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# Studies of Organosulfur Compounds. IX. The Preparation of Organometal IVb Esters of Aromatic Thio Acid

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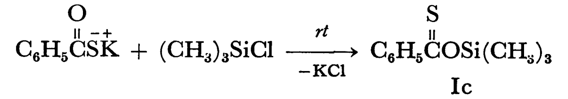
It was found that the reactions of potassium salts of aromatic thio acid with chlorotrimethylsilane gave the corresponding thionoacyloxysilanes [ArC(S)OSi(CH$_3$)$_3$]. On the other hand, the reactions with chlorotrimethylgermanes or -stannane gave the corresponding thiol esters [ArC(O)SM(CH$_3$)$_3$, M: Ge, or Sn] containing the sulfur-metal (IVb) linkage in almost quantitative yields.

During the last decade, a number of reports[1–3] of organometallic sulfur compounds containing silicon, germanium, tin, and lead have been published. However, there have been very few reports[4–6] on any compounds containing the ≡M–S–CO–C≡ (M: IVb element) linkage except the tin compounds; further, many of the reported compounds (mainly tin compounds) have been described in patents [7g–r] without any characterization or description of their physical constants.

In this paper, the results of the reactions of potassium salts of aromatic thio acid with trimethylmetal IVb chlorides will be disclosed in the expectation that the corresponding thiolacyloxy-sialnes, -germanes, and -tins will be obtained.

## Results and Discussion

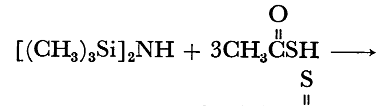
When an equimolar amount of chlorotrimethylsilane was added to a suspension of potassium thiobenzoate in petroleum ether; the color of the reaction mixture changed from colorless to yellow, the subsequent vacuum distillation of the petroleum ether soluble parts gave orange yellow oil with a definite boiling point in almost quantitative yields. Surprisingly, the IR spectrum of this oil showed no absorption band of ν C=O; instead, the absorption bands at 1590 (ν C=C, aromatic), 1250 (δ CH$_3$, scissoring), 1238 (ν C=S), and 953 cm$^{-1}$ (δ CH$_3$, rocking) were observed. The NMR peaks appeared at 9.54 τ (SiCH$_3$, s, 9H) and 1.90—3.20 τ (aromatic, m, 5H). In the visible spectrum, the maximum band at 437 mμ (ε 75) was observed. These results, together with the analytical results, indicate that the liquid is thionobenzoyloxylsilane with the Ic structure (Eq. (1)). By the similar treatment of other



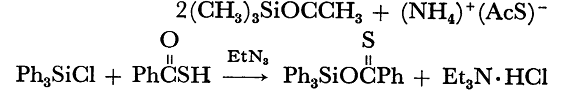
$$C_6H_5\overset{O}{\overset{\|}{C}}S^-K^+ + (CH_3)_3SiCl \xrightarrow[-KCl]{rt} C_6H_5\overset{S}{\overset{\|}{C}}OSi(CH_3)_3 \quad (1)$$

Ic

substituted potassium thiobenzoates with chlorotrimethylsilane, the corresponding thionobenzoyloxysilanes were obtained in excellent yields, as is shown in Table 1. Gornowicz and Ryan[8] reported two methods for the preparation of thionoacyloxysilanes (Eqs. (2) and (3)).



$$[(CH_3)_3Si]_2NH + 3CH_3\overset{O}{\overset{\|}{C}}SH \longrightarrow 2(CH_3)_3SiO\overset{S}{\overset{\|}{C}}CH_3 + (NH_4)^+(AcS)^- \quad (2)$$

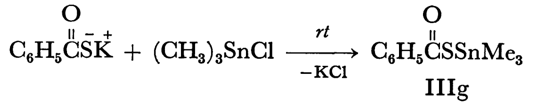


$$Ph_3SiCl + Ph\overset{O}{\overset{\|}{C}}SH \xrightarrow{EtN_3} Ph_3SiO\overset{S}{\overset{\|}{C}}Ph + Et_3N\cdot HCl \quad (3)$$

However, the method reported in this paper is more useful than the method in the literature them because we could avoid using thio acids, which are generally unstable and unpleasant to work with.

The formation of the thion esters (I) might be derived from the strong affinity of silicon to the oxygen atom.

Contrary to the reactions with chlorotrimethylsilane, potassium thiobenzoate reacted readily with chlorotrimethylstannane at 45°C to give the expected (benzoylthio)trimethylstannane (IIIg) as a colorless oil in 98% yield (Eq. (4)). The IIIg structure could be



$$C_6H_5\overset{O}{\overset{\|}{C}}S^-K^+ + (CH_3)_3SnCl \xrightarrow[-KCl]{rt} C_6H_5\overset{O}{\overset{\|}{C}}SSnMe_3 \quad (4)$$

IIIg

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Table 1. Physical properties and elemental analyses of thionobenzoyloxysilanes [X-$C_6H_4C(S)OSi(CH_3)_3$]

| Compd | Substituent X | Bp °C/3 mmHg | Yield % | Color[a] | Formula | Found (Calcd), % | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | Cl | S |
| Ia | *p*-Cl | 94.5 | 92 | O (O) | $C_{10}H_{13}ClOSSi$ | 49.36<br>(49.04) | 5.33<br>(5.35) | 14.00<br>(13.94) | 13.46<br>(13.10) |
| Ib | *m*-Cl | 105 | 98 | O (O) | $C_{10}H_{13}ClOSSi$ | 49.93 | 5.40 | 13.98 | 13.93 |
| Ic | H | 97 | 97 | OY (O) | $C_{10}H_{14}OSSi$ | 57.36<br>(57.08) | 6.88<br>(6.71) | | 15.21<br>(15.25) |
| Id | *p*-$CH_3$ | 117 | 98 | OY (O) | $C_{11}H_{16}OSSi$ | 59.02<br>(58.86) | 7.22<br>(7.19) | | 15.00<br>(14.30) |
| Ie | *m*-$CH_3$ | 113 | 98 | OY (O) | $C_{11}H_{16}OSSi$ | 58.11 | 7.01 | | 14.23 |
| If | *o*-$CH_3$ | 108 | 96 | OY (O) | $C_{11}H_{16}OSSi$ | 58.16 | 7.20 | | 14.16 |
| Ig | *p*-$CH_3O$ | 138 | 98 | OY (O) | $C_{11}H_{16}O_2SSi$ | 54.79<br>(54.94) | 6.69<br>(6.71) | | 13.33<br>(13.24) |
| Ih | *o*-$CH_3O$ | 77 | 95 | OY (O) | $C_{11}H_{16}O_2SSi$ | 54.18 | 6.58 | | 13.91 |

a) O: Orange, OY: Orange yellow, (O): Oil

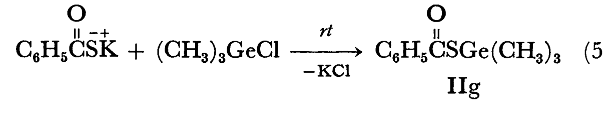
Table 2. Physical properties and elemental analyses of substituted (benzoylthio)trimethylstannanes [X-$C_6H_4C(O)SSn(CH_3)_3$]

| Compd | Substituent X | Mp °C | Yield % | Appearance[a] | Formula | Found (Calcd), % | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | Cl | N | S |
| IIIa | *p*-$NO_2$ | 109 —111.0 | 97 | Y (N) | $C_{10}H_{13}NO_3Sn$ | 34.77<br>(34.70) | 3.77<br>(3.79) | | 4.11<br>(4.05) | 9.33<br>(9.27) |
| IIIb | *m*-$NO_2$ | 79.5— 80.0 | 97 | C (P) | $C_{10}H_{13}NO_3Sn$ | 34.83 | 3.71 | | 4.16 | 9.46 |
| IIIc | *o*-$NO_2$ | 73.0— 73.5 | 98 | C (P) | $C_{10}H_{13}NO_3Sn$ | 34.65 | 3.84 | | 4.23 | 9.22 |
| IIId | *p*-Cl | | 96 | C (O) | $C_{10}H_{13}ClOSSn$ | 35.81<br>(35.79) | 4.01<br>(3.91) | 10.93<br>(10.57) | | 9.83<br>(9.56) |
| IIIe | *m*-Cl | | 95 | C (N) | $C_{10}H_{13}ClOSSn$ | 35.44 | 4.02 | 11.01 | | 9.48 |
| IIIf | *o*-Cl | 64.5— 65.0 | 97 | C (N) | $C_{10}H_{13}ClOSSn$ | 35.01 | 4.00 | 10.73 | | 9.65 |
| IIIg | H | | 99 | C (O) | $C_{10}H_{14}OSSn$ | 40.01<br>(39.89) | 4.79<br>(4.69) | | | 10.68<br>(10.66) |
| IIIh | *p*-$CH_3$ | | 98 | C (O) | $C_{11}H_{16}OSSn$ | 42.33<br>(41.92) | 5.23<br>(5.12) | | | 10.28<br>(10.18) |
| IIIi | *m*-$CH_3$ | | 96 | C (O) | $C_{11}H_{16}OSSn$ | 42.01 | 5.21 | | | 10.33 |
| IIIj | *o*-$CH_3$ | | 97 | C (O) | $C_{11}H_{16}OSSn$ | 41.91 | 5.16 | | | 10.00 |
| IIIk | *p*-$CH_3O$ | 53.0— 54.0 | 98 | C (P) | $C_{11}H_{16}O_2SSn$ | 39.83<br>(39.90) | 4.79<br>(4.87) | | | 9.46<br>(9.69) |
| IIIl | *o*-$CH_3O$ | 69.5— 70.0 | 94 | C (N) | $C_{11}H_{16}O_2SSn$ | 39.88 | 4.83 | | | 9.58 |

a) Y: Yellow, C: Colorless, (N): Needles, (P): Plates, (O): Oil.

assigned by elemental analysis and spectral data: intensive absorption bands at 1631 ($\nu$ C=O) and 775 cm$^{-1}$ ($\delta$ $SnCH_3$) in the IR spectrum, and at 9.43 $\tau$ (Sn–$CH_3$, s, 9H), 1.98—2.50 $\tau$ (aromatic, m, 5H), $J_{^{119}Sn-C-H}=59$ Hz, $J_{^{117}Sn-C-H}=56$ Hz in NMR spectrum. The analogous treatment of other potassium-substituted thiobenzoate with chlorotrimethylstannane gave the corresponding (benzoylthio)trimethylstannanes (IIIa—f and h—l) respectively in quantitative yields (Table 2). The formation of the stannyl esters, III, can be explained by the strong affinity of tin to sulfur atom.

The results obtained above encouraged us to investigate the reactions with chlorotrimethylgermane, bacause germanium is situated between silicon and tin in the peridical table. However, the analogous treatment of potassium thiobenzoate with chlorotrimethylgermane gave (benzoylthio)trimethylgermane (IIg)



$$C_6H_5\overset{\overset{O}{\|}}{C}\overset{-+}{SK} + (CH_3)_3GeCl \xrightarrow[-KCl]{rt} \underset{IIg}{C_6H_5\overset{\overset{O}{\|}}{C}SGe(CH_3)_3} \quad (5)$$

(Eq. 5). The IIg structure was established by elemental analysis and studies of the IR and NMR spectra. In the IR spectrum, intensive absorption bands at 1648 ($\nu$ C=O) and 829 cm$^{-1}$ ($\delta$ $GeCH_3$) were observed. The NMR spectrum showed peaks at 9.33 $\tau$ ($GeCH_3$, s, 9H), and 1.00—2.78 $\tau$ (aromatic, m, 5H). By the analogous treatment of other potassium-substituted thiobenzoates with chlorotrimethylgermane, the corresponding (benzoylthio)trimethylgermanes (IIa—f and h—l) were obtained in excellent yields (Table 3). Germanium would be considered to have a higher affinity to the sulfur atom rather than the oxygen atom.

The silyl thion esters (I) thus obtained were readily hydrolyzed by moisture in air to give hexamethyldisiloxane and the corresponding thiobenzoic acid in almost quantitative yields. However, the germyl thiol esters (II) were fairly stable against moisture and were very slowly hydrolyzed to give hexamethyldigermoxane and the corresponding thiobenzoic acid. On the other hand, the trimethylstannyl thiol esters (III) were a very stable oil or crystals which could be recrystallized

Table 3. Physical properties and elemental analyses of substituted (benzoylthio)trimethylgermanes [(X-$C_6H_4C(O)SGe(CH_3)_3$]

| Compd | Substituent X | Mp °C | Yield % | Appearance[a)] | Formula | Found (Calcd), % C | H | Cl | N | S |
|---|---|---|---|---|---|---|---|---|---|---|
| IIa | *p*-$NO_2$ | 61—62 | 96 | Y (N) | $C_{10}H_{13}NO_3SGe$ | 40.44<br>(40.03) | 4.26<br>(4.37) | | 4.59<br>(4.67) | 10.46<br>(10.70) |
| IIb | *m*-$NO_2$ | 82—83 | 96 | C (N) | $C_{10}H_{13}NO_3SGe$ | 39.94 | 4.33 | | 4.71 | 10.58 |
| IIc | *o*-$NO_2$ | | 98 | SY (O) | $C_{10}H_{13}NOS_3Ge$ | 39.99 | 4.36 | | 4.66 | 11.00 |
| IId | *p*-Cl | | 97 | C (O) | $C_{10}H_{13}ClOSGe$ | 41.46<br>(41.53) | 4.52<br>(4.52) | 12.31<br>(12.25) | | 11.11<br>(11.09) |
| IIe | *m*-Cl | | 98 | C (O) | $C_{10}H_{13}ClOSGe$ | 41.88 | 4.55 | 12.28 | | 11.36 |
| IIf | *o*-Cl | | 98 | C (O) | $C_{10}H_{13}ClOSGe$ | 41.92 | 4.57 | 12.22 | | 11.21 |
| IIg | H | | 96 | C (O) | $C_{10}H_{14}OSGe$ | 47.76<br>(47.10) | 4.58<br>(5.54) | | | 12.96<br>(12.59) |
| IIh | *p*-$CH_3$ | | 98 | C (O) | $C_{11}H_{16}OSGe$ | 49.99<br>(49.15) | 6.07<br>(6.00) | | | 11.42<br>(11.93) |
| IIi | *m*-$CH_3$ | | 99 | C (O) | $C_{11}H_{16}OSGe$ | 48.87 | 6.01 | | | 11.48 |
| IIj | *o*-$CH_3$ | | 98 | C (O) | $C_{11}H_{16}OSGe$ | 49.11 | 6.11 | | | 12.00 |
| IIk | *p*-$CH_3O$ | | 97 | C (O) | $C_{11}H_{16}O_2SGe$ | 46.43<br>(46.39) | 5.70<br>(5.66) | | | 11.58<br>(11.26) |
| IIl | *o*-$CH_3O$ | | 98 | C (O) | $C_{11}H_{16}O_2SGe$ | 46.40 | 5.62 | | | 11.68 |

a) Y: Yellow, C: Colorless, SY: Slight Yellow, (N): Needles, (O): Oil.

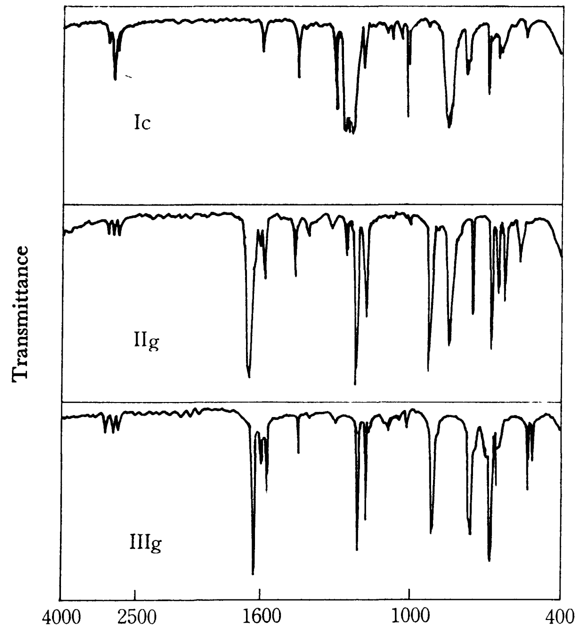


Fig. 1. IR spectra of thionobenzoyltrimethylsilane (Ic), (benzoylthio)trimethylgermane (IIg), and (benzoylthio)trimethyltin (IIIg) (Nujol mull).

from alcohols.

*Spectral Data*. *a) IR Spectra*: The IR spectra of thionobenzoyloxy trimethylsilane (Ic), (benzoylthio)-trimethylgermane (IIg), and -stannane (IIIg) are shown in Fig. 1 as typical examples. Bak *et al.*[9] reported that the two frequencies ($\nu$ C=S and C–S) obtained by a simplified force constant calculation must be looked for in the vicinity of 1200 (C=S) and 700 $cm^{-1}$ (C=S), and that the absorption bands of the C=S band in a series of twenty-one carboxymethyldithio esters were observed between 1190—1225 $cm^{-1}$. Bellamy and Rogasch[10] have reported some results of dithio acid in a variety of solvents. The silyl esters (II) obtained showed necessarily two characteristic strong absorption bands near 1280 and 1240 $cm^{-1}$ on both sides on the absorption band at 1250 $cm^{-1}$ ($\delta$ $SiCH_3$). However, it is difficult to assign the former band to the $\nu$ C=S band because it is situated at a far higher frequency. Further, no the absorption band around 1240 $cm^{-1}$ on (selenobenzoyloxy)trimethylsilane[11] was observed. For these reasons, the absorption band near 1240 $cm^{-1}$ may be considered to be due to the

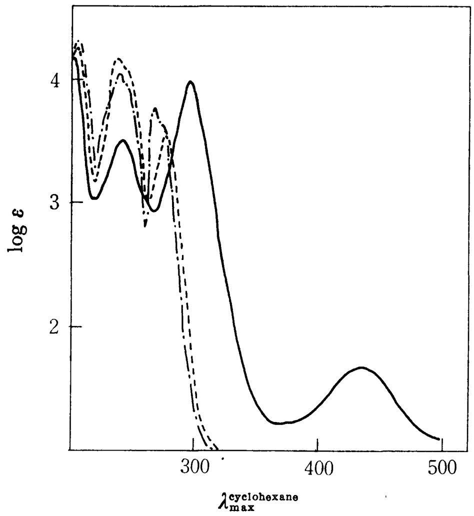


Fig. 2. The electronic spectra of thionobenzyltrimethylsilane (——), (benzoylthio)trimethylgermane (------), and (benzoylthio)trimethyltin (—·—).

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[9] B. Bak, L. Hansen-Nygarred, and C. Pedersen, *Acta Chem. Scand.*, **12**, 1451 (1958).

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[12] All melting points are not corrected. The IR spectra were measured on a JASCO Grating Infrared spectrophotometer IR-G. The UV spectra were recorded on Hitachi 124 spectrophotometer. The NMR spectra were obtained by a JEOL H-60.

C=S stretching band on the silyl esters (I). This result also fits well with the assignment given by Bak *et al.*[9] and Bellamy.[10] In Table 4 the IR absorption bands at near 1240 $cm^{-1}$ are shown.

Gilman and Lichtenwalter[4] reported that the $\nu$ C=O of (benzoylthio)triphenylsilanes appeared at 1690 $cm^{-1}$. The $\nu$ C=O values of the obtained trimethylgermyl (II) and -stannyl esters (III) were observed in the 1645—1677 and 1612—1645 $cm^{-1}$ ranges respectively. These results indicate that the $\nu$ C=O on the esters with a ≡M–S–CO–C≡ linkage (M: Metal IVb) would have a lower frequency shift with an increase in the atomic number of the metal (IVb). These lower frequency shifts are probably caused by either the heavy atomic effect or the higher electron donating properties of IVb elements.

*b) UV and Visible Spectra*: The absorption spectra of (thionobenzoyloxy)trimethylsilane (Ic), (benzoylthio)trimethylgermane (IIg), and stannane (IIIg) are reproduced in Fig. 2, along with the absorption maxima ($\lambda_{max}$) in Table 4. As is shown in Fig. 2 and Table 4, (thionobenzoyloxy)trimethylsilanes have three cha-

TABLE 4. SPECTRAL DATA OF SUBSTITUTED THIONOBENZOYLOXYSILANES (I), (BENZOYLTHIO)TRIMETHYLGERMANES (II) AND STANNANES (III).

| Compd | IR, $cm^{-1}$ (mull) | | | UV, m$\mu$, cyclohexane $\lambda_{max}$ ($\varepsilon$) | | | NMR, ($CCl_4$), $\tau$ | | | $J$(Hz) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\nu$C=S | $\delta$ $SiCH_3$ | | | | | $SiCH_3$ | $CH_3$ | $CH_3O$ | Sn-C-H | Sn-C-H |
| Ia | 1240 | 1250 | 845 | 255<br>(9600) | 302<br>(12000) | 439<br>(94) | 9.54 | | | | |
| Ib | 1240 | 1251 | 850 | 250<br>(6900) | 292<br>(9600) | 443<br>(85) | 9.53 | | | | |
| Ic | 1238 | 1251 | 853 | 247<br>(8000) | 298<br>(9600) | 437<br>(75) | 9.54 | | | | |
| Id | 1238 | 1250 | 852 | 253<br>(8200) | 303<br>(13600) | 436<br>(114) | 9.54 | 7.62 | | | |
| Ie | 1237 | 1250 | 848 | 252<br>(7000) | 300<br>(11500) | 437<br>(97) | 9.54 | 7.62 | | | |
| If | 1236 | 1250 | 850 | 242<br>(8900) | 288<br>(7200) | 427<br>(231) | 9.54 | 7.67 | | | |
| Ig | 1236 | 1257 | 847 | 267<br>(7800) | 321<br>(17700) | 429<br>(150) | 9.54 | | 6.17 | | |
| Ih | 1240 | 1250 | 851 | 246<br>(9100) | 204<br>(5100) | 426<br>(165) | 9.56 | | 6.17 | | |
| | $\nu$ C=O | $\delta$ $GeCH_3$ | | | | | $GeCH_3$ | $CH_3$ | $CH_3O$ | | |
| IIa | 1677[a] | 1239 | 830 | 264<br>(13800) | 287<br>(10000) | | 9.28 | | | | |
| IIb | 1640[a] | 1243 | 833 | 266<br>(22900) | 257<br>(10500) | | 9.30 | | | | |
| IIc | 1658 | 1240 | 832 | 237<br>(9400) | | | 9.30 | | | | |
| IId | 1655 | 1239 | 835 | 250<br>(17000) | 269<br>(12400) | | 9.32 | | | | |
| IIe | 1645 | 1238 | 831 | 240<br>(12000) | 270<br>(8100) | | 9.31 | | | | |
| IIf | 1622 | 1238 | 828 | 241<br>(8000) | 260<br>(4500) | | 9.31 | | | | |
| IIg | 1648 | 1238 | 829 | 240<br>(12900) | 267<br>(8200) | | 9.33 | | | | |
| IIh | 1645 | 1237 | 834 | 249<br>(14300) | 267<br>(12400) | | 9.33 | 7.68 | | | |
| IIi | 1648 | 1245 | 835 | 243<br>(11500) | 267<br>(8500) | | 9.33 | 7.68 | | | |
| IIj | 1649 | 1239 | 830 | 240<br>(11300) | 267<br>(7500) | | 9.33 | 7.63 | | | |
| IIk | 1672 | 1240 | 839 | 222<br>(13200) | 279<br>(19100) | | 9.34 | | 6.16 | | |
| IIl | 1659 | 1240 | 829 | 246<br>(9600) | | | 9.37 | | 6.16 | | |
| | $\nu$ C=O | $\delta$ $SnCH_3$ | | | | | $SnCH_3$ | $CH_3$ | $CH_3O$ | | |
| IIIa | 1622 | 1240 | 780 | 263<br>(12800) | 291<br>(9300) | | 9.35 | | | 60.0 | 56.0 |
| IIIb | 1629 | 1202 | 782 | 226<br>(25100) | | | 9.38 | | | 60.0 | 57.0 |
| IIIc | 1611[a] | 1209 | 782 | | | | 9.37 | | | 62.0 | 58.0 |
| IIId | 1625 | 1240 | 780 | 251<br>(16000) | 278<br>(11700) | | 9.42 | | | 61.0 | 58.2 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| IIIe | 1628 | | 788 | 243<br>(9800) | 274<br>(6800) | 9.40 | | | 60.0 | 67.0 |
| IIIf | 1645[a)] | 1210 | 787 | 243<br>(8400) | 205<br>(5100) | 9.40 | | | 60.0 | 56.4 |
| IIIg | 1631 | 1208 | 775 | 242<br>(11800) | 271<br>(8100) | 9.43 | | | 59.0 | 56.0 |
| IIIh | 1626 | 1217 | 782 | 250<br>(12700) | 275<br>(11200) | 9.43 | 7.68 | | 59.5 | 55.5 |
| IIIi | 1632 | | 783 | 245<br>(10900) | 279<br>(8500) | 9.43 | 7.68 | | 58.0 | 56.2 |
| IIIj | 1633 | 1207 | 775 | 245<br>(9500) | 270<br>(7000) | 9.43 | 7.63 | | 61.0 | 58.0 |
| IIIk | 1620[a)] | 1215 | 777 | | 283<br>(21000) | 9.44 | | 6.14 | 60.0 | 56.2 |
| IIIl | 1622[a)] | 1204 | 782 | 248<br>(9000) | 303<br>(5500) | 9.48 | | 6.16 | 56.2 | 53.0 |

a) KBr

racteristic maximum bands at 240—260 ($\varepsilon$ 5000—10000), 288—305 ($\varepsilon$ 7000—15000), and 426—443 m$\mu$ ($\varepsilon$ 75—230). The former two bands may be ascribed to $\pi \rightarrow \pi^*$ with the latter are $n \rightarrow \pi^*$ transitions of the thiocarbonyl group. On the other hand, the (substituted-benzoylthiotrimethyl)germanes and -stannanes except for those with substituents in the *ortho* position and with a methoxy group in the *para* position, all showed two characteristic maximum absorption bands at 240—260 and 260—290 m$\mu$ with of molecular extinction coefficients over 8000.

## Experimental[12)]

*Materials.* The potassium salts of substituted thiobenzoic acid were prepared by the method described by the literature;[13)] the chlorotrimethylsilane was distilled before use. Chlorotrimethylgermane[14)] and -tin[15)] were prepared similarly.

All the reactions were carried out under nitrogen. Some typical procedures are shown below, while the data are summarized in Tables 1—4.

*Reaction of Potassium Thiobenzoate with Chlorotrimethylsilane.* An equimolar amount of chlorotrimethylsilane was added to a suspension of 1.77 g (0.01 mol) of potassium thiobenzoate in petroleum ether (bp below 45°C), after which the mixture was stirred for 15 min at room temperature. After the removal of the insoluble parts by filtration, the evaporation of the solvent from the filtrate and the vacuum distillation of the residue gave 2.0 g of (benzoylthio)trimethylsilane (Ic).

*Reaction of Potassium Thiobenzoate and Chlorotrimethylgermane.* A solution of an equimolar amount of chlorotrimethylgermane (1.70 g, 0.011 mol) and potassium thiobenzoate in petroleum ether (bp below 45°C) (10 ml) was stirred for 1 hr at room temperature. After the insoluble parts were filtered, the vacuum removal of the solvent and the excess of chlorotrimethylgermane gave 2.37 g of chemically pure (benzoylthio)trimethylgermane (IIg).

*Reaction of Potassium* p*-Nitrothiobenzoate and Chlorotrimethyltin.* A solution of an equimolar amount of chlorotrimethyltin (2.08 g, 0.01 mol) and potassium *p*-nitrothiobenzoate (2.22 g, 0.01 mol) in petroleum ether (bp below 45°C) was refluxed for 1 hr. After the separation of the insoluble parts and the solvent, the recrystallization of the residue from ether–*n*-hexane gave 3.6 g of (*p*-nitrobenzoylthio)trimethyltin (IIIa) as colorless crystals.

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13) S. Kato, T. Mitani, and M. Mizuta, submitted for publication in This Bulletin.

14) a) H. Sakurai, K. Tominaga, T. Watanabe, and M. Kumada, *Tetrahedron Lett.*, **1966**, 5493. b) F. H. Brooks and F. Glockling, "Inorganic Syntheses," Vol. XII, p. 58 (1970).

15) K. A. Kozeschkow, *Ber.*, **66**, 1661 (1933).