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# ORGANO-SILICON, -GERMANIUM AND -LEAD DERIVATIVES OF DIMETHYL- AND DIPHENYL-DITHIOARSINIC ACIDS

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## Summary

Organometallic dimethyl- and diphenyl-dithioarsinates of the type $(C_6H_5)_{4-n}M(S_2AsR_2)_n$ where M = $Si^{IV}$, $Ge^{IV}$, $Pb^{IV}$; R = $CH_3$, $C_6H_5$ and $n = 1$, 2 have been synthesised and characterised by infrared and $^1H$ NMR spectroscopy. The data are consistent with monodentate coordination of the dithioarsinato group to silicon and germanium, but there seems to be bidentate coordination to the organolead moiety.

## Introduction

Organometallic derivatives of dithioacids have received some attention in recent years and preparative procedures and structural data have been reported for Group IV elements with dithiocarboxylates [1], dithiocarbamates [2], dithiophosphates [3,4]. Organotin derivatives received most attention [5–8]. Dithioarsinates have been much less studied than other dithio ligands. The first organometallic derivatives, containing $S_2AsR_2$ ligands, were transition metal complexes, such as $(CO)_4MS_2AsR_2$ (M = Mn, Re) [9] and $(C_5H_5)_2V(S_2AsMe_2)_2BF_4$ [10]. Among the main group derivatives only organoarsenic, $Me_2As(S_2AsMe_2)$ [11] and organotin, $R_nSn(S_2AsR'_2)_{4-n}$ [12,13] derivatives have been prepared, the latter in our laboratory.

The possible analogy with dithiophosphorus ligands, which can exhibit various coordination patterns [14], stimulated us to examine the dithioarsinates in more detail. We describe below the synthesis and characterisation of di- and tri-phenyl-silicon, -germanium and -lead dithioarsinates.

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## Results and discussion

The title compounds were synthesised by treatment of chloro-di- and -triphenyl-silanes, -germanes and -plumbanes with the appropriate amount of sodium dimethyl- and diphenyl-dithioarsinates, in absolute ethanol, acetone or carbon tetrachloride, at room temperature or with heating:

$$\mathrm{Ph_{4-\mathit{n}}MCl_{\mathit{n}}} + \mathit{n}\mathrm{NaS_2AsR_2} \xrightarrow[-\mathit{n}\,\mathrm{NaCl}]{} \mathrm{Ph_{4-\mathit{n}}M(S_2AsR_2)_{\mathit{n}}}$$

$(n = 1;\ \mathrm{M} = \mathrm{Si^{IV}},\ \mathrm{Ge^{IV}}$ and $\mathrm{Pb^{IV}};\ \mathrm{R} = \mathrm{CH_3},\ \mathrm{C_6H_5};$
$n = 2;\ \mathrm{M} = \mathrm{Si^{IV}},\ \mathrm{Pb^{IV}};\ \mathrm{R} = \mathrm{CH_3},\ \mathrm{C_6H_5})$

Some triethyllead derivatives were prepared similarly.

All the derivatives were synthesised under nitrogen; most of them are moisture sensitive, especially the organosilicon and organogermanium dithioarsinates. The dry solids are stable in closed vials for up to two months. The crystalline organolead dithioarsinates are stable, without significant decomposition (no change of melting point and IR spectra after prolonged storage).

### *Spectra and structure*

It was shown earlier [15] that As–S normal vibration modes are practically uncoupled, group-type vibrations; therefore, the assignment of the arsenic–sulfur stretching frequencies for dimethyldithioarsinato derivatives enabled monodentate and bidentate coordination to be distinguished. Difficulties occur only when a distinction between iso- and aniso-bidentate coordination is attempted on the basis of infrared spectra.

It was found that a band at 480 $\mathrm{cm^{-1}}$ is good evidence for the presence of a monodentate dimethyldithioarsinate group [11,12], this band being due to the stretching of an As=S double bond. The infrared spectra of organosilicon and organogermanium dimethyldithioarsinates exhibit a $\nu$(As=S) band at 480 $\mathrm{cm^{-1}}$. The absorption band at 400 $\mathrm{cm^{-1}}$ is assigned to $\nu$(As–S) (As–S single bond). Thus, monodentate coordination of $\mathrm{S_2AsMe_2}$ ligand, and therefore tetrahedral geometry of the silicon and germanium is consistent with these data.

The $^1$H NMR spectra exhibit the expected peaks at $\delta$ 6.48–7.00 ppm due to the

TABLE 1

INFRARED SPECTRA[a] OF THE TITLE COMPOUNDS ($\mathrm{cm^{-1}}$)

| | | | | | |
|---|---|---|---|---|---|
| $\mathrm{Ph_2Si(S_2AsMe_2)_2}$ | 400m | 480ms | 595m | 620m | 495ms |
| $\mathrm{Ph_3Si(S_2AsMe_2)}$ | 405m | 480ms | 595m | 615m | 490ms |
| $\mathrm{Ph_3Ge(S_2AsMe_2)}$ | 410m | 480ms | 600m | 615m | |
| $\mathrm{Ph_2Pb(S_2AsMe_2)_2}$ | 420m | 460s | 598m | 620m | |
| $\mathrm{Ph_3Pb(S_2AsMe_2)}$ | 420m | 460s | 595m | 615m | |
| $\mathrm{Et_3Pb(S_2AsMe_2)}$ | 418w | 470m | 600m | 620m | |
| $\mathrm{Ph_2Si(S_2AsPh_2)_2}$ | 416m | 484m | | | 495ms |
| $\mathrm{Ph_3Si(S_2AsPh_2)}$ | 418m | 485ms | | | 500m |
| $\mathrm{Ph_3Ge(S_2AsPh_2)}$ | 418m | 484m | | | |
| $\mathrm{Ph_2Pb(S_2AsPh_2)_2}$ | 426mw | 460m | | | |
| $\mathrm{Ph_3Pb(S_2AsPh_2)}$ | 425mw | 462m | | | |
| $\mathrm{Et_3Pb(S_2AsPh_2)}$ | 418mw | 470m | | | |

[a] s = strong; ms = medium strong; m = medium; mw = medium weak, w = weak.

TABLE 2

PROPERTIES OF ORGANOMETALLIC DITHIOARSINATES

| | Compound | M.p. (°C) | Net formula | Elemental analysis found/(calcd) (%) | | | $^1$H NMR (ppm) | |
|---|---|---|---|---|---|---|---|---|
| | | | | C | H | As | $\delta$(As-C$H_3$) | $\delta$(C$_6H_5$) |
| 1 | $Ph_2Si(S_2AsMe_2)_2$ | 144 | $C_{16}H_{12}As_2S_4Si$ | 36.48<br>(36.92) | 4.02<br>(4.24) | 28.27<br>(28.84) | 2.06 | 6.26–7.20 |
| 2 | $Ph_3Si(S_2AsMe_2)$ | 128 | $C_{20}H_{21}AsS_2Si$ | 55.83<br>(56.07) | 4.59<br>(4.90) | 17.11<br>(17.52) | 2.06 | 6.40–7.20 |
| 3 | $Ph_3Ge(S_2AsMe_2)$ | 105 | $C_{20}H_{21}AsS_2Ge$ | 50.42<br>(50.78) | 4.11<br>(4.44) | 15.41<br>(15.87) | 2.06 | 6.50–7.25 |
| 4 | $Ph_2Pb(S_2AsMe_2)_2$ | 160-<br>170(dec) | $C_{16}H_{12}As_2S_4Pb$ | 27.03<br>(27.46) | 3.51<br>(3.15) | 21.07<br>(21.45) | 2.06 | 6.60–7.30 |
| 5 | $Ph_3Pb(S_2AsMe_2)$ | 195 | $C_{20}H_{21}AsS_2Pb$ | 39.11<br>(39.52) | 3.15<br>(3.46) | 12.07<br>(12.35) | 2.05 | 6.60–7.30 |
| 6 | $Ph_2Si(S_2AsPh_2)_2$ | 89 | $C_{36}H_{30}As_2S_4Si$ | 55.83<br>(56.25) | 3.68<br>(3.90) | 19.16<br>(19.53) | | 6.28–7.80 |
| 7 | $Ph_3Si(S_2AsPh_2)$ | 76 | $C_{30}H_{25}AsS_2Si$ | 65.01<br>(65.21) | 4.18<br>(4.52) | 13.03<br>(13.58) | | 6.28–7.80 |
| 8 | $Ph_3Ge(S_2AsPh_2)$ | 104 | $C_{30}H_{25}AsS_2Ge$ | 60.07<br>(60.34) | 3.88<br>(4.19) | 12.12<br>(12.57) | | 6.34–7.80 |
| 9 | $Ph_2Pb(S_2AsPh_2)_2$ | 185(dec) | $C_{36}H_{30}As_2S_4Pb$ | 45.11<br>(45.60) | 3.02<br>(3.16) | 15.38<br>(15.85) | | 6.60–7.80 |
| 10 | $Ph_3Pb(S_2AsPh_2)$ | 180<br>(dec) | $C_{30}H_{25}AsS_2Pb$ | 48.98<br>(49.23) | 3.07<br>(3.42) | 9.81<br>(10.26) | | 6.60–7.58 |

phenyl groups attached to silicon, germanium and lead. The signal for $CH_3$ protons is located at $\delta$ 2.06 ppm for dimethyldithioarsinates synthesised, at higher values than for sodium dimethyldithioarsinate [11,12], as expected after the coordination of sulfur atoms, Table 2.

The IR spectra of diphenyldithioarsinato derivatives are more complicated, because of the large number of bands in the 500–400 $cm^{-1}$ region, due to phenyl groups. From data for a large number of metallic and organometallic compounds we expect the $\nu$(As=S) frequency to appear at 480–490 $cm^{-1}$ in the infrared spectra of diphenyldithioarsinates. On the assumption that the phenyl groups do not influence the group character of the As–S normal modes, we made the same correlation as for dimethyldithioarsinic derivatives. The $\nu$(As-S) frequencies occur at lower energies (420–410 $cm^{-1}$), Table 1.

The infrared spectra of organosilicon and organogermanium diphenyldithioarsinates exhibit a band at 484 $cm^{-1}$, and so we assume tetrahedral geometry at silicon and germanium, for both di- and tri-phenyl-substituted compounds containing monodentate dithio groups. The organolead dimethyl- and diphenyl-dithioarsinates show a slightly different picture: two bands (see Table 1) ocuur in the As–S stretchings region, at 420 and 470 $cm^{-1}$ for dimethyldithioarsinates and at 425, 462 $cm^{-1}$ for diphenyl-dithioarsinates. It is difficult to decide between a monomeric or a polymeric structure, involving anisobidentate ligands. A third possibility must also be taken into account, namely a dimeric structure of the type established for $Ph_2SbS_2AsPh_2$ [13] by X-ray diffraction. The IR spectrum of the antimony compound is very similar with that of the lead derivatives discussed above, and a dimeric structure cannot be ruled out at present.

## Experimental

The sodium salts of dimethyl- and diphenyl-dithioarsinic acids were prepared by published methods [16,17]. Organometallic halides were commercial samples. The solvents were dried by standard methods, and distilled. Infrared spectra were recorded on a SPECORD 75 IR C. Zeiss-Jena (DDR) in KBr pellets, in the range 4000–400 $cm^{-1}$. $^1H$ NMR spectra were recorded in $CCl_4$ or $CDCl_3$ (TMS standard) on a TESLA B-487 spectrometer operating at 80 MHz. Carbon and hydrogen microanalyses were performed with a Perkin–Elmer 240B microanalyser.

### *Preparation of organometallic dithioarsinates*

The title compounds were prepared under similar conditions, with small variations from compound to compound. The details are given in Table 3.

The preparations were carried out at 40–50°C except for the lead compounds; these were made at room temperature since decomposition occurred on heating.

Elemental analyses for all the synthesised compounds are given in Table 2.

### *General procedure*

The solution of organometallic chloride in the solvent indicated in Table 3 was added to a solution or suspension of the sodium dimethyl-(diphenyl-)dithioarsinate at room temperature with stirring. The mixture was kept at 40–50°C (except for the lead compounds) with stirring for 1–2 hours. The precipitate of sodium chloride was filtered off and the filtrate was concentrated under reduced pressure. A white or

TABLE 3

PREPARATION OF ORGANOMETALLIC DITHIOARSINATES

| | Compound | Starting materials | | Yields (g(%)) |
|---|---|---|---|---|
| | | $R_nMCl_{4-n}$ | Na dithioarsinate | |
| 1 | $Ph_2Si(S_2AsMe_2)_2$ | $Ph_2SiCl_2$, 0.35 g, 15 ml $CCl_4$ | 0.65 g, 10 ml EtOH | 0.58 (80) |
| 2 | $Ph_3Si(S_2AsMe_2)$ | $Ph_3SiCl$, 0.82 g, 10 ml $CCl_4$ | 0.65 g, 15 ml EtOH | 0.33 g (78) |
| 3 | $Ph_3Ge(S_2AsMe_2)$ | $Ph_3GeCl$, 1.2 g, 20 ml $CCl_4$ | 0.82 g, 20 ml EtOH | 1.24 (72) |
| 4 | $Ph_2Pb(S_2AsMe_2)_2$ | $Ph_2PbCl_2$, 0.65 g, 10 ml $CCl_4$ | 0.65 g, 15 ml EtOH | 0.66 (63) |
| 5 | $Ph_3Pb(S_2AsMe_2)$ | $Ph_3PbCl$, 0.94 g, 20 ml $CCl_4$ | 0.4 g, 20 ml $CCl_4$ | 0.98 (82) |
| 6 | $Ph_2Si(S_2AsPh_2)_2$ | $Ph_2SiCl_2$, 0.50 g, 15 ml $CCl_4$ | 1.26 g, 25 ml $CCl_4$ | 0.98 (63) |
| 7 | $Ph_3Si(S_2AsPh_2)$ | $Ph_3SiCl$, 0.59 g, 15 ml $CCl_4$ | 0.63 g, 20 ml $CCl_4$ | 0.68 (62) |
| 8 | $Ph_3Ge(S_2AsPh_2)$ | $Ph_3GeCl$, 0.68 g, 20 ml $CCl_4$ | 0.63 g, 20 ml $CCl_4$ | 0.64 (68) |
| 9 | $Ph_2Pb(S_2AsPh_2)_2$ | $Ph_2PbCl_2$, 1.3 g, 25 ml $CCl_4$ | 0.86 g, 25 ml acetone | 1.38 (73) |
| 10 | $Ph_3Pb(S_2AsPh_2)$ | $Ph_3PbCl$, 0.95 g, 30 ml acetone | 0.63 g, 25 ml acetone | 1.0 (69) |

slightly yellowish crystalline precipitate was formed in all cases. This was filtered and dried in vacuo over phosphorus pentoxide.

The silicon and germanium compounds are hygroscopic and must be kept under anhydrous conditions. The lead compounds are stable in the atmosphere as solids.

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