Studies on the Thiocarbamoylthiocarbonates. II. Synthesis and Thermal Decomposition of Aryl Thiocarbamoyltrithiocarbonates

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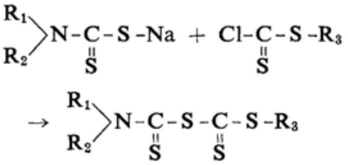
(Received November 24, 1960)

The syntheses and characteristics of *N, N*-disubstituted *O*-aryl *S*-thiocarbamoyldithiocarbonates have been reported previously¹⁾. Aryl esters of *N, N*-disubstituted thiocarbamoyltrithiocarbonic acid were also synthesized by the reaction of aryl chlorodithioformates with sodium or ammonium salts of *N, N*-disubstituted dithiocarbamic acid as shown in Eq. 1.

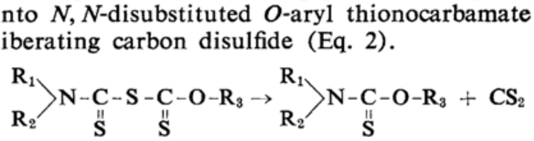


$$\mathrm{R_1R_2N{-}C({=}S){-}S{-}Na + Cl{-}C({=}S){-}S{-}R_3 \rightarrow R_1R_2N{-}C({=}S){-}S{-}C({=}S){-}S{-}R_3} \qquad (1)$$

In this way, various compounds were obtained in good yields as shown in Tables I—IV.

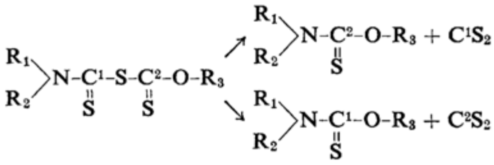
N-Monosubstituted aryl thiocarbamoyltrithiocarbonates could not be obtained, however, by this method, owing to their probable decomposition during the reaction.

As has been described in the previous paper¹⁾, aryl ester of *N, N*-disubstituted *S*-thiocarbamoyldithiocarbonic acid, when kept at a temperature higher than its melting point, decomposes into *N, N*-disubstituted *O*-aryl thionocarbamate liberating carbon disulfide (Eq. 2).



$$\mathrm{R_1R_2N{-}C({=}S){-}S{-}C({=}S){-}O{-}R_3 \rightarrow R_1R_2N{-}C({=}S){-}O{-}R_3 + CS_2} \qquad (2)$$

It is easily seen that two ways are possible to eliminate carbon disulfide, which can be shown in Eqs. 3 and 4.



$$\mathrm{R_1R_2N{-}C^1({=}S){-}S{-}C^2({=}S){-}O{-}R_3 \nearrow R_1R_2N{-}C^2({=}S){-}O{-}R_3 + C^1S_2} \qquad (3)$$

$$\mathrm{R_1R_2N{-}C^1({=}S){-}S{-}C^2({=}S){-}O{-}R_3 \searrow R_1R_2N{-}C^1({=}S){-}O{-}R_3 + C^2S_2} \qquad (4)$$

In order to decide the preferable course of the elimination reaction, the thermal decomposition of the compounds labeled with radioactive sulfur was studied. By the thermal decomposition of *O*-(4-tolyl) *S*-(*N, N*-dimethylthiocarbamoyl)dithiocarbonate (I), in which

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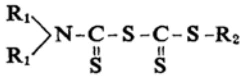
1) A. Kaji, This Bulletin, 34, 254 (1961).

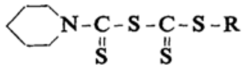
TABLE I. ARYL N,N-DIALKYLTHIOCARBAMOYLTRITHIOCARBONATES



$\begin{array}{l}R_1\\R_1\end{array}\!\!>N-\underset{\underset{S}{\|}}{C}-S-\underset{\underset{S}{\|}}{C}-S-R_2$

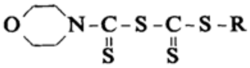
R_1	R_2	Appearance	M. p., °C	Yield %	Formula	Anal.	
						C, % Found (calcd.)	H, % Found (calcd.)
Methyl	Phenyl	Orange prisms	134 ∼134.5	87	$C_{10}H_{11}NS_4$	44.50 (43.96)	4.06 (4.03)
Methyl	2-Tolyl	Orange prisms	80 ∼ 81	75	$C_{11}H_{13}NS_4$	46.60 (45.99)	4.35 (4.53)
Methyl	4-Tolyl	Orange needles	107 ∼108	87	$C_{11}H_{13}NS_4$	46.47 (45.99)	4.99 (4.53)
Methyl	2-Chlorophenyl	Orange pillars	93 ∼ 94	65	$C_{10}H_{10}ClNS_4$	39.45 (39.02)	3.35 (3.25)
Methyl	4-Chlorophenyl	Orange prisms	104 ∼105	81	$C_{10}H_{10}ClNS_4$	39.45 (39.02)	3.21 (3.25)
Methyl	2,4,5-Trichlorophenyl	Orange prisms	112 ∼112.5	94	$C_{10}H_8Cl_3NS_4$	32.08 (31.87)	2.18 (2.12)
Methyl	1-Naphthyl	Orange prisms	97 ∼ 98	58	$C_{14}H_{13}NS_4$	52.30 (52.01)	4.05 (4.02)
Ethyl	Phenyl	Orange needles	68.5∼ 69.5	75	$C_{11}H_{15}NS_4$	47.95 (47.84)	5.05 (4.98)
Ethyl	4-Chlorophenyl	Orange needles	72 ∼ 73	64	$C_{12}H_{14}ClNS_4$	42.50 (42.92)	4.21 (4.17)
Ethyl	2,4,5-Trichlorophenyl	Orange needles	129 ∼130	70	$C_{12}H_{12}Cl_3NS_4$	35.85 (35.60)	2.94 (2.97)
Ethyl	Pentachlorophenyl	Orange prisms	121 ∼122	68	$C_{12}H_{10}Cl_5NS_4$	30.93 (30.80)	2.46 (2.14)
Ethyl	4-Tolyl	Orange needles	66 ∼ 67	60	$C_{13}H_{17}NS_4$	49.42 (49.52)	5.64 (5.40)

TABLE II. ARYL PIPERIDINOTHIOCARBONYLTRITHIOCARBONATES



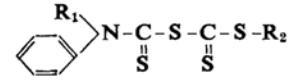
R	Appearance	M. p., °C	Yield, %	Formular	Anal.	
					C, % Found (calcd.)	H, % Found (calcd.)
Phenyl	Orange prisms	76.5∼ 77	60	$C_{13}H_{15}NS_4$	49.75 (49.84)	5.13 (4.79)
4-Tolyl	Orange prisms	108 ∼110	71.5	$C_{14}H_{17}NS_4$	51.62 (51.68)	5.12 (5.20)
4-Chlorophenyl	Orange prisms	135 ∼136	86	$C_{13}H_{14}ClNS_4$	45.37 (44.92)	4.10 (4.03)

TABLE III. ARYL MORPHOLINOTHIOCARBONYLTRITHIOCARBONATES



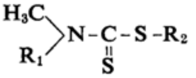
R	Appearance	M. p., °C	Yield, %	Formular	Anal.	
					C, % Found (calcd.)	H, % Found (calcd.)
2-Tolyl	Yellow prisms	104 ∼105	63	$C_{13}H_{15}NOS_4$	47.30 (47.42)	4.48 (4.56)
4-Tolyl	Orange prisms	122 ∼123	67.5	$C_{13}H_{15}NOS_4$	47.57 (47.42)	4.84 (4.56)
2-Chlorophenyl	Orange prisms	114.5∼115.5	67	$C_{12}H_{12}ClNOS_4$	41.45 (41.20)	3.77 (3.43)
2,4,5-Trichlorophenyl	Orange prisms	142 ∼143	86	$C_{12}H_{10}Cl_3NOS_4$	34.85 (34.41)	2.49 (2.39)

TABLE IV. ARYL ARYLTHIOCARBAMOYLTRITHIOCARBONATES



R₁	R₂	Appearance	M. p., °C	Yield %	Formula	Anal.	
						C, % Found (calcd.)	H, % Found (calcd.)
Methyl	4-Tolyl	Orange prisms	98 ～ 99	86	$C_{15}H_{15}NS_4$	54.88 (55.01)	4.50 (4.30)
Methyl	4-Chlorophenyl	Orange prisms	87 ～ 88	74	$C_{15}H_{12}ClNS_4$	48.90 (48.71)	2.87 (3.25)
Phenyl	4-Tolyl	Orange plates	101 ～102	65	$C_{21}H_{17}NS_4$	60.70 (61.31)	4.22 (4.14)
Phenyl	4-Chlorophenyl	Orange prisms	125.5～126.5	54	$C_{20}H_{14}ClNS_4$	55.95 (55.62)	3.30 (3.24)

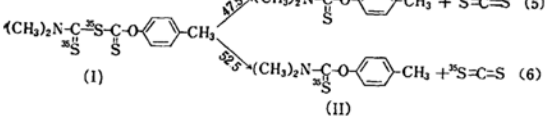
TABLE V. ARYL *N, N*-DISUBSTITUTED-DITHIOCARBAMATES



R₁	R₂	Appearance	M. p., °C	Yield %	Formula	Anal.	
						C, % Found (calcd.)	H, % Found (calcd.)
Methyl	4-Tolyl	Colorless prisms	112～113	77.5	$C_{10}H_{13}NS_2$	56.71 (56.87)	6.21 (6.16)
Methyl	4-Chlorophenyl	Colorless needles	101～103	82	$C_9H_{10}ClNS_2$	47.15 (46.65)	4.13 (4.32)
Phenyl	4-Tolyl	Colorless needles	132～133	76	$C_{15}H_{15}NS_2$	66.25 (65.93)	5.38 (5.49)
Phenyl	4-Chlorophenyl	Colorless lozenges	147～149	80.5	$C_{14}H_{12}ClNS_2$	57.56 (57.24)	4.12 (4.07)

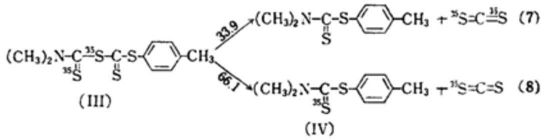
two S atoms in the thiocarbamoylthio group were labeled with $^{35}_{16}S$, radio-active *O*-(4-tolyl) *N, N*-dimethylthionocarbamate (II) was produced. The relative activity of II against I was found to be 0.2625, while the theoretical value, based on Eq. 5 should be zero, and based on Eq. 6, it should be 0.5000.

But this result may be explained if one postulates that the two courses of decomposition (Eqs. 5 and 6) occur simultaneously at the rate of 47.5 : 52.5.



N, N-Disubstituted aryl thiocarbamoyltrithiocarbonates were found to decompose, when kept at temperatures higher than their melting points, into *N, N*-disubstituted aryl dithiocarbamates liberating carbon disulfide. The crystalline decomposition products of some trithiocarbonates are listed in Table V.

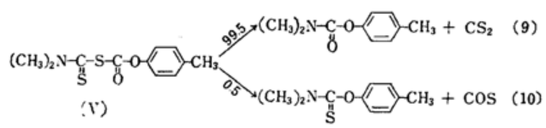
By the thermal decomposition of *S*-(4-tolyl) *S*-(*N,N*-dimethylthiocarbamoyl) trithiocarbonate (III) in which the two S atoms were labeled with $^{35}_{16}S$ similarly as in the case of I, radioactive 4-tolyl *N, N*-dimethyldithiocarbamate (IV) was given. But the relative activity of IV against III was found to be 0.3305. Thus the proportion of the two courses was concluded to be 33.9 : 66.1 (Eqs. 7 and 8) in this case.



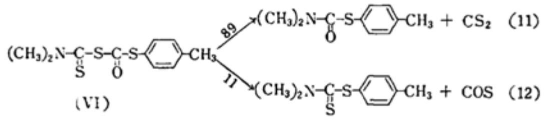
These facts show that the two courses of decomposition can occur simultaneously, but the rate of their occurrence is strongly influenced by substituting O atom with S atom.

To discover what influences would appear when another one of the S atoms was substituted with an O atom, the thermal decomposition of the compounds containing $>C^2=O$ in place of $>C^2=S$ (cf. Eqs. 3 and 4) was studied. This could produce carbon disulfide if the reaction occurred as Eq. 3, or carbon oxysulfide if the reaction followed Eq. 4. By the thermal decomposition of V and VI, both carbon disulfide and carbon oxysulfide were evolved as decomposition fragments in each case (cf. Eqs. 9—12). Also, the volume rates of $CS_2 : COS$ were found to be 99.5 : 0.5 and 89 : 11 respectively, by gas-chromatographic analyses of the above fragments.

These results show that the proportions of the two courses in each case should be 99.5 : 0.5 (Eqs. 9 and 10), and 89 : 11 (Eqs. 11 and 12).



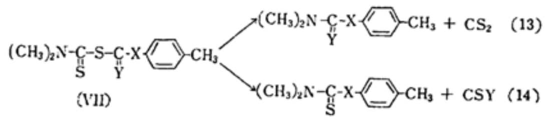
(V)



(VI)

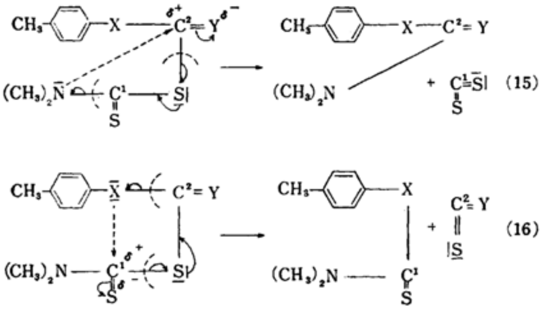
These results show that the proportion of the occurrence of reaction 13 against reaction 14 increases according to the variation of X and Y to S or O atom as follows.

X=Y=0>X=S, Y=0>X=0, Y=S>X=Y=S



(VII)

Summarizing the decomposition reactions mentioned above, it may be concluded that there are two reaction mechanisms on the thermal decomposition reaction of *N*, *N*-disubstituted aryl thiocarbamoylthiocarbonates, which can be written as follows.



(X, Y : O and/or S)

Reaction 15 occurs by co-ordination of $(C^2)^+$ to $\overline{N}$, and reaction 16, by co-ordination of $(C^1)^+$ to $\overline{X}$. The electron density on C^2 and electro-negativity of –X–, which vary according to the variation of X and Y to S or O atom, may have some influence on the reaction courses.

By comparison of the electron densities on C^1 in $\rangle N-\underset{|}{C^1}=S$ and C^2 in $-X-\underset{|}{C^2}=Y$, when both X and Y are O atoms, the electron density on C^2 is far smaller than that on C^1, owing to the greater polarization of $\rangle C=O$ than that of $\rangle C=S$ and greater electro-negativity of –O– than that of –S–. Thus reaction 15 may occur almost exclusively in this case. When X is an S atom, however, the electron density on C^2 increases, for the electro-negativity of –X– becomes smaller owing to replacement of O atom by S atom. This will make not only the co-ordination of $(C^2)^+$ to $\overline{N}$ unfavorable, but also the co-ordination of $(C^1)^+$ to $\overline{X}$ favorable. Thus reaction 16 may occur to some extent in this case. When Y is an S atom, the difference of the electron densities on C^1 and on C^2, due to the respective polarity of $\rangle C=Y$ and $\rangle C=S$, will disappear. Thus the two sorts of co-ordination become concurrent. When X is also an S atom, reaction 16 occurs most easily for the reasons mentioned above.

These situations may explain the relationships between the mechanisms of thermal decomposition of the compounds VII and their structures.

Experimental

Starting Materials.—Sodium or ammonium salts of *N*, *N*-disubstituted-dithiocarbamic acid were synthesized by the known methods[1]. Aryl esters of chlorodithioformic acid were synthesized similarly to aryl chlorothionoformates which were previously reported[1], by the reaction of thiophosgen, thiophenol and sodium hydroxide.

4-Tolyl *N*, *N*-Dimethylthiocarbamoyltrithiocarbonate. — To a solution of 14.3 g. (0.1 mol.) of sodium dimethyldithiocarbamate in 100 cc. of water, was added gradually 20.3 g. (0.1 mol.) of 4-tolyl chlorodithioformate, keeping the temperature at 10~15°C during the reaction period of 2 hr. The reaction mixture produced 25 g. (yield, 87%) of orange crystals with m. p. 105~106°C. Recrystallization from acetone-ethanol gave orange needles of m. p. 107~108°C.

4-Tolyl *N*-Methyl-*N*-phenylthiocarbamoyltrithiocarbonate.—To a suspension of 20 g. (0.1 mol.) of ammonium *N*-methyl-*N*-phenyldithiocarbamate in 100 cc. of acetone, was added gradually 20.3 g. (0.1 mol.) of 4-tolyl chlorodithioformate, keeping the temperature at 5~10°C during the reaction period of 1 hr. The reaction mixture poured into 200 cc. of cold water produced 30 g. (yield, 86%) of orange crystals with m. p. 96~99°C. Recrystallization from acetone-ethanol gave orange prisms with m. p. 98~99°C.

The other esters shown in Tables I—IV were synthesized similarly to the synthesis of the above examples.

***S*-(4-Tolyl) *S*-(*N*, *N*-Dimethylthiocarbamoyl)dithiocarbonate (VI).**—This could also be synthesized in a similar way, by reacting 27.1 g. (0.1 mol.) of *S*-(4-tolyl) chlorothiolformate with 14.3 g. (0.1 mol.) of sodium dimethyldithiocarbamete in 150 cc. of acetone. Yield : 27.8% ; Yellow needles of m. p. 69~70°C.

Found: C, 48.66; H, 4.72; N, 5.33. Calcd. for $C_{11}H_{13}NOS_3$: C, 48.71; H, 4.80; N, 5.17%.

Thermal Decomposition of V and VI.—In a sealed flask (1000 cc. in volume) which was filled with nitrogen gas at 10 mmHg., 2 g. of V or VI was fused at 160°C for 1 hr. After the subsidence of evolution of gas, nitrogen gas was led into the flask until the pressure became 760 mmHg. Further, the ratio of carbon oxysulfied and carbon disulfide, in the gas obtained, was measured by gas-chromatography (column: tricresyl phosphate, at 42.5°C; carrier: H_2).

Thermal Decomposition of Radio-active 4-Tolyl *N*, *N*-Dimethylthiocarbamoyltrithiocarbonate (III).—In an oil bath, 0.575 g. of III (specific activity: 47.84 mc./mol.), synthesized by the reaction between 4-tolyl chlorodithioformate and radio-active sodium *N*,*N*-dimethyldithiocarbamate in which the two S atoms were labeled with $^{35}_{16}S$, was fused at 160°C for 1 hr. in nitrogen atmosphere of 10 mmHg. After the subsidence of evolution of radio-active carbon disulfide, the decomposition product was twice recrystallized from 2.4 cc. of ethanol and produced 0.327 g. (yield, 77.5%) of radio-active 4-tolyl *N*,*N*-dimethyldithiocarbamate (VI), of which the specific activity was 15.81 mc./mol. with m. p. 112~113°C. The relative specific activity of VI against III was 0.3305 (=15.81/47.84).

By the thermal decomposition of radio-active *O*-(4-tolyl) *S*-(*N*,*N*-dimethylthiocarbamoyl)dithiocarbonate (I) (specific activity: 23.85 mc./mol.), radio-active *O*-(4-tolyl) *N*,*N*-dimethylthionocarbamate (II) (specific activity: 6.26 mc./mol.) was produced in a similar way. Thus the relative activity of II against I was 0.2625.

The author wishes to express his sincere thanks to Professor Dr. Ryozo Goto, Kyoto University, for his guidance and encouragement throughout this work. The author also thanks Professor Dr. Hiroshi Watanabe, Konan University, for his helpful advice. He is also grateful to Dr. N. Oda, Mr. M. Kubo, Mr. K. Norishima, Mr. G. Tsuchihashi, Mr. S. Ono and Mr. A. Nomura for gas-chromatographic and elemental analyses, to Dr. K. Taniguchi for his guidance, and to Mr. K. Miyazaki, Mr. K. Hashimoto and Mr. Y. Aoki for their assistance with the experimental work.

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