of ethereal phenyllithium (prepared from 2.1 ml. of bromobenzene and 0.35 g. of lithium wire). Gentle reflux ensued which was maintained by heating for 2 hours. After addition of 50 ml. of dilute hydrochloric acid and evaporation of the ether the aqueous residue was warmed on the steam-bath for 1 hour. The solution was made strongly basic by addition of 35% sodium hydroxide and extracted with ether. Addition of alcoholic hydrogen chloride to the dried extracts precipitated the hydrochloride as a gum which crystallized under acetone to give 0.96 g. of white crystals, m.p. 234–236°. Recrystallization from boiling propyl alcohol raised the melting point to 241–242°.

Anal. Calcd. for $C_{15}H_{20}ClNO$: C. 67.78: H, 7.59: Cl. 13.34. Found: C. 68.10; H. 7.69: Cl, 13.32.

A mixed melting point comparison of this product with that prepared from 3α-tropanyl nitrile and phenylmagnesium bromide[5] resulted in a slight depression. but their infrared spectra were identical.

RENSSELAER. N. Y.

[CONTRIBUTION NO. 553 FROM THE CENTRAL RESEARCH DEPARTMENT. EXPERIMENTAL STATION. E. I. DU PONT DE NEMOURS AND CO.]

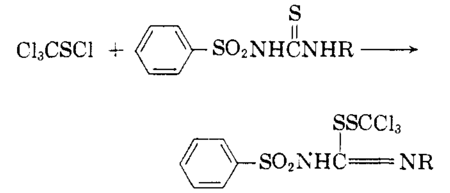
The Reactions of Sulfenyl Chlorides with Thionocarbamates

BY JOHN F. HARRIS, JR.

RECEIVED JUNE 5, 1959

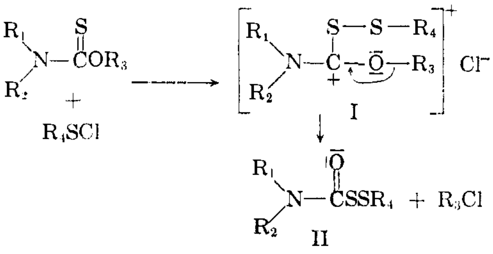
The reaction of sulfenyl chlorides with thionocarbamates has been found to yield alkyl or aryl carbamoyl disulfides. When the reaction is carried out in the presence of base. (dithio)-formimidic esters are obtained.

The sulfenyl halides, RSX, constitute a class of compounds well known for their high degree of reactivity with many types of molecules,[1] *e.g.*, olefins, acetylenes,[2] thiols, amines, ketones and compounds containing activated aromatic nuclei. However, little has been known concerning their reactions with compounds containing the thiocarbonyl group. Recently, one such reaction involving arylsulfonyl thioureas was reported[3]



(1)

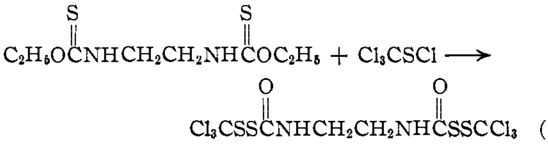
It has now been found that sulfenyl chlorides react readily with another class of thiocarbonyl compounds, the esters of thionocarbamic acids. The products normally obtained are unsymmetrical carbamoyl disulfides. The reaction is conveniently represented by the sequence



(2)

In this scheme the R_4S^+ ion attacks the thionocarbamate at the relatively negative sulfur atom to form the intermediate I. This intermediate expels the alkyl group on the oxygen to produce a carbamoyl disulfide II and an alkyl chloride. The reactions are carried out by mixing equimolar amounts of the reactants in an inert solvent, such as ether or benzene, and allowing the mixture to stand at room temperature for an hour or so. Evaporation of the solvent at room temperature leaves the product in high yield.

The reaction appears to be general and constitutes a convenient route to carbamoyl disulfides of the general type II. Compounds where R_1 and R_2 = H, alkyl, aryl and R_4 = Cl_3C, C_2H_5, *p*-ClC_6H_4, *o*-$NO_2C_6H_4$, have been prepared. The reaction was also successful with a bis-thionocarbamate

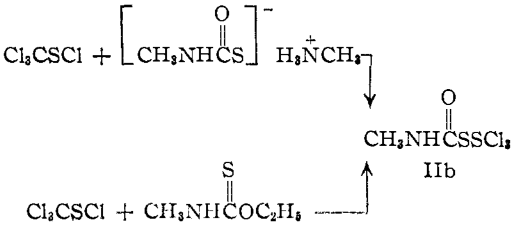


$$C_2H_5O\overset{S}{\overset{\|}{C}}NHCH_2CH_2NH\overset{S}{\overset{\|}{C}}OC_2H_5 + Cl_3CSCl \longrightarrow Cl_3CSS\overset{O}{\overset{\|}{C}}NHCH_2CH_2NH\overset{O}{\overset{\|}{C}}SSCCl_3 \qquad (3)$$

The yields of II are generally better than 70%. In one case, the alkyl chloride was isolated in 73% yield. No compounds represented by II appear to have been described previously. The properties of the examples prepared in this work are recorded in Table I.

The structures of the carbamoyl disulfides II were established by elemental analysis and infared spectroscopy. As expected, the spectra of these compounds exhibit typical amide absorption frequencies (Table II).

Further confirmation of structure II was obtained by the synthesis of trichloromethyl N-methylcarbamoyl disulfide (IIb) by the reaction of trichloromethanesulfenyl chloride and methylammonium N-methylthiocarbamate. This product proved to be identical with the product obtained from the reaction of trichloromethanesulfenyl chloride with N-methylthionocarbamate



$$Cl_3CSCl + \left[CH_3NH\overset{O}{\overset{\|}{C}}S\right]^- H_3\overset{+}{N}CH_3 \longrightarrow CH_3NH\overset{O}{\overset{\|}{C}}SSCl_3 \ (\mathrm{IIb}) \longleftarrow Cl_3CSCl + CH_3NH\overset{S}{\overset{\|}{C}}OC_2H_5 \qquad (4)$$

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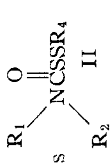
[1] N. Kharasch. S. J. Potempa and H. L. Wehrmeister. *Chem. Revs.*. **39**. 269 (1946).

[2] N. Kharasch and S. J. Assony. THIS JOURNAL. **75**. 1081 (1953).

[3] A. Margot and H. Gysin. U. S. Patent 2.813.902 (1957).

TABLE I

CARBAMOYL DISULFIDES



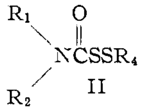
II

	R_1	R_2	R_4	M.p., °C.[a]	Formula	Yield, %	Recrystd. from	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found	Sulfur, % Calcd.	Sulfur, % Found
a	H	H	CCl_3	145–145.5 d.	$C_2H_2Cl_3NOS_2$	78	. . .[c]			6.18[e]	6.24[e]			28.30	28.50
b	H	CH_3	CCl_3	81–81.5	$C_3H_4Cl_3NOS_2$	94	Hexane	14.98	15.32	1.68	1.91	44.22	44.25	26.65	26.66
c	H	$CH_2{=}CHCH_2$	CCl_3	48–49	$C_5H_6Cl_3NOS_2$	62	Pentane	22.52	22.72	2.27	2.67	39.90	39.81	24.05	24.47
d	H	C_2H_5	CCl_3	56–57	$C_4H_6Cl_3NOS_2$	96	Hexane	18.87	19.30	2.38	2.42	41.78	42.07	25.19	25.42
e	H	C_6H_5	CCl_3	88–88.5	$C_8H_6Cl_3NOS_2$	95	Hexane	31.75	32.36	2.00	2.22	35.15	35.18	21.19	21.41
f	H	p-ClC_6H_4	CCl_3	137	$C_8H_5Cl_4NOS_2$	66	$CHCl_3$	28.50	28.71	1.50	1.65	42.08	41.92	19.02	19.11
g	H	CH_3	o-$NO_2C_6H_4$	Dec.[b]	$C_8H_8N_2O_3S_2$	85	. . .[c]	39.33	39.81	3.30	3.41				
h	H	C_6H_5	o-$NO_2C_6H_4$	185–192 d.	$C_{13}H_{10}N_2O_3S_2$	67	. . .[c]	50.97	51.44	3.29	3.36			20.93	21.18
i	H	C_6H_5	p-ClC_6H_4	104–105[d]	$C_{13}H_{10}ClNOS_2$	85	CCl_4	52.78	53.07	3.41	3.44			21.68	21.85
j	H	p-ClC_6H_4	p-ClC_6H_4	116–117[d]	$C_{13}H_9Cl_2NOS_2$	69	CCl_4	47.28	47.52	2.75	2.90			19.42	19.20
k	H	C_6H_5	C_2H_5	64–65	$C_9H_{11}NOS_2$	74	Cyclohexane	50.97	51.44	3.29	3.36			30.06	29.64
l	C_2H_5	C_2H_5	CCl_3	42–43	$C_6H_{10}Cl_3NOS_2$	77	Pentane (−76°)	25.50	25.94	3.57	3.78	37.64	37.28		
m	$Cl_3CSS\overset{O}{\overset{\|}{C}}NHCH_2CH_2NH\overset{O}{\overset{\|}{C}}SSCCl_3$			149.5–150	$C_6H_6Cl_6N_2O_2S_4$	80	Benzene			5.85[c]	5.94[e]	44.40	44.26	26.77	27.14

[a] Uncorrected. [b] This compound crystallized from the reaction mixture in bright yellow needles which turned to an amorphous powder after a few days. [c] Attempts at recrystallization resulted in decomposition. [d] Melting point of crude material. After recrystallization, the compound melted over a large range with decomposition. [e] Nitrogen, %.

TABLE II

INFRARED CHARACTERISTICS OF CARBAMOYL DISULFIDES[a,b]

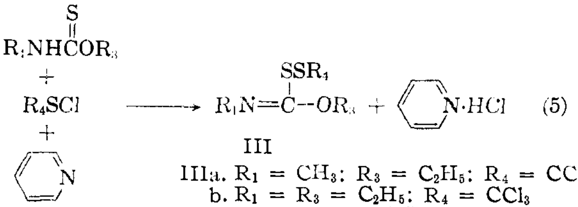


II

R_1	R_2	R_4	Amide bands, wave numbers, cm.$^{-1}$		NH, cm.$^{-1}$
H	CH_3	CCl_3	1695	1504	3401
H	C_2H_5	CCl_3	1692	1508	3401
H	C_6H_5	CCl_3	1709	1522[c]	3401
H	C_6H_5	C_2H_5	1678	1517[c]	3322
H	p-ClC_6H_4	p-ClC_6H_4	1689	1493[c]	3333
C_2H_5	C_2H_5	CCl_3	1695	. .	. .

[a] The assistance of Miss Naomi E. Schlichter of this Laboratory in recording and interpreting the infrared data reported here is gratefully acknowledged. [b] 0.1% in chloroform. [c] Doublet due to aromatic vibration.

If the reactions of the sulfenyl chlorides with monosubstituted thionocarbamates are carried out in the presence of an equivalent of a *t*-amine, *e.g.*, pyridine, it is possible to isolate (dithio)-formidic esters III, which appear to be members of a previously unknown class of compounds[4] Four



(5)

III

IIIa. $R_1 = CH_3$; $R_3 = C_2H_5$; $R_4 = CCl_3$
b. $R_1 = R_3 = C_2H_5$; $R_4 = CCl_3$
c. $R_1 = R_4 = p$-ClC_6H_4; $R_3 = C_2H_5$
d. $R_1 = R_3 = R_4 = C_2H_5$

examples (IIIa, b, c, d) of this class were isolated and characterized; IIIa and IIIb, derived from trichloromethanesulfenyl chloride, were not obtained in high purity since they underwent decomposition during vacuum distillation. After storage in glass at room temperature for several months, gross decomposition was evident. The others (IIIc, IIId) appeared to be little changed after over two years of storage. The infrared spectra of these compounds show a strong absorption band in the 1656–1639 cm.$^{-1}$ region indicative of the carbon–nitrogen double bond.[5]

Treatment of these compounds with anhydrous hydrogen chloride in ether results in the cleavage of the O–alkyl bond and subsequent formation of the corresponding carbamoyl disulfide in high yield. For example, ethyl N-methyl-1-(trichloromethyldithio)-formimidate (IIIa) gave trichloromethyl N-methylcarbamoyl disulfide (IIb) in 94% yield. This reaction probably proceeds through the initial formation of a hydrochloride having the structure of the intermediate I (R_1 = H in reaction 2), which is unstable at room temperature and decomposes spontaneously to the disulfide and the alkyl chloride.

In similar manner, when ethyl N-*p*-chlorophenyl-1-(*p*-chlorophenyldithio)-formimidate was treated

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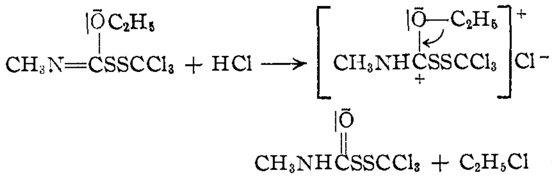
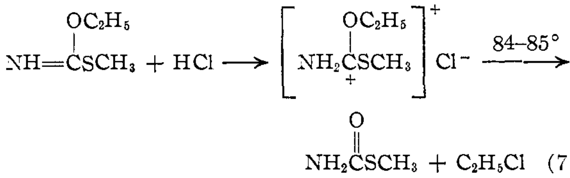
[4] Monosulfide analogs with no substituents on the nitrogen, NH=C(OR)SR, have been described by A. Knorr, *Ber.*, **49**, 1739 (1916).

[5] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 267–271.



$$CH_3N{=}C(\bar{O}C_2H_5)SSCCl_3 + HCl \longrightarrow \left[CH_3NH\overset{+}{C}(\bar{O}{-}C_2H_5)SSCCl_3\right]^+ Cl^- \longrightarrow CH_3NHC({=}\bar{O})SSCCl_3 + C_2H_5Cl \quad (6)$$

with anhydrous hydrogen chloride, *p*-chlorophenyl N-*p*-chlorophenylcarbamoyl disulfide (IIj) was obtained. These reactions appear to be similar to the behavior encountered by Knorr in the preparation and decomposition of the hydrochloride of O-ethyl S-methylimidothiocarbonate[6]



$$NH{=}C(OC_2H_5)SCH_3 + HCl \longrightarrow \left[NH_2\overset{+}{C}(OC_2H_5)SCH_3\right]^+ Cl^- \xrightarrow{84\text{–}85^\circ} NH_2C({=}O)SCH_3 + C_2H_5Cl \quad (7)$$

The isomeric O-methyl S-ethylimidothiocarbonate hydrochloride was reported to decompose in the same manner at 48-49°.[6a,b]

Experimental

Preparation of Thionocarbamates.—Ethyl N-ethylthionocarbamate, ethyl N-phenylthionocarbamate, ethyl N-*p*-chlorophenylthionocarbamate and *n*-butyl N-phenylthionocarbamate, all previously described, were prepared by refluxing a solution of the corresponding isothiocyanate in a large excess of the alcohol in the presence of a tertiary amine.

Ethyl thionocarbamate was prepared by the reaction of aqueous ammonia with O-ethyl S-carboxymethyl xanthate as described by Davies and MacLaren.[7] Similar procedures were used to prepare ethyl N-methylthionocarbamate, ethyl N,N-diethylthionocarbamate and diethyl ethylene-bis-(thionocarbamate), which apparently have not been described previously.

A. Ethyl N-Methylthionocarbamate.—To a stirred and cooled solution of 13.6 g. (0.34 mole) of sodium hydroxide in 150 ml. of water, 32.1 g. (0.34 mole) of chloroacetic acid was added in small portions. This solution was then added to a solution of 54.5 g. (0.34 mole) of potassium ethyl xanthate in 200 ml. of water. After being stirred for a few minutes, the mixture was allowed to stand overnight. The resulting solution of O-ethyl S-carboxymethyl xanthate[8] was then treated with 30 ml. of 45% aqueous methylamine. The resulting mixture was stirred for a few minutes, allowed to stand overnight, and then acidified with glacial acetic acid. The product was removed by three extractions with 150 ml. of ether. The ether solution was extracted once with aqueous sodium bicarbonate, once with water, dried over anhydrous magnesium sulfate, and distilled. There was obtained 22 g. (54%) of ethyl N-methylthionocarbamate as a colorless liquid boiling at 93° (10 mm.), $n^{25}D$ 1.5184-1.5200.

Anal. Calcd. for C_4H_9NOS: C, 40.31; H, 7.61. Found: C, 40.14; H, 7.61.

B. Ethyl N,N-Diethylthionocarbamate.—To a stirred and cooled solution of 20.31 g. (0.113 mole) of O-ethyl S-carboxymethyl xanthate and 4.51 g. (0.113 mole) of sodium hydroxide in 150 ml. of water was added 8.50 g. (0.116 mole) of diethylamine in 25 ml. of water. After the mixture had been allowed to stand overnight, it was acidified with acetic acid and then extracted three times with ether (100 ml., 2 × 50 ml.). The ether solution was shaken first with small increments of an aqueous sodium bicarbonate solution until no more carbon dioxide was liberated, then once with 25 ml. of water, and dried over magnesium sulfate. Upon distillation, there was obtained 12.85 g. (70%) of ethyl N,N-diethylthionocarbamate as an almost colorless liquid distilling at 35-40° (mostly at 40°) (0.1 mm.), $n^{25}D$ 1.4950.

Anal. Calcd. for $C_7H_{15}NOS$: C, 52.13; H, 9.38; S, 19.88. Found: C, 51.66; H, 9.81; S, 20.07.

C. Diethyl Ethylene-bis-(thionocarbamate).—To a stirred and cooled solution of 13.6 g. (0.34 mole) of sodium hydroxide in 150 ml. of water, 32.1 g. (0.34 mole) of chloroacetic acid was added in small portions. This solution was then added to a solution of 54.5 g. (0.335 mole) of potassium ethyl xanthate in 200 ml. of water. This mixture was stirred for a few minutes and then allowed to stand overnight. Ten grams (0.166 mole) of ethylenediamine dissolved in 50 ml. of water was added dropwise with stirring. Precipitation began at once. After the addition was completed, the mixture was stirred a short time and then filtered: wt. of dried product, 21.93 g., m.p. 110.5-112°. Upon cooling of the filtrate an additional 3.4 g. of product, m.p. 111.5-112°, was obtained (64% total yield). After recrystallization from a mixture of 95% ethanol (11 ml./g.) and water (10 ml./g.), there was obtained 19.72 g. of diethyl ethylene-bis-(thionocarbamate) as white prisms melting at 112-112.5°.

Anal. Calcd. for $C_8H_{16}N_2O_2S_2$: C, 40.65; H, 6.82; S, 27.13. Found: C, 41.05; H, 6.85; S, 27.34.

A sample of cyclohexyl N-allylthionocarbamate was kindly supplied by H. E. Cupery of this Laboratory.

Preparation of Sulfenyl Chlorides.—*o*-Nitrobenzenesulfenyl chloride was prepared by the chlorination of bis-(*o*-nitrophenyl) disulfide.[9] *p*-Chlorobenzenesulfenyl chloride was prepared by chlorination of *p*-chlorothiophenol in sulfur dioxide.[10] Ethanesulfenyl chloride was prepared by the chlorination of ethyl disulfide.[11] Trichloromethanesulfenyl chloride was purchased from Distillation Products Industries.

Reactions of Sulfenyl Chlorides with Thionocarbamates to Give Carbamoyl Disulfides II.—All of these reactions were carried out in approximately the same manner. Ethyl esters of the thionocarbamic acids were used except in the preparation of IIc, in which the cyclohexyl ester was used. The reaction of trichloromethanesulfenyl chloride with ethyl N-methylthionocarbamate is described in detail.

A solution of 5.0 g. (0.042 mole) of ethyl N-methylthionocarbamate in 25 ml. of benzene was added to a solution of 7.8 g. (0.042 mole) of trichloromethanesulfenyl chloride in 50 ml. of benzene. The reaction flask was stoppered immediately. After the mixture had stood for one hour, it was poured into a dish and allowed to evaporate to dryness. There remained 9.53 g. (94%) of crude trichloromethyl N-methylcarbamoyl disulfide (IIb). After several recrystallizations from hexane, the product was obtained as white needles melting at 81.5-82.5°.

Anal. Calcd. for $C_3H_4Cl_3NOS_2$: C, 14.98; H, 1.68; Cl, 44.22; S, 26.65. Found: C, 15.32; H, 1.91; Cl, 44.25; S, 26.66.

The properties of the other carbamoyl disulfides prepared in this manner are recorded in Table I.

In a reaction aimed at the isolation of the alkyl chloride, *n*-butyl N-phenylthionocarbamate (20 g. in 50 ml. of ether) and trichloromethanesulfenyl chloride (17.3 g. in 20 ml. of ether) were mixed as described above. The mixture was stirred for four hours, and then all of the volatiles were removed *in vacuo*. Distillation of the condensed volatiles through a spinning band still yielded 6.3 g. (73%) of *n*-butyl chloride, distilling at 78°, $n^{25}D$ 1.3992 (previously reported[12] b.p. 78°, $n^{20}D$ 1.4023).

The Reaction of Trichloromethanesulfenyl Chloride with Methylammonium N-Methylthiocarbamate.—A solution of 7.6 g. (0.0409 mole) of trichloromethanesulfenyl chloride in 75 ml. of benzene was added within 20 minutes to a stirred and cooled suspension of 5.0 g. (0.0409 mole) of methylammonium N-methylthiocarbamate[13] in 75 ml. of benzene. After being stirred for two hours, the mixture was filtered, and the filtrate allowed to evaporate to dryness. There was obtained 5.07 g. (52%) of crude trichloromethyl N-methylcarbamoyl disulfide melting at 70-79°. Several recrystallizations from hexane raised the melting point to 81.5-82.5°.

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(6) (a) A. Knorr, *Ber.*, **49**, 1737 (1916); (b) **50**, 771 (1917).

(7) W. Davies and J. A. MacLaren, *J. Chem. Soc.*, 1436 (1951).

(8) O-Ethyl S-carboxymethyl xanthate can be obtained in crystalline form by acidification of this solution with concentrated hydrochloric acid.

(9) M. H. Hubacher, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 455-457.

(10) R. I. Gunthrie, Ph.D. thesis, Univ. of N. Carolina, 1953.

(11) H. Brintzinger and M. Langheck, *Ber.*, **86**, 557 (1953).

(12) R. H. Wiswall, Jr., and C. P. Smyth, *J. Chem. Phys.*, **9**, 357 (1941).

(13) M. Freund and E. Asbrand, *Ann.*, **285**, 173 (1895).

Anal. Calcd. for $C_3H_4Cl_3NOS_2$: S, 26.65. Found: S. 26.59.

A mixed melting point determination with a sample of trichloromethyl N-methylcarbamoyl disulfide (IIb) prepared from ethyl N-methylthionocarbamate showed no depression.

Preparation of (Dithio)-formimidates. A. Ethyl N-Ethyl-1-(trichloromethyldithio)-formimidate.—A solution of 51.8 g. (0.279 mole) of trichloromethanesulfenyl chloride in 200 ml. of benzene was added dropwise during a period of 50 minutes to a stirred and cooled solution of 37.16 g. (0.279 mole) of ethyl N-ethylthionocarbamate and 22.1 g. (0.279 mole) of pyridine in 200 ml. of benzene. The reaction mixture was stirred for an additional 10 minutes and filtered. The residue was rinsed on the filter with a little benzene. The combined filtrate and rinsings were evaporated *in vacuo* to remove the benzene, and the residue was distilled through a small modified Claisen still. There was obtained 60.85 g. (77%) of crude ethyl N-ethyl-1-(trichloromethyldithio)-formimidate distilling at 88° (0.55 mm.) to 91° (1.0 mm.), $n^{25}\text{D}$ 1.5362–1.5423. Upon redistillation through a small spinning band still fitted with a platinum band, there was obtained a fraction boiling at 87° (0.65 mm.) to 91° (0.70 mm.), $n^{25}\text{D}$ 1.5372–1.5387, infrared max. at 1656 cm.$^{-1}$ C=N (0.1% in chloroform).

Anal. Calcd. for $C_6H_{10}Cl_3NOS_2$: C, 25.50; H, 3.57; S. 22.69. Found: C, 25.97: H. 3.72; S, 22.82.

B. Ethyl N-Methyl-1-(trichloromethyldithio)-formimidate was prepared in a similar manner in 68% yield by the reaction of trichloromethanesulfenyl chloride with a mixture of ethyl N-methylthionocarbamate and pyridine in benzene: b.p. 79° (0.55 mm.) to 89° (1.0 mm.), $n^{25}\text{D}$ 1.5490–1.5499.

Anal. Calcd. for $C_5H_8Cl_3NOS_2$: C, 22.36; H, 3.00; S, 23.87. Found: C, 23.23; H, 3.31; S, 25.87.

C. Ethyl N-Ethyl-1-(ethyldithio)-formimidate was prepared as described above in 92% yield by the addition of 29.1 g. (0.301 mole) of ethanesulfenyl chloride in 75 ml. of benzene to a solution of 40 g. (0.300 mole) of ethyl N-ethylthionocarbamate and 23.8 g. (0.301 mole) of pyridine in 200 ml. of benzene; b.p. 46° (0.05 mm.), $n^{25}\text{D}$ 1.5064, infrared max. at 1642 cm.$^{-1}$ C=N (0.1% in chloroform).

Anal. Calcd. for $C_7H_{15}NOS_2$: C, 43.49; H, 7.80: N, 7.25: S. 33.17. Found: C, 43.73; H, 7.94: N. 7.14; S. 33.45.

D. Ethyl N-*p*-Chlorophenyl-1-(*p*-chlorophenyldithio)-formimidate.—A solution of 22.7 g. (0.127 mole) of *p*-chlorobenzenesulfenyl chloride in 100 ml. of benzene was added during 20 minutes to a stirred and cooled solution of 27.32 g. (0.127 mole) of ethyl N-*p*-chlorophenylthionocarbamate and 10.0 g. (0.126 mole) of pyridine in 200 ml. of benzene. After being stirred for an additional 10 minutes, the mixture was filtered and the filtrate evaporated *in vacuo*. The resulting residue crystallized when cooled to −76°: wt. 42.4 g. (94%), m.p. 30.5–35.5°. After two recrystallizations from pentane at −76°, ethyl N-*p*-chlorophenyl-1-(*p*-chlorophenyldithio)-formimidate was obtained as colorless flat needles melting at 33.5–35°, infrared maximum at 1639 cm.$^{-1}$ C=N (0.1% in chloroform).

Anal. Calcd. for $C_{15}H_{13}Cl_2NOS_2$: C. 50.28; H, 3.66; S. 17.90. Found: C, 50.59; H. 3.86; S, 18.22.

Action of Anhydrous Hydrogen Chloride on (Dithio)-formimidates. A. Methyl N-Methyl-1-(trichloromethyldithio)-formimidate.—Anhydrous hydrogen chloride was bubbled for a few minutes through a solution of 2.0 g. (0.0074 mole) of ethyl N-methyl-1-(trichloromethyldithio)-formimidate in 50 ml. of benzene. The mixture was poured into a dish and allowed to evaporate to dryness. There remained 1.68 g. (94%) of crude trichloromethyl N-methylcarbamoyl disulfide (IIb) melting at 74–79°. Several recrystallizations from hexane raised the melting point to 82–82.5°. Mixed melting point determinations with samples of this compound prepared in the two previously described procedures showed no depression.

B. Ethyl N-*p*-Chlorophenyl-1-(*p*-chlorophenyldithio)-formimidate.—Anhydrous hydrogen chloride was bubbled through a solution of 1.0 g. of ethyl N-*p*-chlorophenyl-1-(*p*-chlorophenyldithio)-formimidate dissolved in 25 ml. of pentane. An oil began to separate immediately which soon solidified. After being allowed to stand for 0.5 hour, the mixture was filtered, and there was obtained 0.80 g. (87%) of crude product. This was recrystallized by dissolving it in 6 ml. of chloroform, filtering, and adding 14 ml. of pentane slowly. There was obtained 0.55 g. of *p*-chlorophenyl N-*p*-chlorophenylcarbamoyl disulfide as white needles. The infrared spectrum substantiated its identity with the product obtained directly from *p*-chlorobenzenesulfenyl chloride and ethyl N-*p*-chlorophenylthionocarbamate.

Anal. Calcd. for $C_{13}H_9Cl_2NOS_2$: S, 19.42. Found: S. 19.41.

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[CONTRIBUTION NO. 517 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

The Chemistry of Some 5-*m*-Dithianones and Dithiacycloalkanones

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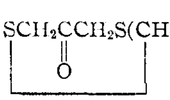
Dithiacycloalkanones, 
$\overset{\llcorner}{S}CH_2\overset{O}{\overset{\|}{C}}CH_2S(CH_2)_n$ where n = 2, 3 and 4, have been prepared by the reaction of *sym*-dichloroacetone with the sodium salt of the appropriate dithiol. The cyclic thioketal, 5-*m*-dithianone (Va), was prepared by saponification and decarboxylation of 4-ethoxycarbonyl-5-*m*-dithianone after first inactivating the ketone group by conversion to a cyclic ketal by reaction with ethylene glycol. Numerous chemical transformations of these cyclic ketones are reported. Some new chemistry of 4-ethoxycarbonyl-5-*m*-dithianone including the separation of keto and enol forms also is described.

The only example of a cyclic ketone containing two ring sulfur atoms is 4-ethoxycarbonyl-5-*m*-dithianone (IIa), reported by Challenger and Miller.[1] These authors reported that hydrolysis of IIa resulted in cleavage of the ring. In an investigation of this reaction as a means for preparing the parent ketone, 5-*m*-dithianone (Va), we have found that the ethoxycarbonyl group can be removed by hydrolysis and decarboxylation if the ketone group is first protected by conversion to a ketal.[1a]

4-Ethoxycarbonyl-5-*m*-dithianone[1] (IIa) was converted to the cyclic ketal IIIa by reaction with

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[1] F. Challenger and S. A. Miller, THIS JOURNAL, 367 (1939).

(1a) Since this manuscript was submitted, A. Lüttringhaus and H. Prinzbach, *Ann.*, **624**, 79 (1959), have reported the direct hydrolysis of IIa to Va in sulfuric acid, as well as the synthesis of several derivatives of IIa also described in this paper.