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STUDIES IN GROUP IV ORGANOMETALLIC CHEMISTRY
XXII. SYNTHESIS OF TIN-GERMANIUM COMPOUNDS BY HYDROGENOLYTIC FISSION OF METAL(IV)-NITROGEN BONDS*

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INTRODUCTION

So far, few examples of compounds containing a Sn–Ge bond have been reported in the literature. Such compounds have been obtained by the interaction of triphenylgermyl–alkali compounds with a triorganotin halide[1,2] (reaction 1) or tin tetrahalide[3] (reaction 2):

$$(C_6H_5)_3GeM + R_3SnX \rightarrow (C_6H_5)_3Ge\text{–}SnR_3 + MX \qquad M = Na, K \qquad (1)$$

$$4(C_6H_5)_3GeLi + SnCl_4 \rightarrow [(C_6H_5)_3Ge]_4Sn + 4\ LiCl \qquad (2)$$

Tetrakis(triphenylgermyl)tin was difficult to isolate in a pure state, because of the occurrence of lithium–chlorine exchange[3]. The predominance of lithium–halogen exchange severely limits the applicability of this type of reactions to the synthesis of more complex Sn–Ge derivatives; *e.g.* from the reaction of triphenyltinlithium with germanium tetrachloride $(Ph_3Sn)_4Ge$ could be isolated in 4% yield only[3].

Recently the hydrogenolytic fission of tin–nitrogen bonds by organotin hydrides was recognized as an important synthetic tool for the preparation of compounds with Sn–Sn bonds[4]. By this method a number of well-defined polytin compounds has been prepared[5,6].

The present paper deals with the preparation of various types of compounds bearing one or more Sn–Ge bonds via hydrogenolysis-type reactions.

PROCEDURE AND DISCUSSION

Reactions of Ge–N bonds with organotin hydrides

Of various organotin nitrogen compounds studied, the rate of hydrogenolysis was found to be highest for (dialkylamino)tin derivatives[7]. Whereas trialkyltin diethylamides and triphenyltin hydride react exothermically, the reaction of tributylgermanium diethylamide and triphenyltin hydride proceeds only slowly in refluxing butyronitrile:

$$(C_4H_9)_3GeN(C_2H_5)_2 + (C_6H_5)_3SnH \rightarrow (C_4H_9)_3Ge\text{–}Sn(C_6H_5)_3 + HN(C_2H_5)_2 \qquad (3)$$

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The diminished reactivity of organogermanium nitrogen compounds is consistent with the occurrence of significant d_π–p_π interaction in the Ge–N as contrasted with the Sn–N bond. Bonding involving this interaction will stabilize the Ge–N bond and will make the free electron pair at the nitrogen atom less available. As already shown for organotin nitrogen compounds this availability is of great importance for the proceeding of the reaction.

In reactions of organotin dihydrides with germanium–nitrogen bonds diethylamino derivatives cannot be used due to the rapid decomposition of the organotin dihydride by diethylamine[8] formed in the reaction. We found that dimethylamine owing to its volatility does not interfere. The synthesis of pentabutylgermyltin monohydride has been achieved according to reaction (4). The progress of the reaction appears from the change in the IR spectrum of the position of the Sn–H absorption (replacement of the band at 1835 cm^{-1} by a band at 1780 cm^{-1}).

$$\underset{\nu(\text{Sn–H})\ 1835\ \text{cm}^{-1}}{(C_4H_9)_3GeN(CH_3)_2+(C_4H_9)_2SnH_2} \rightarrow \underset{\nu(\text{Sn–H})\ 1780\ \text{cm}^{-1}}{(C_4H_9)_3Ge\text{–}Sn(C_4H_9)_2H}+(CH_3)_2NH \quad (4)$$

This hydride may be catalytically decomposed in the presence of diethylamine yielding the linear tetrametal derivative:

$$2\,(C_4H_9)_3Ge\text{–}Sn(C_4H_9)_2H \xrightarrow{(C_2H_5)_2NH} (C_4H_9)_3Ge\text{–}Sn(C_4H_9)_2\text{–}Sn(C_4H_9)_2\text{–}Ge(C_4H_9)_3+H_2\uparrow \quad (5)$$

Similarly, the reaction of organotin hydrides with organotin alkoxides[9] is considerably faster than with organogermanium alkoxides, prolonged refluxing in butyronitrile being required for termination of the latter reaction.

Reactions of Sn–N bonds with organogermanium and organotin hydrides

General remarks on organogermanium hydride reactions. Both triethyl- and triphenyltin diethylamide react under relatively mild conditions with triphenylgermane:

$$R_3SnN(C_2H_5)_2+(C_6H_5)_3GeH \rightarrow R_3Sn\text{–}Ge(C_6H_5)_3+(C_2H_5)_2NH \quad (6)^*$$
$$R = C_2H_5,\ C_6H_5$$

The rate of reaction (6) was compared with that of the corresponding reaction of triphenyltin hydride by measuring the extinction of the Ge–H or Sn–H stretching frequency in the infrared spectrum at appropriate time intervals. Fig. 1 shows that triphenyltin hydride reacts about one thousand times faster than triphenylgermane and clearly illustrates the influence of the polarity of the solvent on the rate of hydrogenolysis with Ph_3GeH.

Whereas triphenylgermane does react with triethyltin diethylamide, the reaction with alkylgermanium hydrides does not proceed under comparative conditions.

The reaction of triphenylgermane with triethyltin (N-hexylformamide) and dibutyltin bis(N-phenylformamide) did not proceed with a measurable rate in refluxing butyronitrile (both compounds readily react with triphenyltin hydride[5]).

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* Contrary to organotin hydrides organogermanium hydrides are not catalytically decomposed by amines[10].

Apparently the lone electron pair at nitrogen in these compounds is not sufficiently available for the reaction to take place.

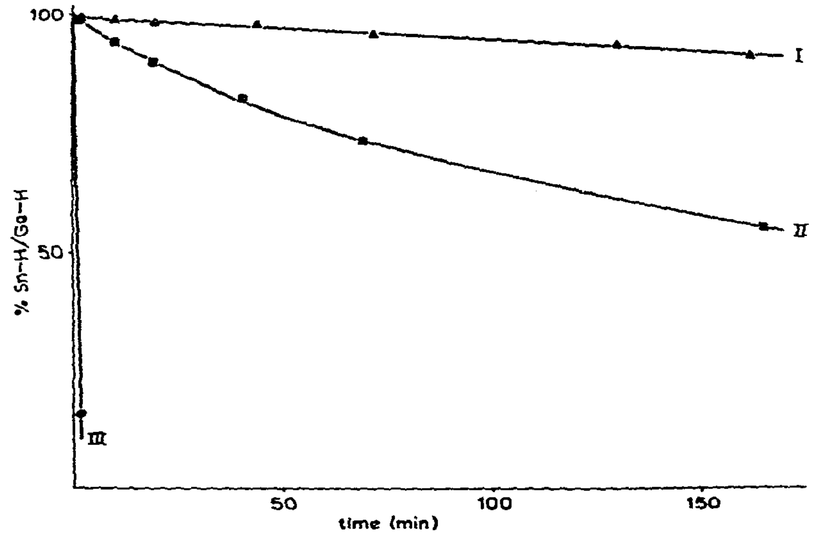


Fig. 1. I, Reaction of triethyltin diethylamide and triphenylgermane in cyclohexane at 20°; II, *idem*, in butyronitrile at 20°; III, triethyltin diethylamide and triphenyltin hydride in cyclohexane at 20°. For experimental details see ref. 7.

The observed solvent and substituent effects suggest that electrophilic attack of the organogermanium hydride hydrogen on nitrogen is involved. Thus the mechanism is likely to be identical with the one demonstrated for the corresponding organotin hydride reaction[7].

Synthesis of Sn–Ge derivatives by hydrogenolysis reactions. The reaction of a bis(dialkylamino)tin derivative with triphenylgermane in a 1 : 1 ratio affords a versatile intermediate (I) containing a Ge–Sn bond:

$$(C_2H_5)_2Sn[N(C_2H_5)_2]_2 + (C_6H_5)_3GeH \rightarrow$$
$$(C_6H_5)_3Ge\text{-}Sn(C_2H_5)_2\text{-}N(C_2H_5)_2 + (C_2H_5)_2NH$$
$$\text{(I)}$$

Reaction of (I) with protic species (*cf.* ref. 11) allows replacement of the diethylamino group by a variety of other functional groups. The Sn–Ge derivatives shown in eqn. (7) have been isolated:

$$\begin{array}{l} \\ (C_6H_5)_3Ge\text{-}Sn(C_2H_5)_2\text{-}N(C_2H_5)_2 \\ \text{(I)} \end{array} \begin{array}{l} \xrightarrow{\frac{1}{2}H_2O} [(C_6H_5)_3Ge\text{-}Sn(C_2H_5)_2\text{-}]_2O + (C_2H_5)_2NH \\ \xrightarrow{C_6H_5C\equiv CH} (C_6H_5)_3Ge\text{-}Sn(C_2H_5)_2\text{-}C\equiv CC_6H_5 + (C_2H_5)_2NH \\ \xrightarrow{C_6H_5OH} (C_6H_5)_3Ge\text{-}Sn(C_2H_5)_2\text{-}OC_6H_5 + (C_2H_5)_2NH \end{array} \quad (7)$$

Hydrogenolysis reactions of (I) with triphenyltin hydride and triphenylgermane led to compounds with three catenated metal atoms:

$$\mathrm{(I)+(C_6H_5)_3GeH \rightarrow (C_6H_5)_3Ge{-}Sn(C_2H_5)_2{-}Ge(C_6H_5)_3+(C_2H_5)_2NH}$$

$$\mathrm{(I)+(C_6H_5)_3SnH \rightarrow (C_6H_5)_3Ge{-}Sn(C_2H_5)_2{-}Sn(C_6H_5)_3+(C_2H_5)_2NH}$$

The reaction with organotin dihydrides gives complications as a result of diethylamine-catalyzed side reactions. As N-phenylformamide is inert towards organotin hydrides under the conditions applied[5], a transamination reaction[12,13] of (I) with N-phenylformamide was carried out and the resulting product (II) used for further syntheses:

$$\begin{array}{l}\mathrm{(C_6H_5)_3Ge{-}Sn(C_2H_5)_2{-}N(C_2H_5)_2+HN(C_6H_5)C(O)H \rightarrow} \\ \qquad\qquad \mathrm{(C_6H_5)_3Ge{-}Sn(C_2H_5)_2{-}N(C_6H_5)C(O)H+(C_2H_5)_2NH} \\ \qquad\qquad\qquad\qquad \mathrm{(II)}\end{array}$$

Reaction of (II) with diorganotin dihydrides in a 2:1 molar ratio affords linear penta-metal derivatives:

$$\begin{array}{l}\mathrm{2(II)+R_2SnH_2 \rightarrow} \\ \mathrm{(C_6H_5)_3Ge{-}Sn(C_2H_5)_2{-}SnR_2{-}Sn(C_2H_5)_2{-}Ge(C_6H_5)_3+2\ HN(C_6H_5)C(O)H} \\ \qquad\qquad\qquad\qquad\qquad\qquad \mathrm{R=C_2H_5,\ C_6H_5}\end{array}$$

From a 1:1 reaction of (II) and diphenyltin dihydride a trimetal monohydride was obtained, which upon catalytic decomposition yielded a linear hexa-metal derivative:

$$\mathrm{(II)+(C_6H_5)_2SnH_2 \rightarrow (C_6H_5)_3Ge{-}Sn(C_2H_5)_2{-}Sn(C_6H_5)_2H+HN(C_6H_5)C(O)H}$$

$$\begin{array}{l}\mathrm{2\,(C_6H_5)_3Ge{-}Sn(C_2H_5)_2{-}Sn(C_6H_5)_2H \xrightarrow{(C_2H_5)_2NH}} \\ \mathrm{(C_5H_5)_2Ge{-}Sn(C_2H_5)_2{-}Sn(C_6H_5)_2{-}Sn(C_6H_5)_2{-}Sn(C_2H_5)_2{-}Ge(C_6H_5)_3+H_2\uparrow}\end{array}$$

Similar reactions were realised with diphenyltin bis(diethylamide), yielding fully arylated products. For example:

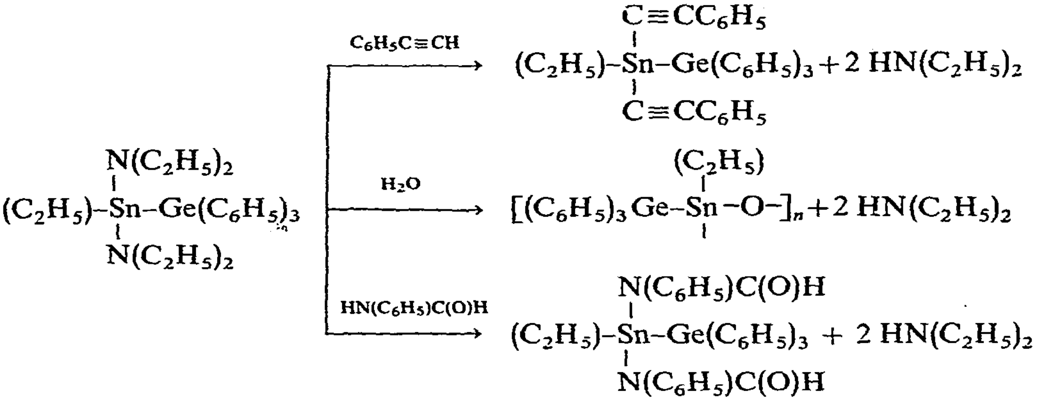
$$\begin{array}{l}\mathrm{(C_6H_5)_3GeH+(C_6H_5)_2Sn[N(C_2H_5)_2]_2 \rightarrow} \\ \qquad\qquad \mathrm{(C_6H_5)_3Ge{-}Sn(C_6H_5)_2{-}N(C_2H_5)_2+HN(C_2H_5)_2} \\ \mathrm{(C_6H_5)_3Ge{-}Sn(C_5H_5)_2{-}N(C_2H_5)_2+H_2O \rightarrow} \\ \qquad\qquad \mathrm{(C_6H_5)_3Ge{-}Sn(C_6H_5)_2{-}OH+HN(C_2H_5)_2} \\ \mathrm{(C_6H_5)_3Ge{-}Sn(C_6H_5)_2{-}N(C_2H_5)_2+HC{\equiv}CC_6H_5 \rightarrow} \\ \qquad\qquad \mathrm{(C_6H_5)_3Ge{-}Sn(C_6H_5)_2{-}C{\equiv}CC_6H_5+HN(C_2H_5)_2}\end{array}$$

It appeared from infrared studies that upon reaction of ethyltin tris(diethylamide) with triphenylgermane one or two diethylamino groups are readily split off. Although model studies show that no steric effect is involved, the third one is cleaved only with difficulty and tris(triphenylgermyl)ethyltin was isolated in 3% yield only.

$$\begin{array}{l}\mathrm{(C_2H_5)Sn[N(C_2H_5)_2]_3+3\ (C_6H_5)_3GeH \rightarrow} \\ \qquad\qquad \mathrm{(C_2H_5)Sn[Ge(C_6H_5)_3]_3+3\ HN(C_2H_5)_2}\end{array}$$

It was possible to isolate the intermediate with one Sn–Ge bond from the

1:1 reaction between triphenylgermane and ethyltin tris(diethylamide). From this intermediate by reaction with water, phenylacetylene or N-phenylformamide the following compounds were prepared:



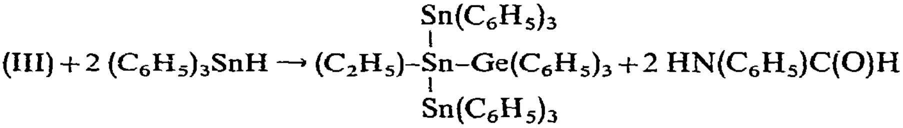
$$(C_2H_5)\text{-}\underset{N(C_2H_5)_2}{\overset{N(C_2H_5)_2}{Sn}}\text{-}Ge(C_6H_5)_3 \xrightarrow{C_6H_5C\equiv CH} (C_2H_5)\text{-}\underset{C\equiv CC_6H_5}{\overset{C\equiv CC_6H_5}{Sn}}\text{-}Ge(C_6H_5)_3 + 2\,HN(C_2H_5)_2$$

$$\xrightarrow{H_2O} [(C_6H_5)_3Ge\text{-}\overset{(C_2H_5)}{Sn}\text{-}O\text{-}]_n + 2\,HN(C_2H_5)_2$$

$$\xrightarrow{HN(C_6H_5)C(O)H} (C_2H_5)\text{-}\underset{N(C_6H_5)C(O)H}{\overset{N(C_6H_5)C(O)H}{Sn}}\text{-}Ge(C_6H_5)_3 + 2\,HN(C_2H_5)_2$$

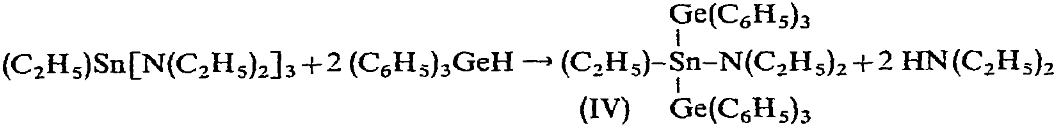
(III)

Reaction of compound (III) with two moles of triphenyltin hydride afforded a branched tetra-metal derivative:



$$(III) + 2\,(C_6H_5)_3SnH \rightarrow (C_2H_5)\text{-}\underset{Sn(C_6H_5)_3}{\overset{Sn(C_6H_5)_3}{Sn}}\text{-}Ge(C_6H_5)_3 + 2\,HN(C_6H_5)C(O)H$$

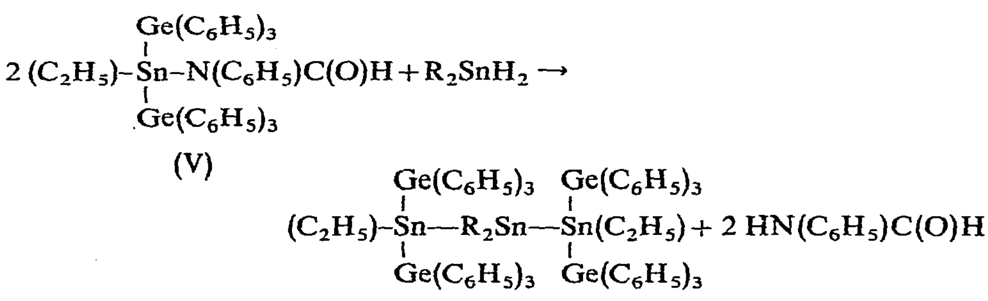
Reaction of the tris(amino)tin compound with triphenylgermane in a 1:2 ratio affords the mono(diethylamino) trimetal derivative (IV) a useful intermediate for further synthesis:



$$(C_2H_5)Sn[N(C_2H_5)_2]_3 + 2\,(C_6H_5)_3GeH \rightarrow (C_2H_5)\text{-}\underset{Ge(C_6H_5)_3}{\overset{Ge(C_6H_5)_3}{Sn}}\text{-}N(C_2H_5)_2 + 2\,HN(C_2H_5)_2$$

(IV)

Hydrolysis of (IV) yields the hydroxide or corresponding oxide, transamination of (IV) the corresponding N-phenylformamido derivative (V). Reactions of the latter with diorganotin dihydrides affords branched polymetal compounds. Reaction in a 2:1 ratio affords hepta-metal derivatives:



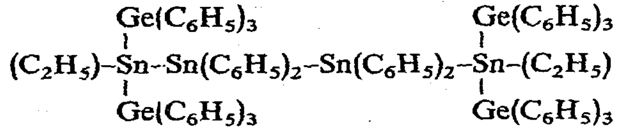
$$2\,(C_2H_5)\text{-}\underset{Ge(C_6H_5)_3}{\overset{Ge(C_6H_5)_3}{Sn}}\text{-}N(C_6H_5)C(O)H + R_2SnH_2 \rightarrow$$

(V)

$$(C_2H_5)\text{-}\underset{Ge(C_6H_5)_3}{\overset{Ge(C_6H_5)_3}{Sn}}\text{—}R_2Sn\text{—}\underset{Ge(C_6H_5)_3}{\overset{Ge(C_6H_5)_3}{Sn}}(C_2H_5) + 2\,HN(C_6H_5)C(O)H$$

(VA) $R = C_4H_9, C_6H_5$

The tetra-metal monohydride obtained by the 1 : 1 reaction of (V) with diphenyltin dihydride, spontaneously decomposes to the octa-metal derivative (VI).



$$(C_2H_5)\text{-}\underset{Ge(C_6H_5)_3}{\overset{Ge(C_6H_5)_3}{Sn}}\text{-}Sn(C_6H_5)_2\text{-}Sn(C_6H_5)_2\text{-}\underset{Ge(C_6H_5)_3}{\overset{Ge(C_6H_5)_3}{Sn}}\text{-}(C_2H_5) \qquad \text{(VI)}$$

Diphenylgermane, but not dibutylgermane is capable of effecting the hydrogenolytic fission of the tin–nitrogen bond. The reaction of triorganotin diethylamides with diphenylgermane in a 2 : 1 ratio affords tri-metal derivatives in good yield:

$$2\ R_3SnN(C_2H_5)_2 + (C_6H_5)_2GeH_2 \rightarrow R_3Sn\text{-}Ge(C_6H_5)_2\text{-}SnR_3 + 2\ HN(C_2H_5)_2$$
$$R = C_2H_5,\ C_6H_5$$

The earlier mentioned intermediate (I) and diphenylgermane in a 2 : 1 ratio afford a penta-metal derivative:

$$2\,\underset{\text{(I)}}{(C_6H_5)_3Ge\text{-}Sn(C_2H_5)_2\text{-}N(C_2H_5)_2} + (C_6H_5)_2GeH_2 \rightarrow$$
$$(C_6H_5)_3Ge\text{-}Sn(C_2H_5)_2\text{-}Ge(C_6H_5)_2\text{-}Sn(C_2H_5)_2\text{-}Ge(C_6H_5)_3 + 2\ HN(C_2H_5)_2$$

Polymeric products containing alternating germanium and tin atoms in the chain have been synthesized starting from bifunctional reactants:

$$n\,(C_6H_5)_2Sn[N(C_2H_5)_2]_2 + n\,(C_6H_5)_2GeH_2 \rightarrow [\text{-}Sn(C_6H_5)_2\text{-}Ge(C_6H_5)_2\text{-}]_n + 2n\,(C_2H_5)_2NH$$
$$n\,(C_2H_5)_2Sn[N(C_2H_5)_2]_2 + n\,(C_6H_5)_2GeH_2 \rightarrow [\text{-}Sn(C_2H_5)_2\text{-}Ge(C_6H_5)_2\text{-}]_n + 2n\,(C_2H_5)_2NH$$

These polymers are slightly yellow coloured compounds, decomposing at about 260°. Owing to their insolubility in common solvents, no molecular weight could be determined. No end groups were found in the infrared spectrum. This presumes a high molecular ring-structure for these compounds.

Attempts to prepare a tin–germanium monohydride analogously to the earlier prepared ditin monohydrides[5b] by a 1 : 1 reaction of a tin–nitrogen compound with diphenylgermane were not successful. *E.g.* from the 1 : 1 reaction of triphenyltin diethylamide and diphenylgermane in refluxing butyronitrile for one hour a pure product containing both tin and germanium could not be isolated. Only 50% of the theoretical amount of diethylamine was formed and the formation of hexaphenylditin indicates that apart from the hydrogenolysis reaction (8) an exchange reaction (9) has taken place.

$$(C_6H_5)_3SnN(C_2H_5)_2 + (C_6H_5)_2GeH_2 \rightarrow (C_6H_5)_3Sn\text{-}Ge(C_6H_5)_2H + HN(C_2H_5)_2 \qquad (8)$$

$$(C_6H_5)_3SnN(C_2H_5)_2 + (C_6H_5)_2GeH_2 \rightarrow (C_6H_5)_3SnH + (C_6H_5)_2Ge(H)N(C_2H_5)_2 \qquad (9)$$
$$\xrightarrow{(C_2H_5)_2NH} (C_6H_5)_3Sn\text{-}Sn(C_6H_5)_3$$

Ultraviolet properties of some tin–germanium compounds

The absorption maxima observed in the near ultraviolet region for a number of tin–germanium derivatives have been summarized in Table 1.

TABLE 1

ULTRAVIOLET SPECTRAL DATA OF VARIOUS TIN–GERMANIUM COMPOUNDS

	Compound	λ_{max}	*log ε*
1	$\mathrm{Bu_3Ge{-}SnPh_3}$	<240	
2	$\mathrm{Bu_3Ge{-}SnPh_2{-}GeBu_3}$	<240	
3	$\mathrm{Ph_3Ge{-}SnEt_3}$	242	4.30
4	$\mathrm{Ph_3Ge{-}SnEt_2{-}GePh_3}$	252	4.49
5	$\mathrm{Ph_3Ge{-}SnEt_2{-}SnPh_3}$	258	4.52
6	$\mathrm{Ph_3Sn{-}GePh_2{-}SnPh_3}$	254	4.50
7	$\mathrm{Ph_3Ge{-}SnPh_3}$	243	4.49
8	$\mathrm{Ph_3Ge{-}SnEt_2{-}SnEt_2{-}SnEt_2{-}GePh_3}$	293[a]	4.36
9	$\mathrm{Ph_3Ge{-}SnEt_2{-}GePh_2{-}SnEt_2{-}GePh_3}$	298	4.47
10	$\mathrm{Ph_3Ge{-}SnEt_2{-}SnPh_2{-}SnPh_2{-}SnEt_2{-}GePh_3}$	302[a]	4.41
11	$\mathrm{Ph_3Ge{-}SnEt_2{-}SnPh_2{-}SnEt_2{-}GePh_3}$	303	4.75
12	$\mathrm{EtSn(GePh_3)_3}$	262	5.09
		269	5.09
13	$\mathrm{Et_{12}Sn_5}$	310	4.33
14	$\mathrm{Et_{14}Sn_6}$	325	4.44

[a] Shoulder.

Strong absorption bands in this region are primarily due to the metal–metal system[14,15]. The absence of phenyl groups as in compounds[5b] 13 and 14 does not prevent the presence of an absorption maximum. The position of λ_{max} is modified by substituents. Substitution of aryl for alkyl groups moves the absorption maximum to higher wavelength. This substituent shift is particularly large for silicon. The difference in wavelength between the maxima of 1,1,1-triphenyl-2,2,2-trimethyldisilane and hexaphenyldisilane amounts to 12 mμ[15,16]. From a comparison of compounds 1, 3 and 7 it appears that the analogous shift for substitution on tin is only 1 mμ and for substitution on germanium is of an unknown value, but larger than 1 mμ. The larger substituent effect for silicon and germanium compared to tin may be connected with a better orbital overlap between phenyl groups and the former elements.

Substitution of tin for germanium causes an upward shift in λ_{max} as appears from a comparison of compound 4 with 5 and of compound 7 with hexaphenylditin, the spectrum of which shows a maximum at 247 mμ.

The UV spectra of the higher members (chains of five and more metal atoms) and particularly those of the branched compounds extend in the visible region, giving these compounds a yellow till red colour. This tailing effect also explains the yellow colour of hexameric and nonameric diethyltin, though no absorption maximum is reported for the spectra of these cyclic compounds in the 300 mμ region[8]. In this region our linear compounds of comparable size all have a distinct absorption band at approximately 300 mμ.

EXPERIMENTAL PART

Since most of the organometallic compounds mentioned in this study are air-sensitive all manipulations were carried out in an atmosphere of dry nitrogen. Cyclohexane and benzene were treated with lithium aluminium hydride and distilled before use in an atmosphere of nitrogen[17]. Butyronitrile was distilled three times from phosphorus pentoxide and once under nitrogen from potassium carbonate. The germanium–nitrogen and tin–nitrogen starting materials were obtained by published procedures[12,18].

The infrared spectra were run using a Perkin and Elmer Infracord model 137 and a Grubb Parson Spectromaster. The ultraviolet spectra were recorded using a Cary model 15 spectrometer.

The Sn–Ge derivatives were purified by column chromatography. The metal content was determined by wet combustion with a mixture of conc. sulphuric acid and fuming nitric acid. Molecular weights were determined by a cryoscopic method.

TABLE 2

COMPOUNDS WITH Ge–Sn BONDS PREPARED

Compound	*Formula*	*Found*	
		% Ge	*% Sn*
$Bu_3Ge-SnPh_3$	$C_{30}H_{42}GeSn$	12.05	19.7
$Bu_3Ge-SnBu_2-SnBu_2-GeBu_3$	$C_{40}H_{90}Ge_2Sn_2$	15.1	24.7
$Bu_3Ge-SnPh_2-GeBu_3$	$C_{36}H_{64}Ge_2Sn$	16.1	19.7
$Ph_3Ge-SnEt_3$	$C_{24}H_{30}GeSn$	14.2	23.2
$Ph_3Ge-SnEt_2-GePh_3$	$C_{40}H_{40}Ge_2Sn$	19.2	15.7
$(Ph_3Ge-SnEt_2)_2O$	$C_{44}H_{50}Ge_2Sn_2O$	14.9	24.3
$Ph_3Ge-SnEt_2-C\equiv CPh$[c]	$C_{30}H_{30}GeSn$	12.7	20.8
$Ph_3Ge-SnEt_2-NEt_2$	$C_{26}H_{35}NGeSn$	13.4	21.9
$Ph_3Ge-SnEt_2-OPh$	$C_{28}H_{30}GeSnO$	12.7	20.7
$Ph_3Ge-SnEt_2-SnPh_3$	$C_{40}H_{40}Sn_2Ge$	8.7	28.3
$Ph_3Ge-SnEt_2-N(Ph)C(O)H$	$C_{29}H_{31}NOGeSn$	12.1	19.8
$Ph_3Ge-SnEt_2-SnEt_2-SnEt_2-GePh_3$	$C_{48}H_{60}Ge_2Sn_3$	12.7	31.2
$Ph_3Ge-SnEt_2-SnPh_2-SnEt_2-GePh_3$	$C_{56}H_{60}Ge_2Sn_3$	11.5	28.2
$Ph_3Ge-SnEt_2-SnPh_2-SnPh_2-SnEt_2-GePh_3$	$C_{68}H_{70}Ge_2Sn_4$	9.4	30.8
$Ph_3Ge-SnPh_2-OH$	$C_{30}H_{26}OGeSn$	12.0	19.7
$Ph_3Ge-SnPh_2-C\equiv CPh$[d]	$C_{38}H_{30}GeSn$	10.3	16.9
$EtSn(GePh_3)_3$	$C_{56}H_{50}Ge_3Sn$	19.4	10.55
$EtSn(GePh_3)(C\equiv CPh)_2$[d]	$C_{36}H_{30}GeSn$	10.8	17.7
$[-Sn(Et)(GePh_3)-O-]_n$	$C_{20}H_{20}GeSnO$	15.6	25.5
$EtSn(GePh_3)(SnPh_3)_2$	$C_{56}H_{50}GeSn_2$	6.3	30.8
$EtSn(GePh_3)_2OH$	$C_{38}H_{36}GeSnO$	18.4	15.0
$EtSn(GePh_3)_2-SnPh_2-Sn(GePh_3)_2Et$	$C_{88}H_{80}Ge_4Sn_3$	15.6	19.1
$EtSn(GePh_3)_2-SnPh_2-SnPh_2-Sn(GePh_3)_2Et$	$C_{100}H_{90}Ge_4Sn_4$	14.55	23.8
$Ph_3Sn-GePh_3$	$C_{36}H_{30}GeSn$	10.8	17.7
$Et_3Sn-GePh_2-SnEt_3$	$C_{24}H_{40}GeSn_2$	11.4	37.4
$Ph_3Sn-GePh_2-SnPh_3$	$C_{48}H_{40}GeSn_2$	7.8	25.4
$Ph_3Ge-SnEt_2-GePh_2-SnEt_2-GePh_3$	$C_{56}H_{60}Ge_3Sn_2$	18.0	19.6
$(-SnPh_2-GePh_2-)_n$	$(C_{24}H_{20}GeSn)_n$	14.6	23.8
$(-SnEt_2-GePh_2-)_n$	$(C_{16}H_{20}GeSn)_n$	18.0	29.4

[a] Insoluble in common organic solvents. [b] Lit.[4] 284–286°. [c] $\nu(C\equiv C)$ 2120 cm^{-1}. [d] $\nu(C\equiv C)$ 2170 cm^{-1}.

Examples of representative methods for preparation are given below. For physical data, analytical results and yields see Table 2.

(Tributylgermyl) triphenyltin

Triphenyltin hydride (3.51 g, 0.01 mole) was added to a solution of tributylgermanium diethylamide (3.16 g, 0.01 mole) in 10 ml butyronitrile. The reaction mixture was refluxed for one hour. The IR spectrum of the mixture failed to show residual Sn–H absorption. After evaporation of the diethylamine and the solvent, the residue was taken up in light petroleum (40–60°) and purified by chromatography on a column of neutral alumina. After removal of the solvent a colorless oil remained, which crystallised after storage at 0°.

(Triphenylgermyl) triethyltin

Triphenylgermane (3.5 g, 0.0114 mol) was added to triethyltin diethylamide (3.18 g, 0.0114 mole). Heating of the mixture at 60° for 2½ h resulted in the gradual

Calculated		*Mol. wt.*		*Yield (%)*	*M.p. (°C)*	n_D^{20}	*Appearance*
% Ge	*% Sn*	*Found*	*Calcd.*				
12.22	19.98	595	594	68	24–25.5		white solid
15.22	24.89			95		1.5213	slight greenish oil
15.60	19.08			36		1.6360	greenish oil
14.24	23.28	524	510	52	45–52		white solid
18.50	15.12	789	784.6	70	133–137		white solid
14.89	24.34	[a]		71	85–95		white solid
12.48	20.40			quant.		1.6501	yellow oil
13.13	21.47			72		1.6085	colourless oil
12.65	20.68			87		1.6443	yellow oil
8.74	28.58	845	831	85	125–129		white solid
12.08	19.75			quant.			colourless oil
12.76	31.29			35		1.6754	white gel
11.76	28.85			25	40		slightly yellow solid
9.63	31.50			24			greenish oil
12.22	19.99	[a]					light green solid
10.70	17.51			77			
20.56	10.55			3	>330		white solid
11.10	18.15			96	40		slight yellow solid
15.53	25.40	[a]		50	dec. 200		yellow solid
6.30	30.92			56	250		slightly yellow solid
18.79	15.36			61	>260		slightly yellow solid
16.27	19.96			26	175		slightly yellow solid
14.12	23.09			70			yellow solid
11.10	18.15			17	282–294		white solid
11.37	37.17	648	638.5	65		1.6119	slightly yellow solid
7.83	25.61			63	169–178		white solid
18.33	19.98			75			white solid
14.52	23.75			51.5	>260		slightly yellow solid
17.98	29.40			74	>260		slightly yellow solid

disappearance of the Ge–H absorption at 2050 cm^{-1}. The reaction product was likewise purified by column chromatography.

1,2-Bis(tributylgermyl)tetrabutylditin

Dibutyltin dihydride (2.47 g, 0.0105 mole) was mixed with tributylgermanium dimethylamide (3.03 g, 0.0105 mole). The temperature was raised to 70–80°. In the IR spectrum the band at 1835 cm^{-1} [ν(Sn–H) of Bu_2SnH_2] was replaced by a band at 1780 cm^{-1} [ν(Ge–Sn–H) of $Bu_3GeSnBu_2H$] in the course of 1 h. The reaction mixture was cooled, 5 ml of diethylamine was added and the mixture was warmed up slowly till 70°. After 6 h the gas evolution was complete.

The residue was, after removal of the diethylamine, purified by column chromatography.

Bis(triphenylgermyl)diethyltin

Triphenylgermane (4.8 g, 0.0157 mole) was added to diethyltin bis(diethylamide) (2.52 g, 0.00785 mole). The reaction mixture was heated for 2 h at 80–90°. The diethylamine formed was stripped off *in vacuo*. The reaction mixture became solid upon cooling. The product was washed twice with light petroleum.

1-(Triphenylgermyl)-1,1-diethyl-2,2,2-triphenylditin

In a distillation apparatus (triphenylgermyl)diethyltin diethylamide (2.68 g, 0.0048 mole) was prepared by heating a 1 : 1 mixture of diethyltin bis(diethylamide) and triphenylgermane at 80° for 1 h followed by removal of volatiles *in vacuo*. At about 90° triphenyltin hydride (1.72 g, 0.0048 mole) was added slowly, whilst the diethylamine was distilled off. When the distillation of diethylamine had stopped, the reaction mixture was heated *in vacuo* at 90° for 1 h. The residue was taken up in benzene/cyclohexane (1 : 1). The hexaphenylditin which had crystallized from the solution after 1 h at 0° was separated by filtration. Evaporation of the filtrate afforded a white, crystalline solid.

Hydrolysis of (triphenylgermyl)diethyltin diethylamide

To 1.6 g (0.0029 mole) of (triphenylgermyl) diethyltin diethylamide prepared as described above a suspension of 0.11 g (100% excess) of water in 10 cc of ether was added slowly. The reaction mixture became turbid. The ether was distilled off and replaced by 5 ml of benzene, which was also distilled off. A slightly turbid colourless oil remained, which crystallized upon standing.

1,3-Bis(triphenylgermyl)hexaethyltritin

To diethyltin bis(diethylamide) (3.21 g, 0.01 mole) triphenylgermane (3.04 g, 0.01 mole) was added. After heating for 1½ h at 80–90°, the diethylamine was evaporated *in vacuo*. N-Phenylformamide (1.21 g, 0.01 mole) was added and the reaction mixture heated for 1½ h at 80–90°. Diethylamine formed was removed *in vacuo*. Diethyltin dihydride (0.89 g, 0.005 mole) in 2 ml butyronitrile was then added. After heating at 100° for 2 h, the Sn–H absorption at 1835 cm^{-1} had disappeared from the IR spectrum. The solvent was replaced by light petroleum causing N-phenylformamide to precipitate. The product was purified by column chromatography of the filtrate.

Compounds [*e.g.* (IV), (V), (VA), (VI)] insoluble in light petroleum or benzene and also in methanol, N-phenylformamide formed in their preparation was separated by extraction with absolute methanol.

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SUMMARY

The synthesis of a variety of linear and branched compounds with Ge–Sn bonds has been described. The synthetic method used involves hydrogenolytic fission of Ge–N and Sn–N bonds with organotin and -germanium hydrides. The ability of the M(IV)–N bond to undergo this reaction has been discussed in terms of the availability of the free electron pair on nitrogen.

The planned synthesis of compounds with up to eight catenated metal atoms has been realized. By partial hydrogenolysis functionally substituted polymetal compounds are obtained which are useful intermediates for further syntheses. Transamination reactions of intermediate organometal diethylamides with N-phenylformamide form an essential step in the preparation of longer-chain compounds.

The ultraviolet spectra of this type of compounds are briefly discussed.

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