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STUDIES OF ORGANOSULFUR COMPOUNDS

X. PREPARATION OF SOME TRIMETHYLMETAL(IVb) ESTERS OF DITHIO ACIDS AND THEIR SPECTRAL PROPERTIES

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SUMMARY

Some trimethylmetal(IVb) esters of dithio acids have been prepared by treatment of the secondary or tertiary amine salts of dithio acids with chlorotrimethylsilane, -germane, or -tin, and their IR, UV and NMR spectra recorded.

INTRODUCTION

Although a number of Group IV organometallic esters such as (II)*, (III)** and (IV)^3 have been reported, the corresponding esters of dithio acids (I), which would be expected to have interesting properties were previously unknown. The preparation of (I) appeared to be difficult, because: (*a*) zinc or lead salts (V) of dithio acids do not react with trialkyl(or aryl)metal(IVb) halides, and (*b*) the hygroscopic nature of sodium or potassium salts (VI) precludes the reaction shown in eqn. (1).


$R\overset{S}{\overset{\|}{C}}SMR'_3$

(I)


$R\overset{O}{\overset{\|}{C}}OMR'_3$

(II)

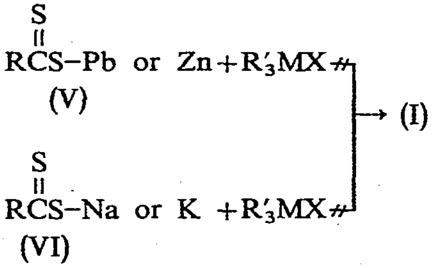

$R\overset{O}{\overset{\|}{C}}SMR'_3$

(III)


$R\overset{S}{\overset{\|}{C}}OMR'_3$

(IV)

R, R' = Alkyl, aryl;
M = Group IVb metal.


$$\left.\begin{array}{l} \underset{(V)}{R\overset{S}{\overset{\|}{C}}S{-}Pb} \text{ or } Zn + R'_3MX \nrightarrow \\ \\ \underset{(VI)}{R\overset{S}{\overset{\|}{C}}S{-}Na} \text{ or } K + R'_3MX \nrightarrow \end{array}\right] \rightarrow (I) \qquad (1)$$

(R, R' = Alkyl, aryl; M = Group IVb metal; X = Halogen.)

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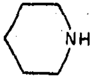
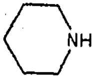
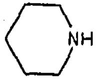
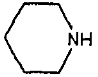
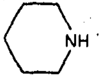
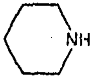
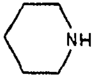
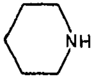
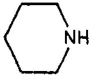
* For M = Si see refs. 1a–1d; for M = Ge see ref. 1e; for M = Sn see refs. 1f and 1 g.

** For M = Si see ref. 2a; for M = Ge see refs. 2b and 2c; for M = Sn see refs. 1d and 1e.

TABLE 1

REACTIONS OF THE AMINE SALTS OF DITHIO ACID WITH TRIMETHYLMETAL(IVb) CHLORIDES

$RC\bar{S}_2\overset{+}{X}H$		$(CH_3)_3MCl$	Solvent[a]	Temp. (°C)	Time (h)	Products	B.p. (°C/mmHg) M.p. (°C)	Yield (%)
R	X	M						
p-$CH_3C_6H_4$	Et_3N	Si	Pet-E	RT	5	p-$CH_3C_6H_4CS_2Si(CH_3)_3$ (Ia)[b]	Oil	98
			THF	50	50	No reaction		
C_6H_5	Et_3N		Pet-E	RT	5	$C_6H_5CS_2Si(CH_3)_3$ (Ib)	Oil	96
			THF	50	24	No reaction		
	Et_2NH		THF	50	48	No reaction		
p-ClC_6H_4	Et_3N		Pet-E	RT	8	p-$ClC_6H_4CS_2Si(CH_3)_3$ (Ic)	Oil	97
	β-Picoline		Pet-E	RT	5			97
			THF	50	24	No reaction		
p-$CH_3C_6H_4$		Ge	Pet-E	RT	0.5	p-$CH_3C_6H_4CS_2Ge(CH_3)_3$ (Id)	Oil	96
C_6H_5			Pet-E	RT	0.5	$C_6H_5CS_2Ge(CH_3)_3$ (Ie)	Oil	98
	β-Picoline		Pet-E	RT	0.5			94
p-ClC_6H_5			Pet-E	RT		p-$ClC_6H_4CS_2Ge(CH_3)_3$ (If)	Oil	95
p-$CH_3C_6H_4$		Sn	Pet-E	RT	10	p-$CH_3C_6H_4CS_2Sn(CH_3)_3$ (Ig)	35–36	98

p-ClC_6H_4			Pet-E		10	p-$ClC_6H_4CS_2Sn(CH_3)_3$ (Ii)	Oil	95
	Et_3N	Ge		RT	5	1-$C_{10}H_7CS_2Ge(CH_3)_3$ (Ij)[c]	Oil	96
1-$C_{10}H_7$				RT	5			95
	Et_3N	Sn		RT	10	1-$C_{10}H_7CS_2Sn(CH_3)_3$ (Ik)[d]	106–107	96
			THF	50	5			95
i-Pr		Si	Pet-E	RT	5	i-$PrCS_2Si(CH_3)_3$ (Il)[e]	37–37.5/0.05	97
		Ge	Pet-E	RT	0.5	i-$PrCS_2Ge(CH_3)_3$ (Im)[d]	44–45/0.03	98
		Sn	Pet-E	RT	10	i-$PrCS_2Sn(CH_3)_3$ (In)[f]	60–61/0.02	98

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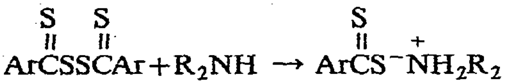
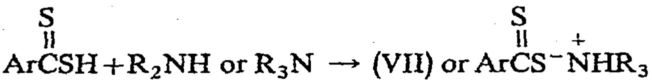
[a] Pet-E: Petroleum ether. [b] Purple. [c] Reddish brown. [d] Orange. [e] Reddish orange. [f] Orange yellow.

In the course of a study of bis(thioaroyl) disulfides, it was found that secondary amine salts (VII) of aromatic dithio acids could be isolated as anhydrous crystals from the reaction of bis(thioaroyl) disulfides with secondary amines[4] [eqn. (2)]. Furthermore, the reaction of dithio acid with secondary or tertiary amines [eqn. (3)][5] was found to provide a convenient route to the amine salts [(VII) and (VIII)] of dithio acids. These results encouraged us to synthesize the title compounds by

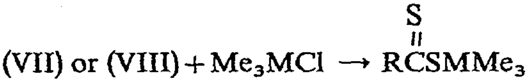


$$\mathrm{Ar\overset{S}{\overset{\|}{C}}SS\overset{S}{\overset{\|}{C}}Ar+R_2NH \longrightarrow \underset{(VII)}{Ar\overset{S}{\overset{\|}{C}}S^{-}\overset{+}{N}H_2R_2}} \qquad (2)$$



$$\mathrm{Ar\overset{S}{\overset{\|}{C}}SH+R_2NH\ or\ R_3N \longrightarrow (VII)\ or\ \underset{(VIII)}{Ar\overset{S}{\overset{\|}{C}}S^{-}\overset{+}{N}HR_3}} \qquad (3)$$

treatment of the amine salts of dithio acid with trimethylmetal(IVb) chloride [eqn. (4)].



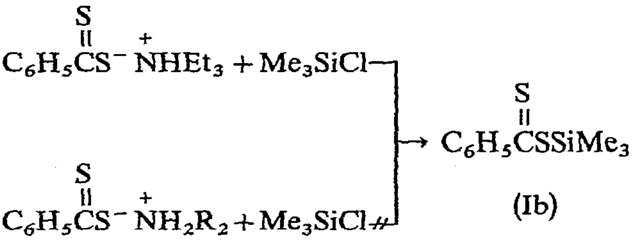
$$\mathrm{(VII)\ or\ (VIII)+Me_3MCl \longrightarrow \underset{(I)}{R\overset{S}{\overset{\|}{C}}SMMe_3}} \qquad (4)$$

(R=Alkyl, aryl; M=Si, Ge, Sn.)

We describe below the preparation of trimethylmetal(IVb) esters (I) of dithio acids and their spectral data.

RESULTS AND DISCUSSION

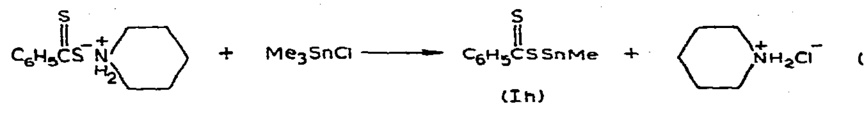
When a suspension of triethylammonium dithiobenzoate in dry petroleum ether was treated with a slight excess of chlorotrimethylsilane at room temperature, (thiobenzoylthio)trimethylsilane (Ib) was obtained in a 96% yield. However, the reaction with the secondary amine salts (piperidinium, diethylammonium etc.) gave no corresponding silyl ester even under more severe conditions.



$$\begin{array}{l} \mathrm{C_6H_5\overset{S}{\overset{\|}{C}}S^{-}\overset{+}{N}HEt_3+Me_3SiCl \longrightarrow \underset{(Ib)}{C_6H_5\overset{S}{\overset{\|}{C}}SSiMe_3}} \\ \mathrm{C_6H_5\overset{S}{\overset{\|}{C}}S^{-}\overset{+}{N}H_2R_2+Me_3SiCl \not\longrightarrow} \end{array} \qquad (5)$$

The structure of (Ib) could be assigned by elemental analysis and spectral data: *viz.* intense absorption bands at 1250 [$\delta(CH_3)$, scissoring], 1240 [$\nu(C{=}S)$], and 953 cm^{-1} [$\delta(CH_3)$, rocking] in the IR spectrum, and resonances at 9.48 ($SiCH_3$, s, 9 H), and 1.75–2.85 τ (C_6H_5, m, 5 H) in NMR spectrum. Analogous treatment of other triethylammonium salts of substituted dithiobenzoate with chlorotrimethylsilane gave the corresponding silyl dithio esters [(Ia) and (Ic)] in excellent yields, as shown in Table 1. However, triethylammonium dithio-1-naphthoate did not react with chlorotrimethylsilane even under severe conditions.

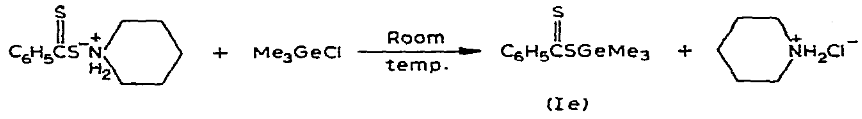
In contrast to the reactions with chlorotrimethylsilane, piperidinium dithiobenzoate reacted readily with chlorotrimethylstannane at room temperature to give the expected (thiobenzoylthio)trimethyltin (Ih) in nearly quantitative yield



(6)

[eqn. (6)]. The structure of (Ih) was confirmed by elemental analysis and studies of spectral data. Thus, the IR spectrum showed absorption bands at 1217 [ν(C=S)] and 778 cm^{-1} [δ(CH_3), rocking], and the NMR spectrum showed peaks at 8.40 ($SnCH_3$, s, 9 H), and 1.90–2.85 τ (C_6H_5, m, 5 H). In the visible region, a maximum was observed at 520 nm (ε 98). Analogous treatment of other piperidinium salts of substituted dithiobenzoate and dithio-1-naphthoate gave the corresponding (thiobenzoylthio)trimethyltin [(Ig) and (Ii)] and (thio-1-naphthoylthio)trimethyltin (Ik) in excellent yields (Table 1). The easier formation of the stannyl esters in comparison with those of the silyl esters can be attributed to the strong affinity of tin for sulfur.

Because germanium lies between silicon and tin in the Periodic Table the reactions with chlorotrimethylgermane were examined. Piperidinium dithiobenzoate readily reacted with chlorotrimethylgermane to give (thiobenzoylthio)trimethylgermane (Ie) quantitatively [eqn. (7)]. The structure of (Ie) was indicated by elemental analysis and studies of IR and NMR spectrum. The IR spectrum showed intense bands at 1218 [ν(C=S)] and 830 cm^{-1} [δ($GeCH_3$), rocking] and the NMR spectrum showed peaks at 9.27 ($GeCH_3$, s, 9 H) and 1.75–2.85 τ (C_6H_5, m, 5 H). Analogous treatment of other piperidinium substituted dithiobenzoates and dithio-1-naphthoate with chlorotrimethylgermane gave the corresponding (thiobenzoylthio)- [(Id) and (If)] and (thio-1-naphthoylthio)trimethylgermanes (Ij) respectively, in excellent yields. Germanium can be regarded as having a stronger affinity than silicon for sulfur.



(7)

In contrast to the behavior of the aromatic analogs, piperidinium dithioisobutyrate readily reacted with chlorotrimethylsilane, germane, and stannane to give the corresponding metalloidal(IVb) esters [(Il)–(In)] in almost quantitative yields [eqn. (8)]. The structures of [(Il)–(In)] were confirmed by elemental analyses

(8)

M = Si,(Il) ; M = Ge,(Im) ; M = Sn,(In)

TABLE 2

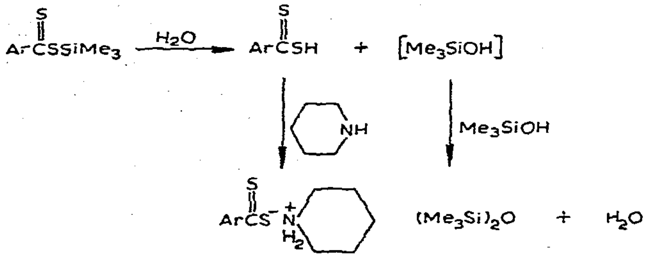
ELEMENTAL ANALYSES

No.	*Compound*	*Formula*	*Analysis found (calcd.) (%)*		
			C	*H*	*S*
(Ia)	$p\text{-}CH_3C_6H_4CS_2Si(CH_3)_3$	$C_{11}H_{16}S_2Si$	55.01 (54.93)	6.72 (6.69)	26.69 (26.67)
(Ib)	$C_6H_5CS_2Si(CH_3)_3$	$C_{10}H_{14}S_2Si$	53.15 (53.03)	6.21 (6.19)	28.56 (28.37)
(Ic)	$p\text{-}ClC_6H_4CS_2Si(CH_3)_3$	$C_{10}H_{13}ClS_2Si^a$	46.22 (46.08)	4.93 (4.99)	24.77 (24.65)
(Id)	$p\text{-}CH_3C_6H_4CS_2Ge(CH_3)_3$	$C_{11}H_{16}S_2Ge$	46.34 (46.35)	5.66 (5.62)	22.55 (22.54)
(Ie)	$C_6H_5CS_2Ge(CH_3)_3$	$C_{10}H_{14}S_2Ge$	44.39 (44.31)	5.23 (5.17)	23.68 (23.71)
(If)	$p\text{-}ClC_6H_4CS_2Ge(CH_3)_3$	$C_{10}H_{13}ClS_2Ge^b$	39.45 (39.36)	4.27 (4.26)	21.09 (21.06)
(Ig)	$p\text{-}CH_3C_6H_4CS_2Sn(CH_3)_3$	$C_{11}H_{16}S_2Sn$	39.92 (39.89)	4.88 (4.84)	19.53 (19.40)
(Ih)	$C_6H_5CS_2Sn(CH_3)_3$	$C_{10}H_{14}S_2Sn$	37.88 (37.87)	4.46 (4.42)	21.31 (20.26)
(Ii)	$p\text{-}ClC_6H_4CS_2Sn(CH_3)_3$	$C_{10}H_{13}ClS_2Sn^c$	34.26 (34.19)	3.76 (3.70)	18.30 (18.29)
(Ij)	$1\text{-}C_{10}H_7CS_2Ge(CH_3)_3$	$C_{14}H_{16}S_2Ge$	52.42 (52.37)	4.99 (4.99)	20.06 (20.01)
(Ik)	$1\text{-}C_{10}H_7CS_2Sn(CH_3)_3$	$C_{14}H_{16}S_2Sn$	45.88 (45.79)	4.39 (4.36)	17.55 (17.50)
(Il)	$i\text{-}C_3H_7CS_2Si(CH_3)_3$	$C_7H_{16}S_2Si$	43.71 (43.68)	8.43 (8.32)	33.46 (33.39)
(Im)	$i\text{-}C_3H_7CS_2Ge(CH_3)_3$	$C_7H_{16}S_2Ge$	35.33 (35.47)	6.84 (6.76)	27.26 (27.11)
(In)	$i\text{-}C_3H_7CS_2Sn(CH_3)_3$	$C_7H_{16}S_2Sn$	29.63 (29.69)	5.67 (5.66)	22.66 (22.69)

[a] Found: Cl, 13.53. Calcd.: Cl, 13.47%. [b] Found: Cl, 11.60. Calcd.: Cl, 11.51%. [c] Found: Cl, 10.09. Calcd.: Cl, 10.00%.

and spectral data as shown in Tables 2 and 3, respectively. The easier formation of the silyl esters (Il) when compared with that of the aromatic dithio acids, can be attributed to the electron donating properties of the isopropyl group.

The metalloidal(IVb) esters (I) of dithio acids were reddish-purple or orange-yellow liquids or crystals. The germyl and stannyl esters were fairly stable and did not



(9)

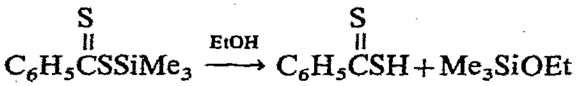
TABLE 3

SPECTRAL PROPERTIES OF TRIMETHYLMETAL(IVB) ESTERS OF DITHIO ACIDS

No.	*Compounds*	*IR (neat) (cm^{-1})* $\delta[CH_3\ (M)]$, $\nu(C{=}S)$	*NMR (CCl_4) (τ)*					*UV (cyclo-C_6H_{12})* λ_{max} *(nm)* (ε_{max})
			M–CH_3(9 H)	*CH_3 (6 H)*	*CH (1 H)*	*p-CH_3 (3 H)*	*Aromatic*	
(Io)	p-$CH_3C_6H_5CS_2CH(CH_3)_2$[a]	1239		8.75 d	6.57 m	7.68 s	1.75–3.00 m	309(12700), 509(127)
(Ip)	$C_6H_5CS_2CH(CH_3)_2$[b]	1230		8.75 d	6.57 m		1.75–2.85 m	296(13200), 509(119)
(Iq)	p-$ClC_6H_5CS_2CH(CH_3)_2$[c]	1239		8.75 d	6.57 m		1.75–2.85 m	306(14300), 511(133)
(Ia)	p-$CH_3C_6H_4CS_2Si(CH_3)_3$	1250, 840, 1240	9.48 s			7.68 s	1.75–3.05 m	310(11000), 533(153)
(Ib)	$C_6H_5CS_2Si(CH_3)_3$	1250, 840, 1240	9.48 s				1.75–2.85 m	298(10800), 531(128)
(Ic)	p-$ClC_6H_4CS_2Si(CH_3)_3$	1250, 845, 1241	9.48 s				1.75–2.85 m	308(13200), 534(137)
(Id)	p-$CH_3C_6H_4CS_2Ge(CH_3)_3$	1237, 830, 1222	9.27 s			7.68 s	1.75–3.05 m	314(14300), 530(149)
(Ie)	$C_6H_5CS_2Ge(CH_3)_3$	1237, 830, 1218	9.27 s				1.75–2.85 m	303(13300), 528(109)
(If)	p-$ClC_6H_4CS_2Ge(CH_3)_3$	1237, 830, 1216	9.27 s				1.70–2.85 m	311(15300), 531(114)
(Ig)	p-$CH_3C_6H_4CS_2Sn(CH_3)_3$	778, 1222	9.40 s			7.68 s	1.75–3.05 m	318(17500), 527(152)
(Ih)	$C_6H_5CS_2Sn(CH_3)_3$	778, 1217	9.40 s				1.75–2.85 m	307(14700), 520(98)
(Ii)	p-$ClC_6H_4CS_2Sn(CH_3)_3$	778, 1214	9.40 s				1.70–2.85 m	314(14500), 525(97)
(Ij)	1-$C_{10}H_7CS_2Ge(CH_3)_3$	1238, 830, 1230	9.27 s				2.50 m	316(20800), 520(270)
(Ik)	1-$C_{10}H_7CS_2Sn(CH_3)_3$	772, 1200	9.40 s				2.50 m	325(16200), 490(247)
(Ir)	i-$C_3H_7CS_2CH(CH_3)_2$[d]	1205		8.75 d	6.57 m			307(8800), 460(119)
(Il)	i-$C_3H_7CS_2Si(CH_3)_3$	1250, 848, 1202	9.55 s	8.75 d	6.57 m			303(11900), 487(121) 306(9500)[e], 483(215)[e]
(Im)	i-$C_3H_7CS_2Ge(CH_3)_3$	1238, 830, 1198	9.31 s	8.75 d	6.57 m			310(13200), 483(127) 313(10600)[e], 478(208)[e]
(In)	i-$C_3H_7CS_2Sn(CH_3)_3$	1200, 778, 1191	9.42 s	8.75 d	6.57 m			319(14700), 473(101) 321(11240)[e], 470(221)[e]

[a] B.p. 105°/0.05 mmHg. Found: C, 62.04; H, 6.59; S, 31.01. $C_{11}H_{14}S_2$ calcd.: C, 62.86; H, 6.67; S, 30.48%. [b] B.p. 86–87°/0.3 mmHg (ref. 5). [c] B.p. 106°/0.02 mmHg. Found: C, 52.44; H, 4.80; Cl, 15.55; S, 27.10. $C_{10}H_{11}ClS_2$ calcd.: C, 52.06; H, 4.77; Cl, 15.40; S. 27.76%. [d] B.p. 35°/0.03 mmHg. Found: C, 52.03; H, 8.62; S, 39.47%. $C_7H_{14}S_2$ calcd.: C, 51.85; H, 8.64; S, 39.51%. [e] Solvent: $CHCl_3$.

change during one week at room temperature, but the silyl esters [(Ia)–(Ic) and (Ie)] were readily hydrolyzed to give trimethylsilanol (which was isolated as hexamethyldisiloxane), and the corresponding dithio acids which were isolated as piperidinium salts [eqn. (9)]. Furthermore, (thiobenzoylthio)trimethylsilane (Ib) reacted readily with ethanol to give the corresponding dithio acid and ethoxytrimethylsilane in excellent yield [eqn. (10)], but no alcoholysis of the stannyl ester (Ih) was observed.



$$C_6H_5\overset{\overset{S}{\|}}{C}SSiMe_3 \xrightarrow{EtOH} C_6H_5\overset{\overset{S}{\|}}{C}SH + Me_3SiOEt \qquad (10)$$

Spectral data

IR spectra. Bak *et al.*[6] have shown by a simplified force-constant calculation that the C=S frequency should be in the vicinity of 1200 and the C–S frequency at about 700 cm^{-1}, and in a series of 21 carboxymethyl dithio esters, the values of ν(C=S) were found to lie between 1190 and 1225 cm^{-1}. Bellamy and Rogasch[7] confirmed Bak's results and solvent effects. Recently, Schmidt *et al.*[8] reported that ν(C=S) for organometal-substituted derivatives of dithiocarbonates of the type $(C_6H_5)_3M{-}S{-}C(S){-}OC_2H_5$ (M = Ge, Sn and Pb) appear near 1040 cm^{-1}. However, ν(C=S) for (thiobenzoyl)trimethylsilane was found by us to be near 1240 cm^{-1} [2c]. The metalloidal (IVb) esters [(Ia)–(Ii)] of aromatic dithio acid obtained had two characteristic intense absorption bands at 1240 and 1050 cm^{-1} (silyl esters), 1220 and 1050 cm^{-1} (germyl esters), and 1215 and 1040 cm^{-1} (stannyl esters), respectively. Furthermore, the esters of dithioisobutyric acid showed 1202 and 1022 cm^{-1} for the silyl compounds (Ie), 1198 and 1020 cm^{-1} for the germyl compounds (Im), and 1187, and 1015 cm^{-1} for the stannyl compound (In). However, it is difficult to assign the lower frequency bands to C=S, because these bands in the case of the amine salts of aromatic and aliphatic dithio acids were observed near 1010[5a] and 970 cm^{-1} [5b], respectively. Thus, the intense absorption band in the 1240–1180 cm^{-1} region can be reasonably attributed to ν(C=S) in the metalloidal (IVb) esters of dithio acid. These assignments are consistent with those for the ν(C=S) in the case of substituted (benzoylthio)trimethylsilanes[2c] and carboxymethyldithio esters[6,7].

Previous reports have shown that ν(C=O) for esters containing the ≡M–S–CO–C≡ linkage [M = Metal(IVb)] have lower frequency shifts with increasing atomic number of metal(IVb)[2c]. Such shifts towards lower frequencies were observed for ν(C=S) in the esters (I) containing the ≡M–S–CS–C≡ linkage [M = Metal(IVb)]. These shifts are probably caused by either the heavy atom effect or the higher electron donating nature of metal(IVb) elements. The IR absorption bands at 1240–1170 cm^{-1} are shown in Table 3.

UV and visible spectra. The absorption spectral curves of (thioisobutyroylthio)-trimethylsilane, -germane, and -tin are shown in Fig. 1, and with the absorption maximum (λ_{max}) are listed in Table 3. As shown in Fig. 1 and Table 3, (thioaroylthio)- and (thioisobutyroylthio)trimethylmetal(IVb) have two characteristic maxima at 300–320 (ε 15000–25000) and 520–530 (ε 100–150, aromatic), or 470–490 nm (ε 70–90, aliphatic), respectively. The former band can be ascribed to the $\pi \rightarrow \pi^*$ and the latter to the $n \rightarrow \pi^*$ transition of the thiocarbonyl group. Interestingly, the $n \rightarrow \pi^*$ transition of the esters (I) show a tendency towards a blue shift while $\pi \rightarrow \pi^*$ transitions

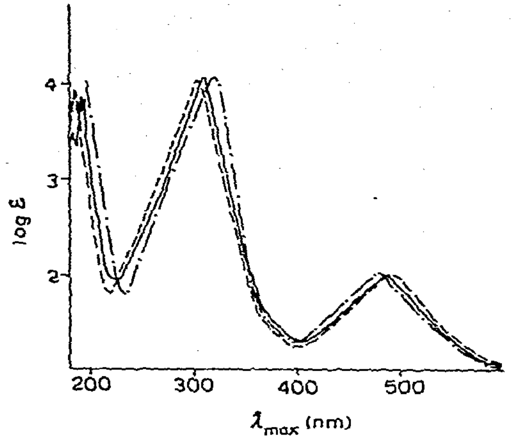


Fig. 1. The electronic spectra of (thioisobutyroylthio)trimethylsilane (----), -germane (——) and -tin (—·—·—).

show a tendency towards a red shift on increasing the atomic number of the metal (IVb). The sequence for the $\pi \rightarrow \pi^*$ transitions is consistent with the order of inductive effects of element (IVb), but the order ($Si > Ge > Sn > C$) of the $n \rightarrow \pi^*$ transition is clearly inconsistent with operation of a simple inductive effect, and may reflect the capacity for $d\pi$–$p\pi$ bonding[9] between the (IVb) element and the sulfur atom.

The large red shift for the $n \rightarrow \pi^*$ transition in comparison with that for the carbon analogues can be interpreted in terms of an interaction between the free electron pair of the sulfur atom lying in the p_y orbital orthogonal to the C=S π-bond system and a sulfur d orbital which is overlapping with a d orbital of silicon, germanium, or tin atom, to form an M–S–C=S superchromophore. A similar explanation for the enhanced extinction coefficients of the $n \rightarrow \pi^*$ transition was given for acylsilanes[10,11] and -germanes[10]. Recently, West *et al.*[12] interpreted this system (Si–C=O) in terms of the molecular orbital correlation diagram, and concluded that the lowering of the energy of the π^* level by a strong $d \rightarrow \pi^*$ bonding was the primary factor, as previously suggested by Orgel[13].

EXPERIMENTAL

The IR spectra were measured on a JASCO grating IR spectrophotometer IR-G. The UV spectra were recorded on a Hitachi 124 spectrophotometer. The NMR spectra were recorded on a JEOL C-60HL instrument, with tetramethylsilane as internal standard. Analyses were carried out by the Elemental Analyses Center of Kyoto University.

Materials

The amine salts of dithio acids were prepared by the method described previously[5] and had m.p.'s as follows: triethylammonium dithiobenzoate[5a], m.p. 61–63°; diethylammonium dithiobenzoate[5a], m.p. 101–102°; piperidinium dithiobenzoate[5a], m.p. 96–97.5°; triethylammonium *p*-methyldithiobenzoate[5a], m.p. 54–56°; triethylammonium *p*-chlorodithiobenzoate[5a], 44–46°; triethylammonium dithio-1-naphthoate[5a], m.p. 129–131°; piperidinium dithio-1-naphthoate[5a], m.p. 130–131°C; piperidinium dithioisobutyrate[5b], m.p. 133–134°. Chlorotrimethylsilane was commercial material, and was purified by careful distillation. Chlorotrimethylgermane (b.p. 125–127°) and -tin (b.p. 153–157°) were prepared by well known procedures from tetrachlorogermane and -tin. Solvents were rigorously dried. Petroleum ether boiling below 45° was used. Reactions and manipulation of samples were carried out under dry nitrogen.

Some typical procedures are shown and the data were summarized in Tables 1–3.

Preparation of (thiobenzoylthio)trimethylsilane (Ib)

A slight excess of chlorotrimethylsilane was added to a suspension of 0.96 g (0.0025 mole) of triethylammonium dithiobenzoate in petroleum ether, and the mixture was stirred at room temperature for 30 min. After the precipitates were filtered, removal of the solvent and the excess of chlorotrimethylsilane *in vacuo* below 40° gave 1.1 g of chemically pure (Ib).

Preparation of (p-chlorothiobenzoylthio)trimethylgermane (If)

A slight excess of chlorotrimethylgermane was added to a suspension of piperidinium *p*-methyldithiobenzoate in petroleum ether, and the mixture was stirred at 50° for 1½ h. After the precipitates were filtered, vacuum distillation of the solvent and the excess of chlorotrimethylgermane below 50° left 1.26 g of chemically pure (If).

Preparation of (p-methylthiobenzoylthio)trimethyltin (Ig)

A mixture of a slight excess of chlorotrimethyltin and 1.1 g (0.0025 mol) of piperidinium *p*-methyldithiobenzoate in ether was stirred at 50° for 2 h. After removal of the precipitates by the filtration, removal of the solvent and the excess of chlorotrimethyltin under vacuum left a residue, which was recrystallized from n-hexane to give 1.45 g of (Ig).

Preparation of (thio-1-naphthoylthio)trimethyltin (Ik)

An equimolar amount of triethylammonium dithio-1-naphthoate (1.37 g, 0.005 mol) and chlorotrimethyltin (1.0 g, 0.005 mol) in petroleum ether was stirred for 8 h. The orange-yellow precipitate was filtered off and extracted with small portions of petroleum ether until the solvent no longer took up color. Evaporation of the solvent from the extracts and recrystallization of the resulting residue from n-hexane or ethanol gave 1.68 g of (Ik).

Preparation of (thioisobutyroylthio)trimethylsilane (Ie)

An equimolar mixture of piperidinium dithioisobutyrate (2.13 g, 0.01 mol) and chlorotrimethylsilane (1.27 g, 0.011 mol) in petroleum ether (15 ml) was stirred at room temperature for 5 h. The precipitate was filtered off, and the solvent and the excess chlorotrimethylsilane were evaporated under vacuum from the filtrate. Vacuum distillation of the residue gave 1.95 g of (Ie).

Hydrolysis of (thiobenzoylthio)trimethylsilane (Ib)

A solution of (Ib) (2.26 g, 0.01 mol) in petroleum ether (15 ml) (b.p. < 35°)

containing a small amount of water was stirred at room temperature for 5 h. After evaporation of the solvent from the reaction mixture, vacuum distillation of the residue below 30° gave 1.20 g [74%, based on the used (Ib)] of hexamethyldisiloxane (dry ice/acetone trap). The IR spectrum of the residue left after the vacuum distillation showed a peak at 2540 cm^{-1} due to ν(SH), and treatment of this residue with piperidine (0.7 g, 0.0085 mol) gave 1.5 g (58%, based on the used (Ib)) of piperidinium dithiobenzoate, m.p. 110–113°, which was identified by comparison of its melting point and IR spectrum with those of an authentic sample.

Reaction of (thiobenzoylthio)trimethylsilane (Ib) with ethanol

An equimolar amount of ethanol (0.92 g, 0.02 mol) and (Ib) (4.52 g, 0.02 mol) was stirred for 20 h at room temperature. Distillation gave 1.88 g [78%, based on used (Ib)] of ethoxytrimethylsilane, b.p. 75° (lit.[16] 75°), IR (neat) 1252 cm^{-1} δ[CH$_3$-(Si)]}. [The IR spectrum of the reaction mixture showed a peak at 2548 cm^{-1} due to ν(SH) of dithiobenzoic acid.]

REFERENCES

1 (a) A. Ladenburg, *Justus Liebigs Ann. Chem.*, 164 (1892) 300;
(b) R. O. Sauer, *J. Amer. Chem. Soc.*, 67 (1945) 1548;
(c) H. A. Schuyten, J. W. Weaver and J. D. Reid, *J. Amer. Chem. Soc.*, 69 (1947) 2110;
(d) L. H. Sommer, G. A. Parker and C. L. Frye, *J. Amer. Chem. Soc.*, 86 (1964) 3280.
(e) M. Lesbre, P. Mazerolles and J. Satge, in D. Seyferth (Ed.), *The Organic Compounds of Germanium*, Wiley, New York, 1971, p. 469.
(f) R. K. Ingham, S. D. Rosenberg and H. Gilman, *Chem. Rev.*, 60 (1960) 459.
(g) R. Okawara and M. Ohara, in A. N. Sawyer (Ed.), *Organotin Compounds* Vol 2, Dekker, New York, 1971, p. 253.
2 (a) H. Schumann, *Advances in Organometallic Chemistry*, Vol. 5, Academic Press, 1966, p. 1.
(b) Ref. (1b) p. 524.
(c) S. Kato, W. Akada, M. Mizuta and Y. Ishii, *Bull. Chem. Soc. Jap.*, 46 (1973) 244.
(d) H. Schumann, I. Schumann-Ruidisch and M. Schmidt, in M. K. Sawyer (Ed.), *Organotin Compounds*, Vol. 2, Dekker, New York, 1971, p. 297.
(e) Ref. (2c).
3 (a) G. A. Gornowicz and J. W. Ryan, *J. Org. Chem.*, 31 (1966) 3439.
(b) Ref. (2c).
4 S. Kato and M. Mizuta, *Int. J. Sulfur Chem., A*, 2 (1972) 27.
5 (a) S. Kato, T. Mitani and M. Mizuta, *Int. J. Sulfur Chem. A*, in press.
(b) S. Kato and M. Mizuta, *Bull. Chem. Soc. Jap.*, 45 (1972) 3492.
6 B. Bak, L. Hansen-Nygarred and C. Pedersen, *Acta Chem. Scand.*, 12 (1958) 1451.
7 L. T. Bellamy and P. F. Rogasch, *J. Chem. Soc.*, (1960) 2218.
8 M. Schmidt, H. Schumann, F. Gliniechi and J. F. Jaggard, *J. Organometal. Chem.*, 17 (1969) 277.
9 (a) J. Lorberth and H. Nöth, *J. Organometal. Chem.*, 19 (1969) 203.
(b) H. Bock and H. Alt, *Chem. Ber.*, 102 (1969) 1534.
(c) A. J. Smith, W. Adcock and W. Kitching, *J. Amer. Chem. Soc.*, 92 (1970) 6140.
(d) J. Schraml and V. Chvalovsky, *Collect. Czech. Chem. Commun.*, 31 (1966) 507.
(e) H. Schumann and P. Reich, *Z. Anorg. Allg. Chem.*, 375 (1970) 72.
(f) H. Schumann and P. Reich, *Z. Anorg. Allg. Chem.*, 377 (1970) 63.
(g) T. A. George, *J. Organometal. Chem.*, 31 (1971) 233.
10 (a) A. G. Brook, M. A. Quigley, C. J. D. Peddle, N. V. Schwartz and C. M. Warner, *J. Amer. Chem. Soc.*, 82 (1964) 5102.
(b) A. G. Brook and J. R. Pierce, *Can. J. Chem.*, 42 (1964) 298.
11 (a) W. K. Musker and R. W. Ashly, *J. Org. Chem.*, 31 (1966) 4237.
(b) W. Musker and G. L. Lasson, *J. Organometal. Chem.*, 6 (1966) 627.

12 (a) D. F. Hamish and R. West, *Inorg. Chem.*, 2 (1963) 1082.
(b) R. West, *J. Organometal. Chem.*, 3 (1965) 314.
13 L. E. Orgel, in E. A. V. Ebsworth (Ed.), *Volatile Silicon Compounds*, Pergamon Press, London, 1963, p. 81.
14 (a) H. Sakurai, K. Tominaga, T. Watanabe and M. Kumada, *Tetrahedron Lett.*, (1966) 5493.
(b) E. H. Brooks and F. Glockling, *Inorganic Syntheses*, Vol. XII, 1970, p. 58.
15 K. A. Kozeschkow, *Chem. Ber.*, 66 (1933) 1661.
16 E. W. Abel, *J. Chem. Soc.*, (1961) 4933.
17 E. Fromm and T. Schmoldt, *Ber. Deut. Chem. Ges.*, 40 (1907) 2861.