{=}CHCH_2N{-}$ group, it is necessary to be concerned only with these structures and not the remainder of the molecule.

TABLE IX

CHLORINE–NITROGEN INTERACTION AS OBSERVED IN SECONDARY AMINES R_1R_2NH

R_1	R_2	MR_D	ΔMR_D
$CH_2{=}C(Cl)CH_2$	n-C_3H_7	37.79	0.25(0.3)[a]
trans-$ClCH{=}CHCH_2$	n-C_3H_7	38.04	
$CH_2{=}C(Cl)CH_2$	$CH_2{=}CHCH_2$	37.24	0.29(0.4)[a]
trans-$ClCH{=}CHCH_2$	$CH_2{=}CHCH_2$	37.53	

[a] See Table X for explanation.

TABLE X

CHLORINE–SULFUR INTERACTION AS OBSERVED IN SULFIDES, R_1SR_2

R_1	R_2	MR_D	ΔMR_D
$CH_2{=}C(Cl)CH_2$	C_2H_5	37.59	0.40(0.5)[a]
trans-$ClCH{=}CHCH_2$	C_2H_5	37.99	
$CH_2{=}C(Cl)CH_2$	n-C_3H_7	42.25	0.45(0.5)[a]
trans-$ClCH{=}CHCH_2$	n-C_3H_7	42.70	

[a] Values in parentheses are the adjusted exaltations obtained by taking into account the intrinsic refractions of the chloroallyl groups.

In order to elucidate the mechanisms which are responsible for these exaltations, more experimental work would have to be done. It would be necessary to differentiate between intra- and intermolecular field effects, inductive effects and electromeric effects.

A brief survey of the literature has revealed that this exaltation phenomenon is also found between 2,3-dichloropropene and *cis*-1,3-dichloropropene (0.5 cc.) and *trans*-1,3-dichloropropene (0.7 cc.),[18] 2,3-dibromo-1-propene[20] and *cis*-1,3-dibromo-propene (0.5 cc.)[21] and 2-bromo-3-chloro-1-propene[22] and *cis*-1-bromo-3-chloro-1-propene (0.6 cc.).[21]

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Experimental[23]

The compounds described in Tables I–IV have been prepared following one of the procedures A–C as noted. The reactants, when commercially available, were used as received without further purification. When unavailable, they were prepared in this Laboratory as described under "Preparation of Intermediates." All of the thiolcarbamates were fractionally distilled through an 18" × 8 mm. tantalum Podbielniak Heli-Grid fractional distillation column provided with external heating jacket. Two differential thermocouples connected to the lower third and upper third of the column helped maintain nearly adiabatic conditions throughout the distillation. Intermediates, which were prepared in larger amounts, were fractionated through a 36" by 25 mm. Todd fractional distillation assembly packed with Hastelloy B Podbielniak Heli-Pak column packing. This column was also provided with two differential thermocouples.

Procedure A. Ethyl Di-*n*-propylthiolcarbamate (18). (a) **Sodium Dispersion Method.**—A suspension of sodium (4.8 g., 0.21 g. at.) in xylene, 150 cc., was heated under argon to 110–120° until the sodium had melted, and then dispersed by stirring at 105–125° for 10 minutes at 4000 r.p.m. with a 1" Simplex Dispersator.[24] The stirring was stopped and the mixture was cooled to 30°. Slow stirring was then started and a solution of 14.3 g. (0.23 mole) of ethanethiol in 25 cc. of dry xylene was added dropwise, maintaining the temperature between 30–40° by external cooling. During the addition of the mercaptan, the mixture changed from an initial pale pink to a dark grayish-purple and finally to a creamish white after all of the sodium had been consumed. (If any doubt exists as to whether all of the sodium has been consumed, a simple rapid test is to add a few drops of the reaction mixture to about 1 cc. of ethanethiol. If any unreacted sodium is present, an evolution of gas bubbles will be observed.) If all of the sodium had been consumed after the addition of the mercaptan, the mixture was heated rapidly to reflux. If any sodium still remained unreacted, a couple of cc. more mercaptan was added and the mixture was slowly heated to reflux. This treatment always consumed unreacted sodium. When reflux was reached, the heating mantle was lowered and 32.8 g. (0.20 mole) of di-*n*-propyl-carbamoyl chloride was added at such a rate so as to promote gentle reflux of the reaction mixture. After the addition was completed, the mixture was refluxed for an additional 0.5 hour, cooled to room temperature, a little Super-Cel was added and the slurry was filtered. The cake was washed with three 25-cc. portions of xylene which were combined with the original filtrate. Most of the solvent was then removed by fractionating the material at atmospheric pressure through a 10" × 25 mm. column packed with Podbielniak Heli-Pak packing at a reflux ratio of 1/1. The distilland was then subjected to fractional distillation through the 18" tantalum Podbielniak Heli-Grid fractional distillation column. There was obtained 34.0 g. (90.0%) of ethyl di-*n*-propylthiolcarbamate. Both the prefraction and pot residue were present in insignificant amounts.

(b) **Sodium Alkoxide Method.**—Sodium (17.5 g. 0.77 mole) was added to 350 cc. of absolute methanol under argon. After solution was complete, the mixture was cooled to 24° and 50 g. (0.81 mole) of ethanethiol was rapidly added with agitation. An exothermic reaction ensued and the temperature rose to 34° without any external cooling. The solution was stirred for an additional 20 minutes at room temperature, then brought to reflux and 200 cc. of methanol was distilled. To the residue was added 250 cc. of xylene

(20) L. F. Hatch, H. E. Alexander and J. D. Randolph, *J. Org. Chem.*, **15**, 654 (1950).

(21) L. F. Hatch and K. E. Harwell, THIS JOURNAL, **75**, 6002 (1953).

(22) L. F. Hatch, I. B. Gordon and J. J. Russ, *ibid.*, **70**, 1093 (1948).

(23) Boiling points are uncorrected. Densities were obtained with a 1-ml. Weld pycnometer, Scientific Glass Apparatus Co., Catalog No. J-550, at a temperature of 30 ± 0.05°. The Zeiss Abbé refractometer was connected to the same constant temperature bath used for density determination. Infrared spectra are from a Perkin–Elmer model 2 double beam recording spectrophotometer equipped with sodium chloride optics.

(24) U. S. Industrial Chemicals Co., "Sodium Dispersions," 2nd edition, New York, N. Y., 1957, pp. 18–23.

and from this mixture 120 cc. of methanol–xylene was distilled. To the residual slurry was again added 250 cc. of xylene and from this mixture 250 cc. of xylene was distilled. Di-*n*-propylcarbamoyl chloride, 125 g. (0.77 mole) was then added over a 10-minute period to the refluxing suspension. It was a very exothermic reaction. The reaction mixture was refluxed for an additional 3 hours and then cooled to 30°. The slurry was filtered and the cake was washed with two 50-cc. portions of xylene which were combined with the original filtrate. The xylene solution was then fractionally distilled through the 36″ × 25 mm. Heli-Pak distillation column. The following fractions were obtained: (1) xylene 183 cc., b.p. 138–139° (760 mm.); (2) an intermediate fraction (154 g.), b.p. 50–136° (30 mm.); (3) ethyl di-*n*-propylthiolcarbamate, 72.5 g. (50%), b.p. 136–138° (30 mm.).

Fraction 2 was analyzed by gas chromatography (didecyl phthalate on firebrick at 175°) and was found to consist of 57% xylene, 24% ethyl di-*n*-propylthiolcarbamate and 19% methyl di-*n*-propylcarbamate. The total yield of ethyl di-*n*-propylthiolcarbamate was, therefore, 76% and methyl di-*n*-propylcarbamate was obtained in a 24% yield.

(*c*) **General Remarks Concerning the Sodium Dispersion Method.**—Primary mercaptans could be reacted with the sodium dispersion at any temperature from 30° to the reflux temperature of the solvent. However, when higher temperatures were used with volatile mercaptans, it was necessary to use a larger excess of mercaptan. This was probably caused by mercaptan being stripped out with the evolved hydrogen without condensing. Secondary and tertiary mercaptans could be reacted at any temperature from 50° to the reflux temperature of the solvent with the exception of *i*-propyl and *i*-butyl mercaptans which required minimum temperatures of 105°.

Other solvents, such as toluene and ethylene glycol dimethyl ether have been used successfully.

It is not necessary to filter the reaction mixture. Addition of water and phase separation is just as satisfactory.

Procedure B. Ethyl *n*-Propylthiolcarbamate (75).—A solution of 10 g. (0.08 mole) of ethyl chlorothiolformate in 20 cc. of ethyl ether was added dropwise at ice-bath temperature to a solution of 9.5 g. (0.16 mole) of *n*-propylamine dissolved in 100 cc. of ethyl ether. It was a very exothermic reaction and crystals of *n*-propylamine hydrochloride formed immediately. The mixture was then filtered and the cake was washed with two 25-cc. portions of ethyl ether. The combined filtrate was then concentrated on the steam-bath and the residual liquid was distilled through the 18″ Podbielniak Heli-Grid fractional distillation column. There was obtained 8.8. g. (74.6%) of ethyl *n*-propylthiolcarbamate. There was no prefraction or pot residue.

General Remarks Pertaining to Procedure B.—It makes no difference whether the amine is added to the alkyl chlorothiolformate or the alkyl chlorothiolformate is added to the amine. Other solvents which have been used are: benzene, petroleum ether, b.p. 30–60°, and *n*-pentane. It is not necessary to filter the cake during the work-up procedure. Addition of water, followed by phase separation and washing the organic phase, first with dilute hydrochloric acid and finally with water, leads to a very pure product.

Instead of using 2 moles of amine per mole of alkyl chlorothiolformate, it is satisfactory to use 1 mole of amine and 1 mole of aqueous sodium hydroxide solution. No apparent hydrolysis of the alkyl chlorothiolformate takes place at ice-bath temperatures. This procedure is advantageous when the amine is not readily available.

Procedure C. 1. Triethylamine Used as Base. (a) Methallyl Diethylthiolcarbamate (154).—Diethylamine (14.6 g., 0.20 mole) and 20.2 g. (0.20 mole) of triethylamine were dissolved in 150 cc. of *t*-butyl alcohol. The solution was cooled to 15° and then 16 g. (0.27 mole) of carbonyl sulfide was passed in with vigorous agitation, maintaining the temperature between 15–20° by cooling with ice. The clear solution was then warmed to 30° with slow stirring and 18.1 g. (0.20 mole) of methallyl chloride was rapidly added. The reaction mixture was then heated slowly to 50° (45 minutes), maintained at 50° for three hours and then heated rapidly to reflux. Distillation of solvent was then begun and 125 cc. of distillate was collected and discarded. The residual slurry was cooled to 30°, diluted with 200 cc. of petroleum ether, b.p. 30–60°, and 50 cc. of water was added. After phase separation, the organic layer was washed with one 50-cc. portion of water, two 50-cc. portions of 5% hydrochloric acid and two 50-cc. portions of water. The petroleum ether solution was then dried over anhydrous magnesium sulfate. The solvent was distilled off on the steam-bath and the residual liquid was fractionally distilled under vacuum. There was obtained 2.0 g. of pre-fraction, b.p. 122–139.8° (30 mm.), reflux ratio 30/1; 21.6 g. (57.6%) of methallyl diethylthiolcarbamate, b.p. 139.8–140.5° (30 mm.), reflux ratio 1/1 and 0.5 g. of residue.

(**b**) **Crotyl Diethylthiolcarbamate (187).**—Diethylamine (29.2 g., 0.40 mole) and 40.4 g. (0.40 mole) of triethylamine were dissolved in 150 cc. of *t*-butyl alcohol. The solution was cooled to 15° and then 32 g. (0.54 mole) of carbonyl sulfide was passed in with vigorous stirring, maintaining the temperature between 15–20° by cooling with ice. The clear solution was then warmed to 30° and the crotyl bromide was added dropwise. The temperature during the addition was maintained at 30–35° by cooling with ice. The slurry was then heated slowly to 50° (30 minutes), held at 50° for two hours and then heated rapidly to reflux. The mixture was then worked up in exactly the same manner as described under (a) above. Fractionation *in vacuo* gave 13.3 g. of a prefraction, b.p. 126.0–148.0° (30 mm.), reflux ratio 45/1; 44.8 g. (60.0%) of crotyl diethylthiolcarbamate, b.p. 148.0–148.5° (30 mm.), reflux ratio 1/1 and 0.4 g. of residue.

2. **Sodium Dispersion Used as Base. Allyl N-Allyl-*n*-propylthiolcarbamate (116).**—Sodium dispersion in xylene[25] (15.3 cc., 0.10 mole) was added to a solution of 9.9 g. (0.10 mole) of N-allyl-*n*-propylamine in 150 cc. of ethylene glycol dimethyl ether. Carbonyl sulfide (8 g., 0.13 mole) was then passed in under the surface of the well stirred mixture (21 minutes), the temperature rising from 20–77° from the heat of the reaction. The reaction mixture was now a turbid greenish-yellow and had a small amount of finely divided solid. Allyl bromide (12.1 g., 0.10 mole) was then added (3 minutes) to the reaction mixture at 55–60°. Salt formed immediately on addition of the allyl bromide. The slurry was then heated to reflux (15 minutes), held at reflux for 15 minutes, cooled to 30°, filtered and the cake was washed with two 50-cc. portions of petroleum ether, b.p. 30–60°. The combined filtrate was concentrated on the steam-bath and the residual liquid was fractionally distilled. There was obtained 13.8 g. (69.2%) of allyl N-allyl-*n*-propylthiolcarbamate, b.p. 151.0–151.2° (30 mm.).

3. **Dialkylamine Used as a Base. 2-Chloroallyl diallylthiol carbamate (176)** was prepared following procedure for 154 except that 2 moles of diallylamine was used per mole of 2,3-dichloro-1-propene instead of 1 mole of diallylamine and 1 mole of triethylamine.

General Remarks Pertaining to Procedure C.—The di- or trialkylamine thiolcarbamate salts were found to be unstable at temperatures above 55°. Decomposition was evidenced by gas evolution. For this reason, reaction temperatures were maintained at 50° or less until a considerable amount of salt had precipitated. This thermal salt decomposition was not encountered in the case of the sodium thiolcarbamates.

The rates of the thiolcarbamate synthesis step varied considerably depending on which R_1 halide was used. The structure of the amine did not have much influence on the rate of this reaction. When allyl bromide, crotyl bromide, propargyl bromide, bromoacetonitrile, 1,3-dichloropropene, 1,3-dibromopropene, chlorodimethyl ether and chlorodimethyl sulfide were used at 30°, salt formation took place within 1 minute if these halides were added rapidly. Salt formation required from 10–25 minutes when methallyl chloride or 2,3-dichloro-1-propene were employed. On the other hand, the reaction mixture required heating at 50° for at least 1 hour before salt crystals formed when 2-bromoethyl ethyl ether was used as the R_1 halide.

The *cis*- and *trans*-3-chloroallyl thiolcarbamates and *cis*-3-bromoallyl thiolcarbamates were prepared from the corresponding *cis*- and *trans*-1,3-dichloropropenes[18,26] and *cis*-1,3-dibromopropene.[21]

Preparation of Intermediates.—The procedure of only one member of a class will be described if in general the same procedure is applicable for the entire class. Otherwise, other examples will be given.

(25) Sodium, 150 g., and 1 g. of oleic acid were dispersed in 600 cc. of xylene and the resulting dispersion was diluted to 1 l. with xylene in a volumetric flask. The resulting dispersion contained 0.1 mole of sodium per 15.3 cc. of solution and was stored in a screw cap bottle. The bottle was shaken vigorously before each use.

(26) L. F. Hatch and H. E. Alexander, THIS JOURNAL, **71**, 1037 (1949).

Dialkylcarbamoyl Chlorides. Di-*n*-propylcarbamoyl Chloride[7].—Anhydrous hydrogen chloride (192 g., 5.25 moles) was passed into a solution of 505 g. (5.00 moles) of di-*n*-propylamine in 2000 cc. of chlorobenzene at 106–113°.

To this slurry was then bubbled in over a 3-hour period, 594 g. (6.00 moles) of phosgene at 115–120°. Since this was an endothermic reaction, heat was continually supplied during the addition. The reaction mixture was then brought to reflux, held at reflux for 0.5 hour, cooled to 110° and stripped free of phosgene by bubbling nitrogen through the solution. The reaction mixture was then fractionally distilled through the 3-ft. HeliPak column. There was obtained 785 g. (96%) of di-*n*-propylcarbamoyl chloride, b.p. 117.5–118.0° (30 mm.).

Alkyl Chlorothiolformates. *n*-Propyl Chlorothiolformate.[2]—A cold solution of 132 g. (3.30 moles) of sodium hydroxide in 1500 cc. of water was added as rapidly as possible to a solution of 326 g. (3.30 moles) of phosgene and 228 g. (3.00 moles) of ethanethiol in 1500 cc. of benzene at −5 to 0°, maintaining this temperature by cooling with a Dry Ice–isopropyl alcohol-bath. The mixture was then stirred at −5° for an additional 0.5 hour. (If the aqueous layer is not basic, more caustic should be added until it becomes alkaline. Otherwise, some undecomposed phosgene may still be present.) The phases were separated, the benzene solution was dried over anhydrous magnesium sulfate and the mixture was then fractionally distilled. There was obtained 250 g. (60%) of *n*-propyl chlorothiolformate, b.p. 59–60° (26 mm.).

Chloroalkyl Chlorothiolformates.[27] **3-Chloropropyl Chlorothiolformate.**—Aluminum chloride (10.6 g., 0.08 mole) was charged to a 4-neck 2-l. flask under argon and 490 g. (4.96 moles) of phosgene was condensed into the flask, cooling with Dry Ice–isopropyl alcohol. The liquid phosgene was then warmed to −5° and 120 g. (1.08 moles) of 3-chloropropanethiol[28] was added over 2 hours with stirring to the refluxing phosgene. No cooling was provided during the addition of the mercaptan and phosgene was condensed and returned to the reaction mixture by means of a Dry Ice condenser. After all of the mercaptan had been added, the mixture was refluxed for an additional 2 hours and the phosgene was then evaporated. The residual liquid was taken up in 1000 cc. of *n*-pentane, filtered, and the solution concentrated on the steam-bath. The residual liquid was then fractionally distilled and there was obtained 106 g. (57%) of 3-chloropropyl chlorothiolformate, b.p. 98.5–99.0° (15 mm.).

Allylalkylamines.[8] **N-Methallylethylamine.**—A solution of 160 g. (4.0 moles) of sodium hydroxide in 500 cc. of water was mixed with 644 g. (10.0 moles) of 70% ethylamine solution and the mixture was heated to 33°. A condenser cooled with ice-water was used to prevent loss of ethylamine. Methallyl chloride (362 g., 4.0 moles) was then added dropwise over 3 hours, maintaining the temperature between 37–40° by adjusting the rate of addition. The mixture was then warmed slowly to reflux (59° pot temperature) over a 2.5-hour interval, refluxed for 0.5 hour and then allowed to cool slowly overnight. The following morning the ethylamine was removed by fractionating the mixture through a 10″ × 1″ Heli-Pak column at a reflux ratio of 3/1, allowing the distilland to reach 65°. The warm mixture was then phase separated and the aqueous phase was extracted with four 100-cc. portions of ethyl ether. The ether extracts were combined with the amine phase and dried first with sodium hydroxide pellets. Partial liquefaction of the caustic pellets took place. The organic phase was then decanted and dried over anhydrous magnesium sulfate. The ether was then removed by distilling through the 10″ Heli-Pak column and the residual liquid was then fractionated through the 3-ft. Heli-Pak column. There was obtained 224 g. (56.6%) of N-methallylethylamine, b.p. 104.2–104.3° (760 mm.).

Miscellaneous. Methyl Di-*n*-propylcarbamate.—Sodium (5.5 g., 0.24 g. at.) was added to 100 cc. of absolute methanol. After all of the sodium had reacted, the solution was heated to reflux and 32.7 g. (0.20 mole) of di-*n*-propylcarbamoyl chloride was slowly added. It was an exothermic reaction and salt formed immediately. The mixture was refluxed for 0.5 hour, cooled and filtered. The cake was washed with 20 cc. of methanol and the combined filtrate was concentrated on the steam-bath. The residual liquid was then fractionally distilled *in vacuo*. There was obtained 17.4 g. (54.7%) of methyl di-*n*-propylcarbamate, b.p. 96.0–96.2° (30 mm.), $n^{30}D$ 1.4256.

Anal. Calcd. for $C_8H_{17}NO_2$: N, 8.80. Found: N, 8.86.

This compound was used as a calibration standard for the gas chromatograph in order to detect its presence in fraction II described under procedure A. Ethyl di-*n*-propylthiolcarbamate (18). (b) Sodium Alkoxide Method.

2-Chloroallyl Ethyl Sulfide.—Sodium dispersion in xylene[25] (34.6 cc., 0.20 mole) was added to 200 cc. of anhydrous benzene. To this mixture was added dropwise a solution of 14.9 g. (0.24 mole) of ethanethiol in 25 cc. of benzene, maintaining the temperature at 30–35° with cooling. The sodium ethylmercaptide was then filtered and the cake was washed with six 50-cc. portions of anhydrous benzene under conditions which excluded moist air from being sucked through the cake. The cake was then transferred to 150 cc. of anhydrous benzene and the slurry was heated to reflux. To the refluxing suspension was then added rapidly 22.2 g. (0.20 mole) of 2,3-dichloro-1-propene. The reaction mixture was refluxed for 4 hours, cooled, filtered and the cake was washed with a little benzene. The filtrate was concentrated on the steam-bath and the residual liquid was fractionally distilled. There was obtained 12.7 g. (46.6%) of 2-chloroallyl ethyl sulfide, b.p. 91.5-92.3° (80 mm.), $n^{30}D$ 1.4918, d^{30}_4 1.0543.

Anal. Calcd. for C_5H_9ClS: Cl, 25.95. Found: Cl, 25.81.

***trans*-3-Chloroallyl ethyl sulfide** was prepared following above procedure except that 22.2 g. (0.20 mole) of *trans*-1,3-dichloropropene was used. Fractionation *in vacuo* gave 15.8 g. (57.5%) of *trans*-3-chloroallyl ethyl sulfide, b.p. 103.5–103.8° (80 mm.), $n^{30}D$ 1.5010, d^{30}_4 1.0597.

Anal. Calcd. for C_5H_9ClS: Cl, 25.95. Found: Cl, 25.83.

2-Chloroallyl *n*-propyl sulfide was prepared following above procedure except that 18.3 g. (0.24 mole) of 1-propanethiol and 22.2 g. (0.20 mole) of 2,3-dichloro-1-propene were employed. Fractionation *in vacuo* gave 16.6 g. (55.3%) of 2-chloroallyl *n*-propyl sulfide, b.p. 109–110.5° (80 mm.), $n^{30}D$ 1.4876, $d^{30}4$ 1.0267.

Anal. Calcd. for $C_6H_{11}ClS$: Cl, 23.53. Found: Cl, 23.47.

***trans*-3-Chloroallyl *n*-propyl sulfide** was prepared following above procedure except that 22.2 g. (0.20 mole) of *trans*-1,3-dichloropropene was used. Fractionation *in vacuo* gave 13.9 g. (46.2%) of *trans*-3-chlorallyl *n*-propyl sulfide, b.p. 120.0–120.8° (80 mm.), $n^{30}D$ 1.4955, d^{30}_4 1.0300.

Anal. Calcd. for $C_6H_{11}ClS$: Cl, 23.53. Found: Cl, 23.62.

Molar Refractions. Precision of the Method.—In the determination of the densities, the pycnometer having an approximate volume of 0.8 cc. was immersed in a constant temperature bath held at a temperature of 30 ± 0.05° for 10 minutes. The room temperature varied from 25–30°. In order to determine the precision of the density determinations, 22 individually complete pycnometer operations were performed on ethyl di-*n*-propylthiolcarbamate, compound 18. The average d^{30}_4 was 0.9543 with extreme values of 0.9538 and 0.9548. The maximum error for a single determination of the refractive index was ±0.0002.

In order to determine whether the observed molecular exaltations in the chloroallyl, bromoallyl and crotyl thiolcarbamates were significant, the lower and upper limits of the densities and refractive indices were incorporated into the Lorentz–Lorenz equation used for the calculation of the molar refractions. The maximum error for a single determination of the molar refraction was found to be less than ±0.02 cc. in all cases. These errors are well below the 0.2–0.9 cc. exaltations which have been observed.

It cannot be definitely stated that all of the thiolcarbamates are 100% pure, but almost all of the samples which were used for molar refraction determinations were center cuts of fractions having only a 1° boiling range or less.

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

(28) B. Sjöberg, *ibid.*, **74B**, 64 (1941).