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# On the Synthesis and the P.M.R. Spectra of (Methylthio) Methyl Germanes and Stannanes.

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*A new synthesis of the compounds* $(CH_3S)_nM(CH_3)_{4-n}$ *(*$M=Ge, Sn$*) is described and their p.m.r. spectra discussed. As well the chemical shift data as the coupling constants* $J_{Sn\text{-}C\text{-}H}$ *and* $J_{Sn\text{-}S\text{-}C\text{-}H}$ *reveal a certain degree of metal-sulphur π-bonding, increasing with increasing value of n. The data are also discussed in terms of relative contributions of four different canonical structures.*

## Introduction

In several previous reports the various parameters determining the chemical shift and indirect spin-spin coupling data in methylgermanium and methyltin compounds have been discussed.[1,2] An interesting problem remained however to be investigated. In the alkoxyalkyl silanes several authors have postulated (p-d) π-bonding in the Si-O-C bonds.[3,4] In organogermanium ant -tin compounds no direct evidence thereof has been advanced. It was therefore decided to study a series of compounds $(CH_3)_nM(X\text{-}CH_3)_{4-n}$ with $M=Ge$, Sn and $X=O$, N, S, as the latter atomic species are known to be possible π-binders. This research was confined to the methyl derivatives for the sake of simplicity in the p.m.r. spectra. This first report will treat only the methylthio compounds.

Several methods have been proposed in the literature to introduce the thiomethyl group on fourth group atoms:[5,6] (1) the reaction of lead mercaptide and $(CH_3)_nMX_{4-n}$, ($X=$halogen) in refluxing benzene or diethylether; (2) the inter-conversion of M-N and M-S bonds. $Me_3MNEt_2+MeSH \rightarrow Me_3MSMe+Et_2NH$.

All these reactions need reactants that are rather difficult to obtain. An attractive way to prepare (methylthio)methyl stannanes was described by Abel and Brady.[7] These authors start with a solution of the methyltin halide in water, to which a 5 per cent excess of methylmercaptan was added in an autoclave. The pressure attained is about 2 atmospheres. To this mixture there was added slowly and under vigorous stirring a solution of sodium hydroxide up to the neutralization point. The (methylthio)methyl stannane separates as a heavy oil and the yields obtained range from 70% to 30% in going from the trimethyl to the monomethyl derivative.

It is however also possible to synthetize these compounds by the alkaline method described above, but under atmospheric pressure. By changing the reaction conditions it was possible to raise the yields for all the reactions to 80% with respect to the methylmetal halide.

## Experimental Section

(a)*Synthesis of (thiomethyl)di- and trimethyl stannanes and germanes.* An appropriate quantity of the methyltin or methylgermanium halide is dissolved in a small volume of water. Methylmercaptan was carefully passed under atmospheric pressure into the solution, while this was slowly neutralized with sodium hydroxide solution (1 N). The methylmercaptan is readily absorbed under these conditions and a heavy oil deposits on the walls of the reaction flask.

(b) *Synthesis of (tris-thiomethyl)methyl germane.* As methyltrichloro germane is not sufficiently soluble in water a slightly modified procedure was elaborated. To the well stirred mixture of the methyltrihalo germane with water, sodium hydroxide pellets were added until all the germanium compound was dissolved. Then the mercaptan is passed through the solution while this is slowly acidified up to a $p_H$ of 4 to 5 by adding dilute hydrochloric acid solution (2 N).

(c) *Synthesis of (tris-thiomethyl)methyl stannane.* Although this compound can be synthetized by the methods outlined in section a, it is rather uncovenient to start with $CH_3SnCl_3$ which is somewhat difficult to prepare. It is therefore easier to start with a solution of $CH_3SnOO(CO_2)K$ in water which can be obtained without difficulty.[8] This solution is slightly alkaline and is treated with methylmercaptan until no more of the latter is absorbed. Neutralization of this solution during the treatment is unnecessary.

In each case these syntheses yield a heavy oil which was separated from the water layer and dried on anhydrous $MgSO_4$. Destillation under atmospheric pressure for $(CH_3)_3GeSCH_3$ and $(CH_3)_3SnSCH_3$, and in

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(1) D. F. Van de Vondel, *J. Organometal. Chem.*, 3, 400-405 (1965).

(2) E. V. Van den Berghe and G. P. Van der Kelen, *J. Organometal. Chem.*, 6, 515-521 (1966).

(3) H. A. Brune, *Chem. Ber.*, 97, 2829 (1964).

(4) T. Ostdick, P. A. McCusker, *Inorg. Chem.*, 6, 98 (1967).

(5) E. W. Abel, D. A. Armitage and D. B. Brady, *J. Organometal. Chem.*, 5, 130-135 (1966).

(6) J. Satgé and M. Lesbre, *Bull. Soc. Chim.*, France, p. 2578 (1965).

(7) E. W. Abel and D. B. Brady, *J. Chem. Soc.*, 1192 (1965).

(8) P. Pfeiffer, *Z. Anorg. Chem.*, 68, 106 (1910).

vacuo for the other compounds gives the pure substances. The purity and identity of the compounds could be derived from their p.m.r. spectra which showed the absence of H containing impurities. Whereas the (thiomethyl)methyl stannanes were already described, the (thiomethyl)methyl germanes are new compounds. The physical constants for the latter are given below:

$CH_3Ge(SCH_3)_3$
b.p. 130° C/15 mm $\delta_4^{20}$ : 1,39 $n_D^{20}$ : 1.5908

$(CH_3)_2Ge(SCH_3)_2$
b.p. 85° C/15 mm $\delta_4^{20}$ : 1,30 $n_D^{20}$ : 1.5470

$(CH_3)_3GeSCH_3$
b.p. 135° C/734 mm $\delta_4^{20}$ : 1,18 $n_D^{20}$ : 1.4792

(d) *Proton magnetic resonance spectra.* The p.m.r. spectra were recorded with a Varian V. 4300-B dual purpose spectrometer at a frequency of 56.4 MHz. Standard experimental conditions were published previously.[1] The chemical shift and coupling constant data are collected in Table I and are graphically presented in Figs. 1 and 2. The germanium compounds were studied as neat liquids. For the tin compounds only data obtained on chloroform solutions are presented. The satellite signals observed in the stannanes and caused by the electron coupled spin-spin interaction between the magnetically active tin isotopes $Sn^{117}$ and $Sn^{119}$ and the protons of the thiomethyl group, did not show the usual splitting for $Sn^{117}$ resp. $Sn^{119}$. Nevertheless these signals were relatively sharp and the coupling constant could be measured quite accurately.

Table I. P.m.r. spectra parameter for methyl(methylthio) stannanes and germanes

| | $\tau_{CH_3}$ | $\tau_{SCH_3}$ | $J_{C^{13}-H}$ | | $J_{Sn-C-H}$ | | $J_{Sn-S-C-H}$ |
|---|---|---|---|---|---|---|---|
| | | | $CH_3$ | $SCH_3$ | | | |
| $Me_3GeSMe$ | 9.61 | 8.09 | 128 | 140 | | | |
| $Me_2Ge(SMe)_2$ | 9.15 | 7.84 | 130 | 140 | | | |
| $MeGe(SMe)_3$ | 8.74 | 7.62 | 132 | 140 | | | |
| $Me_3SnSMe$ | 9.59 | 7.94 | 135 | 142.5 | 54 | 56.5 | 34.2 |
| $Me_2Sn(SMe)_2$ | 9.28 | 7.80 | 135 | 142.5 | 58.5 | 60.5 | 41.2 |
| $MeSn(SMe)_3$ | 9.03 | 7.68 | 135 | 142.5 | 64.5 | 66.5 | 51.7 |

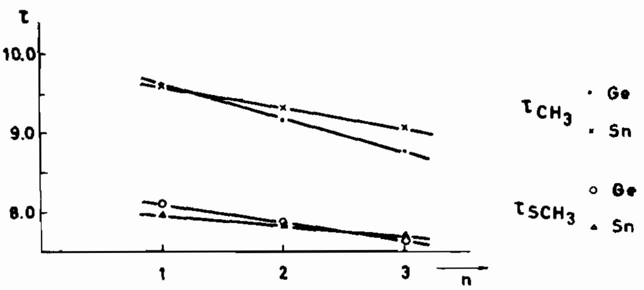


Figure 1. Values for $CH_3$ and $SCH_3$ protons as a function of n in $(CH_3S)_nM(CH_3)_{4-n}$. . Ge, x Sn.

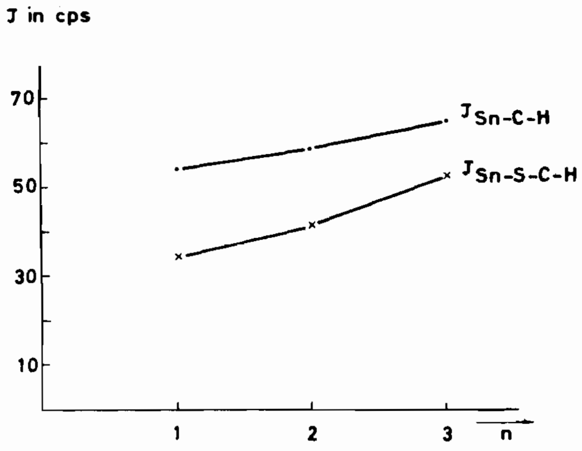


Figure 2. Coupling constants over two (.) and three (x) bonds as a function of n in $(CH_3S)_nSn(CH_3)_{4-n}$.

## Discussion of Results

(a) *Chemical shift data.* The downfield chemical shift of the methyl protons bonded to Ge and Sn increases with progressive introduction of thiomethyl groups. From the graphs in Fig. 1 it can be seen that the increase per thiomethyl group is constant for both Ge and Sn derivatives, but the increase is larger for the Ge than for the Sn compounds. The thiomethyl group being more electronegative than the methylgroup this sequence can be ascribed to the inductive effect.

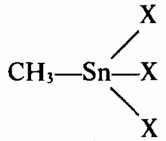
Similar observations are made for the thiomethyl proton chemical shifts. The chemical shift increases with increasing number of thiomethyl substituents, the increment per thiomethyl group is nearly constant and the changes observed in the spectra of the germanes are again larger than those observed for stannanes. This very slight but net decrease of electron density on the thiomethyl group protons can be explained by a corresponding increase of the formal charge on the central atom. In the case of the similar downfield shift of the α-proton resonance of the alkoxy group in alkoxyalkyl silanes $(C_2H_5O)_{4-n}Si(CH_3)_n$ Ostdick and McCusker[4] could prove, with the aid of simultaneous $Si^{29}$ n.m.r. measurements, that these shifts could be explained by a π-bonding contribution that exceeds the inductive effect. For the tin and germanium compounds studied in this work the steady decrease observed for the alkyl protons does not allow to draw an analogous conclusion. The decreasing trend however could be explained only by a slight π-bonding contribution, stimulated (back donation) by the formal charge on the central atom. The tin-sulphur bond will however also have a rather important diamagnetic anisotropy. The simultaneous influence of inductive effect and neighbour anisotropy contributions makes it rather difficult to draw any conclusion concerning the relative importance of (Sn-S) resp. (Ge-S) π-bonding and of other participations.

(b) *Coupling constants.* Due to the high spin quantum number and the quadrupole moment of Ge, it was not possible to observe coupling between Ge and H nuclei. In the germanium compounds only the $C^{13}$-$H^1$ couplings could be measured. For the tin compounds both $J_{Sn\text{-}C\text{-}H}$ and $J_{Sn\text{-}S\text{-}C\text{-}H}$ coupling constants were obtained from the spectra. For the latter however no separate signals for coupling with either $Sn^{117}$ and $Sn^{119}$ could be observed, the four signals collapsing to a relatively sharp and intense doublet.

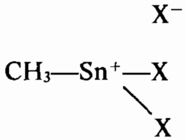
*The coupling over three bonds $J_{Sn\text{-}S\text{-}C\text{-}H}$.* First of all we discuss the tin-proton coupling over sulphur. The data of Table I show that regardless of the degree of substitution the coupling constant $J_{C^{13}\text{-}H}$ of the thiomethyl group proton signals remains unchanged. The electron density and the hybridization in the C-H bonds of the thiomethyl group therefore can be assumed to be unchanged by substitution.

On the other hand both $J_{Sn\text{-}C\text{-}H}$ and $J_{Sn\text{-}S\text{-}C\text{-}H}$ values increase with increasing number of thiomethyl groups (Fig. 2). With respect to the $J_{C^{13}\text{-}H}$ values of the thiomethyl group, the only obvious reason for the trend of the electron coupled spin-spin interaction over three bonds, could be an enhanced electron density in the Sn-S bond.

In a previous study of the p.m.r. spectra and the electrical dipole moments of the methylhalo stannanes contributions of resonance structures of the type C and D were proposed to explain the experimental data. It was shown that for substituents X,



(A)



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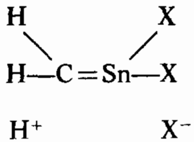
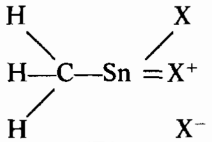


(C)



(D)

of lower electronegativity (iodides) the relative importance of type D contributions exceeded the contribution of type C structure. In the (methylthio)methyl stannanes obviously the same situation is encountered. The constant value of $J_{C^{13}\text{-}H}$ in the tin-compounds also furnishes evidence for the hypothesis that the increase of resonance contributions from type C structures is certainly of secondary importance. The conclusions drawn for the methyhalo stannanes were principally based on the variations of the partial Sn-X moment. It is therefore interesting to note that by two independent experimental methods the same conclusions are reached. Moreover the steady decrease of the τ-values for the thiomethyl group protons, which parallels the increase of $J_{Sn\text{-}S\text{-}C\text{-}H}$, can also be easily understood by these resonance contribution. The observations made in this report then parallel the conclusion reached by Ostdick and McCusker[4] for the methylmethoxy silanes. In the Si-O resp. Sn-S bond the π-bonding increases with increasing number of $OCH_3$ resp. $SCH_3$ groups.

*The coupling over two bonds $J_{Sn\text{-}C\text{-}H}$.* With respect to tetramethyl stannane the $J_{Sn\text{-}C\text{-}H}$ values show an increase of resp. 2, 6.5 and 12 cps on gradual introduction of thiomethyl groups. The latter being more electronegative than the methyl group these results are readily explained by the isovalent rehybridization theory of Bent,[9] i.e. the % s-character of the tin orbital used for bonding with carbon increases. A comparison of these values with those for the methyliodo stannanes[2] (increments resp. 4, 8 and 18 cps) shows that the thiomethyl group must have a lower electronegativity value than iodide. The curve for $J_{Sn\text{-}C\text{-}H}$ versus the number of $SCH_3$ groups is therefore less steep than the similar curve for iodide as a substituent and also less steep than the curve for $J_{Sn\text{-}S\text{-}C\text{-}H}$. This is another observation furnishing evidence for the assumption that the relative increase of the importance of resonance contributions of the type D is higher than this for type C contributions.

*The couplings $C^{13}$-H in the methyl groups bonded to either Sn or Ge.* Whereas the $J_{C^{13}\text{-}H}$ values for the methyl groups in the stannanes are constant within the limits of experimental accuracy, those for the germanes show a slight but distinctly observable increase with increasing number of thiomethyl groups. Simultaneously a steeper decrease of the shielding of the alkyl protons in the germanes versus the values observed in the stannanes is to be noted. Obiously, with relatively weak electronegative substituents, the type C contributions are relatively more important in the germanes than in the stannanes. It seems evident to explain the higher type D contributions by the assumption that tin is more easily polarized than germanium, whereas hyperconjugated structures of the type C would obviously be favored in the germanes where the central atom has less metallic character.

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(9) H. A. Bent, *J. Inorg. Nucl. Chem.*, *19*, 43 (1961).