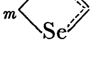
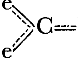
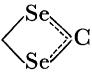
BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 489—491 (1972)

# Reactions of Dibromoalkanes with Dimethyltin Bis(*N*,*N*-dimethylthioseleno- and diselenocarbamates) and Related Compounds

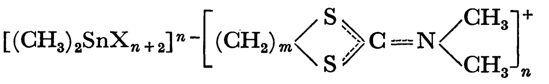
Koji Tanaka and Toshio Tanaka

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

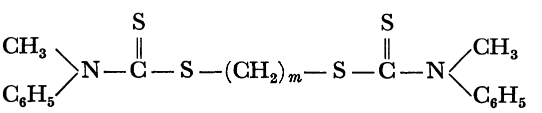
(Received August 11, 1971)

Dimethyltin-bis(*N*,*N*-dimethylthioselenocarbamate), $(CH_3)_2Sn[SSeCN(CH_3)_2]_2$, dimethyltin-bis(*N*,*N*-dimethyldiselenocarbamate), $(CH_3)_2Sn[Se_2CN(CH_3)_2]_2$, and dimethyltin-bis(*N*-methyl-*N*-phenyldiselenocarbamate), $(CH_3)_2Sn[Se_2CN(CH_3)(C_6H_5)]_2$, react with dibromoalkanes to give bis(1-thia-3-selenacycloalkyl-2-dimethylimminium)dimethyltin tetrabromide, $[(CH_3)_2SnBr_4]^{2-}[(CH_2)_m$  $C{=}N(CH_3)_2]_2^+$ ($m=2$, 3), 1,3-diselenacycloalkyl-2-dimethylimminium dimethyltin bromides, $[(CH_3)_2SnBr_{n+2}]^{n-}[(CH_2)_m$  $C{=}N(CH_3)_2]_n^+$ ($n=1$, $m=2$ and $n=2$, $m=3$), and 1,3-diselenacyclopentyl-2-methylphenylimminium bromide, $[(CH_2)_2$  $C{=}N\text{-}(CH_3)(C_6H_5)]^+Br^-$, respectively. The infrared and PMR spectra indicate that the positive charges of 1-thia-3-selena- and 1,3-diselenacycloalkylimminium ions are more delocalized in the higher homologs than in the lower ones.

We have previously reported on the reactions of dihalogenoalkanes with *N*,*N*-dimethyldithiocarbamate and *N*-methyl-*N*-phenyldithiocarbamate complexes of tin(IV), $(CH_3)_2Sn[S_2CN(CH_3)_2]_2$ and $(CH_3)_2Sn[S_2CN(CH_3)(C_6H_5)]_2$.[1,2] The main products of these reactions are 1,3-dithiacycloalkyl-2-dimethylimminium salts (I) and alkylene bis(*N*-methyl-*N*-phenyldithiocarbamate) (II) respectively, depending on the sort of reactant.


(I)

($n=1$ or 2; $m=2$, 3, or 4; X=Cl, Br, or I)


$$\genfrac{}{}{0pt}{}{CH_3}{C_6H_5}\!\!>N-\overset{\overset{S}{\|}}{C}-S-(CH_2)_m-S-\overset{\overset{S}{\|}}{C}-N\!<\!\genfrac{}{}{0pt}{}{CH_3}{C_6H_5}$$
(II)

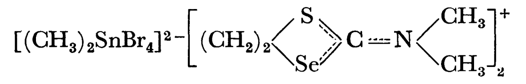
($m=2$, 3, or 4)

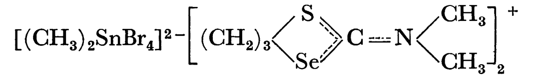
1,3-Dithiacycloalkylimminium ions are considered to be intermediates in the formation of ethylene bis(*N*,*N*-disubstituted-dithiocarbamate).[2,3]

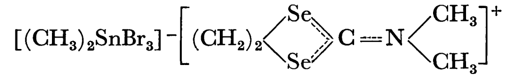
Recently, one of the present authors synthesized some *N*,*N*-dialkylthioseleno-[4] and *N*,*N*-dialkyldiselenocarbamate[5] complexes of tin(IV). The purpose of this paper is to study the reaction of dibromoalkanes with dimethyltin-bis(*N*,*N*-dimethylthioselenocarbamate), $(CH_3)_2Sn[SSeCN(CH_3)_2]_2$, -bis(*N*,*N*-dimethyldiselenocarbamate), $(CH_3)_2Sn[Se_2CN(CH_3)_2]_2$, and -bis(*N*-methyl-*N*-phenyldiselenocarbamate), $(CH_3)_2Sn[Se_2CN(CH_3)(C_6H_5)]_2$ (abbreviated as $(CH_3)_2Sn(dmtsc)_2$, $(CH_3)_2Sn(dmdsc)_2$ and $(CH_3)_2Sn(mpdsc)_2$ respectively).

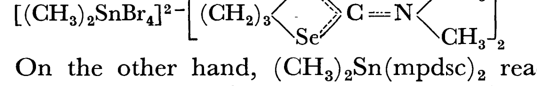
## Results and Discussion

The reactions of $Br(CH_2)_nBr$ ($n=2$, 3) with $(CH_3)_2(dmtsc)_2$ give bis(1-thia-3-selenacycloalkyl-2-dimethylimminium)dimethyltin tetrabromide (III) and (IV), and $(CH_3)_2Sn(dmdsc)_2$ reacts with $Br(CH_2)_nBr$ ($n=2$, 3) to yield 1,3-diselenacycloalkyl-2-dimethylimminiumdimethyltin tribromide and tetrabromide, (V) and (VI):


(III)


(IV)


(V)


(VI)

On the other hand, $(CH_3)_2Sn(mpdsc)_2$ reacts with $Br(CH_2)_2Br$ to preferentially give 1,3-diselenacyclopentyl-2-methylphenylimminium bromide (VII):

---

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

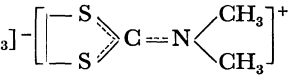
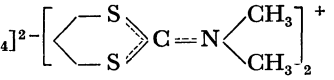
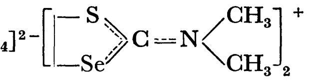
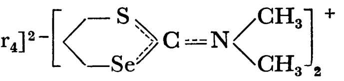
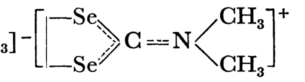
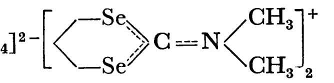
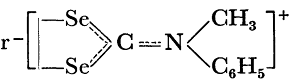
2) T. Tanaka, K. Tanaka, and T. Yoshimitsu, This Bulletin, **44**, 112 (1971).

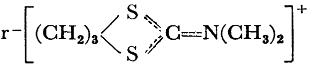
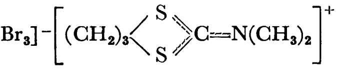
3) T. Nakai, Y. Ueno, and M, Okawara, *Tetrahedron Lett.*, **1967**, 3831; This Bulletin, **43**, 156 (1970).

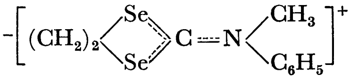
4) T. Kamitani and T. Tanaka, *Inorg. Nucl. Chem. Lett.*, **6**, 91 (1970).

5) T. Kamitani, H. Yamamoto, and T. Tanaka, *J. Inorg. Nucl. Chem.*, **32**, 2671 (1970).

TABLE 1. RELEVANT INFRARED FREQUENCIES ($cm^{-1}$) OF 1,3-DICHALCOGENACYCLOALKYL-2-DIMETHYLIMMINIUM DIMETHYLTIN BROMIDES AND THE RELATED COMPOUNDS[a, b)]

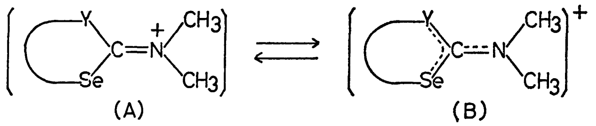
| Compound | | ν(C=N) | $\nu_{as}$(Sn-C) | $\nu_s$(Sn-C) | ν(Sn-Br) |
|---|---|---|---|---|---|
| (Ia) | $[(CH_3)_2SnBr_3]^-$  | 1587 s | 559 s | 511 s | 215 s |
| (Ib)[c)] | $[(CH_3)_2SnBr_4]^{2-}$  | 1538 s | 568m | 505m | 210 s |
| (III) | $[(CH_3)_2SnBr_4]^{2-}$  | 1588 s | 562 s | — | 214 s |
| (IV) | $[(CH_3)_2SnBr_4]^{2-}$  | 1538 s | 561 s | — | 215 s |
| (V) | $[(CH_3)_2SnBr_3]^-$  | 1574 s | 566 s | 511 s | 216 s |
| (VI) | $[(CH_3)_2SnBr_4]^{2-}$  | 1554 s | 564 s | — | ? |
| (VII) | $Br^-$  | 1520 s | — | — | — |

a) Nujol mull. b) The abbreviations used in this table are as follows: s, strong; m, medium. c) This compound is an equimolar mixture of $Br^-$  and $[(CH_3)_2SnBr_3]^-$  .

$Br^-$  (VII)

This is in contrast to the reaction of dimethyltin bis(*N*-methyl-*N*-phenyldithiocarbamate) with $Cl(CH_2)_2Cl$, which yields ethylene bis(*N*-methyl-*N*-phenyldithiocarbamate), besides 1,3-dithiacyclopentyl-2-methylphenylimminium salt.[2)] The difference between these two reactions seems to result from the different solubilities of 1,3-diselena- and 1,3-dithiacyclopentyl-2-methylphenylimminium salts, which are intermediates in the production of ethylene bis(*N*-methyl-*N*-phenylcarbamate) in the 1,2-dihalogenoethane used as the solvent.

The relevant infrared frequencies of the compounds obtained here are listed in Table 1, together with those of the related 1,3-dithiacycloalkyl-2-dimethylimminium compounds. These 1,3-dichalcogenacycloalkylimminium ions exhibit the ν(C=N) bands at relatively high frequencies, suggesting an appreciable double-bond character of the C=N bond. The ν(C=N) frequencies of IV and VI, with the six-membered rings, are lower than those of III and V, which contain the five-membered ring. This tendency may reflect the fact that the higher homologs are more contributed from the canonical structure (B) than from (A), similar to the case of the 1,3-dithiacycloalkyl-2-dimethylimminium cation described in a previous paper.[2)]



(A) (B)

(Y = S or Se)

The ν(C=N) band of VII appears at a frequency considerably lower than those of the other 1,3-dichalcogenacyclopentyl-2-dimethylimminium salts, (III and V). This may be interpreted as indicating the decreasing double-bond character of the C=N bond conjugated with the phenyl group.

As is shown in Table 1, the $(CH_3)_2SnBr_3^-$ ion of V exhibits both asymmetric and symmetric ν(Sn–C) bands, while the $(CH_3)_2SnBr_4^{2-}$ ions of III, IV, and VI show only the asymmetric one. This is consistent with the previous report;[2)] the former is a trigonal bipyramid with two methyl groups located in equatorial positions, while the latter is an octahedron with an almost linear C–Sn–C moiety.

In the PMR spectra, the N–$CH_3$ proton signals of the

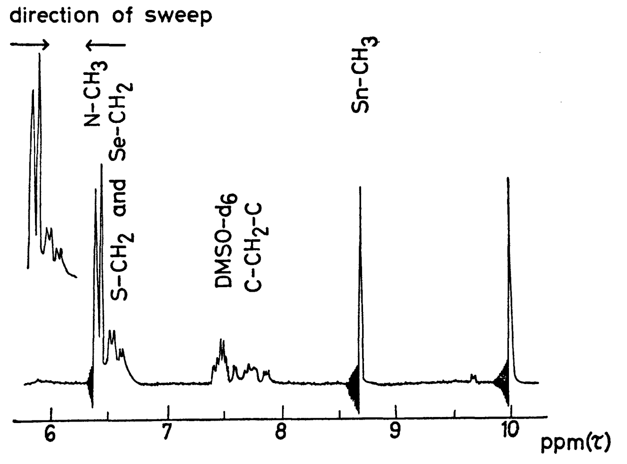


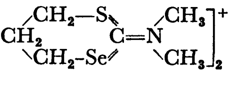
Fig. 1. PMR spectrum $[(CH_3)_2SnBr_4]^{2-}$  in DMSO-$d_6$, 7 wt%.

Table 2. Proton chemical shifts (τ, ppm) and spin-spin coupling constants (Hz) of 1,3-dichalcogenacycloalkyl-2-dimethylimminium dimethyltin bromides and the related compound in DMSO-$d_6$[a)]

| Compound | $\tau$(Sn-CH$_3$) | $\tau$(C-CH$_2$-C) | $\tau$(S-CH$_2$-) and/or $\tau$(Se-CH$_2$-) | $\tau$(N-CH$_3$) | $J$($^{77}$Se-CH$_2$-) | $J$(CH$_2$-CH$_2$-) | $J$($^{119}$Sn-CH$_3$) |
|---|---|---|---|---|---|---|---|
| (Ia) | 8.70 s | — | 5.92 s | 6.44 s | — | — | 114 |
| (Ib) | 8.70 s | 7.78 q | 6.56 s | 6.46 s | — | 7.0 | 114 |
| (III) | 8.71 s | — | 5.86 s [b)] | 6.45 s<br>6.40 s | 10.5 | — | 114 |
| (IV) | 8.70 s | 7.66 s | 6.53 t<br>6.56 t | 6.46 s<br>6.41 s | c) | 6.0 | 114 |
| (V) | 8.70 s | — | 5.78 s | 6.41 s | 10.5 | — | 114 |
| (VI) | 8.70 s | 7.70 q | 6.59 t | 6.42 s | c) | 7.2 | 114 |
| (VII) | — | — | 5.78m | 6.09 s | c) | — | — |

a) The abbreviations used in this table are as follow: s, singlet; t, triplet; q, quintet; m, multiplet.
b) The S-CH$_2$- and Se-CH$_2$- protons were almost magnetically equivalent, resulting in a slightly broad singlet.
c) Not observed for the main signal being multiplet.

1-thia-3-selenacycloalkyl-2-dimethylimminium ion (III and IV) occur as a doublet at room temperature, because the rotation about the C⩵N bond is hindered. The lower-field signal is lower and broader than the higher one (Fig. 1). The former may be assigned to the CH$_3$ protons *trans* to the selenium atom with respect to the C⩵N bond, since the $^{77}$Se (I=1/2, natural abundance 7.58%) could couple more strongly with the *trans*-CH$_3$ protons than with the *cis*-CH$_3$ protons, resulting in a decrease in the height and a broadening of the CH$_3$ proton signal.[4)] As is shown in Table 2, the N—CH$_3$ proton chemical shifts of III are practically in agreement with those of 1,3-dithiacyclopentyl-2-dimethylimminium salt (Ia) and the diselena derivative (V). Quite similarly, the N-CH$_3$ proton spectrum of IV is observed to be a superposition of those of 1,3-dithiacyclohexyl-2-dimethylimminium salt (Ib) and the diselena derivative (VI). The 4- and 6-CH$_2$ proton signals of Ib and VI are a simple triplet due to spin-spin coupling with the 5-CH$_2$ protons, but those of IV shows a doublet of triplets (Fig. 1), although a pair of the lowest signals are concealed by the N-CH$_3$ proton signals. In addition, the 5-CH$_2$ proton signals occur as a complicated multiplet. These results may be due to different magnetic environments of the 4- and 6-CH$_2$ protons attached to the selenium and sulfur atoms respectively.

The $J$($^{119}$Sn-CH$_3$) value of $(CH_3)_2SnBr_3^-$ and $(CH_3)_2SnBr_4^{2-}$ in DMSO-$d_6$ is in agreement with that of $(CH_3)_2SnBr_2$ in the same solvent,[6),7)] which is known to exist as an octahedral complex ion of $(CH_3)_2Sn(DMSO\text{-}d_6)_4^{2+}$.

## Experimental

$(CH_3)_2Sn(dmtsc)_2$,[4)] $(CH_3)_2Sn(dmdsc)_2$,[5)] and $(CH_3)_2Sn(mpdsc)_2$[5)] were prepared elsewhere, while the dihalogenoalkanes are commercially available. The general procedure for the reactions was the same as has been described in the previous paper.[2)]

*Bis(1-thia-3-selenacyclopentyl-2-dimethylimminium)-dimethyltin Tetrabromide (III).* A solution of $(CH_3)_2Sn(dmtsc)_2$ (3.0 g) in 1,2-dibromoethane (20 m*l*) was stirred at 100°C for 10 min to give a yellow precipitate. After the solution had then been cooled to room temperature, the precipitate (III) was filtered off and recrystallized from acetonitrile (4.8 g, 90% yield); mp 146—149°C.

Found: C, 16.71; H, 3.37; N, 3.34%. Calcd for $C_{12}H_{26}N_2S_2Se_2Br_4Sn$: C, 16.78; H, 3.06; N, 3.27%.

*Bis(1-thia-3-selenacyclohexyl-2-dimethylimminium)-dimethyltin Tetrabromide (IV).* A solution of $(CH_3)_2Sn(dmtsc)_2$ (3.0 g) in 1,3-dibromopropane (20 m*l*) was kept at a temperature of about 100°C for 1 hr in order to liberate a yellow precipitate. Recrystallization from acetonitrile then yielded light yellow crystals of IV (4.6 g, 85% yield); mp 104—106°C.

Found: C, 18.65; H, 3.54; N, 3.12%. Calcd for $C_{14}H_{30}N_2S_2Se_2Br_4Sn$: C, 18.96; H, 3.42; N, 3.16%.

*1,3-Diselenacyclopentyl-2-dimethylimminium-dimethyltin Tribromide (V).* A solution of $(CH_3)_2Sn(dmdsc)_2$ (5.0 g) in 1,2-dibromoethane (20 m*l*) had been stirred for 1 hr at 100°C and then filtered; the solid product thus obtained was recrystallized from acetonitrile to give light yellow crystals of V (2.2 g, 65% yield); mp 157—159°C.

Found: C, 13.71; H, 2.58; N, 2.64%. Calcd for $C_{17}H_{16}NSe_2Br_3Sn$: C, 13.32; H, 2.54; N, 2.22%.

*Bis(1,3-diselenacyclohexyl-2-dimethylimminium)-dimethyltin Tetrabromide (VI).* A solution of $(CH_3)_2Sn(dmtsc)_2$ (2.0 g) in 1,3-dibromopropane (20 m*l*) was maintained for 1 hr at 100°C. After it had been cooled to room temperature, yellow solid product (VI) was filtered off and recrystallized from acetonitrile (2.2 g 65% yield); mp 132—133°C.

Found: C, 16.59; H, 2.95; N, 3.06%. Calcd for $C_{14}H_{30}N_2Se_4Br_4Sn$: C, 17.15; H, 3.09; N, 2.86%.

*1,3-Diselenacyclopentyl-2-methylphenylimminium Bromide (VII).* A solution of $(CH_3)_2Sn(mpdsc)_2$ (2.0 g) in 1,2-dibromoethane (20 m*l*) was stirred for 5 min at 100°C to give a yellow precipitate, which was then recrystallized from an acetonitrile-ether mixture to give pale yellow crystals of VIII (0.76 g 69% yield); mp 190—192°C.

Found: C, 31.38; H, 3.21; N, 3.69%. Calcd for $C_{10}H_{12}NSe_2Br$: C, 31.28; H, 3.15; N, 3.65%.

*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 at room temperature, using tetramethylsilane as the internal standard.

We are grateful to the Shinko Chemical Co., Ltd., for supplying the elemental selenium.

---

6) W. Kitching, *Tetrahedron Lett.* **1966**, 3689.
7) T. Tanaka, *Inorg. Chim. Acta*, **1**, 217 (1967).