112 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 112—117(1971) [Vol. 44, No. 1

The Reactions of Dihalogenoalkanes with Dimethyltin Bis(*N*,*N*-dimethyldithiocarbamate) and Related Compounds

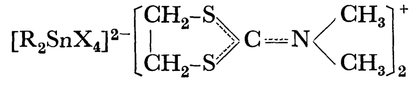
Toshio TANAKA, Koji TANAKA, and Tokio YOSHIMITSU

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-kami, Suita

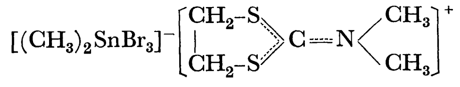
(Received May 7, 1970)

Dimethyltin-bis(*N*,*N*-dimethyldithiocarbamate), $(CH_3)_2Sn[S_2CN(CH_3)_2]_2$, reacts with dihalogenoalkanes to give 1,3-dithiacycloalkyl-2-dimethylimminium dimethyltin halides, $[(CH_3)_2SnX_{n+2}]^{n-}[(CH_2)_m\langle{}^{S}_{S}\rangle C{=}N(CH_3)_2]^+_n$ ($n=1$ or 2; $m=2$, 3, or 4; X=Cl, Br, or I). On the other hand, the reactions between dimethyltin bis(*N*-methyl-*N*-phenyldithiocarbamate), $(CH_3)_2Sn[S_2CN(CH_3)(C_6H_5)]_2$, and dihalogenoalkanes yield preferentially alkylene bis(*N*-methyl-*N*-phenyldithiocarbamate). The difference in reactivity between the two types of complexes is discussed. The infrared and NMR spectra indicate that the positive charge on the dithiacycloalkylimminium ions is more delocalized in the higher homologues. The configurations of dimethyltin trihalide and tetrahalide anions in the solid state and in solution are also presented on the basis of the infrared spectra; the results suggest that, in solution, dimethyltin trihalide anions are more likely to be formed than are dimethyltin tetrahalides.

We have previously reported that some *N*,*N*-dimethyldithiocarbamate complexes of tin(IV), $R_2Sn[S_2CN(CH_3)_2]_2$ (R=CH_3 and C_2H_5) and $(CH_3)_2SnCl[S_2CN(CH_3)_2]$, react with 1,2-dihalogenoethanes to give, preferentially, 1,3-dithiacyclopentyl-2-dimethylimminium compounds, (I) or (II):[1]


(I)

(a): R=CH_3, X=Cl
(b): R=C_2H_5, X=Cl
(c): R=C_2H_5, X=Br


(II)

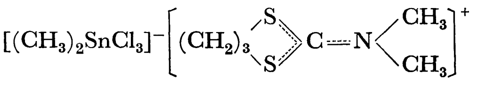
This reaction is different in selectivity from the previously-reported one between sodium *N*,*N*-dimethyldithiocarbamate and 1,2-dihalogenoethanes in some organic solvents, where ethylene bis(*N*,*N*-dimethyldithiocarbamate) was obtained as well as 1,3-dithiacyclopentyl-2-dimethylimminium salts.[2]

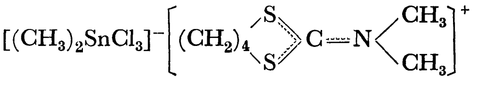
The purpose of the present study is to extend this type of reaction of a variety of dihalogenoalkanes with dimethyltin-bis(*N*,*N*-dimethyldithiocarbamate), $(CH_3)_2Sn[S_2CN(CH_3)_2]_2$, and -bis(*N*-methyl-*N*-phenyldithiocarbamate), $(CH_3)_2Sn[S_2CN(CH_3)(C_6H_5)]_2$ (abbreviated as $(CH_3)_2Sn(dmdtc)_2$ and $(CH_3)_2Sn(mpdtc)_2$ respectively). The former complex reacts with dihalogenoalkanes to form 1,3-dithiacycloalkyl-2-dimethylimminium dimethyltin halides. On the other hand, the reaction of $(CH_3)_2Sn(mpdtc)_2$ with dihalogenoalkanes gives, preferentially, alkylene bis(*N*-methyl-*N*-phenyldithiocarbamates); in the case of 1,2-dichloroethane, 1,3-dithiacyclopentyl-2-methylphenylimminium salt is also produced.

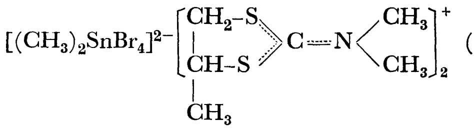
The infrared and PMR spectra of the compounds obtained are discussed from the viewpoint of the delocalization of the positive charge on the dithiacycloalkylimminium cations and of stereochemistry of the dimethyltin halide anions.

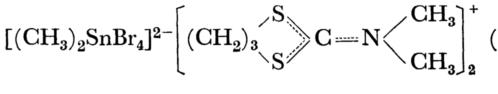
Results and Discussion

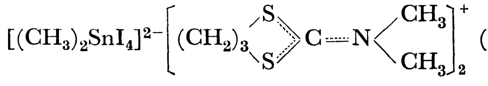
The reaction of $Cl(CH_2)_nCl$ ($n=3$, 4) with $(CH_3)_2Sn(dmdtc)_2$ without a solvent at elevated temperatures yielded 1,3-dithiacycloalkyl-2-dimethylimminium dimethyltin trichlorides, (III) and (IV), while $BrCH_2CHBrCH_3$, $Br(CH_2)_3Br$ and $I(CH_2)_3I$ reacted with $(CH_3)_2Sn(dmdtc)_2$ to give the uni-bivalent compounds, (V), (VI), and (VII), respectively.


(III)


(IV)


(V)


(VI)

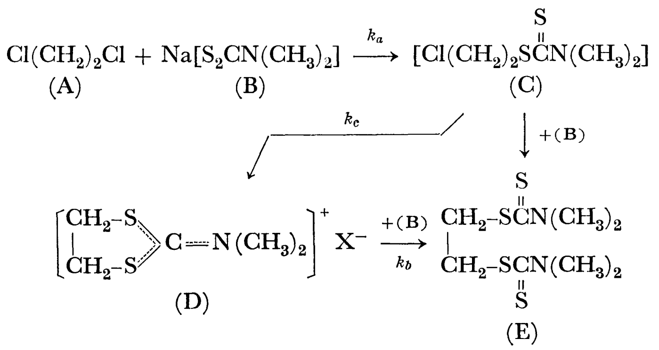

(VII)

The main products in these reactions were 1,3-dithiacycloalkyl-2-dimethylimminium salts, although the yields of III and IV were not very good. Another product expected to be formed, alkylene bis(*N*,*N*-dimethyldithiocarbamates), was not obtained under the present experimental conditions. Recently, the formation of ethylene bis(*N*,*N*-dimethyldithiocarbamate) (E) from 1,2-dichloroethane (A) and sodium *N*,*N*-dimethyldithiocarbamate (B) has been interpreted by the following reaction scheme, involving the intermediate of the isolated anchimetric cation (D), and in which the cyclization of the mono-substituted intermediate (C) occurs very rapidly ($k_c \gg k_a$):[2]

---

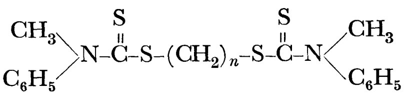
[1] T. Tanaka and T. Abe, *Inorg. Nucl. Chem. Lett.*, **4**, 569 (1968).

[2] T. Nakai, Y. Ueno, and M. Okawara, *Tetrahedron Lett.*, **1967**, 3831; This Bulletin, **43**, 165 (1970).



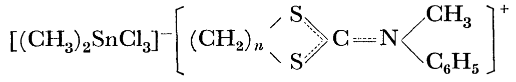
On the basis of this scheme, it may be explained that the reaction of $(CH_3)_2Sn(dmdtc)_2$ with dihalogenoalkanes mainly yielded I—VII, but not the di-substituted products; the I—VII obtained by the cyclization of the mono-substituted products are almost insoluble in dihalogenoalkanes; therefore, it is unlikely that any further reaction of those products with $(CH_3)_2Sn(dmdtc)_2$ will occur. This idea is supported by the results of the reaction of $(CH_3)_2Sn(mpdtc)_2$ with dihalogenoalkanes, as will be described below.

The $(CH_3)_2Sn(mpdtc)_2$ complex reacted with $Cl(CH_2)_2Cl$ to give ethylene bis(*N*-methyl-*N*-phenyldithiocarbamate) (VIIIa) as precipitates. From the filtrate we isolated 1,3-dithiacycloalkyl-2-methylphenylimminium salt (IXa). However, the reactions of $Cl(CH_2)_nCl$ ($n=3$, 4) with $(CH_3)_2Sn(mpdtc)_2$ yielded only alkylene bis(*N*-methyl-*N*-phenyldithiocarbamates) (VIIIb) and (VIIIc), not the corresponding imminium salts, (IXb) and (IXc).



(VIII)

(a) $n=2$, (b) $n=3$, (c) $n=4$



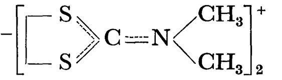
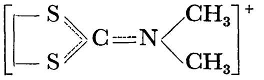
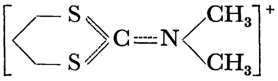
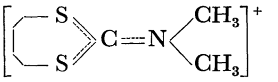
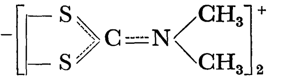
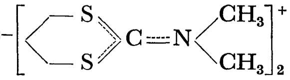
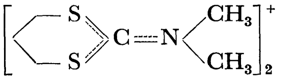
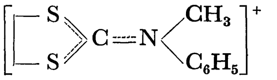
(IX)

(a) $n=2$, (b) $n=3$, (c) $n=4$

In contrast to the dimethylimminium salts (I)—(VII), the methylphenylimminium salt (IXa) is appreciably soluble in dihalogenoalkanes, which act as solvents as well as reactants. IXb and IXc will be more soluble in dihalogenoalkanes than IXa, for they have more dithiacycloalkyl rings. In addition, the reaction rate, k_b, in the scheme described above is much faster than k_a in non-polar aprotic solvents.2) It can reasonably be assumed from these facts that the further reaction of IX with $(CH_3)_2Sn(mpdtc)_2$ will occur to form the di-substituted product (VIII). The infrared spectrum of $(CH_3)_2Sn(mpdtc)_2$ shows the ν(Sn–S) band at 330 cm^{-1}, considerably lower than that of $(CH_3)_2Sn(dmdtc)_2$ (365 cm^{-1}). This lowering in frequency may be related to the bond weakening of the Sn–S bond, which will also enhance the reactivity of the former complex.

The capacity to form both $(CH_3)_2SnX_3^-$ and $(CH_3)_2SnX_4^{2-}$ ions has been known in fluoride,3) chloride, and bromide,4) where the counter cations are Cs^+, $N(CH_3)_4^+$, and $N(C_2H_5)_4^+$, but the iodo-complex has never been isolated. The compound VII is the first iodo-complex anion; this is suggests that some bulky

Table 1. Relevant infrared frequencies (cm^{-1})a) of 1,3-dithiacycloalkyl-2-dimethylimminium dimethyltin halides and the related compoundsb)

	Compound	ν(C=N)	ν_{as}(Sn–C)	ν_s(Sn–C)	ν(Sn–X)
(Ia)	$[(CH_3)_2SnCl_4]^{2-}$ 	1590 s	560 s	515 vw	220 m
(II)	$[(CH_3)_2SnBr_3]^-$ 	1587 s	559 s	511 s	215 s
(III)	$[(CH_3)_2SnCl_3]^-$ 	1541 s	571 m (565 m)	516 m (516 m)	312 s 241 s (325 s) (240 s)
(IV)	$[(CH_3)_2SnCl_3]^-$ 	1461 s	565 m (566 m)	515 m (519 m)	325 s 240 s (326 s) (240 s)
(V)	$[(CH_3)_2SnBr_4]^{2-}$ 	1590 s	568 m (562 m)	— (510 m)	210 s
(VI)	$[(CH_3)_2SnBr_4]^{2-}$ 	1538 s	562 m (561 m)	505 m (511 m)	215 s
(VII)	$[(CH_3)_2SnI_4]^{2-}$ 	1530 s	560 s	518 vw	<200
(IXa)	$[(CH_3)_2SnCl_3]^-$ 	1524 s	578 m (566 m)	506 m (516 m)	256 s, br (326 s) (240 s)

a) Nujol mull and dichloromethane solution; the latter in parentheses.
b) The abbreviations used in this table are as follows: s, strong; m, medium; w, weak; vw, very weak; br, broad.

---

3) C. J. Wilkins and H. M. Haendler, *J. Chem. Soc.*, **1965**, 3174.

4) J. P. Clark and C. J. Wilkins, *J. Chem. Soc.*, *A*, **1966**, 871.

TABLE 2. PROTON CHEMICAL SHIFTS (ppm) AND SPIN-SPIN COUPLING CONSTANTS BETWEEN THE ^{119}Sn AND THE METHYL PROTONS (Hz) OF 1,3-DITHIACYCLOALKYL-2-DIMETHYLIMMINIUM DIMETHYLTIN HALIDES AND THE RELATED COMPOUNDS[a]

Compound	τ(Sn–CH$_3$)	τ(C–CH$_2$–C)	τ(S–CH$_2$)	τ(N–CH$_3$)	τ(C$_6$H$_6$)	J(^{119}Sn–CH$_3$)	Solvent
(Ia)[b]	8.91 s	—	5.95 s	6.44 s	—	116	DMSO-d_6
(II)[b]	8.70 s	—	5.92 s	6.44 s	—	114	DMSO-d_6
(III)	8.73 s	7.70 t	6.56 t	6.37 s	—	90	CH_2Cl_2
(IV)	8.72 s	7.73 m	6.40 m	6.77 s	—	90	CH_2Cl_2
(V)[c]	8.27 s	—	[d]	6.25 [d]	—	86	$CHCl_3$
(VI)	8.34 s	7.58 m	6.51 t	6.33 s	—	86	CH_2Cl_2
(VII)	8.36 s	7.57 t	6.52 t	6.33 s	—	81	$CHCl_2CHCl_2$
(VIIIa)	—	—	6.45 s	6.20 s	2.30 m	—	DMSO-d_6
(VIIIb)	—	8.12 t	6.85 t	6.34 s	2.77 m	—	CH_2Cl_2
(VIIIc)	—	8.39 m	6.85 m	6.28 s	2.70 m	—	CH_2Cl_2
(IXa)	8.75 s	—	5.90 m	6.26 s	2.48 s	90	CH_2Cl_2

a) The abbreviations used in this table are as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad.

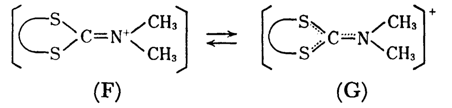
b) These compounds are too insoluble in less donor solvents to measure J(^{119}Sn–CH$_3$) values, but soluble in very polar solvents, such as dimethyl sulfoxide(DMSO). The values of these compounds in DMSO-d_6 are quite similar to those of $(CH_3)_2SnCl_2$ or $(CH_3)_2SnBr_2$ in the same solvent; W. Kitching, *Tetrahedron Lett.*, **1966**, 3689; T. Tanaka, *Inorg. Chim. Acta*, **1**, 217 (1967).

c) τ(C–CH$_3$), 8.26 d.

d) A complicated multiplet. This is also the case of the S–CH chemical shifts.

counter cations make it possible to form dimethyltin iodide anions.

Delocalization of the Positive Charge in the 1,3-Dithiacycloalkyl-2-imminium Cations. The relevant infrared frequencies are listed in Table 1. The compounds, Ia, II, and V all exhibit the ν(C=N) band at relatively high frequencies, suggesting an appreciable double-bond character of the C=N bond and, therefore, a high rotational barrier about it. This idea is supported, although qualitatively, by the PMR spectrum of the compound V (Fig. 1), in which the N–CH$_3$ proton signals are split due to their slightly different magnetic environments. The coalescene temperature is about 125°C in 1,1,2,2-tetrachloroethane, higher than those of most related compounds, such as S-methyl-N,N-dimethyldithiocarbamate, $CH_3SC(S){-}N(CH_3)_2$ (2.5°C in hexane)[5] and N,N-dimethylacetamide, $CH_3C(O){-}N(CH_3)_2$ (87°C as neat liquid),[6] although somewhat lower than that of N,N-dimethylformamide, $HC(O){-}N(CH_3)_2$ (148°C as neat liquid).[6] As is shown in Table 1, the ν(C=N) band shifts to a lower frequency with an increase in the member of the 1,3-dithiacycloalkyl rings. This suggests that the higher homologues receive more contributions from the structure G, resulting in an increase in the electron density on the nitrogen atom. Consistently with this, the N–CH$_3$ proton signal in chloroalkanes is observed at a higher magnetic field with an increase in the size of the dithiacycloalkyl rings, as is shown in Table 2.[7] The participation of the lone-pair electrons of the sulfur atom in π-bonding is sterically more favorable in the higher homologues, resulting in the delocalization of the positive charge.



(F) (G)

With the compound IXa, the ν(C=N) band sppears at a somewhat lower frequency than those of the other compounds with five-membered dithiacycloalkyl rings, Ia, II, and V. This may be interpreted by assuming a conjugation between the C=N bond and the phenyl group.

Stereochemistry of the Dimethyltin Halide Anions. As is listed in Table 1, the 1 : 1 electrolytes, II, III, and IV, in the solid state exhibit two infrared bands due to ν(Sn–C), and the symmetric stretching bands are as strong as the asymmetric ones, indicating that the

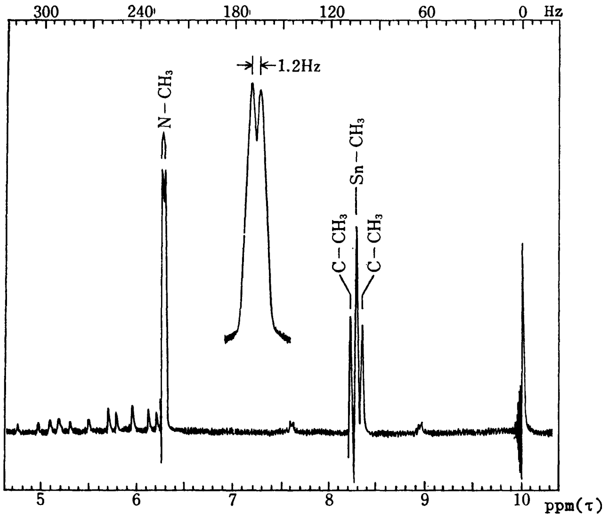
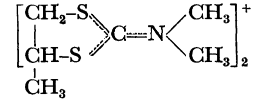


Fig. 1. PMR spectrum of $[(CH_3)_2SnBr_4]^{2-}$·



$\left[\begin{matrix}CH_2{-}S \\ | \\ CH{-}S \\ | \\ CH_3\end{matrix}\!\!>\!C{=}N\!<\!\begin{matrix}CH_3 \\ CH_3\end{matrix}\right]^{+}_{2}$ in chloroform, 6 wt %.

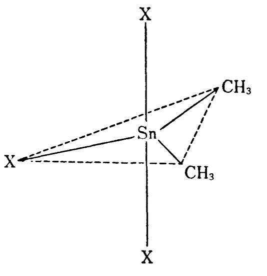
---

[5] C. E. Holloway and M. H. Gitlitz, *Can. J. Chem.*, **45**, 2659 (1967).

[6] M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).

[7] This is not true fot Ia and II, whose τ(N–CH$_3$) values are those of a strong donor solvent; DMSO-d_6.

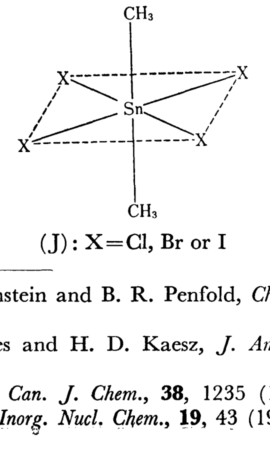
C–Sn–C moiety is not linear. The probable configuration of the $(CH_3)_2SnX_3^-$ anions is a trigonal bipyramid (H), with two methyl groups located in equatorial positions; this is analogous to the structure of the dimethyltin trichloride anion in $[(CH_3)_2SnCl\cdot terpyridyl]^+[(CH_3)_2SnCl_3]^-$, as determined by X-ray analysis.[8]



(H): X=Cl, Br

The spectra of III and IV in dichloromethane closely resemble those of their solid states, except for the region obscured by the solvent. It seems, therefore, that there is essentially no difference between the geometry in the solid state and that in solution for the two compounds. These compounds show a characteristic $J(^{119}Sn–CH_3)$ value of 90 Hz. Extrapolation from the function relating $J(^{119}Sn–CH_3)$ to the apparent *s*-character of the tin atomic orbital in the Sn–C bond[9] indicates a 41% *s*-character, which is much larger than that (33%) expected from the trigonal bipyramid (H). Such a large *s*-character of the tin atomic orbital in the Sn–C bond may possibly be explained by assuming the rehybridization of the tin atomic orbitals due to the electronegativity difference between the methyl group and the chlorine atom.[10] This idea is consistent with the present experimental results that $J(^{119}Sn–CH_3)$ value decreases with a decrease in the electronegativity of the X atom of $(CH_3)_2SnX_3^-$ anions, the bromide and iodide of which result from the dissociation of V, VI or VII in halogenoalkanes, as will be described below.

Of the uni-bivalent electrolytes, Ia, V and VII in the solid state exhibit an intense band due to ν_{as}(Sn–C), while their ν_s(Sn–C) bands are imperceptible. It seems, therefore, that the configuration J with an almost linear C–Sn–C moiety is most plausible for the dimethyltin tetrahalide anions.



(J): X=Cl, Br or I

The spectrum of V in dichloromethane, however, shows the ν_{as}(Sn–C) band shifting to a lower frequency and the ν_s(Sn–C) band occurring distinctly, whereas there is no appreciable change is the spectrum in the other mid-infrared regions (Fig. 2).

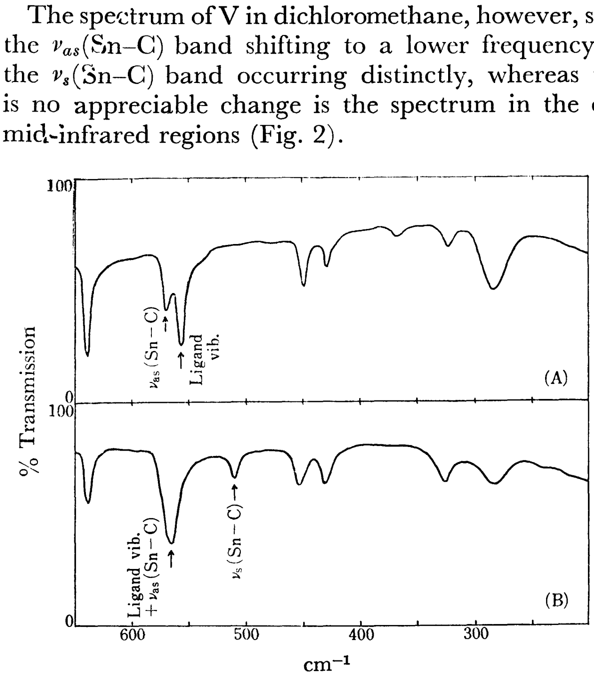
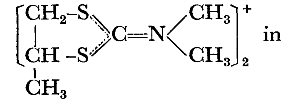


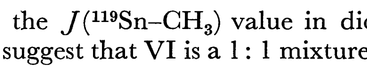
Fig. 2. Infrared spectra of $[(CH_3)_2 SnBr_4]^{2-}\cdot$



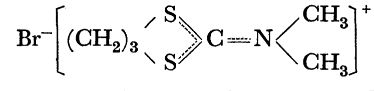
in Nujol (A) and in dichloromethane, 3 wt% (B).

These findings confirm that the $(CH_3)_2SnBr_4^{2-}$ dissociates partly into $(CH_3)_2SnBr_3^-$ and Br^-, and/or $(CH_3)_2SnBr_2$ and $2Br^-$. In view of the $J(^{119}Sn–CH_3)$ value of this compound in chloroform (Table 2), the predominant species may be the $(CH_3)_2SnBr_3^-$ rather than $(CH_3)_2SnBr_2$. The $(CH_3)_2SnI_4^{2-}$ anion of VII is assumed to dissociate similarly into $(CH_3)_2SnI_3^-$, $(CH_3)_2SnI_2$, and I^- in tetrachloroethane, judging from the $J(^{119}Sn–CH_3)$ value (Table 2).

Elemental analysis confirms that the reaction product between $(CH_3)_2Sn(dmdtc)_2$ and $Br(CH_2)_3Br$ has the composition VI, but it has no sharp melting point, even when the recrystallization is repeated. The infrared spectrum of this product in the solid state resembles closely that in solution; particularly, the intensity ratio of the two ν(Sn–C) bands dose not change from the solid state to that in solution. These observations and the $J(^{119}Sn–CH_3)$ value in dichloromethane (Table 2) suggest that VI is a 1 : 1 mixture of X and XI.



(X)



(XI)

There is a remarkable difference in the infrared spectra of IXa between in the solid state and in solution. The spectrum in dichloromethane shows two each of the ν(Sn–C) and ν(Sn–Cl) bands, which are close in frequency to those of III and IV. In the solid state, however, it gives only one broad band due to ν(Sn–Cl), at a very low frequency, and two ν(Sn–C) bands. as is shown in Fig. 3. This indicates that the

---

[8] F. W. B. Einstein and B. R. Penfold, *Chem. Commun.*, **1966**, 780.

[9] J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.*, **83**, 3903 (1961).

[10] H. A. Bent, *Can. J. Chem.*, **38**, 1235 (1960); *Chem. Rev.*, **61**, 275 (1961); *J. Inorg. Nucl. Chem.*, **19**, 43 (1961).

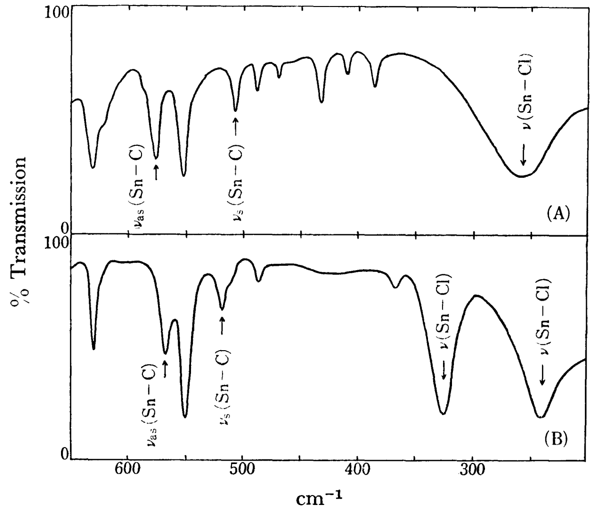
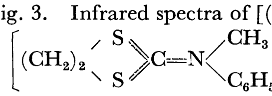


Fig. 3. Infrared spectra of $[(CH_3)_2 SnCl_3]^-\cdot$



$$\left[(CH_2)_2\langle {}^{S}_{S} \rangle C{=}N\langle {}^{CH_3}_{C_6H_5} \right]^+$$

in Nujol (A) and in dichloromethane, 3 wt% (B).

structure of the $(CH_3)_2SnCl_3^-$ ion of IXa in the solid state differs from that in solution, and that it is probably a distorted penta-coordinate.

It may be concluded, from above considerations, that the $(CH_3)_2SnX_4^{2-}$ ions are likely to dissociate into $(CH_3)_2SnX_3^-$ and X^-, and/or partly into $(CH_3)_2SnX_2$ and $2X^-$, even in less polar solvents, such as dichloromethane, and that, therefore, in solution the formation of dimethyltin trihalide anions is more likely than that of the tetrahalides. The electronic spectra of the present 1,3-dithiacycloalkyl-2-dimethylimminium compounds are now under investigation by the authors.

Experimental

Materials. The $(CH_3)_2Sn(dmdtc)_2$ was prepared as has previously been described.[11] The $(CH_3)_2Sn(mpdtc)_2$ was similarly synthesized by the reaction of $(CH_3)_2SnCl_2$ with sodium *N*-methyl-*N*-phenyldithiocarbamate in ethanol; mp 200°C (decomp.).

Found: C, 41.71; H, 4.41; N, 5.34%. Calcd for $C_{18}H_{22}N_2S_4Sn$: C, 42.07; H, 4.32; N, 5.46%.

NMR in dichloromethane: τ(Sn-CH$_3$), 8.55(singlet); τ(N-CH$_3$), 6.37(singlet); τ(C$_6$H$_5$), 2.72(multiplet) ppm; J(^{119}Sn-CH$_3$), 84 Hz. The dihalogenoalkanes used in this experiment are commercially available, except for $I(CH_2)_3I$, which was obtained by the reaction of $Br(CH_2)_3Br$ with NaI in acetone.[12]

General Procedure of the Reactions. The dithiocarbamate complexes of tin(IV) were allowed to react with an excess of dihalogenoalkanes at elevated temperature, without any solvent and under dry nitrogen.

1,3-Dithiacyclohexyl-2-dimethylimminium-dimethyltin Trichloride (III). A solution of $(CH_3)_2Sn(dmdtc)_2$ (3.2 g) in 1,3-dichloropropane (20 m*l*) was refluxed for 3 hr. After the evaporation of an excess of 1,3-dichloropropane under reduced pressure, the resulting solid was repeatedly washed with carbon tetrachloride, and then recrystallized from acetonitrile to give colorless needles (1.0 g, 30% yield); mp 169°C.

Found: C, 23.75; H, 4.61; N, 3.58%. Calcd for $C_8H_{18}NS_2Cl_3Sn$: C, 23.03; H, 4.35; N, 3.36%.

1,3-Dithiacycloheptyl-2-dimethylimminium-dimethyltin Trichloride (IV). A solution of $(CH_3)_2Sn(dmdtc)_2$ (5.0 g) in 1,4-dichlorobutane (20 m*l*) was kept at a temperature of about 120°C for 3 hr. A procedure similar to that used in the case of III and recrystallization from a dichloromethane-petroleum ether mixture yielded colorless needles (1.0 g, 10% yield); mp 56—59°C.

Found: C, 24.87; H, 5.07%. Calcd for $C_9H_{20}NS_2Cl_3Sn$: C, 25.06; H, 4.67%.

Bis(1,3-dithia-4-methylcyclopentyl-2-dimethylimminium)-dimethyltin Tetrabromide (V). A solution of $(CH_3)_2Sn(dmdtc)_2$ (5.0 g) in 1,2-dibromopropane (20 m*l*) was heated to 120°C for 20 min to liberate a white precipitate. After the solution had then been cooled to room temperature, the precipitate V was filtered off and recrystallized from acetonitrile (6.8 g, 70% yield); mp 125—128°C.

Found: C, 20.93; H, 3.86; N, 3.48%. Calcd for $C_{14}H_{30}N_2S_4Br_4Sn$: C, 21.21; H, 3.81; N, 3.53%.

1,3-Dithiacyclohexyl-2-dimethylimminium-bromide (X) and -dimethyltin Tribromide (XI). A solution of $(CH_3)_2Sn(dmdtc)_2$ (5.0 g) in 1,3-dibromopropane (20 m*l*) was treated in a manner similar to that used in the case of V to give a white precipitate of a 1 : 1 mixture of X and XI. Recrystallization from acetonitrile yielded the same mixture (8.3 g, 80% yield).

Found: C, 20.62; H, 3.95; N, 3.42%. Calcd for $C_{14}H_{30}N_2S_4Br_4Sn$: C, 21.21; H, 3.81; N, 3.53%.

Bis(1,3-dithiacyclohexyl-2-dimethylimminium)-dimethyltin Tetraiodide (VII). A mixture of $(CH_3)_2Sn(dmdtc)_2$ (2.0 g) and 1,3-diiodopropane (3 m*l*) was heated at 130°C for 2 hr. After subsequent cooling to room temperature, an excess of 1,3-diiodopropane was filtered out; the solid product thus obtained was recrystallized from a dichloromethane-petroleum ether mixture to give colorless needles VII (4.6 g, 90% yield); mp 143—146°C.

Found: C, 16.76; H, 3.20; N, 2.67%. Calcd for $C_{14}H_{30}N_2S_4I_4Sn$: C, 17.14; H, 3.08; N, 2.85%.

Reaction of $(CH_3)_2Sn(dmdtc)_2$ with $Cl(CH_2)_2Cl$. A solution of $(CH_3)_2Sn(dmdtc)_2$ (5.3 g) in 1,2-dichloroethane was refluxed for 1 hr to give a white precipitate. After the mixture had then been cooled to room temperature, the precipitate VIIIa was filtered off, washed with diethyl ether, and dried *in vacuo* (1.2 g, 53% yield); mp 230°C (decomp.).

Found: C, 55.16; H, 5.34; N, 6.99%. Calcd for $C_{18}H_{20}N_2S_4$: C, 55.07; H, 5.13; N, 7.14%. The filtrate was evacuated under reduced pressure, and a light yellow viscous liquid thus obtained was shaken repeatedly with diethyl ether; the resulting insoluble materials in ether were collected by filtration and washed with carbon tetrachloride, giving a white powder IXa (1.9 g, 39% yield); mp 84—87°C.

Found: C, 30.87; H, 3.79; N, 2.89%. Calcd for $C_{12}H_{18}NS_2Cl_3Sn$: C, 30.97; H, 3.90; N, 3.01%.

*Propylene Bis(*N*-methyl-*N*-phenyldithiocarbamate) (VIIIb).* A solution of $(CH_3)_2Sn(mpdtc)_2$ (5.0 g) in 1,3-dichloropropane (20 m*l*) was heated on a bath at 120°C for 2 hr. After it had then been cooled to room temperature, the solution was evaporated to about a half volume under reduced pressure; the white precipitates which appeared were collected by filtration, and subsequent recrystallization from a dichloromethane - diethyl ether mixture gave colorless needles VIIIb (1.2 g, 37% yield); mp 169°C.

Found: C, 55.97; H, 5.33; N, 6.88%. Calcd for $C_{19}H_{22}N_2S_4$: C, 56.12; H, 5.45; N, 6.89%.

*Butylene Bis(*N*-methyl-*N*-phenyldithiocarbamate) (VIIIc).* This compound was obtained from $(CH_3)_2Sn(mpdtc)_2$ (5.1 g) and 1,4-dichlorobutane (20 m*l*) in a manner similar to that

---

[11] M. Honda, M. Komura, Y. Kawasaki, T. Tanaka, and R. Okawara, *J. Inorg. Nucl. Chem.*, **30**, 3231 (1968).

[12] H. Finkelstein, *Ber.*, **43**, 1528 (1910).

used in the case of VIIIb, and it was recrystallized from the same solvent (1.3 g, 38% yield); mp 135—137°C.

Found: C, 57.12; H, 5.80; N, 6.80%. Calcd for $C_{20}H_{24}N_2S_4$: C, 57.10; H, 5.75; N, 6.66%.

All the compounds isolated were identified by means of their NMR spectra, as are listed in Table 2.

Infrared and NMR Spectra. The infrared spectra were recorded on Hitachi EPI-2G (5000—400 cm^{-1}) and EPI-L (700—200 cm^{-1}) spectrophotometers. The NMR spectra were measured on a Japan Electron JNM-3H-60 spectrometer, operating at 60 MHz and at room temperature, and using tetramethylsilane as the internal standard.