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# On carbon-13 spectra of thio- and dithiocarboxylic acids triorgano group 14 metal esters

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## Abstract

The thiocarbonyl carbon chemical shifts of thio- and dithiocarboxylic acid triorgano group 14 metal esters have been studied in comparison with the carbonyl carbon chemical shifts of the corresponding carboxylic and thiocarboxylic acid derivatives. Triorgano group 14 metal groups cause remarkable downfield shifts of the carbonyl and thiocarbonyl carbon chemical shifts in the esters. The thiocarbonyl carbon chemical shifts of the dithio esters ($i$-$C_3H_7CS_2EMe_3$, E = group 14 element) are correlated linearly with the Allred–Rochow electronegativity of the metals, and with their $\pi-\pi^*$ transition energies except for the silyl esters. The $^{13}C{=}O$ chemical shifts of trimethyltin isobutyrate appear at the lowest field in the carboxylic acid triorgano group 14 metal esters ($RCOOER'_3$, E = group 14 metal). These unusual downfield shifts reflect the polymeric structure of the tin esters. The empirical equation ($\delta(C{=}S) = 1.45\ \delta(C{=}O) - 46.5$ ppm) predicting $^{13}C{=}O$ and $^{13}C{=}S$ chemical shifts, which has been proposed by Kolinowski and Kessler, can not be applied for these triorgano group 14 metal esters and *ortho* substituted benzoates and thio- and dithiobenzoates.

## Introduction

In contrast to carbonyl compounds [1–5], the $^{13}C{=}S$ chemical shifts of thiocarbonyl compounds, especially dithiocarboxylic acid derivatives, have been little investigated [6–8]. Previously we found that the $n-\pi^*$ transitions of the thiocarbonyl group of triorganosilyl dithiocarboxylates appear at the longest wave length region in triorgano group 14 metal dithiocarboxylates ($RCSSER'_3$, E = C, Si, Ge, Sn, Pb) [9]. These results stimulated us to investigate the thiocarbonyl carbon chemical shifts of the dithioesters and their relevant compounds.

In this paper, the $^{13}C{=}S$ chemical shifts of dithiocarboxylic acids triorgano group

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† Deceased.

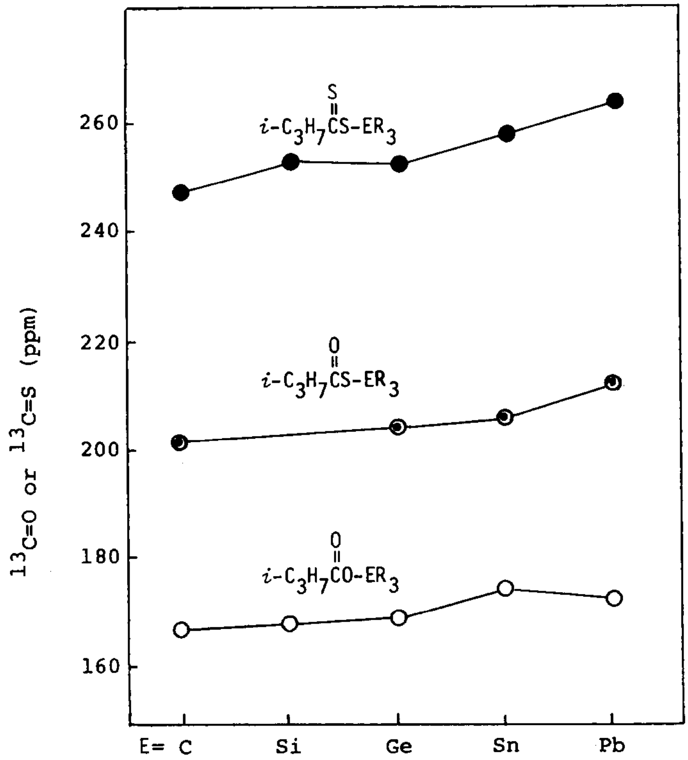


Fig. 1. The carbonyl or thiocarbonyl carbon chemical shifts of triorgano group 14 metal isobutyrates and thio- and dithioisobutyrates.

14 metal esters are discussed by comparison with those of the corresponding carboxylic and thiocarboxylic acid esters.

## Results and discussion

The carbonyl and thiocarbonyl carbon chemical shifts of triorgano group 14 metal isobutyrates and thio- and dithiobutyrates are plotted against the metals in Fig. 1. The triorgano group 14 metal groups induce a downfield shift to the thiocarbonyl carbon resonances and the triorgano silyl group leads to marked downfield shifts compared with other group 14 elements. In the corresponding carboxylic acid triorgano group 14 metal esters, trimethylsilyl isobutyrate does not show a remarkable downfield shift. Presumably, these unusual downfield shifts can be understood in terms of electron delocalization from the C=S bond to the S–Si bond due to the lowering of the S–Si $\sigma^*$ orbital to the C=S $\pi^*$ orbital [10]. It is interesting that the plot of the thiocarbonyl chemical shifts against the Allred–Rochow electronegativities gave a linear correlation except for the silyl ester (Fig. 2). The corresponding carboxylic and thiocarboxylic acid derivatives do not give such a linear correlation.

Previously we found that the n–$\pi^*$ transition bands of the thiocarbonyl group of trimethylsilyl dithiocarboxylates show a marked bathochromic shift compared with

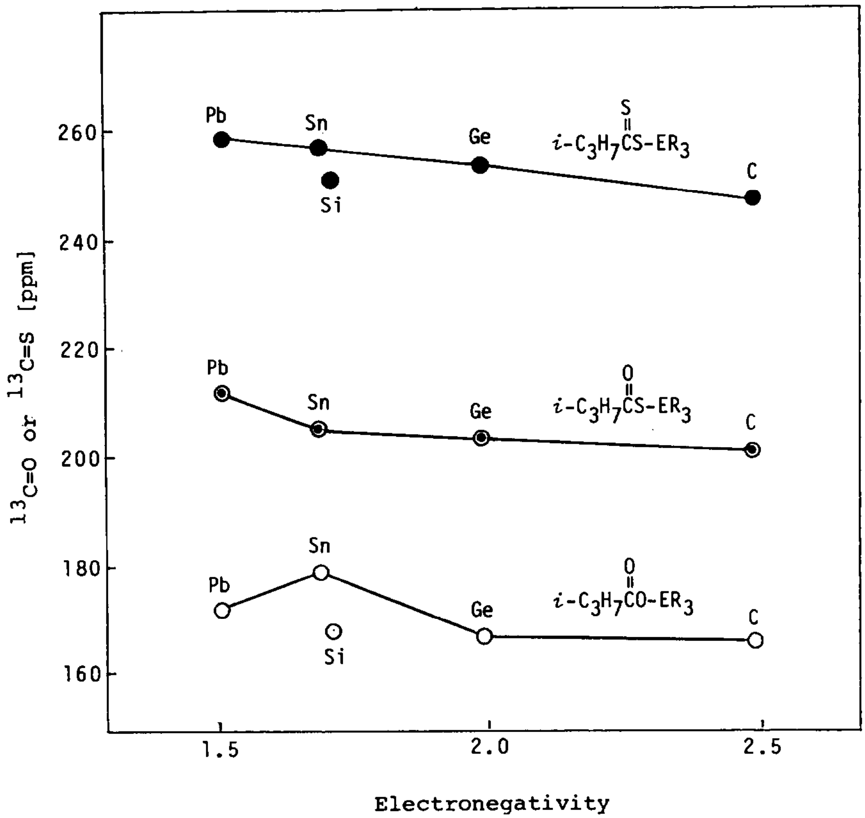


Fig. 2. The plot of the thiocarbonyl carbon chemical shifts against Allred–Rochow's electronegativities of triorgano group 14 metal isobutyrates, thioisobutyrates, and dithioisobutyrates.

the corresponding C, Ge, Sn and Pb dithioesters, while the $\pi$–$\pi^*$ (or n–$\sigma^*$) transition bands of the thiocarbonyl group show a marked hypsochromic shift [9]. This unusual bathochromic shift can be understood in terms of the lowering of the $\pi^*$ orbital due to interaction of the S–Si $\sigma^*$ orbital [10]. The plotting of the $^{13}C{=}S$ chemical shifts against both the n–$\pi^*$ and $\pi$–$\pi^*$ (or n–$\sigma^*$) bands ($\lambda_{max}$) was attempted. Though no linear correlation was obtained against the n–$\pi^*$ transition bands, the plot against the $\pi$–$\pi^*$ (or n–$\sigma^*$) bands resulted in a linear correlation in the Si, Ge, Sn, and Pb esters (Fig. 3).

In contrast to the dithioesters, the $^{13}C$ chemical shifts of trimethyltin isobutyrate is observed at the lowest field in the carboxylic acid triorgano group 14 metal esters ($RCOOER'_3$, E = Group 14 metal) (Fig. 1). This unusual downfield shift reflects the polymeric structure of the tin ester [11]. In the case of the corresponding tin dithioester, the downfield shift is relatively little. In addition, no appreciable downfield shift is observed for the $^{13}C$ chemical shifts of trimethyltin thioisobutyrate (Fig. 1). These results suggest that thio- and dithiocarboxylic acid triorganotin esters are not polymeric, but ester structure. In fact, the measurement of their molecular weights in benzene solution resulted in monomeric structure. Found: 265. $i$-$C_3H_7COSSnMe_3$ calc.: 266.9. Found: 281. $i$-$C_3H_7CSSSnMe_3$ calc.: 282.9).

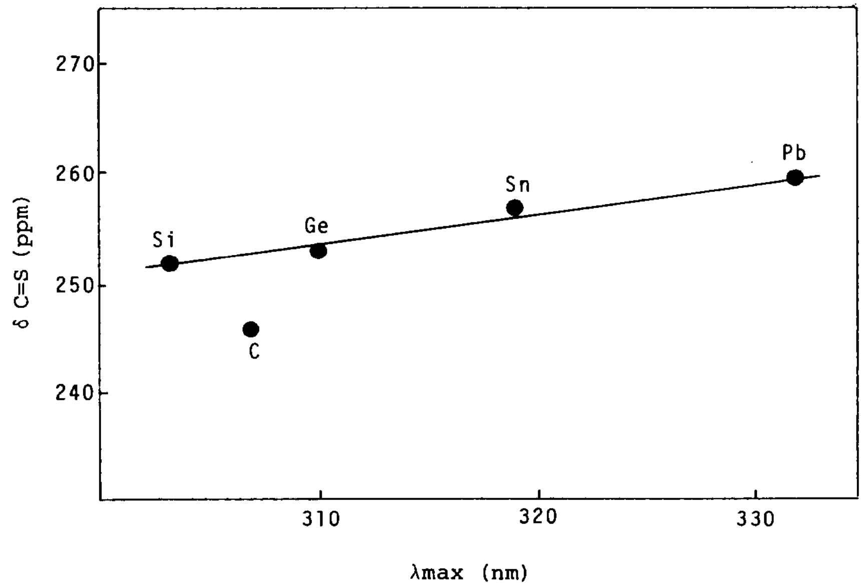
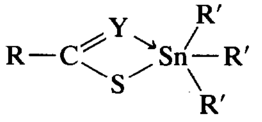


Fig. 3. The plot of thiocarbonyl carbon chemical shifts against $\lambda_{max}$ $\pi-\pi^*$ or $n-\sigma^*$ transition bands of triorgano group 14 metal dithioisobutyrates [*i*-$C_3H_7CSSEMe_3$, E = C, Si, Ge, and Sn; *i*-$C_3H_7CSSPbEt_3$].

The small downfield shifts of the tin dithioester may indicate the structure I, in which the thiocarbonyl sulfur coordinated to the intramolecular tin atom. Similar intramolecularly coordinated structure has been reported for tributyltin thioacetate [12], bis(dithiocarbamato)tin(II) [13,14] and lead(II) complexes [15].



I (Y = O, S)

It has been known that the substituents on the aryl ring in substituted methyl aroylates slightly affect the carbonyl carbon chemical shifts except for the *ortho*-hydroxy substituent [16]. As shown in Table 1, the substituents in substituted benzenedithioic acid methyl esters introduce an upfield shift to the thiocarbonyl carbon resonances and the magnitude of the upfield shifts increases in the order of *para*, *meta*, *ortho* substituents. A similar tendency is also observed for O-trimethylsilyl (X-$C_6H_4CSOSiMe_3$) and *S*-triorgano group 14 metal arenecarbothioates (X-$C_6H_4COSER_3$, E = C, Ge, Sn, Pb) (Table 1).

The empirical equation ($\delta(C{=}S) = 1.45\ \delta(C{=}O) - 46.5$ ppm) predicting $^{13}C$ chemical shifts of C=O or C=S group has been proposed by Kolinowski and Kessler [6]. This equation, however, could not be applied for carboxylic and thio- and dithiocarboxylic and triorgano group 14 metal esters and for the *ortho* substituted benzoic acid and thio- and dithioacid esters. In the case of *ortho* substituted derivatives, the steric hindrance would be influenced.

Table 1

The $^{13}C{=}O$ and $^{13}C{=}S$ chemical shifts of triorgano group 14 metal isobutyrates and thio- and dithioisobutyrates

| R | $ER'_3$ | $^{13}C$ NMR ($CDCl_3$) | |
|---|---|---|---|
| | | $\delta(C{=}S)$ | $\delta(C{=}O)$ |
| $RCS_2ER'_3$ | | | |
| t-$C_3H_7$ | $C(CH_3)_3$ | 247.1 | |
| | $Si(CH_3)_3$ | 252.0 | |
| | $Ge(CH_3)_3$ | 252.9 | |
| | $Sn(CH_3)_3$ | 257.1 | |
| | $Pb(C_2H_5)_3$ | 259.2 | |
| $C_6H_5$ | $C(CH_3)_3$ | 228.9 | |
| | $Si(CH_3)_3$ | 227.3 | |
| | $Ge(CH_3)_3$ | 228.4 | |
| | $Sn(CH_3)_3$ | 230.1 | |
| | $Pb(C_2H_5)_3$ | 231.1 | |
| $RCOSER'_3$ | | | |
| *i*-$C_3H_7$ | $C(CH_3)_3$ | | 200.8 |
| | $Si(CH_3)_3$ | | – |
| | $Ge(CH_3)_3$ | | 203.0 |
| | $Sn(CH_3)_3$ | | 205.7 |
| | $Pb(C_2H_5)_3$ | | 210.5 |
| $RCOOER'_3$ | | | |
| *i*-$C_3H_7$ | $C(CH_3)_3$ | | 165.7 |
| | $Si(CH_3)_3$ | | 166.6 |
| | $Ge(CH_3)_3$ | | 167.8 |
| | $Sn(CH_3)_3$ | | 174.2 |
| | $Pb(C_2H_5)_3$ | | 171.3 |

## Experimental section

The carbon-13 NMR spectra were run on a Hitachi R-22 (22.6 MHz), R-26 (10.0 MHz) and a JEOL JNM-GX-270 (67.8 MHz) spectrometers with computer system for an FT mode using tetramethylsilane as standard in $CDCl_3$, 35–45 °C. The carbon-13 chemical shifts ($\delta$) are believed to be accurate to $\pm 0.2$ ppm. The influence of the concentration (in $CDCl_3$) to the carbonyl and thiocarbonyl carbon shieldings is believed to be within $\pm 0.3$ ppm (for example, $C_6H_5COSH$ 100%: $\delta$ 186.1; 5.3% in $CDCl_3$: $\delta$ 186.3). The proton NMR spectra were recorded on Hitachi R-22 (90 MHz) or R-24 (60 MHz) instruments. The IR spectra were measured on a JASCO grating IR spectrophotometer IR-G. The electron spectra were recorded on Hitachi 124 and 330 spectrophotometers. The measurement of molecular weight and elemental analyses were performed by Alfred Bernhardt Analysis Center, Elbach über Engelskirchen (Germany), or by the Elemental Analysis Center of Kyoto University. Melting points were measured on a Yanagimoto micro melting apparatus and uncorrected.

### *Materials*

t-Butyl dithioisobutyrate and dithiobenzoate were obtained by the reactions of sodium t-butylmercaptide with the corresponding bis(thioacyl) sulfides [17]. *S*-t-

Table 2. Physical properties of carboxylic and thio- and dithiocarboxylic triorgano group 14 metal esters.

| Compounds | M.p. (°C) or b.p. (°C/Torr) | IR (neat) $\nu$(C=O) (cm$^{-1}$) | $^1$H NMR (CDCl$_3$) ($\delta$) | $^{13}$C NMR (CDCl$_3$) ($\delta$) | Yield (%) | Ref. [a] |
|---|---|---|---|---|---|---|
| $i$-$C_3H_7CO_2SiMe_3$ [b] | 114–115/20 | 1720<br>859 [$CH_3$(–Si)] | 0.10 (s, $CH_3$, 9H),<br>1.20 (d, $CH_3$, 6H),<br>2.5 (m, CH, 1H) | 0.0 ($CH_3Si$), 19.0 ($CH_3$), 30.0 (CH), 183.0 (C=O) | 65 | 21 |
| $i$-$C_3H_7CO_2GeMe_3$ [c] | 100–102/10 | 1690<br>840 [$CH_3$(–Ge)] | 0.69 (s, $CH_3$, 9H),<br>1.19 (d, $CH_3$, 6H),<br>2.5 (m, CH, 1H) | 1.7 ($CH_3Ge$), 19.1 ($CH_3$), 34.8 (CH), 183.0 (C=O) | 63 | 2 |
| $i$-$C_3H_7CO_2SnMe_3$ [d] | Solid | 1560<br>780 [$CH_3$(–Sn)] | 0.59 (s, $CH_3$, 9H),<br>1.21 (d, $CH_3$, 6H),<br>2.5 (m, CH, 1H) | −2.0 ($CH_3Sn$), 20.0 ($CH_3$), 35.0 (CH) 182.2 (C=O) | 89 | 23 |
| $i$-$C_3H_7CO_2PbEt_3$ [e] | 119–128 | 1544 | 1.18 (d, $CH_3$, 6H),<br>1.70 (t, $CH_3$, 9H),<br>2.20 (m, $CH_2$, 6H),<br>2.5 (m, CH, 1H) | 12.7 ($CH_3CH_2$), 20.0 ($CH_3\mathit{C}H$), 23.1 ($CH_2Pb$), 31.0 (CH), 183.0 (C=O) | 92 | 24 |
| 2-$CH_3C_6H_4CO_2{}^tBu$ [f] | 84–85/7 | 1714<br>850 [$CH_3$(–C)] | 1.53 (s, $CH_3$, 9H),<br>2.59 (s, $CH_3$, 3H),<br>7.5 (m, Ar, 4H) | 28.1 ($CH_3$), 21.3 ($CH_3Ar$), 78.3 (C), 123.8–137.6 (Ar), 166.3 (C=O) | 84 | |
| 2-$CH_3C_6H_4CO_2SiMe_3$ [g] | 74–75/2 | 1700<br>850 [$CH_3$(–Si)] | 0.05 (s, $CH_3$, 9H),<br>2.62 (s, $CH_3$, 3H),<br>7.5 (m, Ar, 4H) | 0.0 ($CH_3Si$), 21.6, 123.8–137.6 (Ar), 166.9 (C=O) | 64 | 21 |
| 2-$CH_3C_6H_4CO_2GeMe_3$ [h] | Oil | 1680<br>830 [$CH_3$(–Ge)] | 0.70 (s, $CH_3$, 9H),<br>2.62 (s, $CH_3$, 3H),<br>7.6 (m, Ar, 4H) | 1.7 ($CH_3Ge$), 21.6 ($CH_3$), 120.0–140.0, 167.4 (C=O) | 86 | 22 |
| 2-$CH_3C_6H_4CO_2SnMe_3$ [i] | Solid | 1680<br>789 [$CH_3$(–Sn)] | 0.60 (s, $CH_3$, 9H),<br>2.2 (s, $CH_3$, 3H)<br>7.5 (m, Ar, 4H) | −2.0 ($CH_3Sn$), 21.2 ($CH_3$), 126.0–139.4, 172.3 (C=O) | 78 | 23 |
| 2-$CH_3C_6H_4CO_2PbEt_3$ [j] | 104–105 | 1550<br>740 [$CH_2$(–Pb)] | 1.8 (t, $CH_3$, 9H),<br>2.2 (q, $CH_2$, 6H),<br>2.62 (s, $CH_3$, 3H),<br>7.6 (m, Ar, 4H) | 12.8 ($CH_3CH_2$), 21.3 ($CH_3$), 24.8 ($CH_2$), 124.1–138.0 (Ar), 172.9 (C=O) | 78 | 24 |
| $i$-$C_3H_7C(O)S{}^tBu$ [k] | 60–62/21 | 1680<br>970 [$CH_3$–(C)] | 1.20 (d, $CH_3$, 6H),<br>1.52 (s, $CH_3$, 9H),<br>2.7 (m, CH, 1H) | 19.4 ($CH_3C$), 30.0 ($CH_3CH$), 43.6 (CH), 47.0 (C), 200.8 (C=O) | 78 | 18 |
| $i$-$C_3H_7C(O)SGeMe_3$ | 31–32/4 | 1680 | 0.60 (s, $CH_3$, 9H), | 2.6 ($CH_3Ge$), 19.5 ($CH_3$), 45.3 (CH), | 93 | 19 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | 830 [$CH_3$(–Ge)] | 1.10 (d, $CH_3$, 6H),<br>2.7 (m, CH, 1H) | 203.0 (C=O) | | |
| $i$-$C_3H_7C(O)SSnMe_3$ | 42–45/4 | 1660<br>780 [$CH_3$(–Sn)] | 0.60 (s, $CH_3$, 9H),<br>1.17 (d, $CH_3$, 6H),<br>2.79 (m, CH, 1H) | –4.2 ($CH_3$Sn), 19.5, 45.2 (CH), 205.7 (C=O) | 98 | 19 |
| $i$-$C_3H_7C(O)SPbEt_3$ $^l$ | Oil | 1640<br>690 [$CH_2$(–Pb)] | | 13.6 ($CH_3CH_2$), 20.4 ($CH_3$), 24.1 ($CH_2$),<br>45.8 (CH), 210.5 (C=O) | 61 | 19 |
| $C_6H_5COSGeMe_3$ | Oil | See ref. 19 | | 2.1 ($CH_3$Ge), 127.7–138.1 (Ar), 192.8 (C=O) | 89 | 19 |
| 2-$CH_3C_6H_4COSGeMe_3$ | Oil | See ref. 19 | | 2.1 ($CH_3$Ge), 20.6 ($CH_3$), 125.3–139.3 (Ar),<br>195.8 (C=O) | 76 | 19 |
| 4-$CH_3C_6H_4COSGeMe_3$ | Oil | See ref. 19 | | 2.0 ($CH_3$Ge), 21.6 ($CH_3$), 128.0–143.0 (Ar),<br>192.8 (C=O) | 78 | 19 |
| 2-$ClC_6H_4COSGeMe_3$ | Oil | See ref. 19 | | 2.1 ($CH_3$Ge), 126.2–139.4 (Ar), 192.8 (C=O) | 89 | 19 |
| 2-$NO_2C_6H_4COSGeMe_3$ | Oil | See ref. 19 | | 2.1 ($CH_3$Ge), 123.8–145.8 (Ar), 192.0 (C=O) | 74 | 19 |
| $C_6H_5COSSnMe_3$ | Oil | See ref. 19 | | –4.0 ($CH_3$Sn), 128.0–138.3 (Ar), 195.4 (C=O) | 73 | 19 |
| 2-$CH_3C_6H_4COSSnMe_3$ | Oil | See ref. 19 | | –4.1 ($CH_3$Sn), 21.6 ($CH_3$), 123.2–139.1 (Ar),<br>198.2 (C=O) | 80 | 19 |
| 3-$CH_3C_6H_4COSSnMe_3$ | Oil | See ref. 19 | | –4.0 ($CH_3$Sn), 21.5 ($CH_3$), 125.6–138.0 (Ar),<br>195.0 (C=O) | 85 | 19 |
| 4-$CH_3C_6H_4COSSnMe_3$ | Oil | See ref. 19 | | –4.0 ($CH_3$Sn), 21.7 ($CH_3$), 128.7–143.3 (Ar),<br>194.2 (C=O) | 70 | 19 |
| 2-$CH_3OC_6H_4COSSnMe_3$ | 68–70 | See ref. 19 | | –4.2 ($CH_3$Sn), 55.8 ($CH_3$), 112.2–156.8 (Ar),<br>194.8 (C=O) | 92 | 19 |
| 2-$ClC_6H_4COSSnMe_3$ | 62–64 | See ref. 19 | | –4.0 ($CH_3$Sn), 125.9–139.4 (Ar), 195.3 (C=O) | 73 | 19 |
| 4-$ClC_6H_4COSSnMe_3$ | Oil | See ref. 19 | | –4.0 ($CH_3$Sn), 125.9–139.4 (Ar), 195.3 (C=O) | 83 | 19 |
| 2-$NO_2C_6H_4COSSnMe_3$ | 73–75 | See ref. 19 | | –4.0 ($CH_3$Sn), 123.5–145.7 (Ar), 194.6 (C=O) | 81 | 19 |
| 3-$NO_2C_6H_4COSSnMe_3$ | 77–80 | See ref. 19 | | –3.9 ($CH_3$Sn), 123.1–148.3 (Ar), 194.0 (C=O) | 94 | 19 |
| 4-$NO_2C_6H_4COSSnMe_3$ | 107–119 | See ref. 19 | | –4.0 ($CH_3$Sn), 123.1–150.2 (Ar), 194.4 (C=O) | 89 | 19 |
| $i$-$C_3H_7C(S)OSiMe_3$ | 34–35/4 | 1201 (C=S)<br>850 [$CH_3$(–Si)] | 0.40 (s, $CH_3$, 9H),<br>1.20 (d, $CH_3$, 6H),<br>2.9 (m, CH, 1H) | 0.0 ($CH_3$Si), 21.6 ($CH_3$), 46.7 (CH), 228.7 (C=S) | 62 | 19 |
| $C_6H_5C(S)OSiMe_3$ | 90–98/1–3 | See ref. 19 | | 0.0 ($CH_3$Si), 127.3, 128.2, 131.8, 139.0, (Ar),<br>211.0 (C=S) | 78 | 19 |
| 2-$CH_3C_6H_4C(S)OSiMe_3$ | 96–100/1–3 | See ref. 19 | | 0.0 ($CH_3$Si), 21.8 ($CH_3$), 125.0–142.0 (Ar),<br>215.7 (C=S) | 67 | 19 |
| 3-$CH_3C_6H_4C(S)OSiMe_3$ | 102–105/1–2 | See ref. 19 | | 0.0 ($CH_3$Si), 21.4 ($CH_3$), 125.5–138.5 (Ar),<br>215.7 (C=S) | 83 | 19 |

Table 2 (continued)

| Compounds | M.p. (°C) or b.p. (°C/Torr) | IR (neat) $\nu$(C=O) (cm$^{-1}$) | $^1$H NMR (CDCl$_3$) ($\delta$) | $^{13}$C NMR (CDCl$_3$) ($\delta$) | Yield (%) | Ref. [a] |
|---|---|---|---|---|---|---|
| 4-$CH_3C_6H_4C(S)OSiMe_3$ | 115–120/1–4 | | See ref. 19 | 0.0 ($CH_3Si$), 21.4 ($CH_3$), 128.4–142.5 (Ar), 210.9 (C=S) | 83 | 19 |
| 2-$CH_3OC_6H_4(S)OSiMe_3$ | 86–95/3–4 | | see ref. 19 | −2.0 ($CH_3Si$), 54.0 ($CH_3$), 110–162.0 (Ar), 212.0 (C=S) | 92 | 19 |
| 4-$CH_3OC_6H_4C(S)OSiMe_3$ | 110–115/1–2 | | see ref. 19 | 0.0 ($CH_3Si$), 55.0 ($CH_3$), 112.8–163.2 (Ar), 210.4 (C=S) | 83 | 19 |
| 2-$ClC_6H_4C(S)OSiMe_3$ | Oil | | see ref. 19 | 0.0 ($CH_3Si$), 126.3–140.0 (Ar), 211.2 (C=S) | 95 | 19 |
| 3-$ClC_6H_4C(S)OSiMe_3$ | 115–120/1–2 | | see ref. 19 | 0.0 ($CH_3Si$), 126.8–140.8 (Ar), 209.6 (C=S) | 63 | 19 |
| 4-$ClC_6H_4C(S)OSiMe_3$ | 95–101/0.5–1 | | see ref. 19 | 2.0 ($CH_3Si$), 126.0–128.2 (Ar), 208.0 (C=S) | 66 | 19 |
| *i*-$C_3H_7CS_2{}^tBu$ | 73–75/20 | 1225 (C=S) | 1.34 (d, $CH_3$, 6H),<br>1.58 (s, $CH_3$, 9H),<br>3.72 (m, CH, 1H) | 19.1 ($CH_3$), 24.1 ($CH_3CH$), 49.5 (CH), 80.6 (C), 228.9 (C=S) | 8 | 17 |
| $C_6H_5CSSMe$ | 90–95/0.5–1 | 1227 (C=S) | 2.70 (S, $CH_3S$, 3H),<br>7.5 (m, Ar, 4H) | 20.4 ($CH_3$), 127.0–137.1 (Ar), 226.7 (C=S) | 73 | 25 |
| 2-$CH_3C_6H_4CSSMe$ | 99–101/3 | 1247 (C=S) | 2.30 (s, $CH_3$, 3H),<br>2.60 (s, $CH_3S$, 3H),<br>7.4 (m, Ar, 5H) | 19.5 ($CH_3$), 20.5 ($CH_3S$), 125.0–146.6 (Ar), 230.6 (C=S) | 76 | 25 |
| 3-$CH_3C_6H_4CSSMe$ | 144–145/2 | 1259 (C=S) | 2.42 (s, $CH_3$, 3H),<br>2.71 (s, $CH_3S$, 3H),<br>7.6 (m, Ar, 4H) | 20.2 ($CH_3S$), 21.4 ($CH_3$), 123.5–144.8 (Ar), 225.5 (C=S) | 79 | 25 |
| 4-$CH_3C_6H_4CSSMe$ | 111–114/1–3 | 1243 (C=S) | 2.31 (s, $CH_3$, 3H),<br>2.70 (s, $CH_3S$, 3H),<br>7.4 (m, Ar, 4H) | 20.2 ($CH_3S$), 21.4 ($CH_3$), 126.3–142.3 (Ar), 223.3 (C=S) | 76 | 25 |
| 3-$ClC_6H_4CSSMe$ | 105–107/4 | | 2.70 (s, $CH_3$, 3H),<br>7.5 (m, Ar, 4H) | 21.5 ($CH_3$), 124.5–145.5 (Ar), 224.5 (C=S) | 76 | 25 |
| 4-$ClC_6H_4CSSMe$ | 120–122/4 | 1228 | 2.70 (s, $CH_3$, 3H),<br>7.5 (m, Ar, 4H) | 12.2 ($CH_3$), 31.2 ($CH_3$), 127.0–142.0 (Ar), 223.3 (C=S) | 75 | 25 |

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[a] The preparation methods described in the literature were used. [b] Anal. Found: C, 52.49; H, 10.11. $C_7H_{16}O_2Si$ calc.: C, 52.45; H, 10.06%. [c] Anal. Found: C, 40.77; H, 7.89. $C_7H_{16}O_2Ge$ calc.: C, 41.05; H, 7.85%. [d] Anal. Found: C, 33.40; H, 6.42. $C_7H_{16}O_2Sn$ calc.: C, 33.51; H, 6.43%. [e] Anal. Found: C, 30.96; H, 5.80. $C_{10}H_{22}O_2Pb$ calc.: C, 31.48; H, 5.81%. [f] Anal. Found: C, 74.81; H, 8.30. $C_{12}H_{16}O_2$ calc.: C, 74.97; H, 8.39%. [g] Anal. Found: C, 63.10; H, 7.65. $C_{11}H_{16}O_2Si$ calc.: C, 63.43; H, 7.74%. [h] Anal. Found: C, 52.51; H, 6.24. $C_{11}H_{16}O_2Ge$ calc.: C, 52.25; H, 6.38%. [i] Anal. Found: C, 44.73; H, 5.44. $C_{11}H_{16}O_2Sn$ calc.: C, 44.20; H, 5.40%. [j] Anal. Found: C, 39.23; H, 5.22. $C_{14}H_{22}O_2Pb$ calc.: C, 39.15; H, 5.16%. [k] Anal. Found: C, 59.58; H, 10.12. $C_8H_{16}OS$ calc.: C, 59.95; H, 10.06%. [l] Anal. Found: C, 30.10; H, 5.47. $C_{10}H_{22}OSPb$ calc.: C, 30.21; H, 5.58%.

Butyl thioacetate, thioisobutyrate and thiobenzoate were prepared by the reactions of potassium t-butylmercaptide with the corresponding acyl chloride [18]. *O*-Trimethylsilyl [19], *S*-trimethylgermyl [19], *S*-trimethyltin [19] and *S*-triethyllead thiocarboxylates [19], trimethylsilyl dithioisobutyrate [9] and dithiobenzoate [20], and trimethylgermyl [20], trimethyltin [20], and triethyllead dithiocarboxylates [20] were prepared according to the known procedures. Trimethylsilyl carboxylates were prepared by the reactions of chlorotrimethylsilane with the silver salts of the corresponding carboxylic acid [21]. Trimethylgermanium carboxylates were obtained from the reaction of chlorotrimethylgermane and the corresponding sodium carboxylates [22]. Trimethyltin carboxylates were prepared according to the method described in the literature [23]. Triethyllead carboxylates were obtained by the reaction of potassium or piperidinium salts of the corresponding carboxylic acids or by the reaction of the triethyllead hydroxide with the corresponding carboxylic acids [24]. Their yields and spectral data are summarized in Table 2.

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