

## *Studies on the Thiocarbamoylthiocarbonates. I. Synthesis of Aryl Thiocarbamoyldithiocarbonates*

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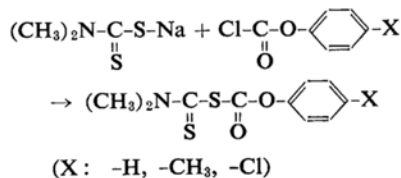
(Received July 26, 1960)

*O*-Alkyl *S*-(*N*, *N*-disubstituted-thiocarbamoyl)-thiocarbonates were studied by Cambron<sup>1)</sup> and Lo<sup>2)</sup>. 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.



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

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
$$(\text{CH}_3)_2\text{N}-\underset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{S}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-\text{C}_6\text{H}_4-\text{X}$$

| X                 | M. p., °C   | Yield, % | Formula  | Anal.                |                      |
|-------------------|-------------|----------|--|----------------------|----------------------|
|                   |             |          |  | C% Found<br>(Calcd.) | H% Found<br>(Calcd.) |
| -H                | 97.5~98.5   | 51.5     | C <sub>10</sub> H <sub>11</sub> NO <sub>2</sub> S <sub>2</sub>   | 49.79<br>(50.43)     | 4.56<br>(4.32)       |
| 4-CH <sub>3</sub> | 105.5~106.5 | 50.5     | C <sub>11</sub> H <sub>13</sub> NO <sub>2</sub> S <sub>2</sub>   | 51.76<br>(51.65)     | 5.10<br>(4.99)       |
| 3-Cl              | 122 ~123    | 24       | C <sub>10</sub> H <sub>10</sub> ClNO <sub>2</sub> S <sub>2</sub> | 43.56<br>(44.09)     | 3.29<br>(3.80)       |

TABLE II. *O*-ARYL *S*-(*N,N*-DIMETHYLTHIOCARBAMOYL)DITHIOCARBONATES
$$(\text{CH}_3)_2\text{N}-\underset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{S}-\underset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{O}-\text{R}$$

| R                           | Appearance        | M. p., °C     | Yield, % | Formula  | Anal.                    |                          |
|-----------------------------|-------------------|---------------|----------|--|--------------------------|--------------------------|
|                             |                   |               |          |  | C %<br>Found<br>(Calcd.) | H %<br>Found<br>(Calcd.) |
| Phenyl                      | Yellow<br>pillars | 68 ~ 69       | 86       | C <sub>10</sub> H <sub>11</sub> NOS <sub>3</sub>                             | 46.30<br>(46.69)         | 3.95<br>(4.28)           |
| 2-Tolyl                     | Yellow<br>prisms  | 74 ~ 75       | 90       | C <sub>11</sub> H <sub>13</sub> NOS <sub>3</sub>                             | 48.20<br>(48.70)         | 5.13<br>(4.80)           |
| 4-Tolyl                     | Yellow<br>needles | 88 ~ 89       | 78       | C <sub>11</sub> H <sub>13</sub> NOS <sub>3</sub>                             | 48.97<br>(48.70)         | 4.71<br>(4.80)           |
| 4-Methoxyphenyl             | Yellow<br>needles | 87.5~88.5     | 80       | C <sub>11</sub> H <sub>13</sub> NO <sub>2</sub> S <sub>3</sub>               | 46.03<br>(45.99)         | 4.42<br>(4.53)           |
| 4-Chlorophenyl              | Yellow<br>prisms  | 104 ~105      | 80       | C <sub>10</sub> H <sub>10</sub> ClNOS <sub>3</sub>                           | 41.40<br>(41.17)         | 3.56<br>(3.43)           |
| 2,4-Dichlorophenyl          | Yellow<br>needles | 138 ~139      | 78       | C <sub>10</sub> H <sub>9</sub> Cl <sub>2</sub> NOS <sub>3</sub>              | 36.95<br>(36.80)         | 2.54<br>(2.76)           |
| 2,4,5-Trichlorophenyl       | Yellow<br>prisms  | 113.5~114.5   | 75       | C <sub>10</sub> H <sub>8</sub> Cl <sub>3</sub> NOS <sub>3</sub>              | 33.34<br>(33.29)         | 1.84<br>(2.22)           |
| 4-Bromophenyl               | Yellow<br>needles | 110 ~111      | 74       | C <sub>10</sub> H <sub>10</sub> BrNOS <sub>3</sub>                           | 35.95<br>(35.71)         | 2.60<br>(2.98)           |
| 2,4,6-Tribromophenyl        | Yellow<br>needles | 118 (decomp.) | 69       | C <sub>10</sub> H <sub>8</sub> Br <sub>3</sub> NOS <sub>3</sub>              | 24.50<br>(24.30)         | 1.49<br>(1.69)           |
| 4-Chloro-2-tolyl            | Yellow<br>prisms  | 113 ~113.5    | 56       | C <sub>11</sub> H <sub>12</sub> ClNOS <sub>3</sub>                           | 43.22<br>(43.20)         | 3.73<br>(3.93)           |
| 2-Chloro-4-tolyl            | Yellow<br>prisms  | 131.5~132.5   | 52       | C <sub>11</sub> H <sub>12</sub> ClNOS <sub>3</sub>                           | 43.50<br>(43.20)         | 3.63<br>(3.93)           |
| 2,6-Dichloro-4-tolyl        | Yellow<br>prisms  | 133 ~134      | 60       | C <sub>11</sub> H <sub>11</sub> Cl <sub>2</sub> NOS <sub>3</sub>             | 39.05<br>(38.82)         | 3.47<br>(3.24)           |
| 4,6-Dichloro-2-tolyl        | Yellow<br>needles | 115 ~116.5    | 56       | C <sub>11</sub> H <sub>11</sub> Cl <sub>2</sub> NOS <sub>3</sub>             | 39.30<br>(38.82)         | 3.41<br>(3.24)           |
| 3,5-Dimethyl-4-chlorophenyl | Yellow<br>prisms  | 113 ~114.5    | 85       | C <sub>12</sub> H <sub>14</sub> ClNOS <sub>3</sub>                           | 44.74<br>(45.07)         | 4.25<br>(4.38)           |
| 2-Phenyl-4-chlorophenyl     | Yellow<br>prisms  | 107 ~108      | 61       | C <sub>16</sub> H <sub>14</sub> ClNOS <sub>3</sub>                           | 52.55<br>(52.24)         | 3.68<br>(3.81)           |
| 2-Biphenyl                  | Yellow<br>needles | 135 ~136      | 84       | C <sub>16</sub> H <sub>15</sub> NOS <sub>3</sub>                             | 57.83<br>(57.66)         | 4.62<br>(4.50)           |
| 4-Acetylphenyl              | Yellow<br>needles | 117.5~118     | 78       | C <sub>12</sub> H <sub>13</sub> NO <sub>2</sub> S <sub>3</sub>               | 48.50<br>(48.16)         | 4.10<br>(4.35)           |
| 2-Methoxycarbonyl-phenyl    | Yellow<br>prisms  | 102.5~103.5   | 60       | C <sub>12</sub> H <sub>13</sub> NO <sub>3</sub> S <sub>3</sub>               | 45.80<br>(45.71)         | 4.10<br>(4.13)           |
| 4-Nitrophenyl               | Yellow<br>prisms  | 114 ~115      | 90       | C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> S <sub>3</sub> | 40.05<br>(39.75)         | 3.52<br>(3.31)           |
| 1-Chloro-2-naphthyl         | Yellow<br>prisms  | 126.5~127     | 91       | C <sub>14</sub> H <sub>12</sub> ClNOS <sub>3</sub>                           | 49.20<br>(49.20)         | 3.60<br>(3.51)           |
| 1-Bromo-2-naphthyl          | Yellow<br>prisms  | 141 ~142      | 76       | C <sub>14</sub> H <sub>12</sub> BrNOS <sub>3</sub>                           | 43.55<br>(43.52)         | 2.92<br>(3.11)           |

TABLE III. *O*-ARYL *S*-(*N,N*-DIETHYLTHIOCARBAMOYL)DITHIOCARBONATES  
 $(C_2H_5)_2N-C(=S)-S-C(=S)-O-R$

| R                           | Appearance     | M. p., °C        | Yield, % | Formula                 | Anal.                    |                          |
|-----------------------------|----------------|------------------|----------|-------------------------|--------------------------|--------------------------|
|                             |                |                  |          |                         | C %<br>Found<br>(Calcd.) | H %<br>Found<br>(Calcd.) |
| 2-Biphenyl                  | Yellow plates  | 76 ~ 77          | 72       | $C_{18}H_{19}NOS_3$     | 60.30<br>(59.83)         | 5.34<br>(5.26)           |
| 2-Chloro-4-tolyl            | Yellow needles | 93 ~ 94          | 81       | $C_{13}H_{16}ClNOS_3$   | 47.15<br>(46.78)         | 5.15<br>(4.80)           |
| 2,6-Dichloro-4-tolyl        | Yellow needles | 91.5 ~ 93        | 70       | $C_{13}H_{15}Cl_2NOS_3$ | 42.85<br>(42.39)         | 3.92<br>(4.08)           |
| 3,5-Dimethyl-4-chlorophenyl | Yellow needles | 92 ~ 93          | 69       | $C_{14}H_{18}ClNOS_3$   | 48.45<br>(48.35)         | 4.57<br>(5.18)           |
| 2,4,6-Tribromophenyl        | Yellow needles | 114<br>(decomp.) | 69       | $C_{12}H_7Br_3NOS_3$    | 27.40<br>(27.59)         | 2.82<br>(2.30)           |
| 2-Nitro-4-tolyl             | Yellow scales  | 104.5 ~ 105.5    | 84       | $C_{13}H_{16}N_2O_3S_3$ | 46.17<br>(45.35)         | 4.75<br>(4.65)           |
| 2-Naphthyl                  | Yellow prisms  | 62 ~ 63          | 64.5     | $C_{16}H_{17}NOS_3$     | 57.08<br>(57.31)         | 5.25<br>(5.07)           |
| 1-Chloro-2-naphthyl         | Yellow prisms  | 143 ~ 144        | 60       | $C_{16}H_{16}ClNOS_3$   | 52.50<br>(51.96)         | 4.40<br>(4.33)           |
| 3-Chloro-2-naphthyl         | Yellow needles | 107.5 ~ 108.5    | 72       | $C_{16}H_{16}ClNOS_3$   | 51.80<br>(51.96)         | 4.57<br>(4.33)           |
| 1-Bromo-2-naphthyl          | Yellow prisms  | 142 ~ 144        | 73       | $C_{16}H_{16}BrNOS_3$   | 46.10<br>(46.38)         | 3.67<br>(3.86)           |

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

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

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

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

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

| R <sub>1</sub> | R <sub>2</sub>  | Appearance     | M. p., °C | Yield, % | Formula  | Anal.                    |                          |
|----------------|-----------------|----------------|-----------|----------|--|--------------------------|--------------------------|
|                |                 |                |           |          |  | C %<br>Found<br>(Calcd.) | H %<br>Found<br>(Calcd.) |
| Methyl         | 4-Tolyl         | Yellow prisms  | 98~99     | 72       | C <sub>16</sub> H <sub>15</sub> NOS <sub>3</sub>   | 57.95<br>(57.66)         | 4.11<br>(4.50)           |
| Methyl         | 4-Chloro-phenyl | Yellow prisms  | 133~134   | 85       | C <sub>15</sub> H <sub>12</sub> ClNOS <sub>3</sub> | 51.20<br>(50.92)         | 3.72<br>(3.39)           |
| Phenyl         | 4-Tolyl         | Orange needles | 110~111   | 73       | C <sub>21</sub> H <sub>17</sub> NOS <sub>3</sub>   | 63.90<br>(63.80)         | 4.51<br>(4.30)           |
| Phenyl         | 4-Chloro-phenyl | Orange prisms  | 118~119   | 60       | C <sub>20</sub> H <sub>14</sub> NOS <sub>3</sub>   | 58.00<br>(57.76)         | 3.36<br>(3.37)           |

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

| R <sub>1</sub>           | R <sub>2</sub>         | Appearance           | M. p., °C   | Yield, % | Formula   | Anal.                     |                           |
|--------------------------|------------------------|----------------------|-------------|----------|---|---------------------------|---------------------------|
|                          |                        |                      |             |          |   | C, %<br>Found<br>(Calcd.) | H, %<br>Found<br>(Calcd.) |
| Dimethyl-amino           | 4-Tolyl                | Colorless pillar     | 95 ~ 96     | 62       | C <sub>10</sub> H <sub>13</sub> NOS                 | 61.80<br>(61.53)          | 6.59<br>(6.67)            |
| Dimethyl-amino           | 4-Chlorophenyl         | Colorless needles    | 58 ~ 59     | 64       | C <sub>9</sub> H <sub>10</sub> ClNOS                | 50.45<br>(50.12)          | 4.31<br>(4.64)            |
| Dimethyl-amino           | 2,4,5-Trichloro-phenyl | Colorless prisms     | 136 ~ 137   | 72.5     | C <sub>9</sub> H <sub>8</sub> Cl <sub>3</sub> NOS   | 38.38<br>(37.96)          | 2.37<br>(2.81)            |
| Dimethyl-amino           | 4-Acetylphenyl         | Slight amber needles | 102.5~103.5 | 61.5     | C <sub>11</sub> H <sub>13</sub> NO <sub>2</sub> S   | 59.26<br>(59.19)          | 5.83<br>(5.83)            |
| Morpholino               | 1-Chloro-2-naphthyl    | Colorless plates     | 138 ~ 139   | 81       | C <sub>15</sub> H <sub>14</sub> ClNO <sub>2</sub> S | 58.80<br>(58.54)          | 4.23<br>(4.55)            |
| <i>N</i> -Methyl-anilino | 4-Chloro-phenyl        | Colorless needles    | 104 ~ 105.5 | 78       | C <sub>14</sub> H <sub>12</sub> ClNOS               | 60.05<br>(60.54)          | 4.19<br>(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.

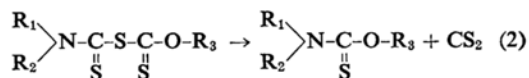
*O*-Aryl *S*-(*N*-monosubstituted-thiocarbamoyl)-dithiocarbonates could not be isolated by the reaction between aryl chlorothionoformates and sodium *N*-monoalkyl- or *N*-monoaryl-dithiocarbamates, because of their decomposition during the reaction period.

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.

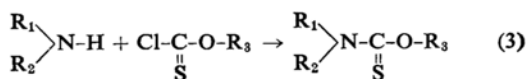
The substituents of the aryl group, as shown

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.



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.



### Experimental

**Starting Materials.**—Sodium or ammonium salts of *N,N*-disubstituted-dithiocarbamic acid were synthesized by the known methods<sup>3)</sup>. 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.

The author wishes to express his sincere thanks to Professor Dr. Ryozo Goto, Kyoto University, for his guidance and encouragement throughout this work.

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

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