Studies on the Thiocarbamoylthiocarbonates. I. Synthesis of Aryl Thiocarbamoyldithiocarbonates

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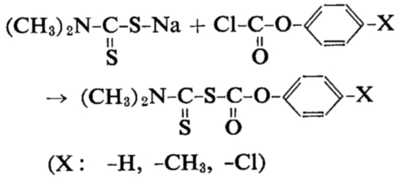
O-Alkyl *S*-(*N*, *N*-disubstituted-thiocarbamoyl)-thiocarbonates were studied by Cambron[1] and Lo[2]. Lo reported that these alkyl esters, except isopropyl ester, were unstable and decomposed even at room temperature. No report on the aryl esters of this thiocarbonic acid has been given. The present author succeeded in the synthesis of these aryl esters.

Results and Discussion

Aryl chloroformates reacted with sodium dimethyldithiocarbamate in acetone, giving *O*-aryl *S*-(*N*, *N*-dimethylthiocarbamoyl) thiocarbonates as shown in Table I.



(X: -H, $-CH_3$, -Cl) (1)

But these esters were unstable and decomposed even at room temperature within a few weeks.

Aryl chlorothionoformates reacted with sodium or ammonium dialkyldithiocarbamates, giving various *O*-aryl *S*-(*N*, *N*-dialkylthiocarbamoyl) dithiocarbonates in good yields as

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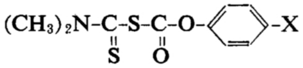
[1] A. Cambron, *Can. J. Res.*, 2, 341 (1930).

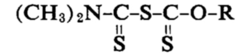
[2] C. Lo and W. E. Craig, Japanese Pat. 253207 (1958).

TABLE I. *O*-ARYL *S*-(*N*,*N*-DIMETHYLTHIOCARBAMOYL)THIOCARBONATES



X	M. p., °C	Yield, %	Formula	Anal.	
				C% Found (Calcd.)	H% Found (Calcd.)
-H	97.5～ 98.5	51.5	$C_{10}H_{11}NO_2S_2$	49.79 (50.43)	4.56 (4.32)
4-CH_3	105.5～106.5	50.5	$C_{11}H_{13}NO_2S_2$	51.76 (51.65)	5.10 (4.99)
3-Cl	122 ～123	24	$C_{10}H_{10}ClNO_2S_2$	43.56 (44.09)	3.29 (3.80)

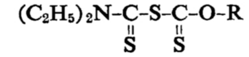
TABLE II. *O*-ARYL *S*-(*N*,*N*-DIMETHYLTHIOCARBAMOYL)DITHIOCARBONATES



$$(CH_3)_2N-\underset{\underset{S}{\|}}{C}-S-\underset{\underset{S}{\|}}{C}-O-R$$

R	Appearance	M. p., °C	Yield, %	Formula	Anal.	
					C % Found (Calcd.)	H % Found (Calcd.)
Phenyl	Yellow pillars	68 ～ 69	86	$C_{10}H_{11}NOS_3$	46.30 (46.69)	3.95 (4.28)
2-Tolyl	Yellow prisms	74 ～ 75	90	$C_{11}H_{13}NOS_3$	48.20 (48.70)	5.13 (4.80)
4-Tolyl	Yellow needles	88 ～ 89	78	$C_{11}H_{13}NOS_3$	48.97 (48.70)	4.71 (4.80)
4-Methoxyphenyl	Yellow needles	87.5～ 88.5	80	$C_{11}H_{13}NO_2S_3$	46.03 (45.99)	4.42 (4.53)
4-Chlorophenyl	Yellow prisms	104 ～105	80	$C_{10}H_{10}ClNOS_3$	41.40 (41.17)	3.56 (3.43)
2,4-Dichlorophenyl	Yellow needles	138 ～139	78	$C_{10}H_9Cl_2NOS_3$	36.95 (36.80)	2.54 (2.76)
2,4,5-Trichlorophenyl	Yellow prisms	113.5～114.5	75	$C_{10}H_8Cl_3NOS_3$	33.34 (33.29)	1.84 (2.22)
4-Bromophenyl	Yellow needles	110 ～111	74	$C_{10}H_{10}BrNOS_3$	35.95 (35.71)	2.60 (2.98)
2,4,6-Tribromophenyl	Yellow needles	118 (decomp.)	69	$C_{10}H_8Br_3NOS_3$	24.50 (24.30)	1.49 (1.69)
4-Chloro-2-tolyl	Yellow prisms	113 ～113.5	56	$C_{11}H_{12}ClNOS_3$	43.22 (43.20)	3.73 (3.93)
2-Chloro-4-tolyl	Yellow prisms	131.5～132.5	52	$C_{11}H_{12}ClNOS_3$	43.50 (43.20)	3.63 (3.93)
2,6-Dichloro-4-tolyl	Yellow prisms	133 ～134	60	$C_{11}H_{11}Cl_2NOS_3$	39.05 (38.82)	3.47 (3.24)
4,6-Dichloro-2-tolyl	Yellow needles	115 ～116.5	56	$C_{11}H_{11}Cl_2NOS_3$	39.30 (38.82)	3.41 (3.24)
3,5-Dimethyl-4-chlorophenyl	Yellow prisms	113 ～114.5	85	$C_{12}H_{14}ClNOS_3$	44.74 (45.07)	4.25 (4.38)
2-Phenyl-4-chlorophenyl	Yellow prisms	107 ～108	61	$C_{16}H_{14}ClNOS_3$	52.55 (52.24)	3.68 (3.81)
2-Biphenylyl	Yellow needles	135 ～136	84	$C_{16}H_{15}NOS_3$	57.83 (57.66)	4.62 (4.50)
4-Acetylphenyl	Yellow needles	117.5～118	78	$C_{12}H_{13}NO_2S_3$	48.50 (48.16)	4.10 (4.35)
2-Methoxycarbonylphenyl	Yellow prisms	102.5～103.5	60	$C_{12}H_{13}NO_3S_3$	45.80 (45.71)	4.10 (4.13)
4-Nitrophenyl	Yellow prisms	114 ～115	90	$C_{10}H_{10}N_2O_3S_3$	40.05 (39.75)	3.52 (3.31)
1-Chloro-2-naphthyl	Yellow prisms	126.5～127	91	$C_{14}H_{12}ClNOS_3$	49.20 (49.20)	3.60 (3.51)
1-Bromo-2-naphthyl	Yellow prisms	141 ～142	76	$C_{14}H_{12}BrNOS_3$	43.55 (43.52)	2.92 (3.11)

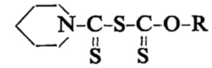
TABLE III. *O*-ARYL *S*-(*N,N*-DIETHYLTHIOCARBAMOYL) DITHIOCARBONATES



$(C_2H_5)_2N-\underset{\underset{S}{\|}}{C}-S-\underset{\underset{S}{\|}}{C}-O-R$

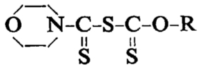
R	Appearance	M. p., °C	Yield, %	Formula	Anal.	
					C % Found (Calcd.)	H % Found (Calcd.)
2-Biphenylyl	Yellow plates	76 ~ 77	72	$C_{18}H_{19}NOS_3$	60.30 (59.83)	5.34 (5.26)
2-Chloro-4-tolyl	Yellow needles	93 ~ 94	81	$C_{13}H_{16}ClNOS_3$	47.15 (46.78)	5.15 (4.80)
2,6-Dichloro-4-tolyl	Yellow needles	91.5~ 93	70	$C_{13}H_{15}Cl_2NOS_3$	42.85 (42.39)	3.92 (4.08)
3,5-Dimethyl-4-chlorophenyl	Yellow needles	92 ~ 93	69	$C_{14}H_{18}ClNOS_3$	48.45 (48.35)	4.57 (5.18)
2,4,6-Tribromophenyl	Yellow needles	114 (decomp.)	69	$C_{12}H_{12}Br_3NOS_3$	27.40 (27.59)	2.82 (2.30)
2-Nitro-4-tolyl	Yellow scales	104.5~105.5	84	$C_{13}H_{16}N_2O_3S_3$	46.17 (45.35)	4.75 (4.65)
2-Naphthyl	Yellow prisms	62 ~ 63	64.5	$C_{16}H_{17}NOS_3$	57.08 (57.31)	5.25 (5.07)
1-Chloro-2-naphthyl	Yellow prisms	143 ~144	60	$C_{16}H_{16}ClNOS_3$	52.50 (51.96)	4.40 (4.33)
3-Chloro-2-naphthyl	Yellow needles	107.5~108.5	72	$C_{16}H_{16}ClNOS_3$	51.80 (51.96)	4.57 (4.33)
1-Bromo-2-naphthyl	Yellow prisms	142 ~144	73	$C_{16}H_{16}BrNOS_3$	46.10 (46.38)	3.67 (3.86)

TABLE IV. *O*-ARYL *S*-(PIPERIDINOTHIOCARBONYL) DITHIOCARBONATES



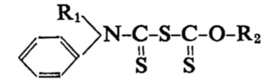
R	Appearance	M. p., °C	Yield, %	Formula	Anal.	
					C % Fonnd (Calcd.)	H % Found (Calcd.)
Phenyl	Yellow needles	95~ 96	61	$C_{13}H_{15}NOS_3$	52.70 (52.53)	4.84 (5.05)
4-Tolyl	Yellow needles	102~103	74	$C_{14}H_{17}NOS_3$	53.90 (54.02)	5.15 (5.47)
2-Naphthyl	Yellow needles	127~128	71	$C_{17}H_{17}NOS_3$	59.10 (58.79)	4.85 (4.90)
1-Chloro-2-naphthyl	Yellow needles	131~132	76	$C_{17}H_{16}ClNOS_3$	53.42 (53.47)	4.25 (4.19)

TABLE V. *O*-ARYL *S*-(MORPHOLINOTHIOCARBONYL) DITHIOCARBONATES



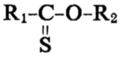
R	Appearance	M. p., °C	Yield, %	Formula	Anal.	
					C % Found (Calcd.)	H % Found (Calcd.)
4-Tolyl	Yellow needles	136 ~137	51.5	$C_{13}H_{15}NO_2S_3$	50.20 (49.84)	4.75 (4.79)
4-Chlorophenyl	Yellow needles	134 ~135	53.5	$C_{12}H_{12}ClNO_2S_3$	43.55 (43.18)	3.69 (3.60)
2-Biphenylyl	Yellow needles	130.5~131	53	$C_{18}H_{17}NO_2S_3$	57.35 (57.60)	4.15 (4.53)
2-Methoxycarbonyl-phenyl	Yellow prisms	115 ~116	72	$C_{14}H_{15}NO_4S_3$	47.73 (47.06)	3.75 (4.20)
1-Chloro-2-naphthyl	Yellow needles	149 ~150	73	$C_{16}H_{14}ClNO_2S_3$	50.31 (50.07)	3.78 (3.65)

TABLE VI. *O*-ARYL *S*-(ARYLTHIOCARBAMOYL)DITHIOCARBONATES



R_1	R_2	Appearance	M. p., °C	Yield, %	Formula	Anal. C % Found (Calcd.)	Anal. H % Found (Calcd.)
Methyl	4-Toyl	Yellow prisms	98~ 99	72	$C_{16}H_{15}NOS_3$	57.95 (57.66)	4.11 (4.50)
Methyl	4-Chlorophenyl	Yellow prisms	133~134	85	$C_{15}H_{12}ClNOS_3$	51.20 (50.92)	3.72 (3.39)
Phenyl	4-Tolyl	Orange needles	110~111	73	$C_{21}H_{17}NOS_3$	63.90 (63.80)	4.51 (4.30)
Phenyl	4-Chlorophenyl	Orange prisms	118~119	60	$C_{20}H_{14}NOS_3$	58.00 (57.76)	3.36 (3.37)

TABLE VII. *O*-ARYL *N,N*-DISUBSTITUTED-THIONOCARBAMATES



$$R_1-\underset{\underset{S}{\|}}{C}-O-R_2$$

R_1	R_2	Appearance	M. p., °C	Yield, %	Formula	Anal. C, % Found (Calcd.)	Anal. H, % Found (Calcd.)
Dimethylamino	4-Tolyl	Colorless pillar	95 ~ 96	62	$C_{10}H_{13}NOS$	61.80 (61.53)	6.59 (6.67)
Dimethylamino	4-Chlorophenyl	Colorless needles	58 ~ 59	64	$C_9H_{10}ClNOS$	50.45 (50.12)	4.31 (4.64)
Dimethylamino	2,4,5-Trichlorophenyl	Colorless prisms	136 ~137	72.5	$C_9H_8Cl_3NOS$	38.38 (37.96)	2.37 (2.81)
Dimethylamino	4-Acetylphenyl	Slight amber needles	102.5~103.5	61.5	$C_{11}H_{13}NO_2S$	59.26 (59.19)	5.83 (5.83)
Morpholino	1-Chloro-2-naphthyl	Colorless plates	138 ~139	81	$C_{15}H_{14}ClNO_2S$	58.80 (58.54)	4.23 (4.55)
N-Methylanilino	4-Chlorophenyl	Colorless needles	104 ~105.5	78	$C_{14}H_{12}ClNOS$	60.05 (60.54)	4.19 (4.32)

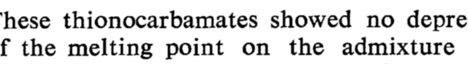
shown in Tables II—V. *O*-Aryl *S*-(*N*-alkyl-*N*-arylthiocarbamoyl)dithiocarbonates and *O*-aryl *S*-(*N*, *N*-diarylthiocarbamoyl)dithiocarbonates were also given by the similar reaction and listed in Table VI. In these reactions, water, methanol, ethanol, acetone and benzene can be used as the reaction medium. These aryl esters of *S*-(*N*, *N*-disubstituted-thiocarbamoyl)-dithiocarbonic acid, isolated as yellow or orange crystals when recrystallized from acetone-ethanol, were stable at room temperature.

O-Aryl *S*-(*N*-monosubstituted-thiocarbamoyl)-dithiocarbonates could not be isolated by the reaction between aryl chlorothionoformates and sodium *N*-monoalkyl- or *N*-monoaryl-dithiocarbamates, because of their decomposition during the reaction period.

It was concluded that both of the two hydrogen atoms connected with the nitrogen atom of the thiocarbamoyl group must be substituted to stabilize these dithiocarbonates.

The substituents of the aryl group, as shown in Tables II—VI, did not have such strong effects on the stability of the esters which were kept at a lower temperature than their respective melting points.

Aryl esters of *S*-(*N*, *N*-disubstituted-thiocarbamoyl)dithiocarbonic acid decomposed when heated at the melting points for a long period, giving carbon disulfide and *O*-aryl *N*, *N*-disubstituted thionocarbamate as shown in Table VII.



$$\genfrac{}{}{0pt}{}{R_1}{R_2}\!>\!N-\underset{\underset{S}{\|}}{C}-S-\underset{\underset{S}{\|}}{C}-O-R_3 \rightarrow \genfrac{}{}{0pt}{}{R_1}{R_2}\!>\!N-\underset{\underset{S}{\|}}{C}-O-R_3 + CS_2 \quad (2)$$

These thionocarbamates showed no depression of the melting point on the admixture with *O*-aryl *N*, *N*-disubstituted-thionocarbamates prepared from *N*, *N*-disubstituted-amines and aryl chlorothionoformates.

$$\genfrac{}{}{0pt}{}{R_1}{R_2}\!>\!N-H + Cl-\underset{\underset{S}{\|}}{C}-O-R_3 \rightarrow \genfrac{}{}{0pt}{}{R_1}{R_2}\!>\!N-\underset{\underset{S}{\|}}{C}-O-R_3 \quad (3)$$

Experimental

Starting Materials.—Sodium or ammonium salts of *N, N*-disubstituted-dithiocarbamic acid were synthesized by the known methods[3]. Aryl esters of chlorothionoformic acid were prepared as follows: To a solution of 1 mol. of thiophosgen and 1 mol. of phenol in chloroform was added gradually 1 mol. of sodium hydroxide (5% aqueous solution) under vigorous agitation. The temperature was kept at 5~10°C during the reaction period of 30 min. The chloroform layer was washed with water and dried over calcium chloride. The removal of chloroform gave esters which could be used in the following reaction without further purification.

***O*-(3, 5-Dimethyl-4-chlorophenyl) *S*-(*N, N*-dimethylthiocarbamoyl)dithiocarbonate.**—To a solution of 14.3 g. (0.1 mol.) of sodium dimethyldithiocarbamate in 100 cc. of water was added gradually 23.5 g. (0.1 mol.) of 3, 5-dimethyl-4-chlorophenyl chlorothionoformate keeping the temperature at 10~15°C during the reaction period of 2 hr. By the filtration of the reaction mixture, 27.2 g. (yield, 85%) of yellow crystals with m. p. 112~114°C were obtained. Recrystallization from acetone-ethanol gave yellow prisms with m. p. 113~114.5°C.

***O*-(4-Chlorophenyl) *S*-(*N*-methyl-*N*-phenylthiocarbamoyl)dithiocarbonate.**—To a solution of 20 g. (0.1 mol.) of ammonium *N*-methyl-*N*-phenyldithiocarbamate in 200 cc. of acetone was added gradually 21 g. (0.1 mol.) of 4-chlorophenyl chlorothionoformate keeping the temperature at 5~10°C during the reaction period of 1 hr. The reaction mixture, poured into 500 cc. of cold water, gave 31 g. (yield, 85%) of yellow precipitates with m. p. 132~134°C. Recrystallization of the preceipitates from acetone-ethanol gave yellow prisms with m. p. 133~134°C.

The other esters shown in Tables II—VI were synthesized in the similar way.

4-Tolyl *N, N*-dimethylthionocarbamate. — In an oil bath, 0.45 g. of *O*-(4-tolyl) *S*-(*N, N*-dimethylthiocarbamoyl)dithiocarbonate was kept at 160°C for 1 hr. After the subsidence of evolution of carbon disulfide, the reaction mixture was cooled to room temperature. Twice repeated recrystallization of the reaction mixture from 0.5 cc. of ethanol, gave 0.2 g. (yield, 62%) of 4-tolyl *N, N*-dimethylthionocarbamate with m. p. 95~96°C.

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[3] Houben-Weyl, "Methoden der organischen Chemie", 9, Georg Thieme Verlag, Stuttgart (1955), p. 826.