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SYNTHESIS OF GROUP IV ORGANOMETALLIC POLYMERS AND RELATED COMPOUNDS

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UTRECHT, THE NETHERLANDS

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FOREWORD

This work was prepared by the Institute for Organic Chemistry, T.N.O., Utrecht, the Netherlands, under USAF Contract No. AF 61(052)-218. The contract was initiated under Project No. 7023, Task No. 73666, and was continued under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication," Task No. 734203, "Fundamental Principles Determining the Behavior of Macromolecules." The work was administered under the direction of the European Office of Aerospace Research, United States Air Force, Brussels, Belgium.

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The work was carried out under the supervision of Prof. G. J. M. Van der Kerk, Director of the Institute for Organic Chemistry T.N.O., Utrecht, the Netherlands.

This technical report has been reviewed and is approved.

William E. Gibbs

WILLIAM E. GIBBS,
Chief, Polymer Branch
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ABSTRACT

The synthesis and characterization have been described of linear polymers, having a carbon chain regularly interrupted by the Group IV elements silicon, germanium, tin, or lead. Such polymers have been obtained by means of:

a) Poly-addition reactions involving an organotin dihydride and either a dienic, a diynic, or a monoynic compound.

b) Wurtz-type poly-condensations involving appropriate combinations of p-chlorophyenyl and chloro derivatives of the Group IV elements.

The synthesis and polymerization of vinyl-type Group IV organometallic monomers is dealt with briefly.

Furthermore, interesting Group IV metal-containing heterocycles have been prepared and also a few polymers containing, in addition to Group IV atoms, other hetero-elements in their backbone.

All polymer-forming reactions have been studied by carrying out model reactions on a low-molecular weight level.

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The preparation and characterization have been reported of various low-molecular and polymeric compounds, the majority of which have not been described before. Essential data of about two hundred compounds (successively numbered from 1 through 207) are presented in the tables listed below. The compounds, the number of which has been marked with an asterisk, are compiled in Table 25.

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SECTION I

ADDITION REACTIONS INVOLVING ORGANOTIN HYDRIDES AND UNSATURATED COMPOUNDS

A. Discussion

In the years 1955-1958 at our Institute much attention had been paid to the information of tin-carbon bonds by the reaction of organotin hydrides with carbon-carbon unsaturated compounds (References 32-35). When our organometallic polymer program was initiated it was decided to apply this reaction principle to the synthesis of organotin polymers. Aspects of the chemistry of organotin hydrides related to the possibility of preparing polymers have been discussed before (References 20, 30, 31). Some points will be recalled briefly as this will lead to a better appreciation of the scope of the polymer-forming reaction.

Adducts are formed upon reaction of triorganotin monohydrides with a variety of mono-substituted terminal olefins (References 33, 34):

$$R_3SnH + CH_2{=}CH\text{-}R' \longrightarrow R_3SnCH_2CH_2R' \qquad (I)$$

Reactions involving triphenyltin hydride proceed smoothly at moderate temperatures (70°-100°). Both the reaction time (usually a few hours, sometimes as short as a few minutes) and the yield (generally high, in some cases quantitative) depend on the substituent R'. Trialkyltin hydrides react slower and only if the olefinic bond is activated sufficiently by R' (e.g., when R' represents an aryl group).

Where investigated (e.g., n-octene, acrylonitrile, styrene) the organotin group was found to have added to the terminal olefinic carbon atom. Although polar effects influence the rate of the reaction, steric factors mainly determine its course. Terminal addition seems to be the rule.

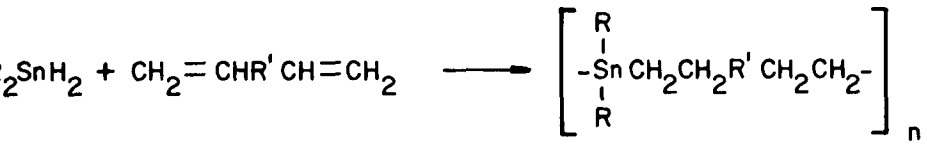
After the completion of the greater part of this work catalysts for the addition of organotin hydrides to unreactive olefins have been reported (References 36-39). Addition of the less-reactive trialkyltin hydrides to nonactivated double bonds has been realized using catalytic amounts of free radical producing compounds (References 36, 37) or organo-aluminium (References 37, 38). However, the simultaneous occurrence of side-reactions (References 14, 37) may restrict the applicability of the free radical catalysis for polymer formation (compare also Reference 39). Catalysis by alkylaluminium compounds, which have been found to be inactive in addition reactions of the analogous trialkylsilicon and germanium hydrides (Reference 15; compare also Reference 40), has not been investigated thoroughly yet.

Similar reactions have been realized using acetylenic derivatives as the unsaturated partner (Reference 34):

$$R_3SnH + HC{\equiv}C\text{-}R' \longrightarrow R_3SnCH{=}CHR' \xrightarrow{R_3SnH} R_3SnCH_2CHR'SnR_3 \qquad (II)$$

However, the reactivity of organotin hydrides towards carbon-carbon triple bonds is much higher than towards olefinic double bonds. Mostly, these reactions proceed exothermally in the absence of any added catalyst. Consequently, when applying one mole of a monohydride per mole of a monoacetylenic compound, only the olefinic adduct is being formed. Similarly, when applying two moles of a monohydride, two separate reaction steps can be distinguished, the second one requiring more severe conditions.

Considering the foregoing, the possibility of applying this reaction principle to the synthesis of polymers is evident. Upon reaction of an organotin dihydride with an appropriate diolefine (preferably an α,ω-diene) linear polymers are being formed under incorporation of organotin groups in the main chain:



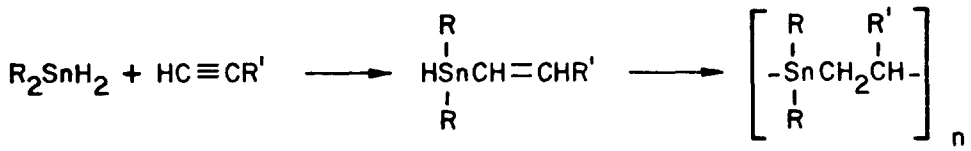
(III)

Starting from acetylenic compounds as the unsaturated reaction partner, and making use of the earlier mentioned marked difference in reactivity of the organotin hydride towards double and triple bonds, two different routes leading to polymers can be followed:

1. Reaction of an α,ω-diyne with an organotin dihydride in a 1:1 ratio under very mild conditions will result in the formation of a linear polymer. In this case the reaction ends after conversion of the triple bonds into double bonds:

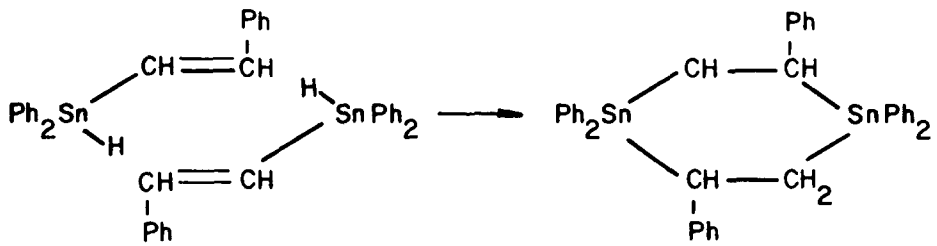
(IV)

2. Reaction of a monoacetylenic compound with an organotin dihydride again in an exactly 1:1 ratio will proceed in two steps, viz. formation of an olefinic organotin monohydride and subsequently, at higher temperature, homopoly-addition of this monomer:



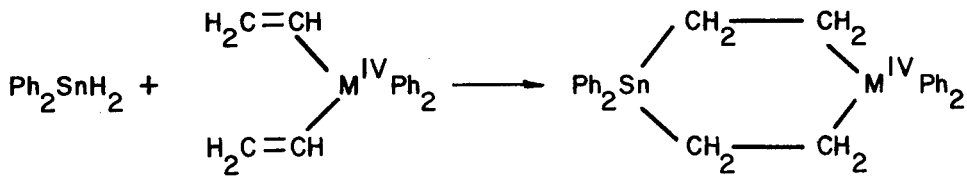
(V)

However, two molecules of the 1:1 addition intermediate may form a six-membered cyclic dimer with the two tin atoms in 1,4-position. This reaction course has in fact been observed upon reaction of diphenyltin dihydride with phenylacetylene (Reference 41). As noted from an absorption peak at 988 cm^{-1}, originating from the C-H bending vibration of trans-disubstituted ethylene groups, the olefinic intermediate has the trans-structure, its formation presumably being promoted by steric factors (see also Section VI-C). The trans-structure, in its turn, favors the formation of the distannacyclohexane system:



(VI)

Dienic or diynic compounds having the two unsaturated groups in a sterically favorable position have also been found to yield cyclic oligomers in addition to linear polymers. Reaction of diphenyltin dihydride with divinyl organometallic derivatives yields the bimetallic cyclohexane analogues (cyclic monomers) as the main product (Reference 41):



(VII)

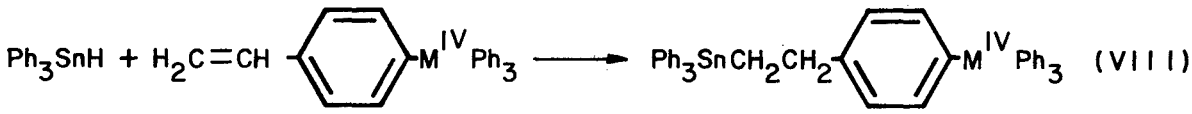
M^{IV} = Si and Ge

Reaction of organotin dihydrides with 1,5-hexadiyne in addition to the expected polymers yields 1-stanna-2,6-cycloheptadiene derivatives (see Section I-C).

B. Synthesis of Low-Molecular and Polymeric Adducts from Organotin Hydrides and Olefinic Compounds

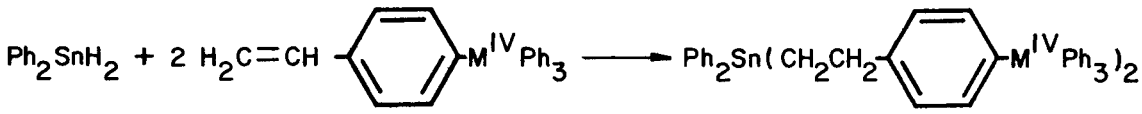
Considering the foregoing it would seem that the presence of voluminous aryl groups in the dienic reactants, to be used in poly-addition reactions with organotin dihydrides, will sterically disfavor ring-formation and at the same time will activate the double bonds. For this reason 1,4-divinylbenzene (1*), 3,9-divinylspirobi(meta-dioxan), p,p'-diisopropenylbiphenyl (2*) and the diphenyldi-p-styrenyl derivatives of germanium, tin, and lead (see also Section II-B) were selected as dienic components.

Optimal conditions for polymer-formation have been determined by carrying out model reactions of the mono-p-styrenyl derivatives of germanium, tin, and lead both with triphenyltin hydride and diphenyltin dihydride, as well as of the di-p-styrenyl derivatives with triphenyltin hydride:



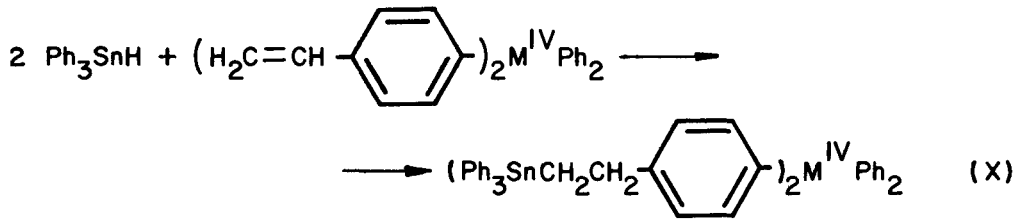
(VIII)

3-5, M^{IV} = Ge, Sn, and Pb resp.



(IX)

6-8, M^{IV} = Ge, Sn, and Pb resp.



(X)

9-11, M^{IV} = Ge, Sn, and Pb resp.

From each type of reaction the expected addition products were obtained in good yields. The compounds obtained in these reactions are listed in Table 1.

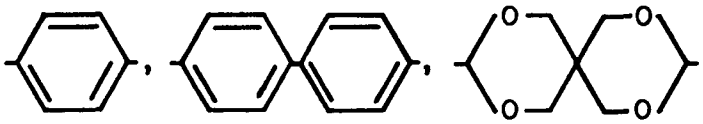
It thus appears, that contrary to vinyl and allyl groups, which are reductively cleaved from lead by phenyltin hydrides (Reference 42), the p-styrenyl group remains unaffected. Abnormal products which previously had been found to result from reactions involving vinyl or allyl derivatives (Reference 42), e.g.,

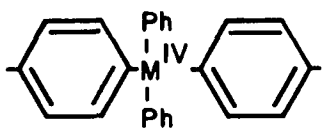
$$2\ Ph_3M^{IV}CH{=}CH_2 + Ph_2SnH_2 \longrightarrow Ph_3M^{IV}CH_2CH_2SnPh_3 \qquad (XI)$$

have not been isolated.

The polymer-forming reactions of 1,4-divinylbenzene, 3,9-divinylspirobi(meta-dioxan) and the diphenyldi-p-styrenyl derivatives of germanium, tin, and lead with diphenyltin dihydride (1:1 molar ratio) yielded glasslike products, which according to analytical results and solubility properties, are indeed strictly poly-addition polymers. Obviously the occurrence of vinyl-type polymerization may be excluded:

$$R_2SnH_2 + H_2C{=}C(R')\text{-}R''\text{-}C(R'){=}CH_2 \longrightarrow \left[-\underset{R}{\overset{R}{Sn}}-CH_2-\underset{R'}{CH}-R''-\underset{R'}{CH}-CH_2- \right]_n \qquad (XII)$$

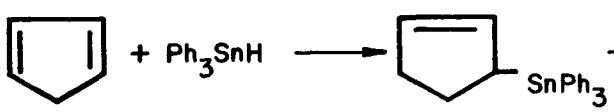
12-15, R'' = 

16-24, R'' = 

The polymers derived from alkyltin dihydrides seem to be more or less crosslinked, judging from their solubility behavior. The mechanism responsible for crosslinking is not well understood. It is conceivable, however, that owing to the somewhat smaller reactivity of dialkyltin dihydrides as compared with diphenyltin dihydrides towards double bonds both vinyl-type polymerization and occasional decomposition of Sn-H groups with formation of Sn-Sn groups leads to the occurrrence of branched structures.

The polymers obtained in reaction (XII) are presented in Table 2 and Table 3.

The reaction of cyclopentadiene with organotin dihydrides did not yield the expected products. As noted from model reactions the reactivity of the remaining double bond in the monoaddition product (25*) from triphenyltin hydride and cyclopentadiene is insufficient for uncatalyzed addition:



(XIII)

Most probably 1,4-addition occurs in the formation of the 1:1 adduct (compare also Reference 43).

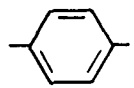
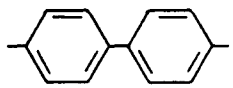
TABLE 1

Addition Products from p-Styrenyl-Substituted Group IV Metal Derivatives and Organotin Hydrides (VIII, IX, X)

NO.	COMPOUND	FORMULA	REACTION TEMP. (°C)	TIME (HRS.)	RECRYST-SOLVENT	MELTING POINT (°C)	YIELD (%)	REFERENCES
3	$Ph_3SnCH_2CH_2$-C$_6$H$_4$-$GePh_3$	$C_{44}H_{38}GeSn$	90	3	EtAc[a]	201-203	80	2, 23
4	$Ph_3SnCH_2CH_2$-C$_6$H$_4$-$SnPh_3$	$C_{44}H_{38}Sn_2$	90	3	EtAc	184-186	81	2, 23
5	$Ph_3SnCH_2CH_2$-C$_6$H$_4$-$PbPh_3$	$C_{44}H_{38}SnPb$	70	3	EtAc	177-179	85	3, 23
6	$Ph_2Sn(CH_2CH_2$-C$_6$H$_4$-$GePh_3)_2$	$C_{64}H_{56}Ge_2Sn$	75	2	Acet[b]	168-169	79	3, 23
7	$Ph_2Sn(CH_2CH_2$-C$_6$H$_4$-$SnPh_3)_2$	$C_{64}H_{56}Sn_3$	75	2	Acet	~ 75[d]	84	3, 23
8	$Ph_2Sn(CH_2CH_2$-C$_6$H$_4$-$PbPh_3)_2$	$C_{64}H_{56}SnPb_2$	75	2	Acet	~ 70[d]	81	3, 23
9	$(Ph_3SnCH_2CH_2$-C$_6$H$_4$-$)_2GePh_2$	$C_{64}H_{56}GeSn_2$	90	3	Acet	207-209	90	3, 23
10	$(Ph_3SnCH_2CH_2$-C$_6$H$_4$-$)_2SnPh_2$	$C_{64}H_{56}Sn_3$	100	3	Acet	183-185	77	3, 23
11	$(Ph_3SnCH_2CH_2$-C$_6$H$_4$-$)_2PbPh_2$	$C_{64}H_{56}Sn_2Pb$	70	3	Ligr[c]	180-182	89	3, 23

[a]Ethyl acetate; [b]Acetone; [c]Ligroin; [d]Amorphous solids.

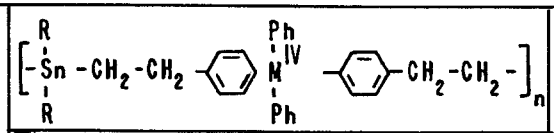
TABLE 2
Polymers from Dienic Compounds and Organotin Dihydrides (XII)

NO.	$\left[-\underset{R}{\overset{R}{Sn}}-CH_2-\underset{R'}{CH}-R''-\underset{R'}{CH}-CH_2-\right]_n$			FORMULA	APPEARANCE OF POLYMER	SOLUBILITY	T MELT (°C)	$\overline{M}_w$	REFERENCES
	R	R′	R″						
12	Pr	H		$(C_{16}H_{26}Sn)_n$	soft, tacky viscous flow	-	-	-	5, 30, 31
13	Ph	H	id.	$(C_{22}H_{22}Sn)_n$	glasslike	C_6H_6; $CHCl_3$	70	110.000 33.000[a]	5, 6, 8 23, 30, 31
14	Bu	Me		$(C_{26}H_{38}Sn)_n$	very viscous	-	-	-	5, 30
15	Ph	H		$(C_{23}H_{28}O_4Sn)_n$	glasslike	C_6H_6; $CHCl_3$	90	19.000	6, 23, 30, 31

[a]Osmometric measurement ($\overline{M}_n$)

TABLE 3

Polymers from Di-p-Styrenyl-Substituted Group IV Metal Derivatives and Organotin Dihydrides (XII)

NO.	 R	M^{IV}	FORMULA	APPEARANCE OF POLYMER	SOLUBILITY	T MELT (°C)	$\overline{M}_w$	REFERENCES
16	Pr	Ge	$(C_{34}H_{40}GeSn)_n$	tough $\xrightarrow{100°}$ rubbery	C_6H_6(slightly)	240		7, 30, 31
17	Ph	Ge	$(C_{40}H_{36}GeSn)_n$	hard, brittle	C_6H_6; $CHCl_3$	110	27.000	5, 6, 23, 30, 31
18	Pr; Ph (1:1)[a]	Ge	$(C_{37}H_{38}GeSn)_n$	hard $\xrightarrow{120°}$ rubbery	C_6H_6(slightly)	250		7, 30, 31
19	Pr	Sn	$(C_{34}H_{40}Sn_2)_n$	tough $\xrightarrow{130°}$ rubbery	swells in C_6H_6	> 260		5, 7, 30, 31
20	Bu	Sn	$(C_{36}H_{44}Sn_2)_n$	hard, slightly tough	id.			5, 30, 31
21	Ph	Sn	$(C_{40}H_{36}Sn_2)_n$	hard, brittle	C_6H_6; $CHCl_3$	100	48.000, 29.000[b]	5, 6, 8 23, 30, 31
22	Pr; Ph (1:1)[a]	Sn	$(C_{37}H_{38}Sn_2)_n$	hard $\xrightarrow{90°}$ rubbery	C_6H_6	130		7, 30, 31
23	Pr	Pb	$(C_{34}H_{40}SnPb)_n$	tough $\xrightarrow{90°}$ rubbery	C_6H_6(slightly)	230		7, 30, 31
24	Ph	Pb	$(C_{40}H_{36}SnPb)_n$	hard, brittle	C_6H_6; $CHCl_3$	70	14.000	5, 6, 23, 30, 31

[a]Equimolecular mixture of Pr_2SnH_2 and Ph_2SnH_2; [b]Osmometric measurement ($\overline{M}_n$).

Molecular weights of the polymers, determined by means of ultra-centrifuge measurements* according to Archibald (Reference 44) or osmometrically** are presented in Tables 2 and 3. It appears from these data that the attainment of appreciable molecular weights is possible. Interfering reactions, such as the thermal breakdown of the rather unstable Sn-H bond apparently do not occur under the reaction conditions used. A broad molecular weight distribution may be expected for this type of polymer-forming reaction (hydrogen transfer polymerization). This is confirmed by the large differences between $\overline{M}_n$ and $\overline{M}_w$ observed ($\overline{M}_w$ emphasizes the high, $\overline{M}_n$ the low values).

In general, polymer-melt temperatures are quite low. Interchain forces will be rather weak, because of lack of hydrogen bonding. Moreover, the relatively large metal atoms and their bulky substituents will hamper effective Van der Waals interaction between the chains and crystallization. The X-ray diffraction*** pattern of polymer 13 revealed its amorphous structure. The low-molecular addition compounds 7 and 8 behaved similarly: they failed to crystallize and showed an abnormally low melting point.

The mechanical properties of the polymers obtained from diphenyltin dihydride are poor. Clear films cast from a chloroformic solution are brittle as are the fibers drawn from a hot melt of these materials.

The results of thermogravimetric tests on some poly-addition polymers (Chevenard thermobalance, N_2 atmosphere, heating 2.5° per min.) are presented in Table 4****. Temperature at which 5 and 50 percent weight loss has occurred ($T_{5\%}$ and $T_{50\%}$), residual weight at 950° (RW) and the percentage of inorganic elements in the original polymer are given. As it appears from these data these poly-addition polymers are, under the conditions employed in this test, stable up to about 300°C, quite according to expectation in view of the stability of the bonds present in these polymers.

The compounds and polymers, containing both germanium and tin or both lead and tin, display in their infrared spectra distinctive "X-sensitive" absorptions associated with the presence of phenyl- and p-phenylene-M^{IV} groups in the molecule (see also Section VII), the relative intensities of which are indicative of the ratio in which these groups are present. In Figure 1 these absorptions for M^{IV}-Ge and Sn (bands at 1090 cm^{-1} and 1075 cm^{-1} respectively) of four compounds containing both germanium and tin are shown.

1,4-Divinylbenzene (1*) was purified via the 1,4-dihydrobromo derivative (26*). p-p'-Diisopropenyl-biphenyl (2*) was obtained by a Wurtz coupling reaction involving p-chloro-α-methylstyrene (see Section II-B). The organotin hydrides were prepared as previously described (Reference 45).

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*These measurements were carried out at the Central Laboratory T.N.O., Delft, under the direction of Dr. D. T. F. Pals.

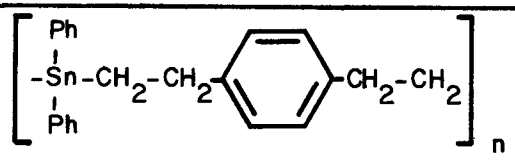
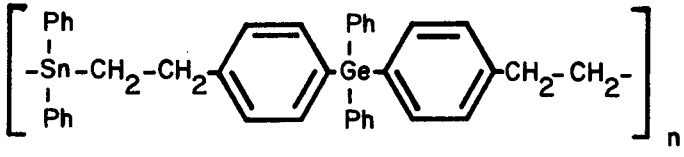
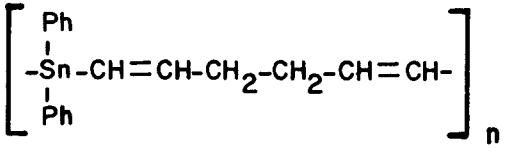
**These measurements were carried out at the Directorate of Materials and Processes, Deputy of Technology, Wright-Patterson AFB, Ohio.

***The authors are indebted to Prof. A. F. Peerdeman, Laboratory for Crystallography, State Univ. of Utrecht, for the X-ray diffraction measurement.

****The authors are indebted to Dr. G. F. L. Ehlers (Aeronautical Systems Division, Wright-Patterson AFB, Ohio) for these measurements.

TABLE 4

Thermogravimetric Analysis of Some Group IV Metal Poly-Addition Polymers

No.	Polymer	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	RW (%)	% of Inorg. Elements	References
13		300	385	28	29.3	8,30,31
17		325	460	30	27.1	8,30,31
37		280	355	27	33.6	8,30,31

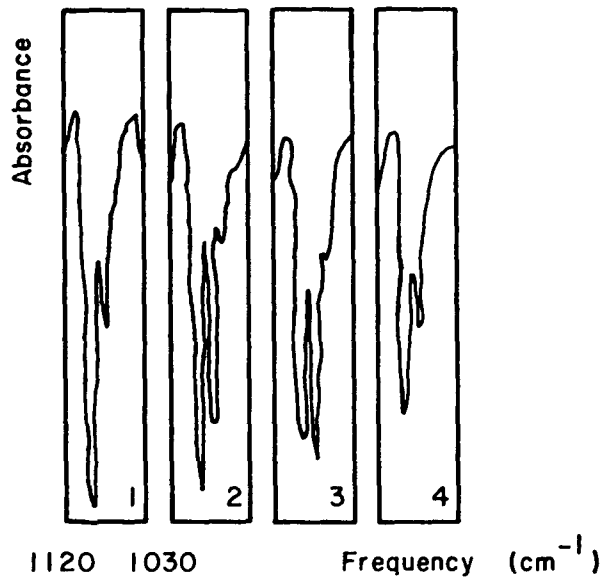


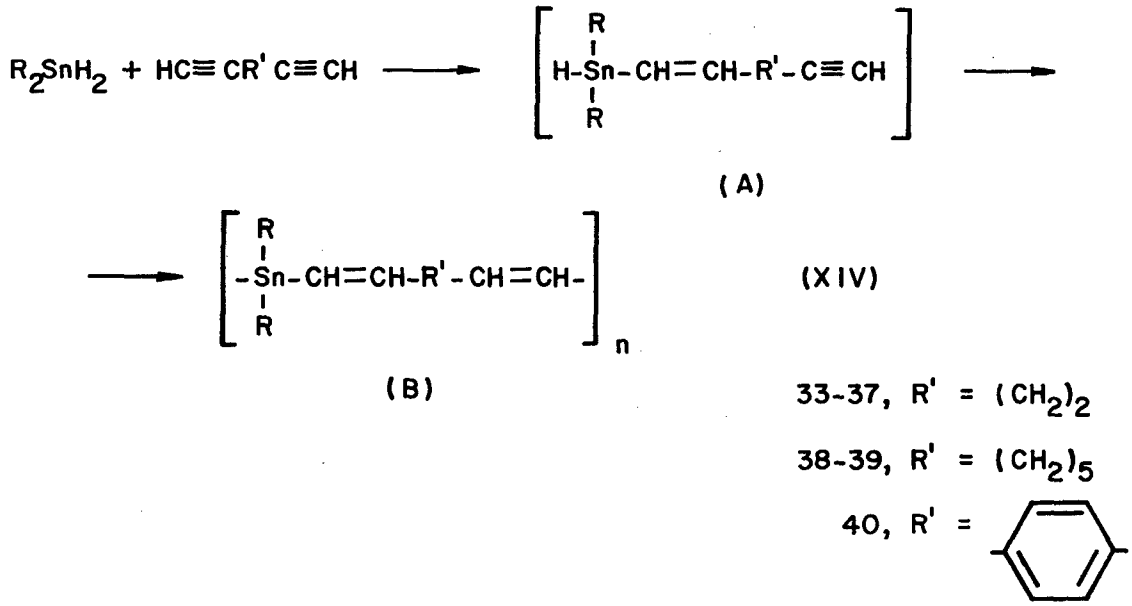
Figure 1. Infrared Absorption Spectra (1120-1030 cm^{-1}) of: 1. $C_{64}H_{56}Ge_2Sn$ (6); 2. $C_{44}H_{38}GeSn$ (3); 3. $C_{64}H_{56}GeSn_2$ (9); 4. $(C_{40}H_{36}GeSn)_n$ (17)

All reactions involving organotin hydrides were carried out under nitrogen in order to eliminate oxidative degradation of the organotin hydrides. Low reaction temperatures (60°-110°) were employed in the polymer-forming reactions in order to prevent disproportionation of the dihydrides leading to mono- and trifunctional hydrides which would act as chain-stopping and crosslinking agents, respectively.

The progress of the reaction can be determined very easily by I.R. absorption measurements. The disappearance of the characteristic Sn-H stretching vibration in the 1800-1840 cm^{-1} region (5.5μ), see References 46, 47, together, of course, with the disappearance of vinyl absorption bands is the most clear-cut indication that the reaction has gone to completion.

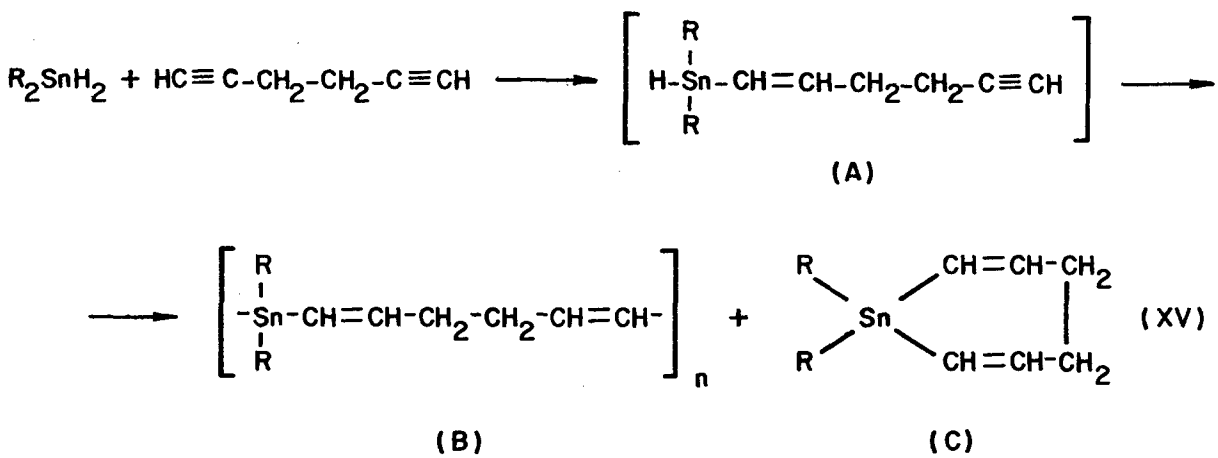
C. Synthesis of Cyclic Monomers and Linear Polymers from Organotin Hydrides and Acetylenic Compounds

As outlined above linear heteropolymers containing tin-ethylenic groups in the main chain may be obtained from organotin dihydrides and α,ω-diynes, such as 1,5-hexadiyne, 1,8-nonadiyne, and 1,4-diethynylbenzene. Such reactions will proceed via the intermediate formation of a compound (A) containing a tin-hydrogen, a carbon-carbon double, and a carbon-carbon triple bond:



In general these compounds react with considerable evolution of heat, calling for the use of a diluent. The reactions were carried out initially in n-hexane and finally after removal of the solvent at 100°. In each case investigated the reaction product was soluble in benzene, but the infrared spectrum was completely devoid of residual Sn-H or acetylenic absorption.

The polymers derived from 1,5-hexadiyne range from a rubberlike elastic solid (R = Ph) to viscous liquids (R = Me, Et, Pr, Bu). When heated in vacuo (150°-250° at 10^3 mm Hg), the liquid polymers change to rubberlike, benzene-insoluble solids (polymers 33 and 34, R = Me, Et) or to benzene-soluble, elastic near-solids (polymers 35 and 36, R = Pr, Bu). This was accompanied by distilling-off a liquid having the same analytical composition as the remaining polymer. The absence of Sn-H and acetylenic absorption in the infrared spectra excludes the open structure (A) for these volatile products. Apparently the primary intermediate (A) partly reacts intramolecularly with formation of the cyclic monomer (C):

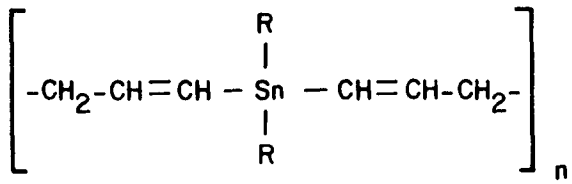


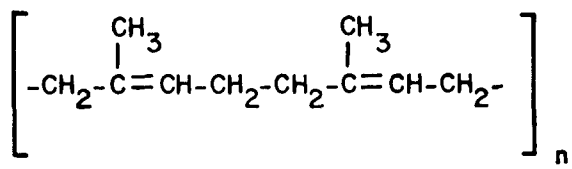
This picture is in accordance with the infrared characteristics observed in the spectra of the cyclic monomers: presence of the ν C = C absorption band at 1590 cm^{-1} and the ring vibration at 785 cm^{-1} (see also Section VI-C), absence of the strong trans-vinylene absorption

present in the corresponding polymers at 987 cm^{-1}. The 2,6-cycloheptadiene derivatives isolated are presented in Table 5. The polymers obtained in Reaction XIV are presented in Table 6.

The reactions of diphenyltin dihydride with 1,4-pentadiyne-3-ol (43*) and with 3-phenyl-1,4-pentadiyne-3-ol (44*) afforded brown brittle polymers, which, owing to partial resinification of the diyne, did not have the correct composition. Derivatives of 1-stanna-2,5-cyclohexadiene could not be isolated. Similarly, only polymeric products were obtained in poly-additions involving 1,8-nonadiyne (45*).

The hexadienyltin polymers show some structural resemblance to natural rubber. Apart from the presence of methyl groups, every second $-CH_2CH_2-$ group in natural rubber has been replaced by a dialkyltin or a diphenyltin group:





Replacement of the ethylene group in this type of organotin polymer by the pentamethylene group results in the loss of the rubberlike properties. All efforts to vulcanize this "tin-rubber" using several vulcanizing systems have been in vain, whereas this polymer, as appeared from oxygen-absorption measurements, will not be very suitable for purposes in which oxidation-resistant rubbers have to be applied*. The results of a thermogravimetric test on this polymer has been presented in Table 4.

Molecular weights of the benzene-soluble polymers, determined by means of ultracentrifuge measurements** are presented also in Table 6. As might be expected, the degrees of polymerization of the polymers obtained by diyne-dihydride poly-additions are appreciably higher than those mentioned in the previous section dealing with dienes.

Although trialkylgermanium hydrides have been reported to add quantitatively to terminal acetylenes (Reference 48), only low-molecular-weight polymers resulted from the reaction of organogermanium dihydrides and α-ω-diynes. In spite of the rather drastic reaction conditions (7 days at 120° without a solvent; chloroplatinic acid catalysis), the polymers obtained from diphenyl- and dibutylgermanium dihydride and 1,5-hexadiyne displayed residual Ge-H and acetylenic absorption in their infrared spectrum, indicative of a low degree of polymerization. The phenylgermanium polymer (42) showed none of the rubberlike properties

*The authors are indebted to Dr. J. W. H. Zijp and Mr. G.A. Gerritse of the Rubber Institute, T.N.O., Delft, the Netherlands, for carrying out these measurements.

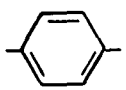
**These measurements were carried out at the Central Laboratory, T.N.O., Delft, the Netherlands, under the direction of Dr. D. T. F. Pals.

TABLE 5

1-Stanna and 1-Germa-2, 6-Cycloheptadiene Derivatives (XV)

No.	R	M^{IV}	Formula	Boiling Point (°C / mm)	n_D^{20}	Yield (%)	References
27	Me	Sn	$C_8H_{14}Sn$	30-32/0.2	1.5280	16	5,24
28	Et	Sn	$C_{10}H_{18}Sn$	74-76/5	1.5308	20	5,24
29	Pr	Sn	$C_{12}H_{22}Sn$	64-65/0.02	1.5213	17	5,24
30	Bu	Sn	$C_{14}H_{26}Sn$	90-92/0.08	1.5174	28	5,24
31	Ph	Sn	$C_{18}H_{18}Sn$	147-150/0.3	1.6226	12	5,24
32	Bu	Ge	$C_{14}H_{26}Ge$	100-105/0.5	1.4920	2	7,24

TABLE 6
Polymers from Diynic Compounds and Organotin or Germanium Dihydrides (XIV)

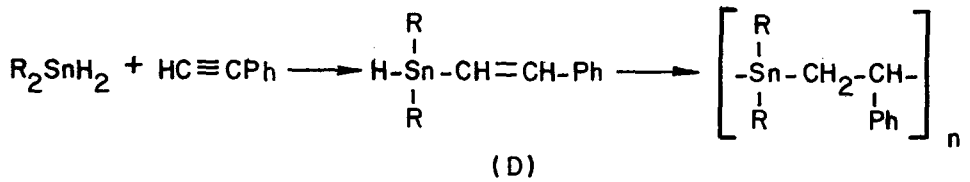
NO.	$\left[\begin{matrix}R\\ \vert \\ -M^{IV}\\ \vert \\ R\end{matrix}\right.-CH=CH-R'-CH=CH-\Big]_n$			FORMULA	APPEARANCE OF POLYMER[a]	SOLUBILITY[a]	$\overline{M}_w$	REFERENCES
	R	M^{IV}	R'					
33	Me	Sn	$-(CH_2)_2-$	$(C_8H_{14}Sn)_n$	rubbery solid	swells in C_6H_6	-	5, 24, 30, 31
34	Et	Sn	id.	$(C_{10}H_{18}Sn)_n$	id.	id.	-	5, 24, 30, 31
35	Pr	Sn	id.	$(C_{12}H_{22}Sn)_n$	soft, slightly elastic, viscous flow	C_6H_6	50.000	5, 24, 30, 31
36	Bu	Sn	id.	$(C_{14}H_{26}Sn)_n$	soft, slightly viscous	id.	50.000	5, 24, 30, 31
37	Ph	Sn	id.	$(C_{18}H_{18}Sn)_n$	rubberlike, completely resilient	C_6H_6(partly)	75.000[b]	5, 8, 24, 30, 31
38	Bu	Sn	$-(CH_2)_5-$	$(C_{17}H_{32}Sn)_n$	very viscous oil	C_6H_6; $CHCl_3$	45.000	8, 24, 30, 31
39	Ph	Sn	id.	$(C_{21}H_{24}Sn)_n$	soft, tacky, viscous flow	id.	100.000	8, 24, 30, 31
40	Ph	Sn		$(C_{22}H_{18}Sn)_n$	solid $\xrightarrow{160°}$ rubbery	C_6H_6	65.000	6, 24, 30, 31
41	Bu	Ge	$-(CH_2)_2-$	$(C_{14}H_{26}Ge)_n$	rubberlike	-	-	7, 24
42	Ph	Ge	id.	$(C_{18}H_{18}Ge)_n$	tacky, near-solid	C_6H_6	10.000	7, 24

[a]After heating in vacuo; [b]$\overline{M}_w$ of benzene-soluble fraction.

of its organotin analogue. Attempts to demonstrate the presence of the cyclic monomer in this polymer were unsuccessful, whereas on heating the butylgermanium polymer (41) in vacuo a small quantity of the cyclic monomer (32) was isolated.

Similarly, both cyclic dimers and polymers may be expected from the reaction of organotin dihydrides and monoacetylenic compounds, such as phenylacetylene. However, in these studies no attempts have been made to separate the six-membered heterocycles (compare Equation VI) from the reaction products. The isolation and characterization of the cyclic dimer from diphenyltin dihydride and phenylacetylene had been reported previously (Reference 41).

The first step, i.e., the formation of a β-styryltin hydride (D) proceeds exothermally; the succeeding polymerization requires prolonged heating at 90°-130°:



(XVI)

(D)

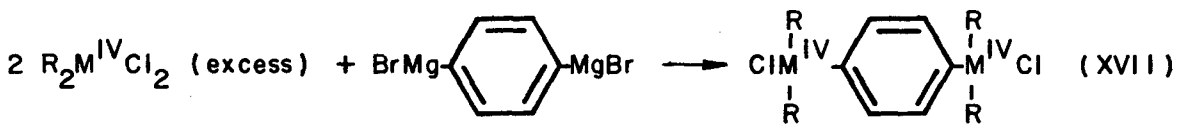
46-48, R = Pr, Bu, and Ph

The low-molecular weight polymeric products thus obtained are listed in Table 7.

Phenylacetylene, 1,5-hexadiyne, 1,8-nonadiyne (45*), and 1,4-pentadiyne-3-ol (43*) were obtained according to published methods (compare Reference 24). 3-Phenyl-1,4-pentadiyne-3-ol (44*) was obtained from the reaction of ethynylmagnesium bromide with phenylethynylketone. p-Diethynylbenzene (49*) was prepared from crude divinylbenzenes via the p-tetrabromo derivative (50*). Diphenyl- and dibutylgermanium dihydride were obtained by $LiAlH_4$-reduction of the respective halides. Dibutylgermanium dibromide (51*) was prepared from diphenylgermanium dibromide via dibutyldiphenylgermane (52*).

D. Synthesis of Low-Molecular and Polymeric Adducts from Organotin Hydrides and Vinyl Derivatives of Group IV Metals Containing the p-Phenylene Group

As discussed in Section I-A reactions involving organotin dihydrides and divinyl-organometallics will result mainly in the formation of cyclic products. With this in mind some divinyl derivatives of a novel type have been synthesized according to:



(XVII)

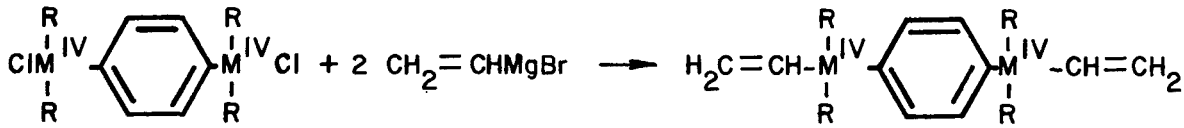
53*-55*, M^{IV} = Si or Sn

R = Me or Ph

TABLE 7

Polymers from Phenylacetylene and Organotin Dihydrides (XVI)

No.	$\underset{R}{\underline{\left[\begin{array}{c} R \\ \mid \\ -Sn-CH_2-CH- \\ \mid \qquad\quad \mid \\ R \qquad\quad Ph \end{array}\right]}}$	Formula	Appearance of Polymer	Solubility	T Melt (°C)	$\bar{M}_w$	References
46	Pr	$(C_{14}H_{22}Sn)_n$	very viscous oil	C_6H_6	-	3.400	5,6,24,30, 31
47	Bu	$(C_{16}H_{26}Sn)_n$	id.	id.	-	-	5,24,30,31
48	Ph	$(C_{20}H_{18}Sn)_n$	hard, brittle	id.	80	-	5,30,31

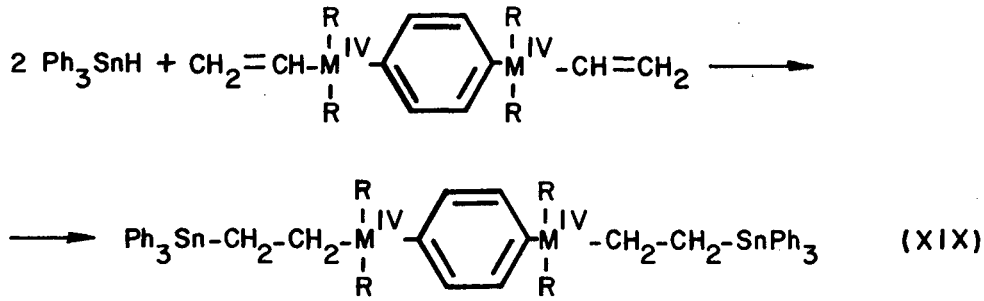


(XVIII)

56-58, M^{IV} = Si or Sn

R = Me or Ph

These compounds, which have been listed in Table 8 were expected to yield solely linear polymers upon reaction with organotin dihydrides as a result of the presence of the p-phenylene group. However, reaction of these compounds with triphenyltin hydride, although affording the expected products (see Table 9):



(XIX)

59-61, M^{IV} = Si or Sn

R = Me or Ph

was accompanied by some decomposition. Reaction with diphenyltin dihydride did not produce products with any appreciable molecular weight, considerable evolution of gas, and formation of metallic tin being observed. Apparently the p-phenylenedivinyl derivatives are susceptible to the reducing action of the organotin hydrides.

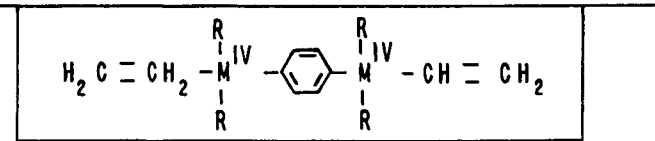
E. Synthesis of Low-Molecular and Polymeric Adducts from p-Phenylene-Bis(Dimethyltin Hydride) and Olefinic and Acetylenic Compounds

As described in the previous sections organometallic polymers having appreciable molecular weights can be obtained by means of poly-addition reactions involving organotin dihydrides and unsaturated compounds. However, the softening points of these polymers are low. One possible way to increase the crystallinity, and with that the softening temperatures, of these poly-addition polymers is by introducing an enhanced rigidity into the polymer backbone. This may be accomplished by introducing p-phenylene groups into the polymer backbone. The phenylene groups may form a part either of the dienic compound or of the tin hydride. Poly-addition reaction using several dienic compounds containing the p-phenylene group have been described in previous sections. Poly-addition reactions using p-phenylene-bis-(dimethyltin hydride) are described in the present section.

p-Phenylene-bis(dimethyltin hydride) (62*) has been obtained by reduction of the corresponding dichloride (55*):

TABLE 8

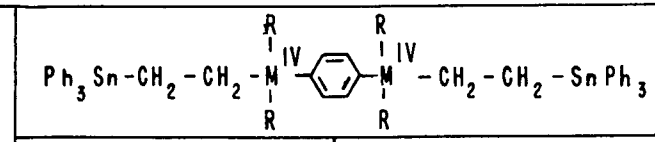
Divinyl Derivatives of Group IV Metals Containing the p-Phenylene Group (XVIII)



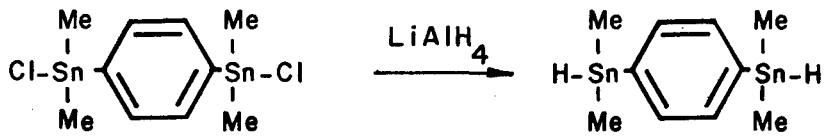
NO.	M^{IV}	R	FORMULA	BOILING POINT (°C / mm)	n_D^{20}	YIELD (%)	REFERENCES
56	Si	Me	$C_{14}H_{22}Si_2$	85.5-87/0.4	1.5112	75	10, 31
57	Si	Ph	$C_{34}H_{30}Si_2$	95-110[a]	-	44	10, 31
58	Sn	Me	$C_{14}H_{22}Sn_2$	97/0.003	1.5633	37	10, 31

TABLE 9

Addition Products from Divinyl Organometallics Containing the p-Phenylene Group and Triphenyltin Hydride (XIX)



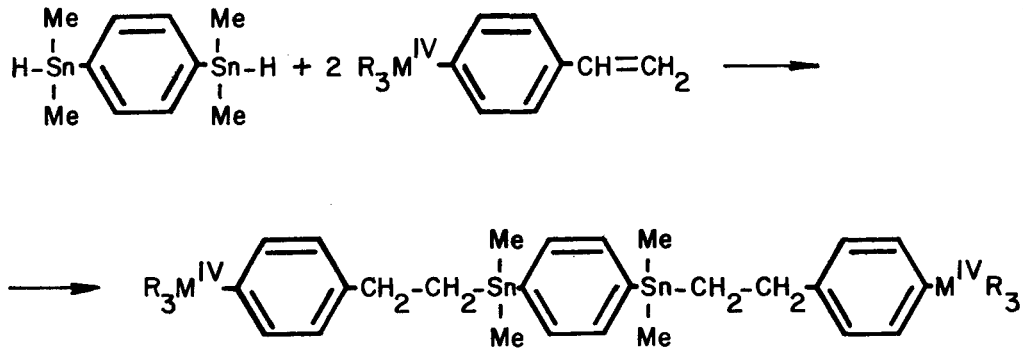
NO.	M^{IV}	R	FORMULA	MELTING POINT (°C)	YIELD (%)	REFERENCES
59	Si	Me	$C_{50}H_{54}Si_2Sn_2$	130-135	74	10, 31
60	Si	Ph	$C_{70}H_{62}Si_2Sn_2$	162-172	42	10, 31
61	Sn	Me	$C_{50}H_{54}Sn_4$	189-198	27	10, 31



(XX)

(62*)

For an insight into the reactivity of this hydride a few model reactions were carried out with mono-p-styrenyl derivatives of germanium, tin, and lead. The 2:1 addition products obtained are listed in Table 10:



(XXI)

63, R = Me M^{IV} = Sn

64-66, R = Ph M^{IV} = Ge, Sn, and Pb resp.

Since each tin atom of the present organotin hydride bears two aliphatic groups the behavior of the compound towards unsaturated carbon-carbon bonds much more resembles that of alkyltin hydrides than of aryltin hydrides. Therefore fairly long reaction periods are necessary to complete the addition reactions. The 2:1 adducts are colorless amorphous solids which show a wide melting range. Repeated crystallization from appropriate solvents did not yield sharp-melting, crystalline compounds, although according to analytical and infrared data these solids must be fairly pure. Lack of crystallinity, which also is encountered in the addition products 7 and 8 (Table 1) seems to be inherent to this type of molecules.

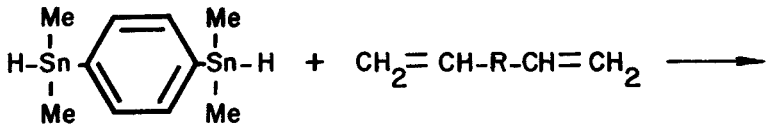
TABLE 10

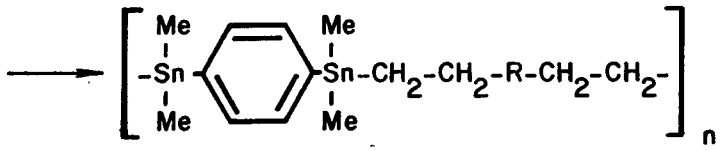
Addition Products from p-Styrenyl-Substituted Group IV Metal Derivatives and p-Phenylene-Bis(Dimethyltin Hydride) (XXI)

NO.	COMPOUND (R = -Sn(Me)$_2$-C$_6$H$_4$-Sn(Me)$_2$-)	FORMULA	REACTION TEMP (°C)	TIME (HRS)	MELTING POINT[a] (°C)	YIELD[a] (%)	REFERENCES
63	Me_3Sn-C$_6$H$_4$-CH_2-CH_2-R-CH_2-CH_2-C$_6$H$_4$-$SnMe_3$	$C_{32}H_{50}Sn_4$	85	26	64-68	40 (46)	13, 27
64	Ph_3Ge-C$_6$H$_4$-CH_2-CH_2-R-CH_2-CH_2-C$_6$H$_4$-$GePh_3$	$C_{62}H_{62}Ge_2Sn_2$	70	30	125-145	47 (53)	12, 13, 27
65	Ph_3Sn-C$_6$H$_4$-CH_2-CH_2-R-CH_2-CH_2-C$_6$H$_4$-$SnPh_3$	$C_{62}H_{62}Sn_4$	70	18	124-136	54 (76)	12, 13, 27
66	Ph_3Pb-C$_6$H$_4$-CH_2-CH_2-R-CH_2-CH_2-C$_6$H$_4$-$PbPh_3$	$C_{62}H_{62}Sn_2Pb_2$	85	16	115-130	23 (53)	13, 27

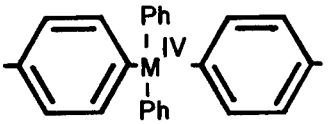
[a]After repeated recrystallizations; yields after only one crystallization are given in parenthesis; see also discussion.

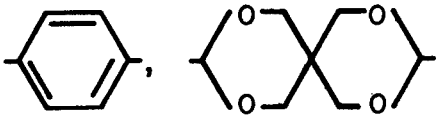
The poly-addition reactions of p-phenylene-bis(dimethyltin hydride) with several dienic, acetylenic, and diacetylenic compounds afforded polymeric products which showed close resemblance to the corresponding polymers derived from diphenyltin dihydride:

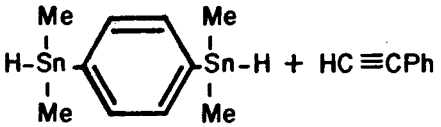


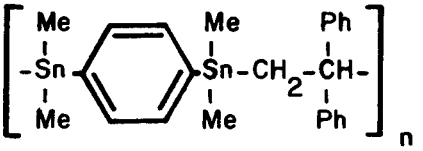


(XXII)

67,68 R = 

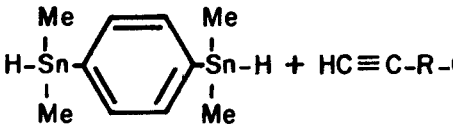
69,70 R =  resp.

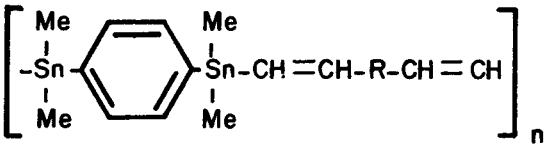




(XXIII)

(71)





(XXIV)

72-74 R = $-(CH_2)_2-$, $-(CH_2)_5-$ and

resp.

A survey of the polymers thus obtained is given in Table 11. The polymers 67, 70, 72, and 73 have been subjected to molecular weight determinations by means of ultra-centrifuge measurements*.

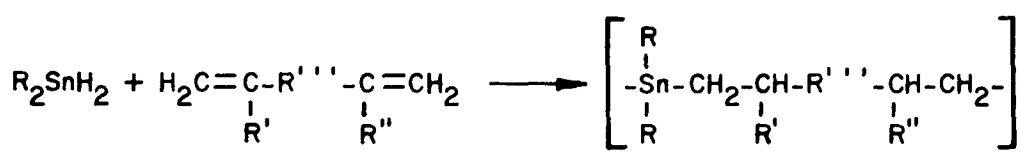
Exact molecular weights could not be determined by this method, due to a very broad molecular weight distribution of the polymer sample. The weight-average molecular weights of all of these four polymers are about 100.000 ($\bar{n} = \sim 120\text{-}200$). It has to be stressed that the experiments indicate that only about less than 10 percent of each sample has a molecular weight of a few hundred-thousands, whereas the bulk of the samples has a molecular weight of approximately only a few ten thousands.

In spite of these rather high molecular weights the softening points of the above described polymers just like those of the polymers obtained from organotin dihydrides, are low. Obviously this unfavorable behavior is inherent to this type of organometallic poly-addition polymers. This may be due to the absence of intermolecular forces, which is also demonstrated by the lack of crystallinity of several monomeric compounds. Hydrogen-bonding can not occur and van der Waals interaction between the molecules will be hampered by the bulky organometallic group.

F. Synthesis of Polymers from Organotin Dihydrides and Unsaturated Esters and Amides

Another way to increase the melting point of polymers is by favoring chain interaction by introducing polar groups into the polymer main chain. To this purpose organotin dihydrides were reacted with difunctionally unsaturated esters and amides.

The poly-addition reactions of organotin dihydrides with ethyleneglycol diacrylates, methacrylic anhydride, allyl methacrylate and diallyl diglycolate yielded tin-containing polyesters:



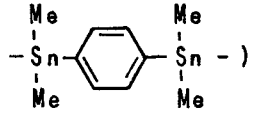
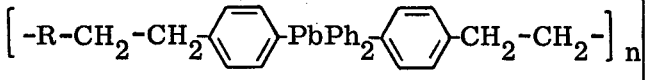
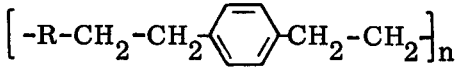
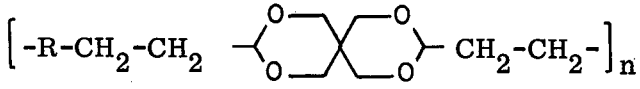
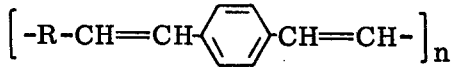
(XXV)

75-79, R''' = organic group containing at least one ester (anhydride) function

*See Reference 44 and footnote on page 8.

TABLE 11

Polymers from Unsaturated Compounds and p-Phenylene-Bis(Dimethyltin Hydride) (XXII-XXIV)

NO.	POLYMER (R = )	FORMULA	APPEARANCE OF POLYMER	SOLUBILITY	T MELT (°C)	REFERENCES
67		$(C_{38}H_{42}Sn_3)_n$	hard, brittle	C_6H_6	95	13, 14, 27
68		$(C_{38}H_{42}Sn_2Pb)_n$	id.	id.	95	13, 27
69		$(C_{20}H_{28}Sn_2)_n$	hard	id.	100	14, 27
70		$(C_{21}H_{34}O_4Sn_2)_n$	id.	id.	90	13, 14, 27
71	$\left[-R-CH_2-CH(Ph)-\right]_n$	$(C_{18}H_{24}Sn_2)_n$	glasslike	id.	65	14, 27
72	$\left[-R-CH{=}CH-(CH_2)_2-CH{=}CH-\right]_n$	$(C_{16}H_{24}Sn_2)_n$	rubbery, slightly tacky	id.	-	13, 14, 27
73	$\left[-R-CH{=}CH-(CH_2)_5-CH{=}CH-\right]_n$	$(C_{19}H_{30}Sn_2)_n$	very viscous slightly rubbery	id.	-	13, 14, 27
74		$(C_{20}H_{24}Sn_2)_n$	hard, brittle crosslinked	-	-	13, 27

The weight-average molecular weight of the polyesters determined by means of the Archibald method (Reference 44) was found to be 150.000 ($\bar{n} = \sim 320$, polymer 76), 25.000 ($\bar{n} = \sim 60$, polymer 78), and 75.000 ($\bar{n} = \sim 150$, polymer 79).

Upon heating diphenyltin dihydride with N,N'-alkylene-bis-acrylamides low-melting brittle polymers soluble in dimethylformamide were obtained:

$$Ph_2SnH_2 + H_2C{=}CH\text{-}CO\text{-}NH\text{-}(CH_2)_x\text{-}NH\text{-}CO\text{-}CH{=}CH_2 \longrightarrow$$

$$\longrightarrow \left[\begin{array}{c} Ph \\ | \\ -Sn- \\ | \\ Ph \end{array} CH_2\text{-}CH_2\text{-}CO\text{-}NH\text{-}(CH_2)_x\text{-}NH\text{-}CO\text{-}CH_2\text{-}CH_2\text{-} \right]_n \qquad \text{(XXVI)}$$

80-82, x = 2,6 and 9

The polymers obtained in Reactions XXV and XXVI are listed in Table 12.

The N,N'-alkylene-bis-acrylamides (83*-85*) were obtained from acryloyl chloride and the corresponding diamines. The addition reactions were carried out as described in previous sections.

As may be derived from these and formerly described experiments the addition of the tin-hydrogen group to unsaturated carbon-carbon bonds may be applied successfully to the synthesis of high-molecular weight polymers containing organotin groups in the polymer backbone. In spite of the rather superficial characterization of the polymers obtained in this synthetic study, we believe, however, that it may safely be concluded that polymers, obtained in this way, in general will be very viscous liquids or low-melting solids. Interchain forces inevitably tend to be very weak as a consequence of the presence of the bulky organotin group in the polymer main chain.

TABLE 12

Ester or Amide Group Containing Organotin Dihydride Addition Polymers

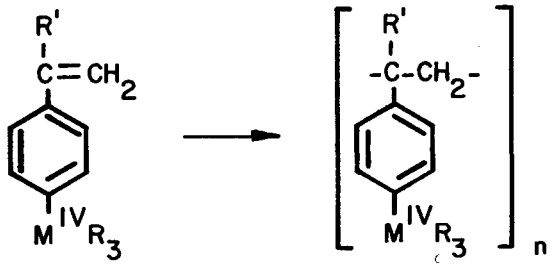
NO.	$\left[-\underset{R}{\overset{R}{Sn}}-CH_2-\underset{R'}{CH}-R'''-\underset{R''}{CH}-CH_2-\right]_n$				FORMULA	APPEARANCE OF POLYMER	SOLUBILITY	T MELT (°C)	$\overline{M}_w$	REFERENCES
	R	R'	R''	R'''						
75	Pr	H	H	$-COOCH_2CH_2OOC-$	$(C_{14}H_{26}O_4Sn)_n$	tough	-	-	-	30
76	Ph	Me	Me	id.	$(C_{22}H_{26}O_4Sn)_n$	very tacky cold-flowing	C_6H_6	-	150.000	12, 27
77	Ph	Me	Me	-COOCO-	$(C_{20}H_{22}O_3Sn)n$	hard, brittle	-	-	-	30
78	Ph	H	Me	$-CH_2OOC-$	$(C_{19}H_{22}O_2Sn)_n$	very tacky cold-flowing	C_6H_6	-	25.000	12, 27
79	Ph	H	H	$-CH_2OOCCH_2OCH_2COOCH_2-$	$(C_{22}H_{26}O_5Sn)_n$	id.	id.	-	75.000	12,27
80	Ph	H	H	$-CONH(CH_2)_2NHCO-$	$(C_{20}H_{24}N_2O_2Sn)_n$	hard, brittle	DMF	120	-	14, 27
81	Ph	H	H	$-CONH(CH_2)_6NHCO-$	$(C_{24}H_{32}N_2O_2Sn)_n$	id.	id.	110	-	14, 27
82	Ph	H	H	$-CONH(CH_2)_9NHCO-$	$(C_{27}H_{38}N_2O_2Sn)_n$	id.	id.	100	-	14, 27

SECTION II

PREPARATION AND POLYMERIZATION OF GROUP IV ORGANOMETALLIC DERIVATIVES OF STYRENE, α-METHYLSTYRENE, ISOPRENE, AND ACRYLIC ESTERS

A. Discussion

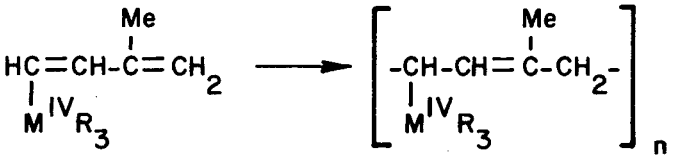
When this program was started it was decided to synthesize a number of Group IV organometallic derivatives of styrene and α-methylstyrene and to study their homopolymerization. Vinyl-type polymerization of these monomers will lead to carbon-chain polymers with organometallic groups attached to the main chain:



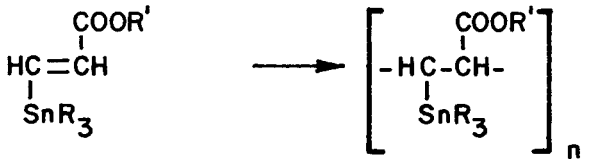
(XXVII)

R' = Me or H

Similarly, homopolymerizations involving Group IV organometallic derivatives of isoprene and acrylic esters may lead to polyisoprenes and polyacrylates in which the metal atoms are attached directly to the polymer main chain:



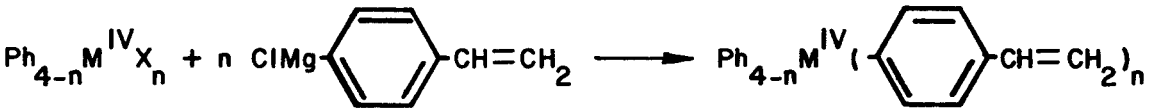
(XXVIII)



(XXIX)

B. Synthesis of Group IV Organometallic Derivatives of Styrene and α-Methylstyrene

The triphenylmono- and diphenyldi-p-styrenyl derivatives of germanium tin and lead were obtained by interaction of p-vinlyphenylmagnesium chloride (Reference 49) with the appropriate organometallic halides:



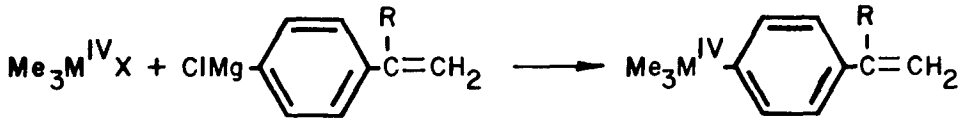
(XXX)

86-91, M^{IV} = Ge, Sn, and Pb

n = 1 and 2

Triphenyl-p-styrenylsilane, due to steric factors cannot be obtained in this way. Attempts at synthesis via the reaction of p-chlorostyrene with triphenylsilyllithium (Reference 50) were also unsuccessful (Reference 21). The compounds 86-91 have been listed in Table 13.

Trimethyl-p-styrenyl and trimethyl-p-α-methylstyrenyl derivatives of silicon, germanium, tin, and lead were obtained in the same way (see also Table 14):



(XXXI)

93-100, M^{IV} = Si, Ge, Sn, and Pb

R = H or Me

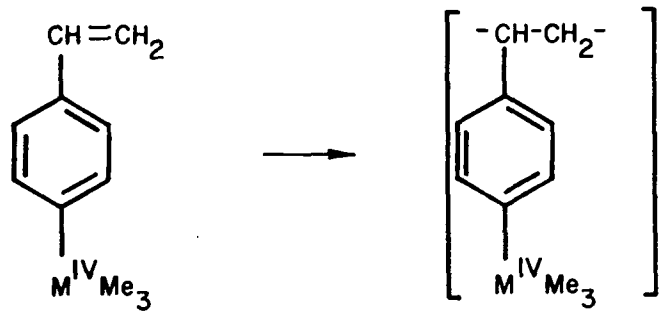
p-Chloro-α-methylstyrene (101*) was obtained by dehydration of p-chlorophenyldimethylcarbinol, prepared from p-chlorophenylmagnesium chloride and acetone.

p-Tert-butylstyrene (92), which has been included in our polymerization experiments, was obtained by dehydration of p-tert-butylphenylmethylcarbinol (102*).

Infrared spectra of these compounds revealed, aside from the bands associated with the presence of the p-phenylene and either the phenyl or the methyl groups (see Section VII), bands characteristic of the vinyl groups, e.g., at 910 cm^{-1} (strong, = CH_2 deformation out-of-plane at 988 (medium strong, -CH out-of-plane deformation) and at ~1625 cm^{-1} (weak, C = C stretching). Contrary to previous assignments (Reference 21, 22) the band occurring near 1380 cm^{-1} must be attributed to C-C stretching vibrations of the 1,4-disubstituted aromatic nucleus (see also Section VII).

C. Homopolymerization of Group IV Organometallic Derivatives of Styrene and α-Methyl-Styrene

The styrene monomers 92-96 polymerized readily at 70°-90° in the presence of free radical initiators, preferably 2,2'-azo-bis-isobutyronitrile to give the polystyrenes 103-107:



(XXXII)

103-107, M^{IV} = C, Si, Ge, Sn, and Pb resp.

These are clear, colorless solids, soluble in aromatic solvents and chloroform. The organo-lead polymer, provided its molecular weight is high enough, only swells in these solvents. Thermal polymerization is also possible but this requires prolonged heating at ~140°.

TABLE 13

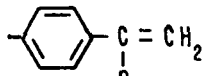
Triphenylmono- and Diphenyldi-p-Styrenyl Derivatives of Germanium, Tin, Lead (XXX)

NO.	$Ph_{4-n}M^{IV}(-C_6H_4-CH=CH_2)_n$		FORMULA	RECRYST – SOLVENT	MELTING POINT (°C)	YIELD (%)	REFERENCES
	M^{IV}	n					
86	Ge	1	$C_{26}H_{22}Ge$	ethanol	116-117	67	2, 3, 21
87	Sn	1	$C_{26}H_{22}Sn$	id.	112-113[a]	78	2, 3, 21
88	Pb	1	$C_{26}H_{22}Pb$	id.	110-111	77	3, 21
89	Ge	2	$C_{28}H_{24}Ge$	ethanol-propanol 1:1	139-140	62	2, 3, 21
90	Sn	2	$C_{28}H_{24}Sn$	ethanol	108-109	65	2, 3, 21
91	Pb	2	$C_{28}H_{24}Pb$	id.	96-97	65	3, 21

[a]Reported (Reference 49) m.p: 105.5-108°.

TABLE 14

Trimethyl-p-Styrenyl and Trimethyl-p-α-Methylstyrenyl Derivatives of Group IV Elements (XXXI)

NO.	Me_3M^{IV} 		FORMULA	BOILING POINT (°C/mm)	n_D^{20}	d_4^{20}	YIELD (%)	REFERENCES
	M^{IV}	R						
92	C	H	$C_{12}H_{16}$	57-59/0.2[a]	1.5267[a]	0.8866	-	4, 22
93	Si	H	$C_{11}H_{16}Si$	98-99/17[b]	1.5225[b]	0.8944[b]	73	4, 22
94	Ge	H	$C_{11}H_{16}Ge$	39-41/0.05	1.5400	1.1060	71	4, 22
95	Sn	H	$C_{11}H_{16}Sn$	53-54/0.0001	1.5648	1.3020	81	3, 4, 22
96	Pb	H	$C_{11}H_{16}Pb$	60-61/0.0015	1.6070	1.7278	67	3, 4, 22
97	Si	Me	$C_{12}H_{18}Si$	68-70/0.7[c]	1.5208[c]	0.8835[c]	71	4, 22
98	Ge	Me	$C_{12}H_{18}Ge$	55-57/0.3	1.5344	1.0936	57	4, 22
99	Sn	Me	$C_{12}H_{18}Sn$	49-51/0.0003	1.5574	1.2743	61	4, 22
100	Pb	Me	$C_{12}H_{18}Pb$	69-71/0.001	1.5963	1.6816	56	4, 22

[a]Reported (Reference 51) b.p.: 99-100°/14 mm, n_D^{25} : 1.5245;

[b]Reported (Reference 52) b.p.: 101-101.5°/20 mm, n_D^{20} : 1.5221, d_4^{20}: 0.8979;

[c]Reported (Reference 52) b.p.: 110-111°/20 mm, n_D^{20} : 1.5188, d_4^{20}: 0.8828.

A rather interesting dependency was found to exist between the nature of the metal atom and the rate of polymerization. A quantitative study revealed the sequence Pb > Si > C > Ge > Sn (see also Figure 2).

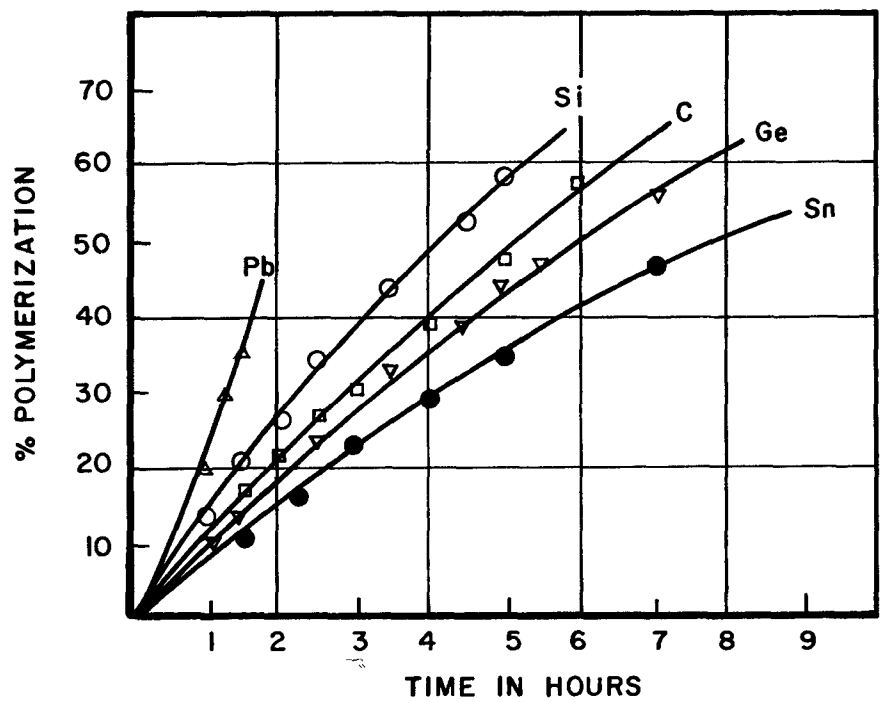
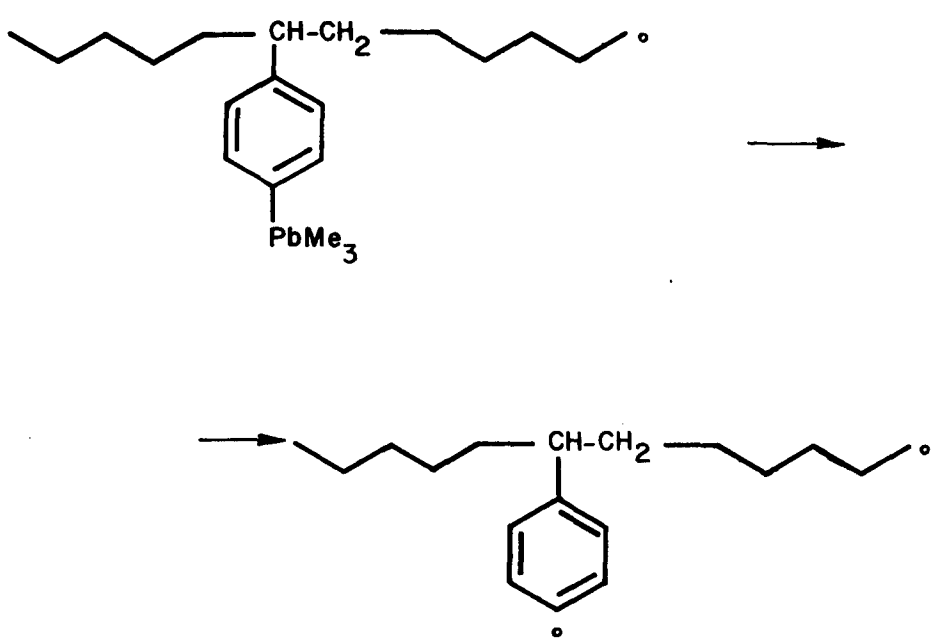


Figure 2. Plot of Percentage Polymerization Against Time for Monomers $\underline{p}$-$Me_3M^{IV}C_6H_4CH=CH_2$ (70.0°; 0.10 Mole % 2,2'-Azo-Bis-Iso-Butyronitrile)

Homolytic cleavage of lead-carbon bonds during polymerization, providing a source of extra chain-initiating radicals, is probably responsible for the higher rate of polymerization of the styrenyllead monomer:



(XXXIII)

A consequence of the phenomenon is the formation of a crosslinked polymer. The sequence Si > C > Ge > Sn is best related to a decreasing electron-attracting effect of the organometallic substituents. It might be that for silicon electron-attraction as a result of $d\pi$-$p\pi$ interaction with the styrenyl group surpasses the effect of electronegativity which decreases in the order C, Si, Ge, and Sn. Korshak et al. (Reference 53) have found a similar sequence Si > C > Ge > Sn for the polymerization of vinyl-substituted organometallics. Recently Polyakova et al. (Reference 54) reported a similar sequence for the degree of polymerization of Group IV substituted polystyrenes, obtained by radical-initiated polymerization under high pressure.

The polymer containing silicon, germanium, and tin has a softening point in the range of 170°-180° and, in finely divided form, can be pressed into transparent colorless films or sheets at elevated temperature (~190°) and pressure (~200 kg/cm^2). The brittleness of these films decreases in the order Sn > Ge > Si.

The thermal stability of these carbon-chain polymers is determined by the temperature at which the depolymerization reaction starts. In Table 15 the results of a thermogravimetric analysis (heating in air at a rate of 5° per min.) are presented. From these figures it appears that the order of stability of these polymers is Si ≈ Ge > Sn > Pb > C (see also Reference 55).

Copolymerization experiments involving Group IV organometallic styrenes have recently been reported (Reference 56). Similarly, p-trimethylgermyl-,p-trimethyltin- and p-trimethylleadstyrene in the presence of 2,2'-azo-bis-isobutyronitrile readily copolymerize with styrene and methyl methacrylate to give glasslike copolymers.

The organometallic derivatives of α-methylstyrene listed in Table 14 do not undergo thermal or radical-initiated polymerization under the conditions given for the styrene monomers, whereas the triphenyl-substituted derivatives listed in Table 13 readily undergo peroxide-initiated polymerization to give transparent, rather brittle, glasslike polymers. Recently the radical-initiated polymerization of Group IV derivatives of α-methylstyrene under high pressure (6000 atm.) has been reported (Reference 57).

D. Synthesis and Attempted Polymerization of Group IV Organometallic Derivatives of Isoprene and Acrylic Esters

To obtain a polymerizable organotin-substituted isoprene first triethyltin hydride was reacted with ethynyldimethylcarbinol:

$$Et_3SnH + HC{\equiv}C\text{-}CMe_2OH \longrightarrow \underset{(108^*)}{Et_3SnCH{=}CH\text{-}\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{C}}\text{-}OH} \qquad \text{(XXXIV)}$$

However, all attempts to dehydrate this compound have been in vain.

An alternative route, i.e., dehydration of the acetylenic carbinol followed by the addition reaction with triethyltin hydride was also unsuccessful. The addition reaction did not proceed in an unequivocal way, a mixture of the 1:1 and the 2:1 adduct had been obtained the separation of which could not be fully achieved:

TABLE 15

Thermal Degradation of Group IV Organometallic Polystyrenes

No.	Polystyrenes Tested M^{IV}	Temp. of Initial Weight-Loss (°C)	Ultimate Temp. (°C)	% Weight-Loss after Heating	References
103	C	ca. 150	725	100	7
104	Si	ca. 310	730	90	7
105	Ge	ca. 310	700	89	7
106	Sn	ca. 220	640	68	7
107	Pb	ca. 180	700	61	7

$$Et_3SnH + HC{\equiv}C\text{-}C(CH_3){=}CH_2 \longrightarrow Et_3SnCH{=}CH\text{-}C(CH_3){=}CH_2 \; (109^*) \; + \; Et_3SnCH{=}CH\text{-}CH(CH_3)\text{-}CH_2SnEt_3\,(?) \; (110^*) \qquad \text{(XXXV)}$$

Similarly, the reaction of triethyltin hydride with 1-methoxy-1-buten-3-yne failed to give a pure product:

$$Et_3SnH + HC{\equiv}C\text{-}CH{=}CH\text{-}OCH_3 \longrightarrow Et_3SnCH{=}CH\text{-}CH{=}CH\text{-}OCH_3 \; (111^*) \qquad \text{(XXXVI)}$$

The fraction obtained after several fractionations still contains some 2:1 adduct.

To obtain trialkylstannyl derivatives of acrylic esters trialkyltin hydrides were reacted with propiolic esters. However, the course of the reaction is not unambiguous. Besides the addition of tin hydride across the triple bond (see also Table 16) substitution of the acidic hydrogen of the acetylenic part of the propiolate by the trialkyltin group also occurs. The latter yields trialkylstannyl derivatives of propiolic esters. The tin-ethylenic bond in the compound thus formed is easily hydrolyzed producing the organotin hydroxide and propiolic ester. These two compounds may react with each other to give the trialkyltin salt of propiolic acid. Model reactions of organotin methoxides and hydroxides with propiolic esters confirmed this picture.

$$R_3SnH + HC{\equiv}C\text{-}COOR' \longrightarrow R_3Sn\text{-}CH{=}CH\text{-}COOR' \qquad \text{(XXXVII)}$$

112-115, R = Me, Et
R' = Me, Et

$$R_3SnH + HC{\equiv}C\text{-}COOR' \longrightarrow R_3Sn\text{-}C{\equiv}C\text{-}COOR' \qquad \text{(XXXVIII)}$$

116*, R = Et
R' = Me

$$R_3Sn\text{-}C{\equiv}C\text{-}COOR' + H_2O \rightleftharpoons R_3SnOH + H\text{-}C{\equiv}C\text{-}COOR' \qquad \text{(XXXIX)}$$

$$R_3SnOH + H\text{-}C{\equiv}C\text{-}COOR' \rightleftharpoons HC{\equiv}C\text{-}COOSnR_3 + R'OH \qquad \text{(XL)}$$

117*, 118*, R = Me and Et resp.

The homopolymerization of these organotin acrylic esters under the influence of Ziegler-Natta catalysts was attempted, using the following systems:

a. $Et_3Al/VOCl_3$ (15:1) or $EtAlX_2/VOCl_3$ (15:1) "Bakelite" catalyst
b. $Et_3Al/VOCl_3$ (2:1) "Copolymerization catalyst (Reference 58)
c. $Et_3Al/TiCl_4$ (3:1) "Ziegler-Natta" catalyst (Reference 59)

However, in these cases no polymerization was observed.

TABLE 16

Esters of β-Trialkylstannylacrylic Acid from Propiolic Esters and Trialkyltin Hydrides (XXXVII)

No.	R_3Sn-CH=CH-COOR' R	R'	Formula	Boiling Point (°C/mm)	n_D^{20}	Yield (%)	References
112	Me	Me	$C_7H_{14}O_2Sn$	83-88/27	1.4784	42	11,12,13
113	Me	Et	$C_8H_{16}O_2Sn$	74-76/12	1.4700	35	12,13
114	Et	Me	$C_{10}H_{20}O_2Sn$	73-75/4	1.4900	48	11,12,13
115	Et	Et	$C_{11}H_{22}O_2Sn$	85-87/1	1.4860	44	12,13

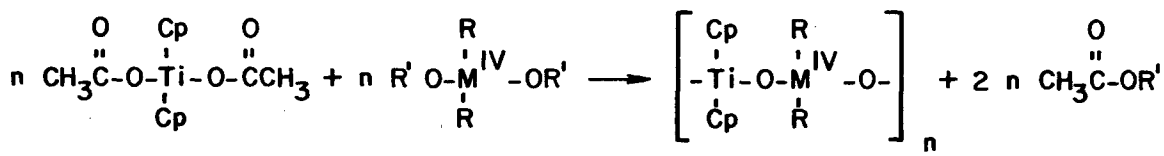
Acrylic acid with a trimethylsilyl group attached to the α-carbon atom was prepared also (119*). Attempts to synthesize the methyl ester of this acid, involving diazomethane, resulted in impure products. Recently the synthesis (Reference 60) and homopolymerization (Reference 61) of α-trialkylstannylacrylic alkyl esters at high temperatures (~250°) have been reported.

SECTION III

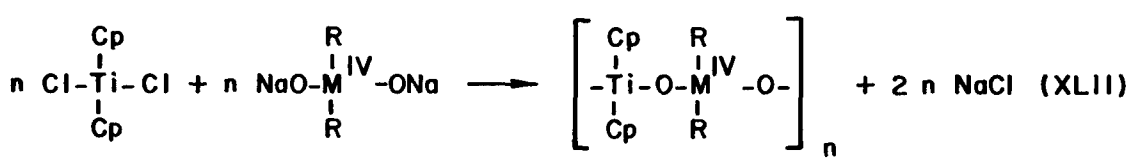
BIS-CYCLOPENTADIENYLTITANOXANE DERIVATIVES OF GROUP IV METALS

A. Discussion

Among the biscyclopentadienyl derivatives of the transition metals, ferrocene especially has excellent thermal stability. It is to be expected that the thermal behavior of certain derivatives of similar sandwich compounds derived from titanium and vanadium will be more or less comparable. Therefore, the introduction of bis-cyclopentadienyltitanium or -vanadium groups might result in thermostable structures with attractive physical properties. Of the many synthetic approaches which can be considered, the reaction of bis-cyclopentadienyltitanium diacetate with a dialkyl- or diaryl-M^{IV}-dialcoholate or of bis-cyclopentadienyltitanium dichloride with a disodium dialkyl- or diaryl-M^{IV}-diolate may be mentioned.



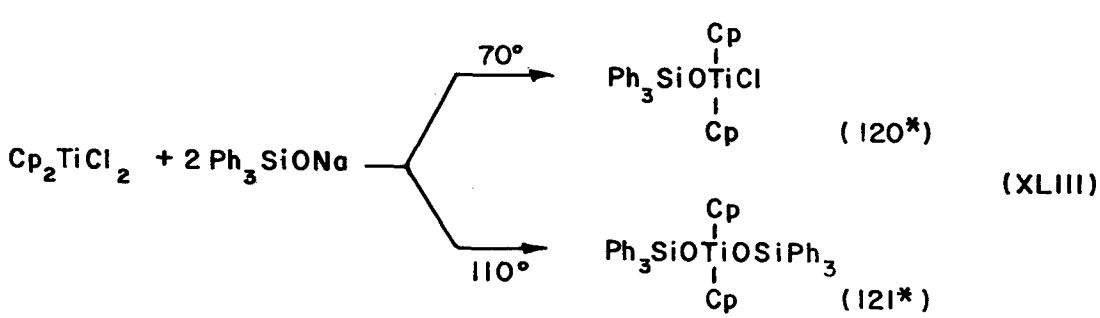
(XLI)



(XLII)

B. Synthesis of Triphenylsiloxy Derivatives of Bis-Cyclopentadienyltitanium

The suitability of Equation XLII for polymer formation was studied in a model reaction by reacting monofunctional sodium triphenylsilanolate with difunctional bis-cyclopentadienyltitanium dichloride in toulene. Contrary to the findings of Gutmann and Meller (Reference 62), who were unable to isolate any condensation product, this reaction afforded triphenylsiloxy- and bis-triphenylsiloxy-bis-cyclopentadienyltitanium derivatives. It was found that depending on the reaction temperature employed, one or two chlorine atoms are replaced by the triphenylsiloxy group:

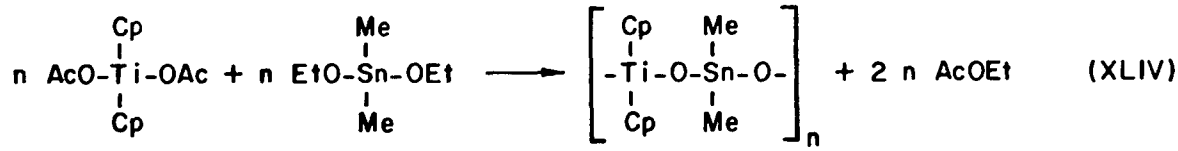


(XLIII)

Tetrakis-triphenylsiloxy-titanium (122*) was isolated in very low yield from the residue of the reaction at 110°. Neither the formation of compound 120 in the 110° reaction, nor of compound 121 in the 70° reaction could be demonstrated.

C. Attempted Synthesis of Bis-Cyclopentadienyltitanoxane Polymers of Group IV Metals

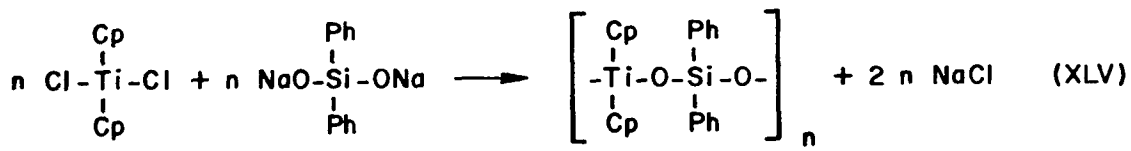
The above described route XLI appeared very unpromising due to the extreme sensitivity towards moisture of bis-cyclopentadienyltitanium diacetate (123*). Moreover, this compound possesses marked thermal instability which necessitates the application of a low reaction temperature in the reaction with a dialcoholate. Reaction with dimethyltin diethylate, expected to proceed according to:



(124)

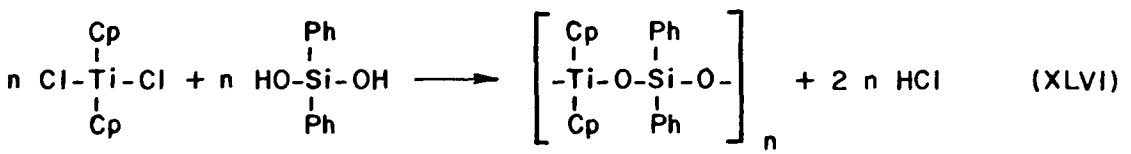
did not result in the formation of polymeric material containing Ti-O-Sn bonds. Bis-cyclopentadienyltitanium oxide and polymeric dimethyltin derivatives appeared to be the main products.

The successful preparation of triphenylsiloxy derivatives from bis-cyclopentadienyltitanium dichloride and sodium triphenylsilanolate has led us to study the polymer-forming reaction of disodium diphenylsilanediolate with bis-cyclopentadienyltitanium dichloride:



(125)

The reaction of Cp_2TiCl_2 with $Ph_2Si(ONa)_2$ in toluene at 90° afforded sodium chloride and an orange-yellow solid (125a) with m.p. ~180°. Separate analysis for both Si and Ti of this product indicated a Si/Ti ratio greater than 1. Since the disodium diolate most probably is not sufficiently pure for high-polymer formation, the direct condensation of diphenylsilane diol with bis-cyclopentadienyltitanium dichloride was carried out also:



(125)

It is apparent that the presence of a HCl-receptor such as an organic base will favor the occurrence of co-polycondensation. Upon addition of Cp_2TiCl_2 to a toluenic solution of $Ph_2Si(OH)_2$, containing an equimolecular quantity of aniline, at 90° yielded aniline-HCl and an orange-colored product (125b) melting at ~ 155°. Analyses of this product indicated a Ti/Si ratio greater than 1 (~1.3), which (together with the presence of residual chlorine) might be explained by assigning to these compounds an oligomeric structure with chloro-bis-cyclopentadienyl end-groups ($n \approx 4$).

To attain higher molecular weights further experiments were carried out under more forced conditions, yielding a light-tan, benzene-soluble, infusible powder. Elementary analyses suggested that appreciable cleavage of cyclopentadienyl-titanium bonds had occurred. The high Ti/Si ratio (~1.8) cannot be explained by assuming an oligomeric structure with titanium end-groups and must be connected with the presence of Ti-O-Ti bonds in the polymer chain.

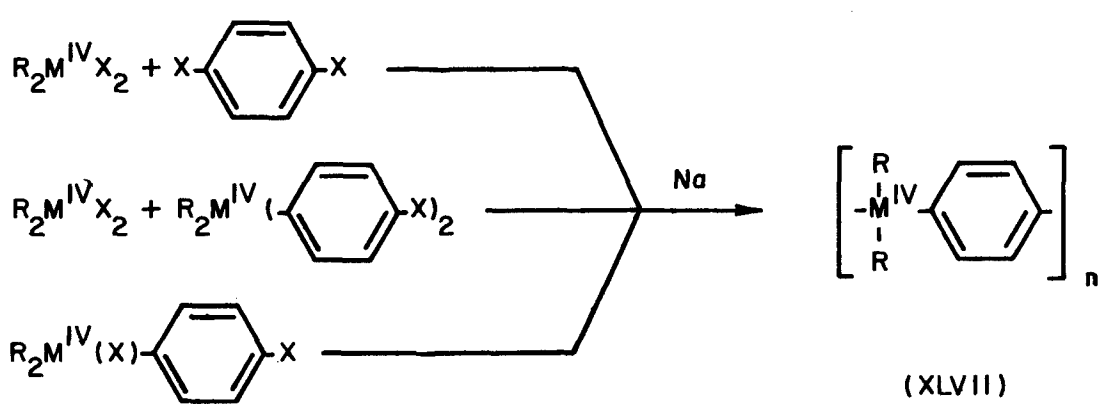
SECTION IV

WURTZ-TYPE CONDENSATIONS LEADING TO GROUP IV ORGANOMETALLIC OLIGOMERS AND POLYMERS CONTAINING THE p-PHENYLENE GROUP

A. Discussion

The poly-addition polymers described in the first section of this report in spite of their appreciable molecular weights have low softening points. This was ascribed to the low degree of crystallinity or even amorphous state of these polymers. It is well known that a high degree of crystallinity is favored by, among other factors, rigidity of the polymer backbone, a feature that can be promoted by putting inflexible rings, e.g., the p-phenylene group into the polymer chain. It is inherent to the poly-addition reaction (addition of Sn-H to $H_2C{=}CH$-) that polymers obtained by this reaction contain ethylene groups. Thus, polymers consisting of a chain of Group IV elements linked through p-phenylene groups have to be prepared by other methods. Such polymers should have crystalline properties and thus melt much higher than the poly-addition polymers. With a view to the thermal and oxidative stability of the silicon-phenyl bond (tetraphenylsilane may be distilled open to the atmosphere at 430° without decomposition; see Reference 63) the silicon-containing oligomers and polymers of this type might be expected to have good stability in particular. Although the germanium-phenyl and the tin-phenyl bond are inherently less stable, p-phenylenegermanium and p-phenylenetin polymers will be about the most stable organic polymers which can be devised from these elements anyhow.

Since the Wurtz-type condensation reaction is very well suited to the establishment of M^{IV}-aryl bonds, this method was selected because of its simplicity and versatility. Each of the following reaction types might be employed for the synthesis of polymers:

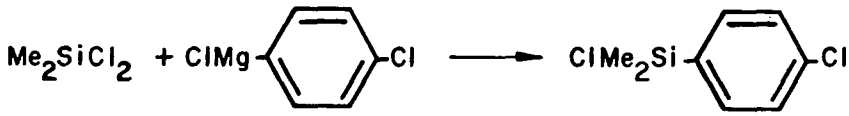


(XLVII)

The oligomeric members of this class of compounds were prepared by essentially similar methods and subsequently their properties were studied.

B. Synthesis of Oligomeric and Polymeric p-Phenylenesilanes

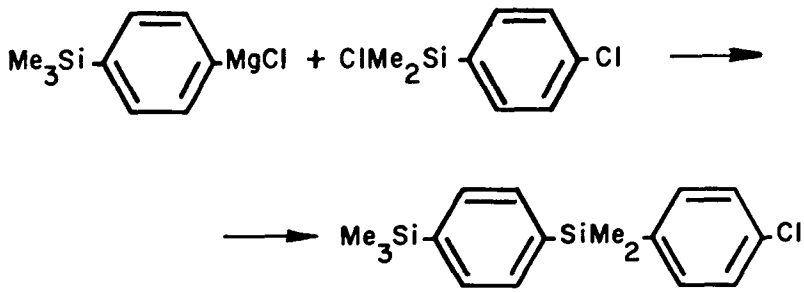
The starting materials required for this study were prepared by conventional methods. p-Chlorophenyl-trimethylsilane (126*), bis(p-chlorophenyl)dimethylsilane (127*), p-chlorophenyltriphenylsilane (128*) and bis(p-chlorophenyl)diphenylsilane (129*) were prepared using slightly modified published procedures. Chloro-p-chlorophenyldimethylsilane (130*) was obtained from p-chlorophenylmagnesium chloride and dichloro-dimethylsilane:



(XLVIII)

(130*)

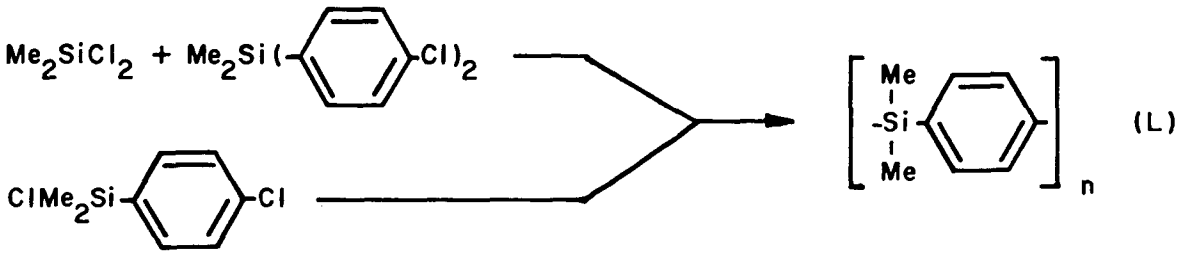
The preparation of p-bis(chlorodimethylsilyl)benzene (53*) and p-bis(chlorodiphenylsilyl)-benzene (54*) has been mentioned in Section I.D. The isolation of the last-mentioned compound was accomplished via the di-ethoxy derivative (131*). p-Chlorophenyl-dimethyl-(p-trimethylsilylphenyl)silane (132*) was obtained by Grignard coupling of p-chloromagnesium phenyl-trimethylsilane and chloro-p-chlorophenyldimethylsilane:



(XLIX)

A number of oligomeric model compounds were prepared by the reaction of appropriate combinations of mono- and bifunctional p-chlorophenyl and chlorosilanes with a suspension of sodium sand in refluxing toluene. In each case the expected product was isolated in satisfactory yield (Table 17). Whereas the methyl-substituted p-phenylenesilane oligomers 133-137 and the mixed compound 140 are readily soluble in the common organic solvents, the very high-melting completely phenyl-substituted products 138 and 139 are sparingly soluble in boiling aromatic solvents or dimethylformamide only.

The successful preparation of the oligomeric p-phenylenesilanes led us to carry out under similar conditions polymer-forming reactions of appropriate combinations of bi-functional p-chlorophenyl and chlorosilanes (Table 18). Poly-dimenthyl-p-phenylenesilane (141, 142) was obtained by two routes as shown in the next equation:

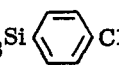
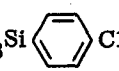
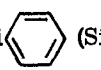


(L)

Each of the reactions mentioned in Table 18 afforded polymeric products the analyses of which are in accord with the proposed structure. The formation of Si-Si bonds, which must be considered possible in this type of reaction, most probably does not occur. Moreover, Korshak et al. (Reference 65), who recently reported the poly-condensation of a haloaryl- and an odd four haloalkyl-halosilanes under similar conditions, were unable to demonstrate the presence of such bonds in their products, at least by chemical means.

TABLE 17

Some Oligomeric p-Phenylenesilanes Obtained by Wurtz-Type Condensations

NO.	COMPOUND	FORMULA	OBTAINED FROM		M. p. °C	RECRYST. SOLVENT	YIELD (%)	REFERENCE
			CHLOROSILANE	p - CHLOROPHENYLSILANE				
133	Me_3Si $SiMe_3$[a]	$C_{12}H_{22}Si_2$	Me_3SiCl	Me_3Si Cl	94-96[d]	ethanol	60	7, 26
134	$Me_3Si($ $SiMe_2)_2Me$	$C_{20}H_{32}Si_3$	Me_2SiCl_2	2 Me_3Si Cl	78-81	propanol	48	7, 26
135	$Me_3Si($ $SiMe_2)_3Me$	$C_{28}H_{42}Si_4$	$ClMe_2Si$ $SiMe_2Cl$	2 Me_3Si Cl	131-133	ethanol	37	7, 26
136	$Me_3Si($ $SiMe_2)_4Me$	$C_{36}H_{52}Si_5$	Me_2SiCl_2	2 Me_3Si $SiMe_2$ Cl	170-173	acetone	53	8, 26
137	$Me_3Si($ $SiMe_2)_5Me$	$C_{44}H_{62}Si_6$	$ClMe_2Si$ $SiMe_2Cl$	2 Me_3Si $SiMe_2$ Cl	187-191	toluene	47	8, 26
138	Ph_3Si $SiPh_3$	$C_{42}H_{34}Si_2$	Ph_3SiCl	Ph_3Si  Cl	337-341	DMF[b,c]	33	8, 26
139	$Ph_3Si($ $SiPh_2)_2Ph$	$C_{60}H_{48}Si_3$	Ph_2SiCl_2	2 Ph_3Si  Cl	365-368	xylene[c]	45	8, 26
140	Ph_3Si  $(SiMe_2$ $)_2$- -$SiPh_3$	$C_{58}H_{54}Si_4$	$ClMe_2Si$ $SiMe_2Cl$	2 Ph_3Si Cl	220-222	DMF[b]	48	8, 26

[a]Magnesium in THF was used as the condensing agent;

[b]dimethylformamide;

[c]by continuous extraction;

[d]Clark et al. (Reference 64) reported m.p. 88° for this compound.

TABLE 18

Some Poly-p-Phenylenesilanes Obtained by Wurtz-Type Condensations

NO.	POLYMER	FORMULA	OBTAINED FROM		MELTING POINT[a] (°C)	YIELD (%)	$\overline{M}_n$[b]	D.P.[c]	REFERENCE
			CHLOROSILANE	p-CHLOROPHENYLSILANE					
141a	$(-Si(Me)_2-C_6H_4-)_n$	$(C_8H_{10}Si)_n$	Me_2SiCl_2	$Me_2Si(-C_6H_4-Cl)_2$	200-225	15	3800	28	9,10,26
141b					155-210	54	1800	13	9,10,26
142a	$(-Si(Me)_2-C_6H_4-)_n$	$(C_8H_{10}Si)_n$	$ClMe_2Si-C_6H_4-Cl$	$ClMe_2Si-C_6H_4-Cl$	190-210	17	2100	16	9,10,26
142b					170-185	40	1800	13	9,10,26
143	$(-Si(Me)_2-C_6H_4-Si(Ph)_2-C_6H_4-)_n$	$(C_{26}H_{24}Si_2)_n$	Me_2SiCl_2	$Ph_2Si(-C_6H_4-Cl)_2$	155-170	76	2400	6	9,10,26
144a	$(-Si(Me)_2-C_6-H_4-Si(Me)_2-C_6H_4-Si(Ph)_2-C_6H_4-)_n$	$(C_{34}H_{34}Si_3)_n$	$ClMe_2Si-C_6H_4-SiMe_2Cl$	$Ph_2Si(-C_6H_4-Cl)_2$	190-210	14	2900	6	9,10,26
144b					175-195	34	2800	5	9,10,26
145a	$(-Si(Me)_2-C_6H_4-Si(Ph)_2-C_6H_4-Si(Ph)_2-C_6H_4-)_n$	$(C_{44}H_{38}Si_3)_n$	$ClPh_2Si-C_6H_4-SiPh_2Cl$	$Me_2Si(-C_6H_4-Cl)_2$	215-245	18	2600	4	9,10,26
145b					135-155	22	-	-	9,10,26
146a	$(-Si(Ph)_2-C_6H_4-)_n$	$(C_{18}H_{14}Si)_n$	$ClPh_2Si-C_6H_4-SiPh_2Cl$	$Ph_2Si(-C_6H_4-Cl)_2$	>360	52	-	-	9,10,26
146b					235-260	12	2100	8	9,10,26

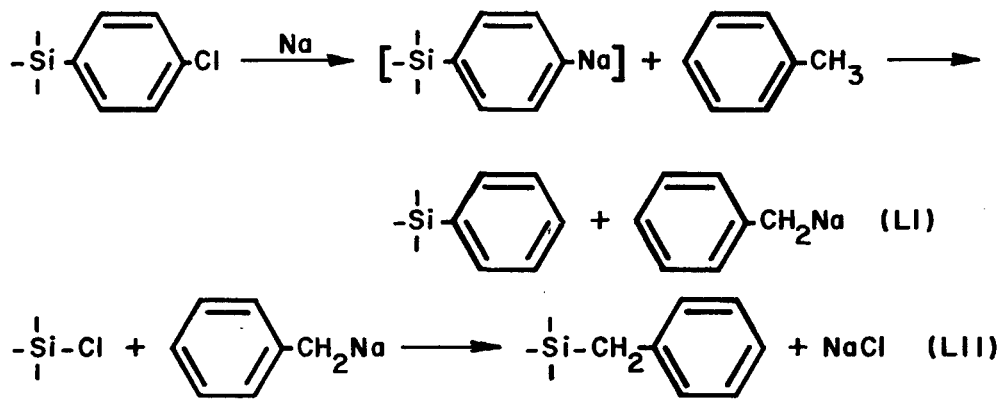
[a]Temperatures at which softening starts and at which a clear melt is obtained are given;

[b]ebullioscopic measurement in benzene;

[c]see also structural unit given in the second column.

The polymers are soluble (144a and 145a sparingly) in hot aromatic solvents (with the exception of 146a, compare compounds 138 and 139), but insoluble in aliphatic hydrocarbons and alcohols. They were obtained as colorless powders by preparation with methanol from their toluenic solution or as amber-colored, brittle resins by evaporation of the solvent.

The poly-p-phenylenesilanes contain on the average only 10-30 p-phenylene groups per molecule. It would seem that the attainment of high molecular weights is hampered by the limited solubility of this type of compounds, resulting in the precipitation of already relatively low molecular weight species from the reaction medium. The choice of toluene, one of the best solvents for this type of polymer, as the reaction medium has the disadvantage that it may undergo metallation by reactive organosodium derivatives such as phenylsodium to give benzylsodium (Reference 66). When it is assumed that this type of poly-condensation involves the intermediate formation of organosodium derivatives, reaction of the latter with the solvent, i.e., toluene, instead of with a chlorosilyl group will result in chain-termination by each of the two following consecutive reactions:



Thus, instead of p-chlorophenyl and chlorosilyl end-groups the polymer would contain phenyl and benzyl-silicon end-groups. This mechanism of termination which would seem to prevent the attainment of appreciable molecular weights finds support in the observed low residual chlorine content of the polymer fractions isolated; e.g., polymer 143 with $\overline{M}_n = 2400$ (ebullioscopic) contains 0.39 percent residual chlorine, whereas the calculated value assuming two chlorine-containing end-groups is 2.95 percent. The presence of siloxane groups likely to result from the hydrolysis of chlorosilyl end-groups could not be detected by infrared spectroscopy. The infrared spectra of the polymers were compared with those of the corresponding model compounds mentioned in Table 17. The spectra support the proposed structure, differences occurring in the relative intensities rather than in the position of the various absorptions (compare also Section VII).

A first insight into the thermal behavior of some representative poly-p-phenylenesilane samples was obtained by determining with a Chevenard thermobalance the weight-loss occurring on heating the samples gradually and continuously up to 900° at a rate of 2.5°/min. under nitrogen*. The temperature at which loss in weight starts and the percentage weight-loss at various temperatures between 400° and 900° are presented in Table 19. Some typical weight-loss curves are shown in Figure 3.

*Thermogravimetric curves were determined by Dr. G. F. L. Ehlers (Nonmetallic Materials Laboratory, Aeronautical Systems Division, Wright-Patterson AFB, Ohio) and at the Institute for Physical Chemistry T.N.O., Utrecht, under the direction of Dr. W. M. Smit.

TABLE 19

Weight-Loss of Poly-p-Phenylenesilanes upon Heating at Gradually Increasing Temperature

NO.	POLYMER	TEMP. OF INITIAL WEIGHT-LOSS (°C)	WEIGHT-LOSS AT TEMP. (°C) OF					REFERENCES
			400	450	500	600	900	
141a	$[-SiMe_2-C_6H_4-]_n$	400	-	2	22	56	58	11, 12, 26
142b	id.	390	1	4	33	65	67	10, 11, 12, 26
143	$[-SiMe_2-C_6H_4-SiPh_2-C_6H_4-]_n$	330	2	9	16	49	53	10, 12, 26
144a	$[-SiMe_2-C_6H_4-SiMe_2-C_6H_4-SiPh_2-C_6H_4-]_n$	350	1	7	30	47	47	10, 12, 26
145a	$[-SiMe_2-C_6H_4-SiPh_2-C_6H_4-SiPh_2-C_6H_4-]_n$	485	-	-	1	44	46	10, 12, 26
146a	$[-SiPh_2-C_6H_4-]_n$	310	2	5	20	30	35	11, 12, 26
146b	id.	315	5	7	30	58	59	10, 11, 12, 26

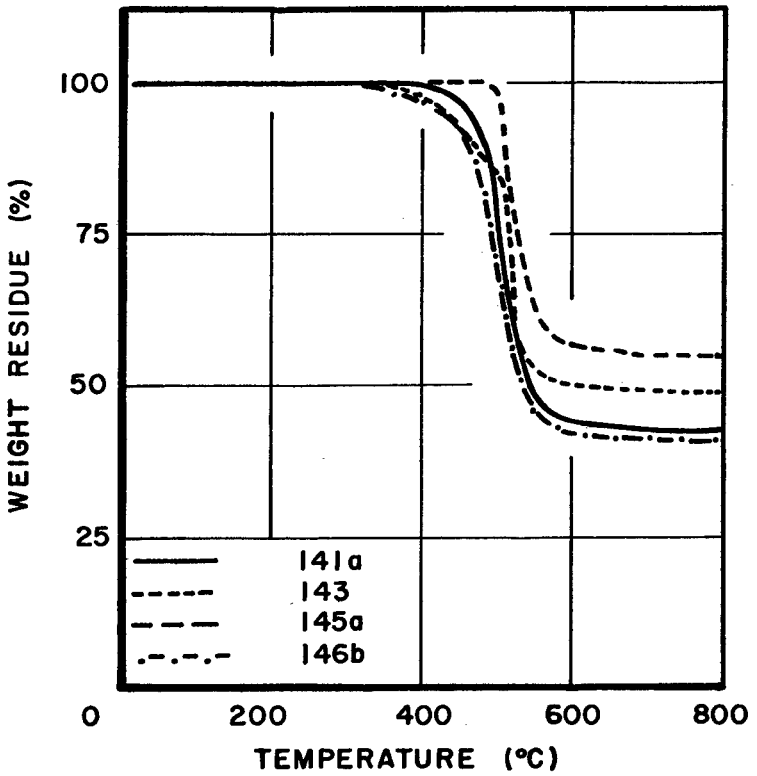


Figure 3. Plot of Weight-Residue against Temperature (Heating Rate 2.5°/Min.; N_2 Atmosphere) for Some Poly-p-Phenylenesilanes

All samples show no loss in weight whatever during the initial heating period, then a rapid weight-loss over a narrow temperature range occurs to give an apparently stable residue, which in addition to silicon must contain other elements in view of the considerable remaining weight-percentage (e.g., 144a, 145a, 146a).

It is our opinion that the present type of thermogravimetric data should not be interpreted directly in terms of thermal stability. We believe that the thermal stabilities per se of all these compounds having in common a p-phenylenesilane backbone do not differ much; so, there must be other factors which determine the marked differences in the thermal behavior between the several samples. Among these factors volatility, in particular of low molecular constituents of the sample, must be mentioned first.

The thermal behavior of four samples of a p-phenylenesilane, having the structure $(-C_6H_4SiMe_2-)_n$ and differing only in degree of polymerization, are shown in Figure 4.

With increasing degree of polymerization the temperature of initial weight-loss shifts towards higher temperatures, whereas the weight-percentage of the ultimate residue remaining after heating up to 900°C, increases. The pure pentamer (137, n = 5) starts to lose weight at 325°C, but weight-losses at temperatures of 400° and 500°C are 55 and 80 percent respectively. The pure trimer (135, n = 3) starts to lose weight at 245°C and the weight-losses at temperatures of 400° and 500°C are 90 and 97 percent respectively.

These facts seem to support our concept that in addition to thermal degradation, volatility of the sample must also play a part.

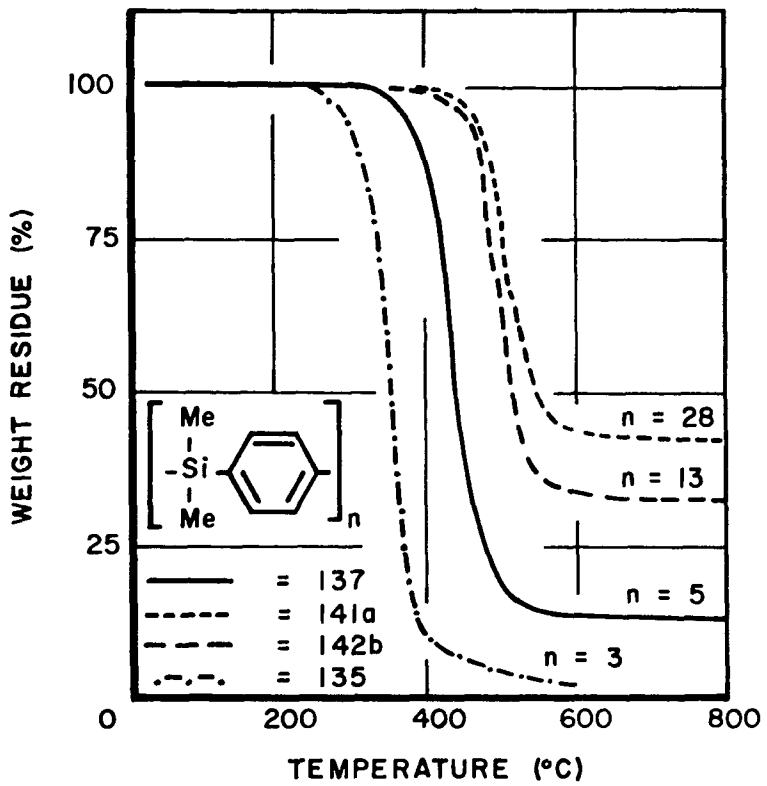
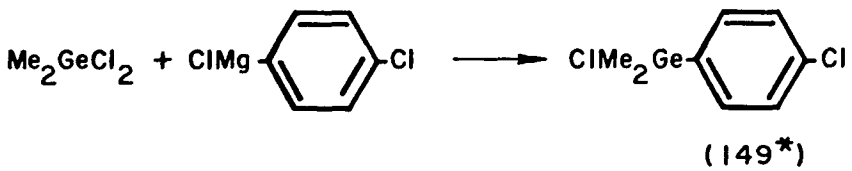


Figure 4. Plot of Weight-Residue against Temperature (Heating Rate 2.5°/Min.; N_2 Atmosphere) for Four Samples of a Poly-p-Phenylenesilane of Different Molecular Weights

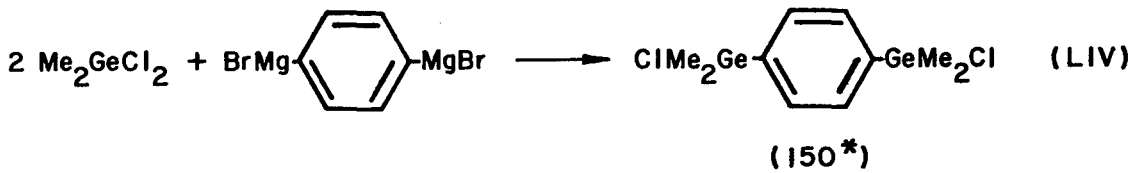
C. Synthesis of Oligomeric and Polymeric p-Phenylenegermanes

The starting materials required for this study were prepared by a conventional Grignard synthesis or a coupling reaction with p-chlorophenyllithium. p-Chlorophenyltrimethylgermane (147*) was prepared from trimethylgermanium bromide and p-chlorophenylmagnesium chloride; bis(p-chlorophenyl)dimethylgermane (148*) was obtained by the reaction of dimethylgermanium dichloride with p-chlorophenyllithium. An attempt to synthesize p-chlorophenyldimethylgermanium chloride (149*) from p-chlorophenyllithium and dimethylgermanium dichloride (1:1 ratio) yielded only impure bis(p-chlorophenyl)dimethylgermane. The wanted compound was obtained, however, from p-chlorophenylmagnesium chloride and dimethylgermanium dichloride:



(LIII)

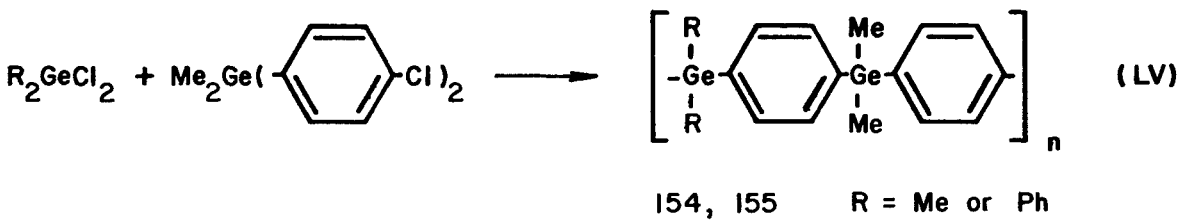
p-Bis(chlorodimethylgermyl)benzene (150*) was synthesized according to:



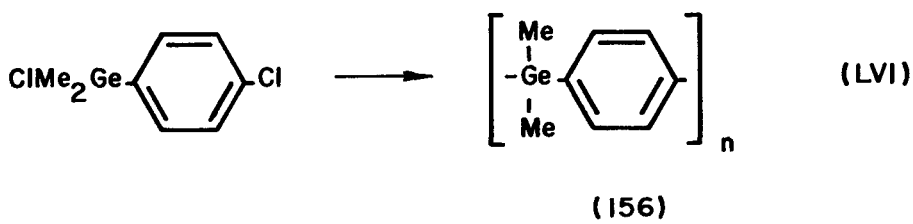
This compound was purified via the polymeric oxide.

A number of oligomeric model compounds were prepared by the reaction of appropriate combinations of p-chlorophenyl- and chlorogermanes with a suspension of sodium sand in refluxing toluene (Table 20). The yields obtained in these model reactions are similar to those obtained in experiments leading to the silicon analogues (preceding section, Table 17).

These results induced us to carry out a few Wurtz-type condensations involving bifunctional p-chlorophenyl- and chlorogermanes (Table 20):



Polymeric products, which, according to analytical and infrared data, have the proposed structure, were obtained from the reaction mixtures. Similar poly-condensation reactions involving p-chlorophenyldimethylgermanium chloride yielded only small amounts of low-melting products:



The polymers 154 and 155 obtained in this way, contain on the average only ten p-phenylenegermane units per molecule. Again the attainment of high molecular weights may be hampered by factors as limited solubility of the polymeric products formed or chain-termination via metallation of the solvent. The absence of reactive end-groups, as appears both from elementary analysis (e.g., Cl, found: 0.16%; calcd. for $Cl(GeMe_2C_6H_4)_{12}Cl$: 3.20%) and infrared spectroscopy, suggests that the previously formulated mechanism of chain-termination (Section IV-B) also applies in this case. The presence of any Ge-Ge bonds could not be demonstrated by chemical means.

D. Attempted Synthesis of Oligomeric and Polymeric p-Phenylenestannanes

The starting materials p-chlorophenyltrimethyltin (157*), p-bromophenyltrimethyltin (158*) and bis(p-chlorophenyl)dimethyltin (159*) were prepared in the usual way by a Grignard synthesis involving methyltin chlorides and p-halogenophenylmagnesium halide. p-Chlorophenyldimethyltin chloride (160*) was obtained in low yield from dimethyltin dichloride and p-chlorophenylmagnesium chloride:

TABLE 20

Some Oligomeric and Polymeric p-Phenylenegermanes Obtained by Wurtz-Type Condensations

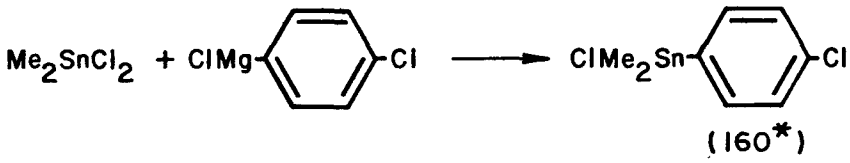
NO.	COMPOUND OR POLYMER	FORMULA	OBTAINED FROM		RECRYST. SOLVENT	MELTING POINT (°C)	YIELD (%)	MOL.[a] WEIGHT	REFER-ENCES
			CHLOROGERMANE	p-CHLOROPHENYLGERMANE					
151	$Me_3Ge-C_6H_4-GeMe_3$	$C_{12}H_{22}Ge_2$	Me_3GeCl	$Me_3Ge-C_6H_4-Cl$	ethanol	105-107	60	-	15, 28
152	$Me_3Ge(-C_6H_4-GeMe_2)_2Me$	$C_{20}H_{32}Ge_3$	Me_3GeCl	$Me_2Ge(-C_6H_4-Cl)_2$	ethanol	94-96	50	488[c]	12, 28
153	$Me_3Ge(-C_6H_4-GeMe_2)_3Me$	$C_{28}H_{42}Ge_4$	$ClMe_2Ge-C_6H_4-GeMe_2Cl$	$Me_3Ge-C_6H_4-Cl$	ligroin	137-139	41	-	15, 28
154a	$(-GeMe_2-C_6H_4-)_n$	$(C_8H_{10}Ge)_n$	Me_2GeCl_2	$Me_2Ge(-C_6H_4-Cl)_2$	-	145-175[b]	37	2100[d]	13, 28
154b						165-190[b]	4	-	15
155a	$(-GeMe_2-C_6H_4-GePh_2-C_6H_4-)_n$	$(C_{26}H_{24}Ge_2)_n$	Ph_2GeCl_2	$Me_2Ge(-C_6H_4-Cl)_2$		110-130[b]	38	1850[d]	13, 28
155b						170-200[b]	3	-	15

[a]Molecular weights were determined using a Mechro Lab Vapor pressure osmometer;

[b]temperatures at which softening starts and at which a clear melt is obtained;

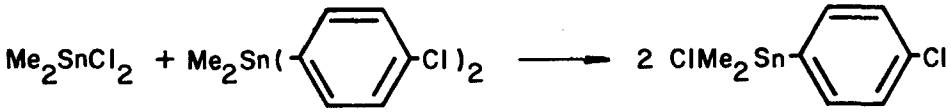
[c]calculated: mol. weight 490,3;

[d]$\overline{M}_n$.



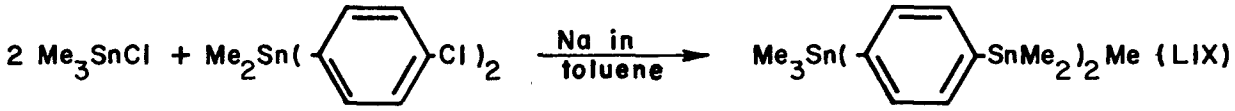
(LVII)

A redistribution reaction involving dimethyltin dichloride and bis(p-chlorophenyl)dimethyltin gave better results:

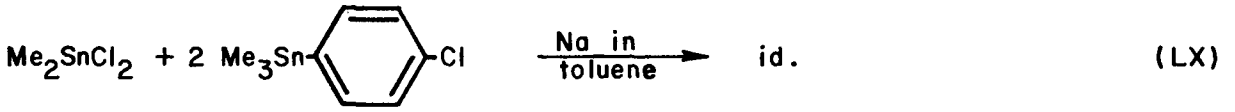


(LVIII)

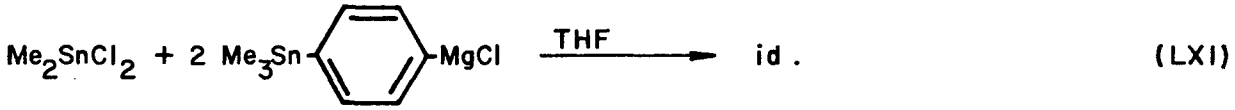
The model reaction of trimethyltin chloride and p-chlorophenyltrimethyltin with sodium in refluxing toluene proceeded very sluggishly, bis(p-trimethyltin)benzene (161*) was obtained in only 40 percent yield. The synthesis of the dimer bis(p-trimethyltinphenyl)dimethyltin (162*) was attempted by each of the following routes:



(LIX)



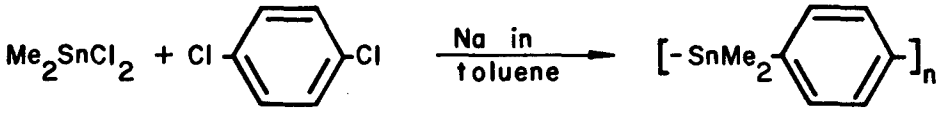
(LX)



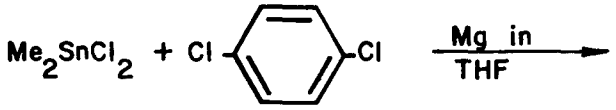
(LXI)

In each case the reaction product consisted of a mixture from which the wanted product could be isolated in pure form in a yield of only 5-10 percent. Peculiarly enough, bis(p-trimethyltin)benzene (161) was isolated in yields up to 40 percent.

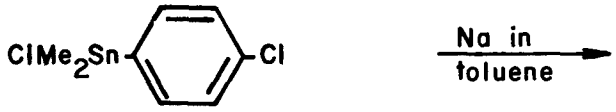
With a view to the unfavorable results obtained with the monomeric compounds, it is not surprising that our attempts to obtain p-phenylenetin polymers have remained unsuccessful. Experiments, according to each of the following equations, were carried out:



(LXII)



(LXIII)



(LXIV)

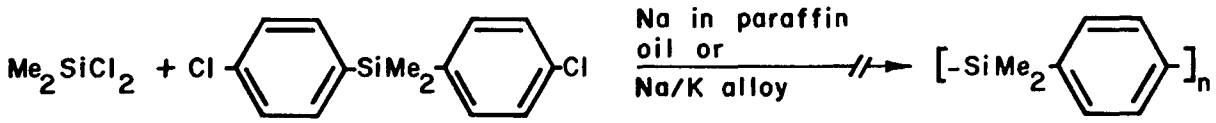
Most of the starting material was recovered from Reaction LXII. Reaction LXIII yielded only oily products with a wide boiling range. Similarly, the self-condensation of p-chlorophenyldimethyltin chloride afforded a liquid, the analysis of which was not in accordance with the expected product.

In view of these unfavorable results we have discontinued this line of work.

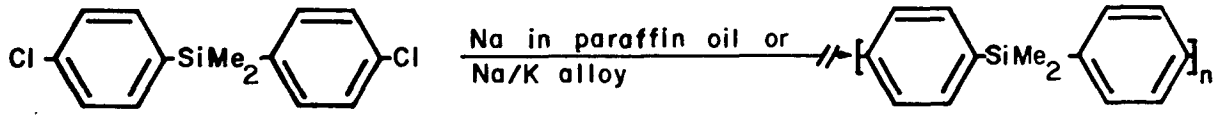
E. Investigation of Other Condensing Agents

In the previous sections the synthesis has been described of poly-p-phenylenesilanes and -germanes by means of Wurtz-type poly-condensation reactions of appropriate combinations of bifunctional p-chlorophenyl and chlorosilanes or -germanes with sodium sand in toluene as the condensing agent. However, under these conditions only low-molecular weight polymers were obtained. Therefore we have looked into the possibility of obtaining these structures by means of other condensing agents (compare also Section V).

Poly-condensation of dichlorodimethylsilane with bis(p-chlorophenyl)dimethylsilane (127) or homopoly-condensation of the latter using a sodium dispersion in paraffin oil or a liquid sodium potassium alloy did not yield the expected products:



(LXV)

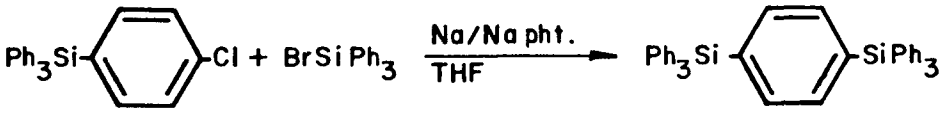


(LXVI)

All products obtained after fractionation consisted of low-melting fractions, soluble in aromatic solvents, and an extremely high-melting fraction, insoluble in any type of solvent tried. The solubility and the melting points of the polymer fractions suggest that initially low-molecular weight (linear) chains are formed, which on further condensation are cross-linked. The infrared spectra of the infusible polymer samples obtained in the homopoly-condensation reactions show an absorption at the frequency characteristic of the Si-O-Si vibration. This fact, together with the high silicon content of these fractions, suggests that silicon-carbon bonds are broken both by sodium and by sodium-potassium alloy in the homopoly-condensation reaction.

Very recently Wurtz-type condensations, using a sodium-naphthalene solution in tetrahydrofuran as the condensing agent, have been described (Reference 67).

In order to investigate the applicability of this homogeneous system to the preparation of p-phenylenesilanes sodium-naphthalene was reacted with triphenylbromosilane and p-chlorophenyltriphenylsilane (128*) in THF:



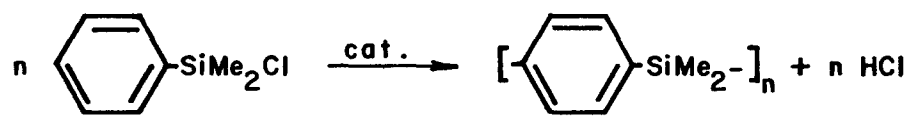
(LXVII)

Carrying out the reaction at about 60°C more than the calculated amount of sodium was consumed. It is likely that phenyl-silicon bonds are cleaved at this temperature by the reactive sodium complex.

To avoid this side-reaction the reaction temperature was lowered to 0°C. However, p-bis-(triphenylsilyl)benzene was obtained now in only 17 percent yield, whereas the starting material Ph_3SiBr was recovered in only 40 percent yield.

These results indicated that these systems most probably are not suitable for the preparation of high molecular weight poly-p-phenylenesilanes.

The possibility of preparing poly-p-phenylenesilanes by means of a Friedel-Crafts reaction has been studied also. To this purpose chlorodimethylphenylsilane (163*) was heated with a few Friedel-Crafts catalysts:



(LXVIII)

After heating the compound with 1 percent of catalyst ($BF_3 \cdot Et_2O$, $SbCl_3$ or $FeCl_3$) at 200°-230° for 14 hrs., the starting material was recovered in 91-93 percent yield. Heating the compound with 1 percent of $AlCl_3$ at 230° for 13 hrs. yielded 84 percent of the starting material, together with a few percent of low-boiling products.

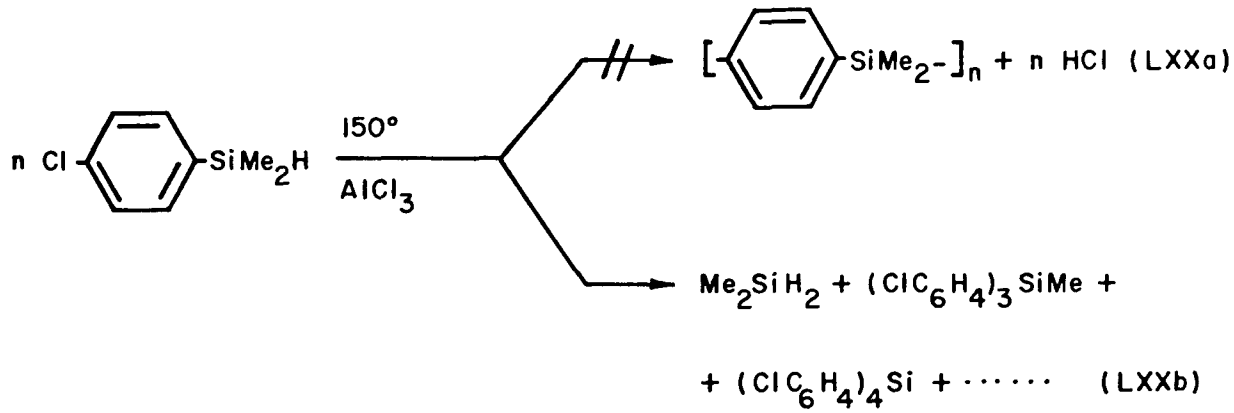
Heating 10 g (0.06 mole) of $PhMe_2SiCl$ with 1 g (0.0075 mole) of $AlCl_3$ at 140° for 13 hrs. yielded a mixture of compounds in which the starting material was no longer present. The following compounds were identified: Me_3SiCl (0.02 mole), Ph_4Si (0.004 mole), Ph_3SiOH (from Ph_3SiCl, 0.01 mole) and an oil, obviously a siloxane:

$$PhMe_2SiCl \xrightarrow[140°]{AlCl_3} Me_3SiCl + Ph_3SiCl + Ph_4Si + \ldots\ldots \qquad \text{(LXIX)}$$

Heating 10 g of $PhMe_2SiCl$ with 1 g of $FeCl_3$ at 210° for 10 hrs. yielded a low-boiling fraction (Me_3SiCl, yield about 8%) and a high-boiling one, obviously impure starting material (yield about 80%).

A similar study with p-chlorophenyldimethylsilane (164*) has been carried out. After heating this compound with 10 percent of $FeCl_3$ at 200° for 12 hrs., the starting material was recovered in about 70 percent yield.

Heating 8 g (0.044 mole) of the hydride with 0.4 g (0.003 mole) of $AlCl_3$ at 150° for 8 hrs., yielded a volatile compound (obviously dimethylsilane, 0.012 mole) and 7.0 g of a mixture of compounds, in which the starting material was no longer present. Infrared spectroscopy and elementary analysis point to the presence of compounds like tris-(p-chlorophenyl)-methylsilane and tetrakis(p-chlorophenyl)silane. Obviously the silicon hydride, just like the chloride, disproportionates under the influence of aluminium chloride:



From these experiments it was concluded that Friedel-Crafts reactions under these circumstances are not suitable for polymer formation.

SECTION V

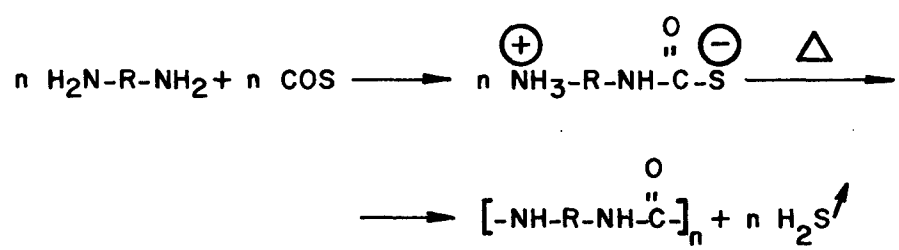
SYNTHESIS AND DEGRADATION OF GROUP IV ORGANOMETALLIC DERIVATIVES OF ORGANIC SALTS

A. Discussion

Efforts to synthesize poly-p-phenylenesilanes and -germanes, polymers of a type that exhibits a considerable thermal stability (750°-950°F), have been described in the preceding chapter. However, the Wurtz-type condensation used for their preparation does not allow the attainment of high-molecular weight products. No other routes leading directly to polymers of this type have been mentioned in the literature and we have been unable to devise any useful suggestion along this line.

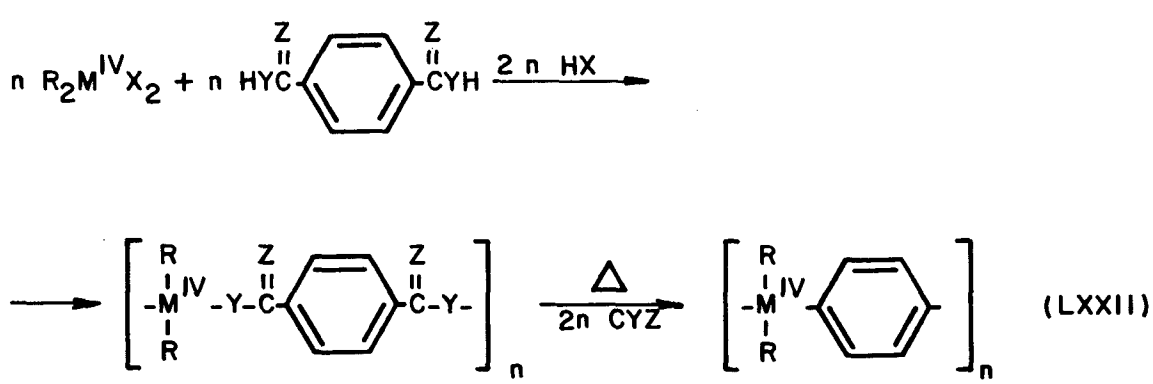
Lack of appropriate polymerization methods is a general problem in the preparation of really thermostable polymers. Although the synthesis of several novel low-molecular (organo)metallic compounds of promising thermal stability has been reported in the literature, suitable techniques for carrying out these reactions on a high-polymeric level are not available. A solution of this problem may be a two-step procedure, in which first a high-molecular weight pre-polymer is prepared by a usual technique and subsequently this pre-polymer is transformed by a, preferably simple, procedure into the final, inherently insoluble and infusible, thermostable polymer.

The solid state polymerization of alkylenediamine-thiocarbamic acid salts to high-molecular weight polyureas (Reference 68), under generation of hydrogen sulphide, is one of the earliest examples of this type of polymerization:



(LXXI)

A potential application of this principle to the preparation of IVth group organometallic polymers containing the p-phenylene group, would seem to be a combination of a polycondensation process and a decarboxylation or similar reaction in the solid state, e.g.:



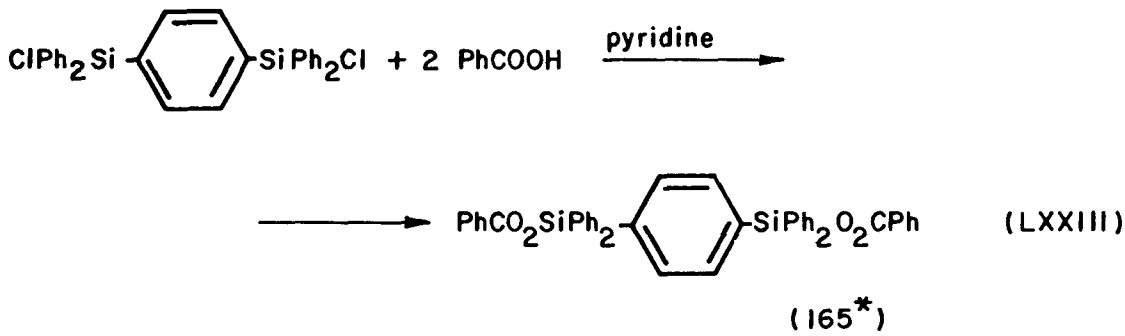
(LXXII)

Y = O,S Z = O,S

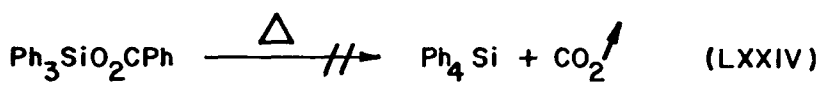
B. Synthesis and Attempted "Decarboxylation" of Group IV Organometallic Cyanoacetates, Benzoates, Thiobenzoates, and Dithiobenzoates

The decarboxylation and related reactions of Group IV organometallic derivatives of organic salts, which may produce aryl- Group IV metal bonds, has been studied on the monomeric level. To this purpose a number of appropriate organosilicon and -tin carboxylates, thiobenzoates and dithiobenzoates were synthesized.

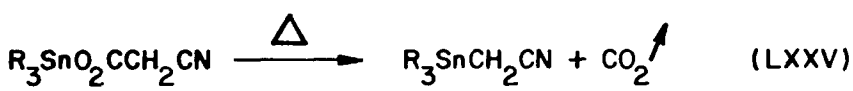
p-Phenylene-bis(diphenylsilylbenzoate) (165*) was obtained by the reaction of p-bis-(chlorodiphenylsilyl)benzene (54) with benzoic acid in the presence of pyridine:



Triphenylsilyl benzoate (166*) was similarly prepared. However, all attempts to decarboxylate these compounds at various temperatures (up to 300°C) and pressures were unsuccessful. No weight loss was observed and the infrared spectra remained unchanged:

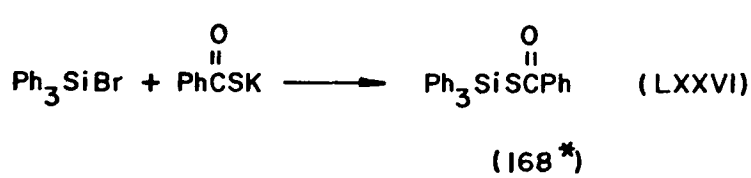


Organotin cyanoacetates are readily decarboxylated to cyanomethyltin compounds (Reference 69):



The positive result with the organotin cyanoacetate suggested a corresponding experiment with a silyl cyanoacetate. Triphenylsilyl cyanoacetate (167*), prepared by the reaction of bromotriphenylsilane with potassium cyanoacetate, was heated at 200°C/16 mm for several hours. Again, no decarboxylation was detected. Apparently the $-SiO_2C-$ structure is thermally quite stable.

Our attention was then directed towards a similar study of the corresponding thiobenzoates and dithiobenzoates. Triphenylsilyl thiobenzoate (168*) was prepared by the reaction of potassium thiobenzoate with bromotriphenylsilane in refluxing toluene:



The high boiling point of this compound (about 200°/0.02 mm) without any decomposition suggested a considerable thermal stability. Further attempts to eliminate carbon oxysulphide at elevated temperatures were unsuccessful.

All attempts to isolate pure triphenylsilyl dithiobenzoate from potassium dithiobenzoate and triphenylbromosilane have failed because of its extreme hydrolytic susceptibility resulting in the formation of triphenylsilanol. The organotin analogues, triphenyltin thiobenzoate (169*) and dithiobenzoate (170*), were readily prepared by similar procedures and are hydrolytically much more stable. Triphenyltin thiobenzoate did not change upon heating at 220°C for prolonged periods. Attempts to eliminate carbon disulphide from triphenyltin dithiobenzoate at elevated temperatures resulted in a complex mixture of solid and liquid reaction products which could not be separated. Among these products triphenyltin thiophenolate (171*), independently prepared from triphenyltin hydride and thiophenol, did not seem to be present.

The negative results obtained in this study make successful reactions on a polymeric level highly improbable.

C. Synthesis and Desulphination of Organotin Sulphinates

In the previous section the synthesis of Group IV organometallic benzoates, thiobenzoates, and dithiobenzoates has been described. Attempts to eliminate carbon dioxide, carbon oxysulphide or carbon disulphide at various temperatures and pressures were unsuccessful. It has been reported in the literature (Reference 70) that arylsulphinic acids react with mercuric chloride or acetate to yield arylmercuric salts. Therefore it seemed worth our while to investigate similar reactions involving arylsulphinates of Group IV elements. To this purpose a few organotin arylsulphinates were prepared and their behavior at elevated temperatures was studied.

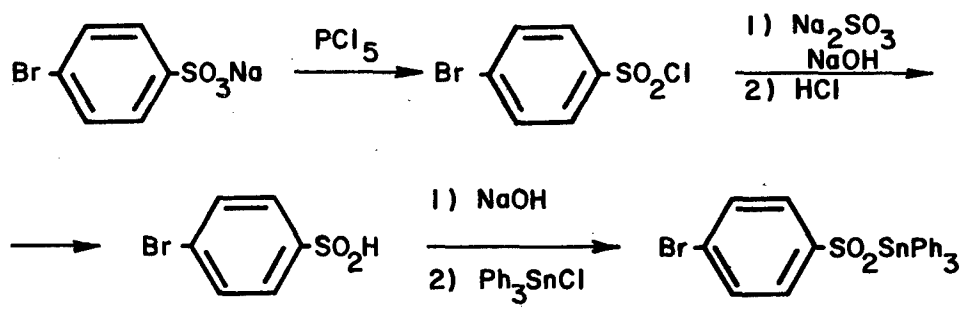
Triphenyltin benzenesulphinate (172*) was prepared by an interfacial condensation of triphenyltin chloride (in ether) with sodium benzenesulphinate (in water):

$$Ph_3SnCl + NaO_2SPh \longrightarrow \underset{(172^*)}{Ph_3SnO_2SPh} + NaCl \qquad \text{(LXXVII)}$$

Diphenyltin bis(benzene sulphinate) (173*) was obtained in the same way. An attempt to prepare diphenylchlorotin benzenesulphinate by a similar condensation reaction yielded a 1:1 complex of diphenylchlorotin benzenesulphinate and diphenyltin oxide (174*):

$$2\ Ph_2SnCl_2 + NaO_2SPh + H_2O \longrightarrow \underset{(174^*)}{Ph_2Sn(Cl)O_2Ph.Ph_2SnO} + NaCl + 2\ HCl \qquad \text{(LXXVIII)}$$

Triphenyltin p-tolylsulphinate (175*) and triphenyltin p-acetylaminobenzenesulphinate (176*) were obtained as described above. Triphenyltin p-bromobenzenesulphinate (177*) was prepared by the following sequence of reactions:



(LXXIX)

(177*)

Upon heating triphenyltin p-tolylsulphinate at about 235°/0.2 mm during 25 minutes a gas was evolved and the solid melted, yielding after cooling a mixture of compounds. Pure compounds could not be isolated, but the fractions obtained upon recrystallization obviously consist of triphenyl-p-tolyltin and tetraphenyltin. The infrared spectra of these mixtures, in particular the C-H out-of-plane vibration of 1,4-disubstituted benzenes at about 800 cm^{-1}, showed that the decomposition reaction under these conditions yielded about 30 percent of triphenyl-p-tolyltin and 10 percent of tetraphenyltin. Obviously redistribution of the triphenyltin group had also played a part:

$$Ph_3SnO_2SR \xrightarrow{\Delta} Ph_3SnR + SO_2 + Ph_4Sn + \cdots\cdots \qquad \text{(LXXX)}$$

Further information about the decomposition reaction was obtained from a series of experiments in each of which the reaction products were isolated and the sulphur dioxide liberated was titrated. To this purpose triphenyltin benzenesulphinate was decomposed by heating during 20 min. at about 225° at several pressures. The gaseous products were trapped in long tubes cooled by liquid air. The contents of the tubes were subsequently bubbled through a 2 N potassium hydroxide solution. The resulting solution was analyzed by titration with iodine and sodium thiosulphate. The results of these experiments are presented in Table 21.

From this table can be derived that:

a. Tetraphenyltin is formed by redistribution of the triphenyltin group in about 25 percent yield, irrespective of the pressure.

b. Tetraphenyltin is formed by elimination of sulphur dioxide in yields varying from about 10 percent at 200 mm to about 30 percent at very low pressures.

c. The part of the sulphinate that is not consumed in a. or b. decomposes into into low-melting products.

Obviously, the present mode by which the reaction is accomplished tends to be not very suitable for the formation of a phenyl-tin bond, unless catalysts are found that promote desulphination reaction and, at the same time, allow the temperature at which desulphination occurs to be reduced, thus suppressing the redistribution reaction.

Catalysts, that favor the elimination of sulphur dioxide from salts of arylsulphinic acids, have not been reported. Only the decomposition has been described (Reference 71) of a few arylsulphinic acids to the corresponding benzenes by heating in solvents, preferably pyridine.

A few preliminary experiments along that line have been carried out. Triphenyltin benzenesulphinate was heated with pyridine or quinoline. However, only small amounts of tetraphenyltin were isolated. Similar negative results have been obtained using small amounts of copper, cupric oxide, or mercuric chloride as a catalyst. Copper seems to enhance the formation of tetraphenyltin by redistribution.

TABLE 21

Decomposition of Triphenyltin Benzenesulphinate by Heating at ~ 255°C

PRESSURE (mm Hg)	SULPHINATE (mg)	WEIGHT-LOSS (mg)	SULPHUR DIOXIDE DETERMINED BY TITRATION		LOW-MELTING PRODUCTS (mg)	TETRAPHENYLTIN ISOLATED		% Ph_4Sn MINUS+++ % SO_2
			(mg)	(%)+		(mg)	(%)+	
205	2467	-**	29.0	9.1	1287	693	32.6	23.5
14	2451	73	75.5	23.6	1305	957	44.9	21.3
4	2459	136	99.5	30.9	1106	1112	52.0	21.1
1.5	2448	148	96.6	30.1	963	1173	55.1	25.0
0.2	2439	154	101.4	31.8	957	1188	56.0	24.2

*Yields are based on the reaction: $Ph_3SnO_2SPh \longrightarrow Ph_4Sn + SO_2$.

**Not determined.

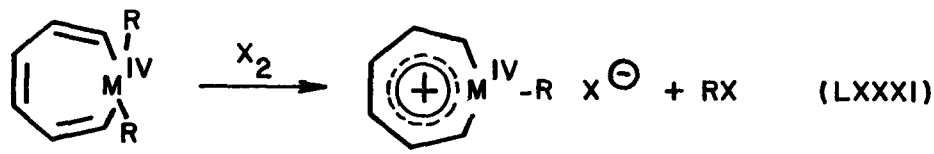
***I.e., tetraphenyltin formed by redistribution.

SECTION VI

AN APPROACH TO THE SYNTHESIS OF A QUASI-AROMATIC SILA- AND STANNATROPYLIUM ION

A. Discussion

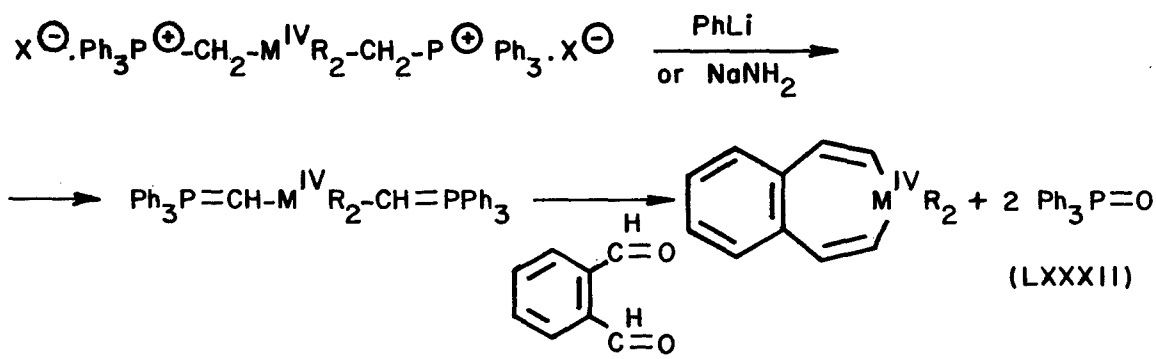
As a sideline of our investigations efforts have been made towards the preparation of unsaturated Group IV organometallic heterocycles, in particular Group IV metallo -2,4,6-cycloheptatriene derivatives. These compounds are of interest because in principle, they may aromatize to form a tropylium-ion structure, e.g.:



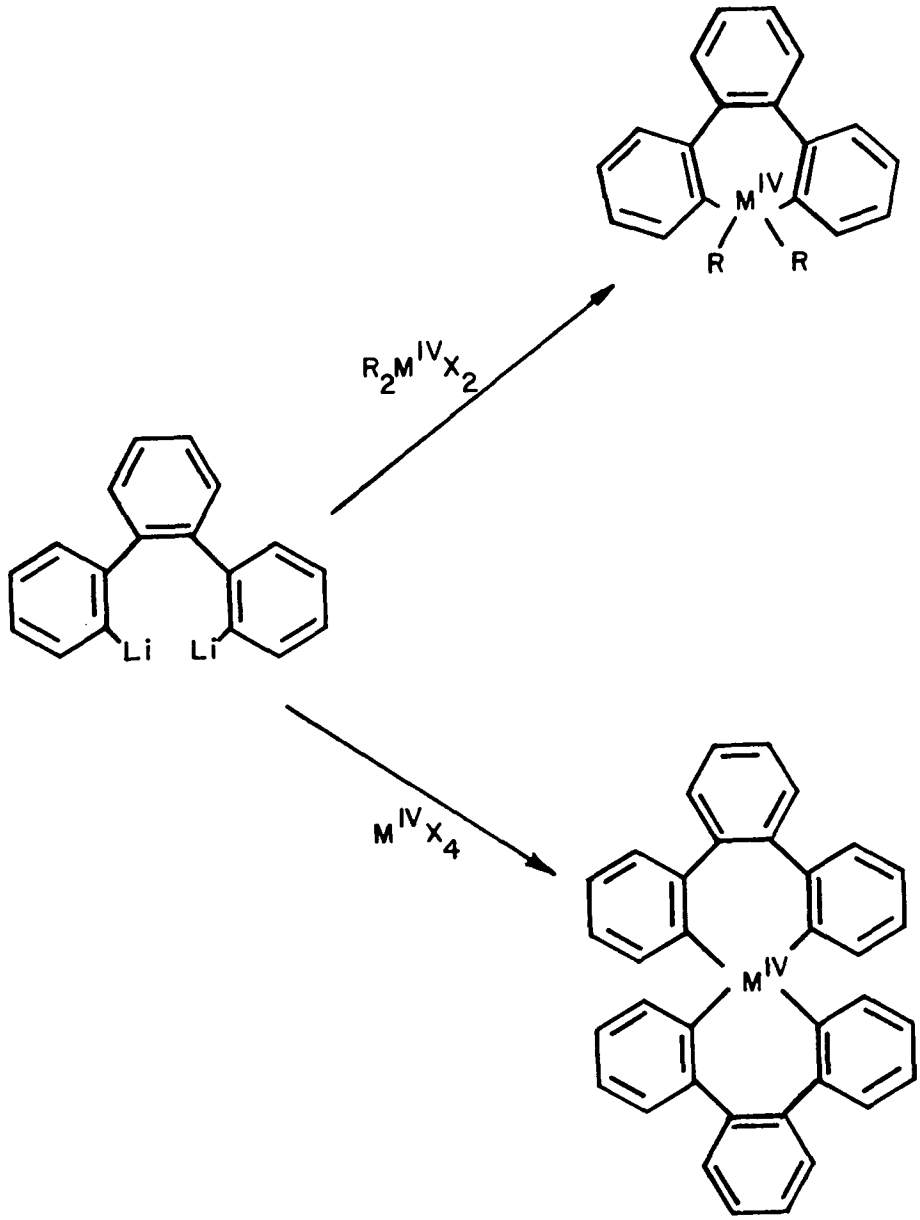
(LXXXI)

A study of these compounds and in particular of their aromatized derivatives, although mainly of interest from a theoretical point of view, might be of value for Group IV organometallic polymer chemistry too.

The following reaction routes were selected for the synthesis of these seven-membered unsaturated Group IV organometallic heterocycles:

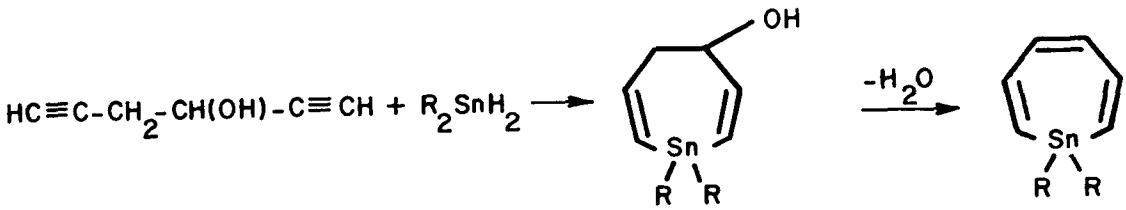


(LXXXII)

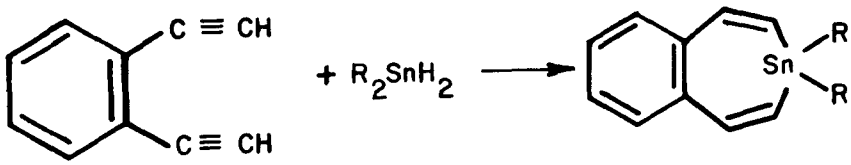


(LXXXIII)

(LXXXIV)



(LXXXV)



(LXXXVI)

B. Attempted Syntheses of Group IV Metal-Containing Heterocycles via the Wittig Reaction or via Condensation Reactions with o,o"-Terphenylenedilithium

Recently Wittig and coworkers (Reference 72) reported the synthesis of unsaturated seven- and eight-membered cyclic compounds via the Wittig reaction; 1,2-benzo-1,3,5-cycloheptatriene, 1,2-benzo-1,3,6-cycloheptatriene, and 1,2-benzo-1,3,7-cyclooctatriene could be prepared by this method. These successful syntheses induced us to investigate the applicability of this type of reaction to the preparation of unsaturated metal-containing heterocycles (LXXXII, M^{IV} = Si, Ge, Sn; R = Me, Ph). To this purpose some experiments have been carried out, directed to the synthesis of halogenomethyl-substituted organosilicon and organotin compounds and their triphenylphosphonium derivatives.

Bis(iodomethyl)dimethylsilane (178*) was obtained by the reaction of bis(chloromethyl)-dimethylsilane with sodium iodide in acetone. The triphenylphosphonium derivative of this compound (179*) was easily prepared by heating with triphenylphosphine:

$$2\ Ph_3P + (ICH_2)_2SiMe_2 \longrightarrow I^{\ominus}.Ph_3P^{\oplus}\text{-}CH_2\text{-}SiMe_2\text{-}CH_2\text{-}P^{\oplus}Ph_3.I^{\ominus}$$

(178*) (179*) (LXXXVII)

To obtain similar organotin compounds bis(bromoethyl)tin dibromide (180*) was prepared from tin tetrabromide and diazomethane according to published methods (References 73, 74). Phenylation of this compound with two equivalents of phenylmagnesium bromide or phenyllithium afforded bis(bromoethyl)phenyltin bromide (181*) as the main product. All attempts to introduce a second phenyl group in this molecule were without success. A similar situation had been found (References 75, 76) in the synthesis of aryl-substituted halomethyltin compounds from aryltin halides and diazomethane. Only chloromethyldiphenyltin chloride had been obtained (Reference 75) from the reaction of diphenyltin dichloride with an excess of diazomethane. Introduction of a second methylene radical seems to be impossible. Similarly, triphenyltin chloride does not react at all with diazomethane (References 75, 76).

The possibility of obtaining halogenomethyltin compounds via organolithium compounds was studied also. To obtain chloromethyltriphenyltin triphenyltinlithium, prepared by a procedure described by Tamborski et al. (Reference 77), was reacted with an equimolecular amount of bromochloromethane. Interaction of the reactants at room temperature yielded considerable amounts of hexaphenylditin and methylene-bis(triphenyltin), but no chloromethyltriphenyltin was found. Carrying out the reaction at low temperatures (-65°C) again yielded considerable amounts of hexaphenylditin together with a low-melting solid, from which, however, after treatment with sodium iodide in acetone, triphenyltin iodide was obtained. Obviously halogen-metal interchange plays an important part in this type of reaction, yielding triphenyltinhalide (isolated as the iodide), which partly reacts with triphenyltinlithium affording hexaphenylditin. The formation of methylene-bis(triphenyltin) may be explained by several reaction routes. Cleavage of this compound by iodine yielded diphenyl(triphenylstannyl methyl)tin iodide and phenyliodide instead of the product aimed at viz. iodomethyltriphenyltin.

A few experiments were carried out directed to the preparation of the seven-membered silicon-containing heterocycle from the triphenylphosphonium derivative of bis(iodomethyl)-dimethylsilane and o-phthaldialdehyde according to Equation LXXXII. However, all efforts to isolate the heterocycle were in vain. Infrared spectra of the products obtained from the reaction mixture showed the presence of Si-O bonds.

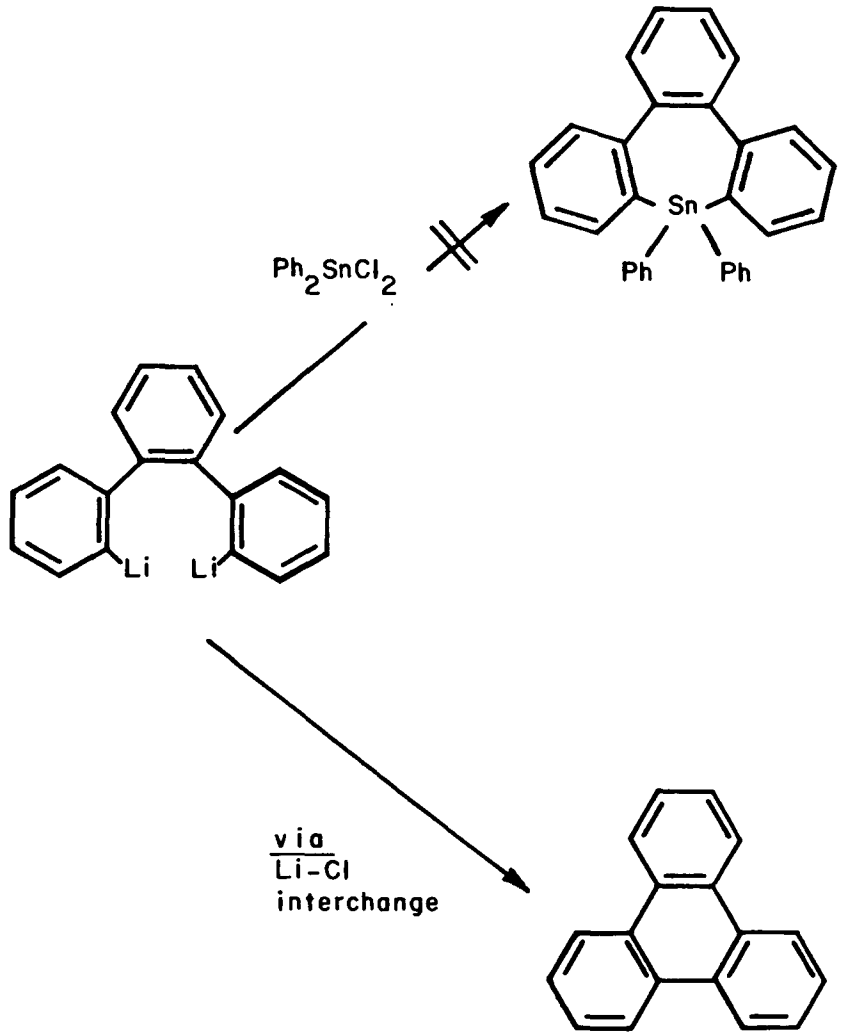
Very recently Gilman and Tomasi (Reference 78) obtained similar results viz.:

$$R_3SiCH{=}PPh_3 \xrightarrow{Ph_2C{=}O} R_3SiO^{\ominus} + Ph_2C{=}CH\text{-}P^{\oplus}Ph_3 \longrightarrow$$

$$\longrightarrow R_3SiOH + Ph_2C{=}C{=}PPh_3 \xrightarrow{PH_2C{=}O} Ph_2C{=}C{=}CPh_2 + Ph_3P{=}O$$

(LXXXVIII)

We have looked also into the possibility of obtaining seven-membered tin-containing heterocycles from aryldilithium compounds and tin halides. To this purpose o,o''-terphenylenedilithium, prepared from o-terphenylene-mercury-cyclic dimer (Reference 79), was brought into reaction with diphenyltindichloride. Although a reaction occurred, all attempts to isolate the expected compound from the reaction mixture were without success. On the other hand considerable amounts of o-triphenylene were found to be present. Obviously metal-halogen interchange has occurred:



(LXXXIII)

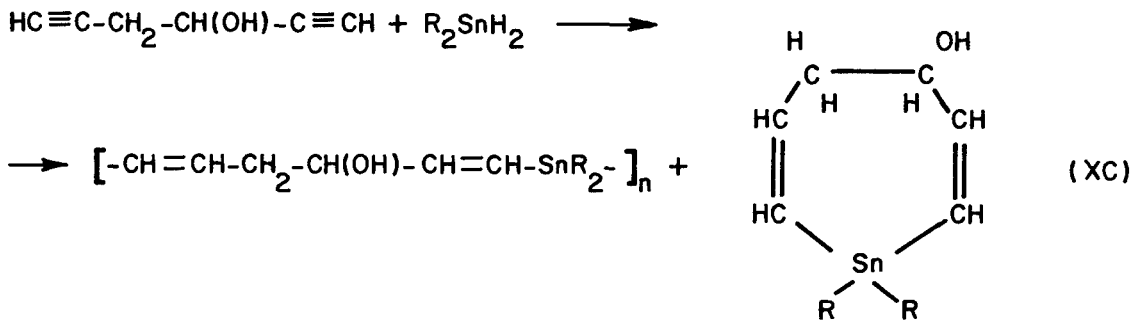
(LXXXIX)

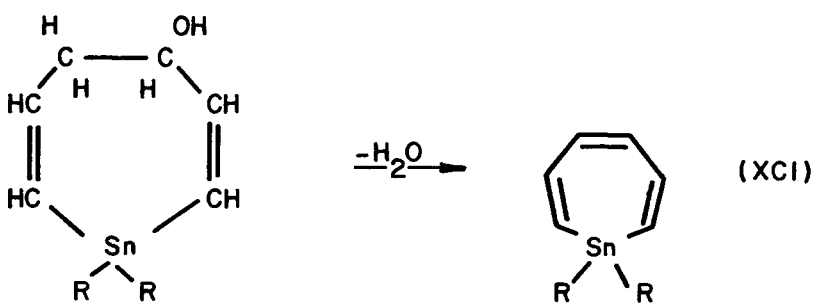
Because organohalogenosilanes show a lesser tendency towards metal-halogen exchange it is to be expected that similar condensation reactions involving silicon halides will result in the formation of the wanted heterocycles.

C. Synthesis of Linear and Cyclic Tin-Containing Compounds by Means of Organotin Hydride Addition Reactions

As outlined in Section I addition of organotin dihydrides to bifunctionally unsaturated compounds may yield tin-containing heterocycles, the formation of which is mainly governed by steric factors. Therefore, the possibility of obtaining 1-stannacycloheptatriene-2,4,6 derivatives via organotin hydride addition reactions has been studied also.

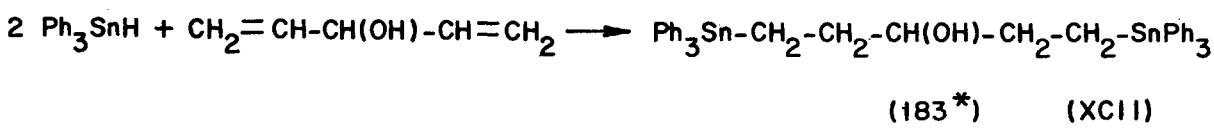
In Section I.C. the addition of organotin dihydrides to hexadiyne has been described, yielding, in addition to polymeric products, small amounts of 1-stannacycloheptadiene-2,6 derivatives. This induced us to investigate the reaction between organotin dihydrides and 1,5-hexadiyne-3-ol. It was to be expected that in addition to polymers also cyclic monomers would be formed, which could possibly be dehydrated to yield the wanted unsaturated heterocycles:





In order to study the addition reaction of organotin hydrides with unsaturated compounds containing a hydroxyl function some model reactions were carried out. To this purpose triphenyl- and triethyltin hydride were brought into reaction with divinylcarbinol and divinylglycol respectively.

Upon reacting triphenyltin hydride with divinylcarbinol a tacky very viscous oil was obtained. As appeared from analytical and infrared data addition had occurred in the usual way:



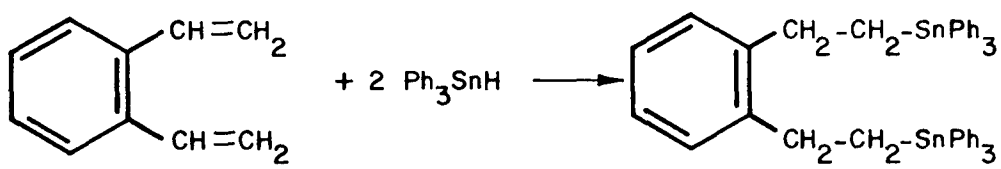
Reacting triphenyltin hydride with divinylglycol did not yield the expected 2:1 adduct. Similar experiments with triethyltin hydride and the unsaturated alcohols did not yield pure products though addition had occurred.

These rather disappointing results made a successful synthesis of the seven-membered heterocycle according to Equation XC highly improbable. In fact the pure cyclic monomer was not isolated from reaction mixtures obtained from hexadiyne-3-ol and diethyl- or diphenyltin dihydride. Only low-melting polymeric materials were obtained.

1,5-Hexadiyne-3-ol (184*) was obtained by the reaction of propargylaldehyde with allenylmagnesium chloride, according to Sondheimer et al. (Reference 80). The addition reactions were carried out as described previously.

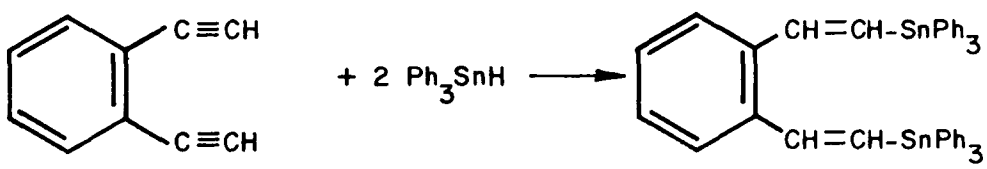
A tin hydride addition reaction which, in view of the nature and the position of the unsaturated groups, may lead directly to the formation of the unsaturated seven-membered heterocycle, is the reaction of organotin dihydrides with o-diethynylbenzene. Therefore the reaction of organotin hydrides with this compound was investigated. Addition reactions with the corresponding dienic compound, o-divinylbenzene, were included in this study.

Some model experiments were carried out with organotin monohydrides and the unsaturated compounds. Addition of triphenyltin hydride to o-divinyl- or o-diethynylbenzene afforded the 2:1 adducts in satisfactory yield (see also Table 22);



(XCIII)

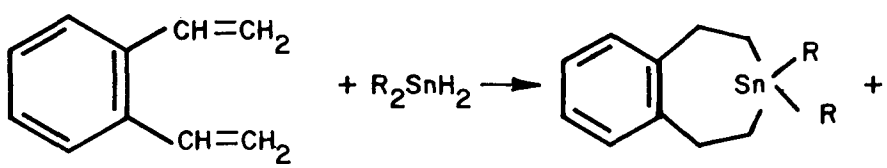
(185)



(XCIV)

(186)

Subsequently, organotin dihydrides were brought into reaction with o-divinylbenzene. From the reaction of diphenyltin dihydride with the unsaturated compound, in addition to a polymer, a cyclic monomer and a cyclic dimer were obtained. Other products were not isolated:



187, R = Ph

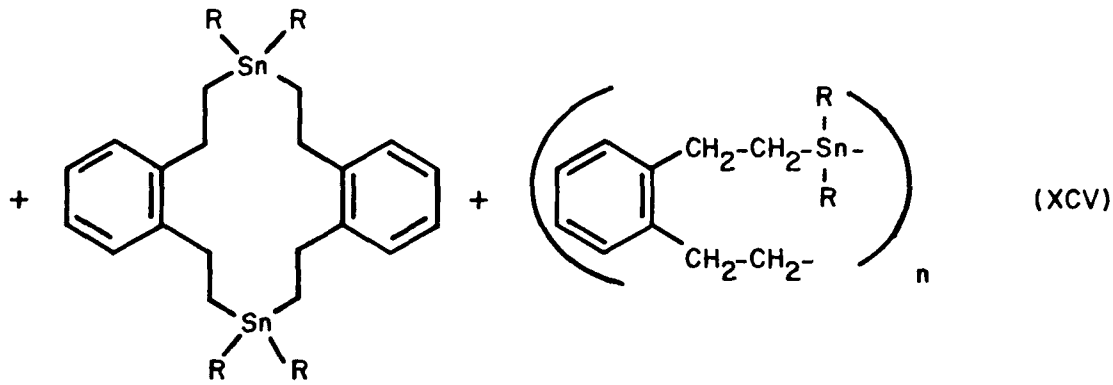
188, R = Et

TABLE 22

Addition Products Obtained from Organotin Hydrides and o-Divinyl- or o-Diethynylbenzene (XCIII-XCVI)

NO.	COMPOUND OR POLYMER		MELTING POINT (°C)	YIELD (%)	MOL. WEIGHT FOUND BY MECHROLAB. MEAS.		INFRARED BANDS (cm^{-1})				REFERENCES
							1580 C=C	990 TRANS	$_H C=C^H$	780 RING	
185	$C_{46}H_{42}Sn_2$	(832.23)	111-114	85	-	-	oo[f]	oo		oo	19
186	$C_{46}H_{38}Sn_2$	(828.20)	140-145	50	-	-	m	oo		oo	16, 19
187	$C_{22}H_{22}Sn$	(405.11)	98-100	10	401[d] 392	402 395	oo	oo		vs	10, 11, 12, 16, 19, 29
188	$C_{14}H_{22}Sn$	(309.02)	-[a]	10	309	-	oo	oo		vs	17, 18, 19, 29
189	$C_{44}H_{44}Sn_2$	(810.22)	277-282	10	790	-	oo	oo		w	10, 11, 16, 19, 29
190	$(C_{22}H_{22}Sn)_n$	$(405.11)_n$	~60-70	70	-	-	oo	oo		oo	10, 11, 16, 19, 29
191	$(C_{14}H_{22}Sn)_n$	$(309.02)_n$	-	77	-	-	(m)	(m)		oo	19, 29
192	$C_{12}H_{14}Sn$	(276.94)	41-42[b]	6	281	-	s	oo		vs	19, 29
193	$C_{14}H_{18}Sn$	(304.97)	-[c]	17	301 295	312 312	s	oo		vs	18, 19, 29
194	$C_{18}H_{18}Sn$	(353.04)	-	5	445[e]	-	s	w		vs	29
195	$C_{36}H_{36}Sn_2$	(706.07)	184-186	25	700	-	m	vs		w	29
196	$C_{44}H_{36}Sn_2$	(802.16)	282-285	12	749 802	722 -	s	vs		w	12, 13, 16, 19, 29
197	$(C_{12}H_{14}Sn)_n$	$(276.94)_n$	-	75	-	-	m	s		oo	29
198	$(C_{14}H_{18}Sn)_n$	$(304.97)_n$	-	50	-	-	-	-		-	29
199	$(C_{18}H_{18}Sn)_n$	$(353.04)_n$	-	67	-	-	s	s		m[g]	19, 29
200	$(C_{22}H_{18}Sn)_n$	$(401.08)_n$	~ 60-80	75	-	-	m	w		w[g]	12, 13, 19, 29

[a]B.p: 93°-98°/0.08, n_D^{20}: 1.5616; [b]b.p: 88°-90°/0.4, n_D^{20}: 1.6108; [c]b.p. 96°/0.4, n_D^{20}: 1.5983; [d]cryoscopic measurements in diphenyl, M.W.: 402, 418, and 413; [e]cyclic monomer contaminated with some polymer; [f]oo = only weak or no absorption observed, w = weak, m = medium, s = strong, vs = very strong; [g]absorption in this region may be due to the presence of small quantities of the monomeric heterocycle present in the polymer sample.



(XCV)

189, R = Ph

190, R = Ph

191, R = Et

A similar experiment involving diethyltin dihydride yielded only the cyclic monomer and a polymer. So far the cyclic dimer, most probably also present in the reaction mixture, could not be isolated by the usual techniques.

The successful results obtained in the above described experiments led us to carry out under similar conditions (gentle heating in inert solvents) addition reactions involving organotin dihydrides and o-diethynylbenzene. However, from the reaction of diphenyltin dihydride with o-diethynylbenzene only the fourteen-membered heterocycle and a polymer could be obtained. All efforts to isolate the cyclic monomer were in vain.

As has been mentioned in Section I the addition of organotin hydrides to acetylenic bonds may produce trans-and cis-products dependent on the steric course of the addition and on any subsequent isomerization. The addition of triphenyltin hydride to phenylacetylene at room temperature exclusively produced the trans-product (either occurrence of cis-addition or isomerization of the cis-product), the addition of triphenyltin hydride to propargyl alcohol obviously furnished both isomers (Reference 34). It seems therefore that, when voluminous groups are attached to both reactants (e.g., phenyl groups), either trans-addition (formation of cis-products) is hindered by steric factors, or the initially formed cis-product readily isomerizes under these conditions. So, the formation of the cyclic monomer from diphenyltin dihydride and o-diethynylbenzene under these circumstances becomes highly improbable.

However, very recently it has been reported (Reference 81) that upon the addition of triphenyltin hydride to phenylacetylene at -70°, 91 percent of the adduct formed (no yield specified) has the cis-configuration (occurrence of trans-addition). The cis-product at room temperature readily isomerizes to the trans-product. Similarly, by carrying out the reaction of diphenyltin dihydride and o-diethynylbenzene at -70°, initial trans-addition might sterically make possible addition of the second Sn-H group to the second ethynyl group with formation of the cyclic monomer. Subsequent isomerization, if at all possible, would be of no concern.

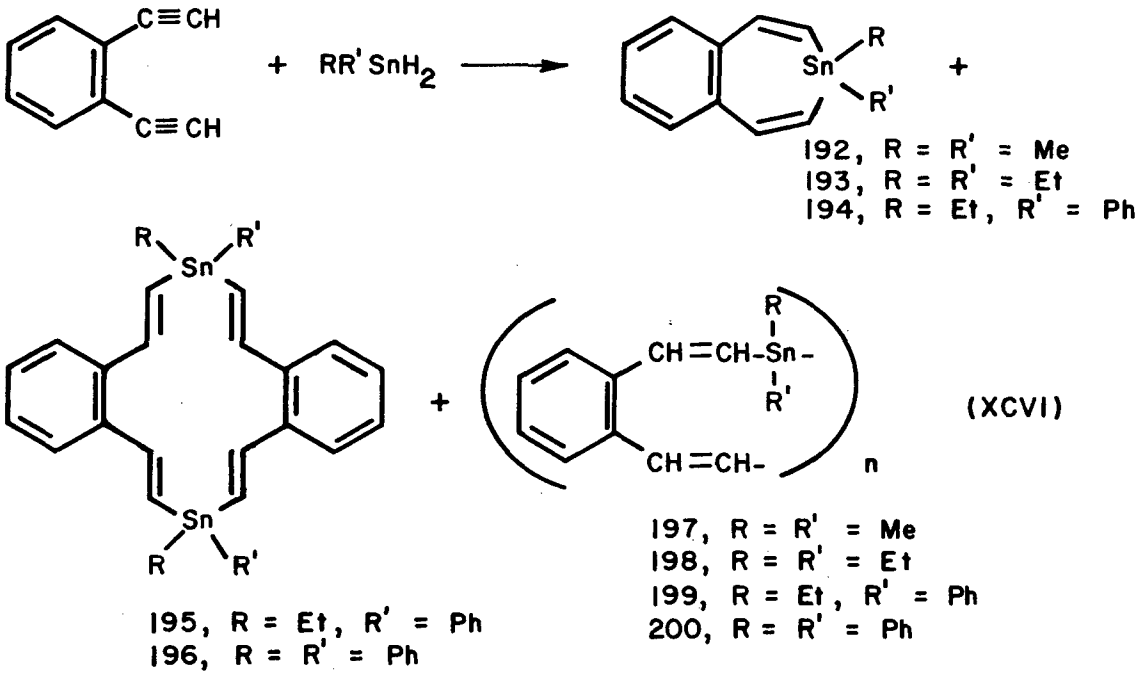
In order to test this possibility diphenyltin dihydride was reacted with o-diethynylbenzene at -70°C. However, again the cyclic monomer could not be isolated from the reaction mixture, although the polymers obtained in these low-temperature experiments showed an increased amount of cis-bonds.

Trimethyltin hydride when added to phenylacetylene at 40° afforded 58 percent of the cis-adduct (30% conversion in 24 hrs see Reference 81). Because of the more favorable cis-trans

ratio at higher temperatures of trimethyltin hydride-adducts, similar experiments were carried out with dimethyl-, ethylphenyl-, and diethyltin dihydride respectively and o-diethynylbenzene.

The reaction of dimethyl- and diethyltin dihydride with o-diethynylbenzene afforded, in addition to polymeric products, small amounts of the cyclic monomers, which were purified by distillation at reduced pressure. No attempts were made to isolate the cyclic dimers from the reaction mixtures, though they may be present as well.

From the reaction mixture obtained from ethylphenyltin dihydride and the diynic compound a high-melting crystalline product (cyclic dimer) and a low-melting product were isolated. The low-melting product was separated into a high and a low molecular weight fraction. The latter fraction consisted of almost pure monomer as appeared from molecular weight determinations and degradation with iodine (Section VI.D).



Some data on the oligomeric and polymeric products obtained in these addition reactions (XCIII-XCVI), the identities of which were established by infrared spectroscopy, molecular weight determinations, vapor-phase chromatography, and elementary analysis, are collected in Table 22. As can be seen from this table at least one absorption in the 780 cm^{-1} region seems to be characteristic of the seven-membered heterocycles. A similar band has been observed in the infrared spectra of the 1-stannacycloheptadiene-2,6 derivatives described in Section I.C, but in the infrared spectra of the corresponding polymers only a very weak band is observed at about 800 cm^{-1}. The band at 780 cm^{-1} may be skeletal vibration of the seven-membered tin-containing heterocycle.

The addition reactions were carried out as described previously. Ethylphenyltin dihydride (201*), not described before, was obtained in very low yield via the reaction sequence:

$$PhSnCl_3 + 3\ EtMgBr \longrightarrow PhSnEt_3 \xrightarrow{SnCl_4} Et_2SnCl_2 + EtPhSnCl_2 \longrightarrow$$

$$\xrightarrow{LiAlH_4} Et_2SnH_2 + EtPhSnH_2 \qquad (XCVII)$$

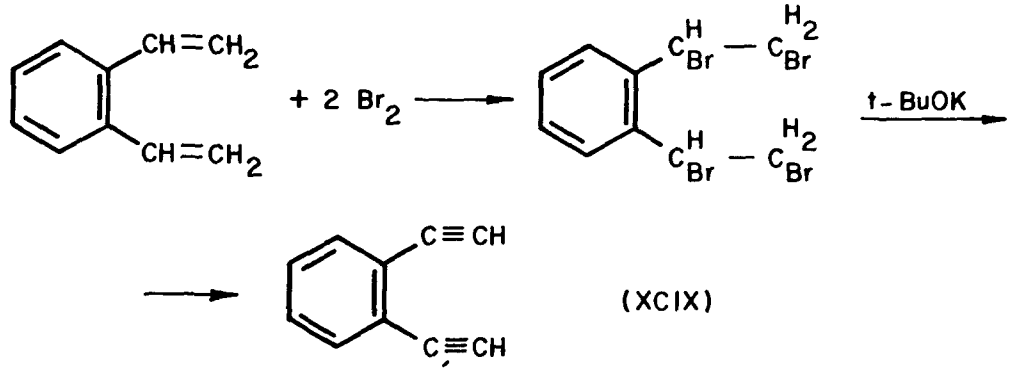
(201*)

Cleavage of two phenyl groups from ethyltriphenyltin by iodine and reduction of the resulting iodide gave better results:

$$Ph_3SnCl + EtMgBr \longrightarrow Ph_3SnEt \xrightarrow{I_2} EtPhSnI_2 \xrightarrow{LiAlH_4} EtPhSnH_2$$

(201*) (XCVIII)

o-Divinylbenzene (202*) was synthesized from o-oxylene, via o-di(bromomethyl)benzene, o-di(ethoxycarbonylmethyl)benzene and o-di(2-hydroxyethyl)benzene according to published methods (References 82, 83). o-Diethynylbenzene (203*) was obtained by bromination of o-divinylbenzene, followed by dehydrobromination of the tetrabromo product (References 84, 85):



(XCIX)

(203*)

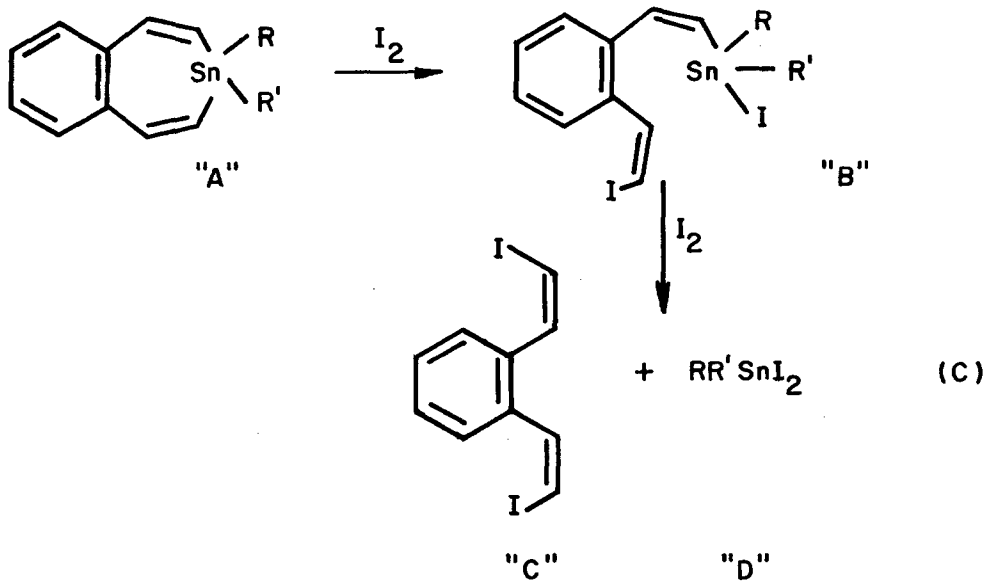
D. Degradation of Stannacycloheptatriene Derivatives by Iodine

As has been outlined before our interest was focused on stannacycleheptatriene-2,4,6 derivatives with a positive charge on the tin atom, because such a system may have a more or less aromatic character. To this purpose 3,3-dimethyl-, 3,3-diethyl-, and 3-ethyl-3-phenyl-3-benzostannepin were reacted with iodine using toluene, benzene, chloroform, or ether as a solvent. However, consumption of one equivalent of iodine did not yield the expected products. Instead of splitting off the aryl group or one of the alkyl groups attached to the tin atom, the seven-membered heterocycle was opened. A second equivalent of iodine reacted much slower; probably the first reaction is facilitated by a substantial strain in the heterocycle.

The course of these reactions was studied by means of GLC and IR spectroscopy. A semi-quantitative study was carried out by treating a benzenic solution of 3,3-diethyl-3-benzostannepin gradually with the theoretical amount of iodine dissolved in the same solvent. The

solutions thus obtained were analyzed by GLC and IR spectroscopy. The data are collected in Table 23.

As may be derived from these data the heterocycle "A" is opened during the addition of the first equivalent of iodine yielding product B. This product is converted by a second equivalent of iodine yielding products "C" and "D". During the consumption of the first equivalent of iodine small amounts of product B are converted already into products C and D.



Very small amounts of products C and D were isolated. The identity of the latter, diethyltin diiodide, was confirmed by the gaschromatogram and infrared spectrum of a synthesized sample.

Upon reacting 3,3-dimethyl-3-benzostannepin with iodine the heterocycle suffered ring fission in the same way, yielding ultimately dimethyltin diiodide (not isolated) and product "C" (GLC-characteristic). 3-Ethyl-3-phenyl-3-benzostannepin behaved similarly.

Product "C" was identified as o-bis-(β-iodovinyl)benzene (204*), most probably the pure cis-cis isomer. A similar degradation has been proposed by Freedman (Reference 86) for the reaction of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-stannacyclopentadiene with bromine.

In none of these cases product "B" was isolated in pure form, but attempts have been made to establish the nature of the iodine atoms present in it. To this purpose a sample was isolated by evaporation of th solvent from a reaction mixture of equivalent amounts of 3,3-diethyl-3-benzostannepin and iodine in benzene. Iodine analyses of this product indicate that all iodine is benzene. Iodine analyses of this product indicate that all iodine added is present in the form of high-boiling compounds and that about 50 percent of the iodine added is attached to tin. This fact, together with GLC and infrared data and the identification of products "C" and ' D" justify our opinion about the existence and structure of compound B.

As may be derived from the experiments described above introduction of an ionic Sn-X bond in 1-stannacycloheptatriene-2,4,6 derivatives in this way is higly improbable.

In view of the interesting theoretical aspects implied we have planned to continue our studies in this field of Group IV organometallic chemistry. Some reaction routes which may

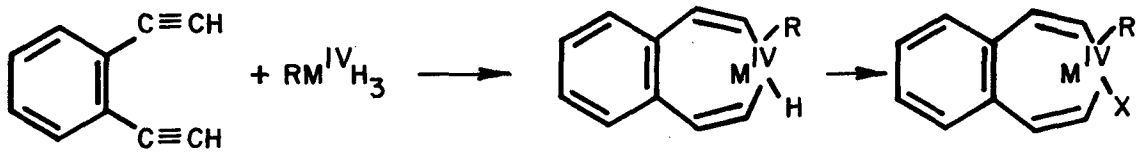
TABLE 23

The Reaction of 3.3-Diethyl-3-Benzostannepin with Iodine in Benzene (C)

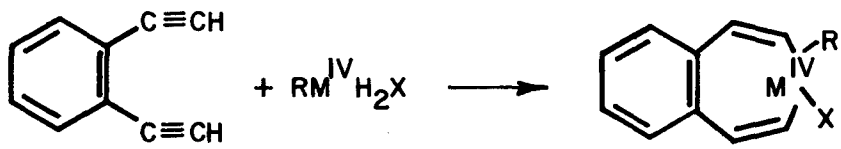
REACTION MIXTURE OF	AREA (mm^2) OF GLC - PEAKS WITH A RETENTION TIME OF			ABSORBANCE OF INFRARED BANDS WITH A FREQUENCY OF					% A AND % C CALCD. FROM		
	9 MIN.	16 MIN.	20 MIN.	1595 cm^{-1}	1575 cm^{-1}	1295 cm^{-1}	1180 cm^{-1}	780 cm^{-1}	II (A)	VIII (A)	III (C)
	I	II	III	IV	V	VI	VII	VIII			
0.10 mmol A (blanc)	0	590	0	0.00	0.14	0.00	0.03	0.47	100	100	0
0.10 mmol A + 0.05 mmol I_2	0	380	40	0.01(sh)	0.09	0.05	0.04	0.31	65	66	5
0.10 mmol A + 0.10 mmol I_2	110	80	70	0.02	0.04	0.12	0.05	0.06	14	13	9
0.10 mmol A + 0.15 mmol I_2	200	0	350	0.03	0.02	0.19	0.08	0.00	0	0	43
0.10 mmol A + 0.18 mmol I_2	360	0	740	0.03	0.00	0.26	0.11	0.00	0	0	90
peak or band is char. of compound	D	A	C	C(+B?)	A(+B?)	C(+B?)	D(+...)	A	-	-	-

lead to the formation of the compounds aimed at and which presently are under investigation have been described below:

(CI)



(CII)



(CIII)

SECTION VII

INFRARED SPECTROSCOPY OF GROUP IV ORGANOMETALLIC COMPOUNDS IN THE ROCKSALT REGION

In the course of this study numerous infrared spectra of reaction mixtures and products obtained have been recorded. Various low-molecular and polymeric Group IV organometallic compounds have been characterized in this way. Moreover, infrared spectroscopy has proved to be a useful tool in the determination of the progress of several reactions, in particular, of tin hydride addition reactions.

Some infrared data are presented in Table 24, specifically, those characteristic of vinyl, p-styrenyl, phenyl, and p-phenylene derivatives of Group IV elements. Some of these absorptions, although not directly originating from vibrations of the metal atoms themselves, show characteristic shifts to lower frequencies as the weight of the metal atom(s) in the molecule increases. For a detailed discussion of these bands the reader is referred to published reports (References 21-29, 41, 42, 46, 87).

The infrared spectra were obtained using a Perkin-Elmer Infracord Model 137 Spectrophotometer. The potassium bromide pressed disk technique was used for all the solid samples (denoted by sld. in Table 24); however, the liquids (denoted by liq.) were recorded in 0.010-0.025 mm cells with sodium chloride windows.

The synthesis of the greater part of the Group IV organometallic compounds compiled in Table 24 have been described in the preceding chapters. The p-phenylene derivatives, p-bis-(triphenylgermyl)benzene (205*), p-bis(triphenylstannyl)benzene (206*) and p-bis(triphenylplumbyl)benzene (207*), the preparation of which has not been mentioned in the preceding sections, were obtained by a conventional Grignard procedure from p-dibromobenzene and the respective triphenyl Group IV metal halides.

TABLE 24

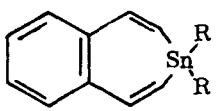
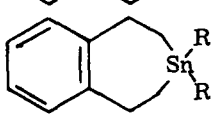
Some Infrared Absorption Characteristics of Group IV Organometallic Compounds

REGION (cm^{-1})	COMPOUND	INFRARED ABSORPTION BANDS[a] (cm^{-1})				ASSIGNMENTS
		Si	Ge	Sn	Pb	
~2150	Et_3M^{IV}-C≡C-COOMe (liq.)	-	-	2150 s	-	(M^{IV})-C≡C-(R) str. vibr.
2100-1800	$Et_3M^{IV}H$ (liq.)	2096 vs	2004 vs	1812 vs	-	M^{IV}-H str. vibr.
	$Ph_3M^{IV}H$ (liq.)	-	-	1838 vs	-	
	$Ph_2M^{IV}H_2$ (liq.)	-	2045 vs	1855 vs	-	
~1625	p-Me_3M^{IV}-C_6H_4-CH=CH_2 (liq.)	1631 m	1621 m	1616 m	1618 m	(R)-C=C str. vibr.
~1580	$Ph_3M^{IV}CH=CH_2$ (sld.)	1587[b] m	1587[b] w	1580[b] w	1572[b] m	(M^{IV})-C=C str. vibr.
	$Ph_2M^{IV}(CH=CH_2)_2$ (sld.)	1587[b] s	1590[b] m	1587[b] m	-	
~1580	Ph_4M^{IV} (sld.)	1587 w	1587 w	1580 vw	1567 w	C-C str. vibr. of -C_6H_5 nucleus
	p-Ph_3M^{IV}-C_6H_4-$M^{IV}Ph_3$ (sld.)	1588 w	1582 w	1577 w	1568 m	
~1575	p-Me_3M^{IV}-C_6H_4-Cl (liq.)	1580 s	1577 m	1572 s	-	C-C str. vibr. of -C_6H_4-nucleus
~1480	Ph_4M^{IV} (sld.)	1485 m	1484 m	1475 m	1471 m	C-C str. vibr. of -C_6H_5- nucleus
	p-Ph_3M^{IV}-C_6H_4-$M^{IV}Ph_3$ (sld.)	1487 m	1482 s	1474 s	1472 s	
~1475	p-Me_3M^{IV}-C_6H_4-Cl (liq.)	1484 s	1475 s	1474 s	-	C-C str. vibr. of -C_6H_4-nucleus
~1425	Ph_4M^{IV} (sld.)	1428 s	1429 s	1425 s	1422 s	C-C str. vibr. of -C_6H_5-nucleus
	p-Ph_3M^{IV}-C_6H_4-$M^{IV}Ph_3$ (sld.)	1428 vs	1429 vs	1425 vs	1425 vs	
~1390	$Ph_3M^{IV}CH=CH_2$ (sld.)	1395 m	1393 m	1387 m	1381 w	$(M^{IV}$-C)=CH_2 def. vibr.(in-plane)
	$Ph_2M^{IV}(CH=CH_2)_2$(sld.)	1393 s	1395 s	1389 s	-	
~1375	p-Me_3M^{IV}-C_6H_4-Cl (liq.)	1379 s	1376 s	1376 s	-	
	p-Ph_3M^{IV}-C_6H_4-$M^{IV}Ph_3$ (sld.)	1373 m	1372 m	1371 m	1368 m	C-C str. vibr. of -C_6H_4- nucleus
	p-Me_3M^{IV}-C_6H_4-$M^{IV}Me_3$ (sld.)	1373 m	1372 m	1365 m	-	

TABLE 24 (Continued)

REGION	COMPOUND	INFRARED ABSORPTION BANDS[a] (cm^{-1}) Si	Ge	Sn	Pb	ASSIGNMENTS
~1245	$Ph_3M^{IV}CH{=}CH_2$ (sld.)	1258 m	1258 m	1244 m	1225 m	(M^{IV})-CH= def. vibr. (in-plane)
	$Ph_2M^{IV}(CH{=}CH_2)_2$ (sld.)	1258 m	1263 s	1245 s	-	
1250-1150	p-Me_3M^{IV}-C_6H_4-CH=CH_2 (liq.)	1248 vs	1232 s	1181 m	1149 w	(M^{IV})-CH_3 sym. def. vibr. (in-plane)
	p-Me_3M^{IV}-C_6H_4-$M^{IV}Me_3$ (sld.)	1248 vs	1232 s	1181 m	-	
1130-1075	p-Ph_3M^{IV}-C_6H_4-$M^{IV}Ph_3$ (sld.)	1129 s	1112 m	1092 m	1075 vw	"X-sensitive" vibr. of -C_6H_4- nucleus
	p-Me_3M^{IV}-C_6H_4-$M^{IV}Ph_3$ (sld.)	1127 s	1112 m	1091 m	-	
~1100	p-Me_3M^{IV}-C_6H_4-Cl (liq.)	1111 m	1096 s	1095 vs	-	id. (sym.?)
~1075	p-Me_3M^{IV}-C_6H_4-Cl (liq.)	1086 vs	1074 vs	1064 vs	-	id. (asym.?)
1110-1060	Ph_4M^{IV} (sld.)	1110 vs	1088 s	1073 s	1062 s	"X-sensitive" vibr. of -C_6H_5 nucleus
	p-Ph_3M^{IV}-C_6H_4-$M^{IV}Ph_3$ (sld.)	1110 vs	1089 vs	1074 vs	1062 m	
~1025	Ph_4M^{IV} (sld.)	1030 m	1028 m	1022 m	1018 m	C-H def. vibr. (in-plane) of -C_6H_5 nucleus
	p-Ph_3M^{IV}-C_6H_4-$M^{IV}Ph_3$ (sld.)	1030 w	1026 m	1021 m	1017 m	
~1015	p-Ph_3M^{IV}-C_6H_4-$M^{IV}Ph_3$ (sld.)	1020 vw	1017 m	1012 m	1008 m	C-H def. vibr. (in-plane) of -C_6H_4- nucleus
	p-Me_3M^{IV}-C_6H_4-$M^{IV}Me_3$ (sld.)	(1020)[c]	1019 m	1012 m	-	
	p-Me_3M^{IV}-C_6H_4-Cl (liq.)	1018 s	1014 vs	1015 vs	-	
~1000	Ph_4M^{IV} (sld.)	999 m	999 m	998 m	997 s	"ring" vibr. of -C_6H_5 nucleus
	p-Ph_3M^{IV}-C_6H_4-$M^{IV}Ph_3$ (sld.)	999 m	999 m	998 s	997 s	
~1000	$Ph_3M^{IV}CH{=}CH_2$ (sld.)	1000[b] s	999[b] s	996[b] s	997[b] s	(M^{IV})-CH= def. vibr. (out-of-plane)
	$Ph_2M^{IV}(CH{=}CH_2)_2$ (sld.)	1005[b] vs	1001[b] vs	1000[b] vs	-	
~990	p-Me_3M^{IV}-C_6H_4-CH=CH_2 (liq.)	990 s	988 s	988 s	988 s	(R)-CH= def. vibr. (out-of-plane)
~990	$Pr_3SnCH{=}CHPh$ (liq.)	-	-	987 vs	-	(Sn)(H)C=C(H)(R) def. vibr. (out-of-plane)

TABLE 24 (Continued)

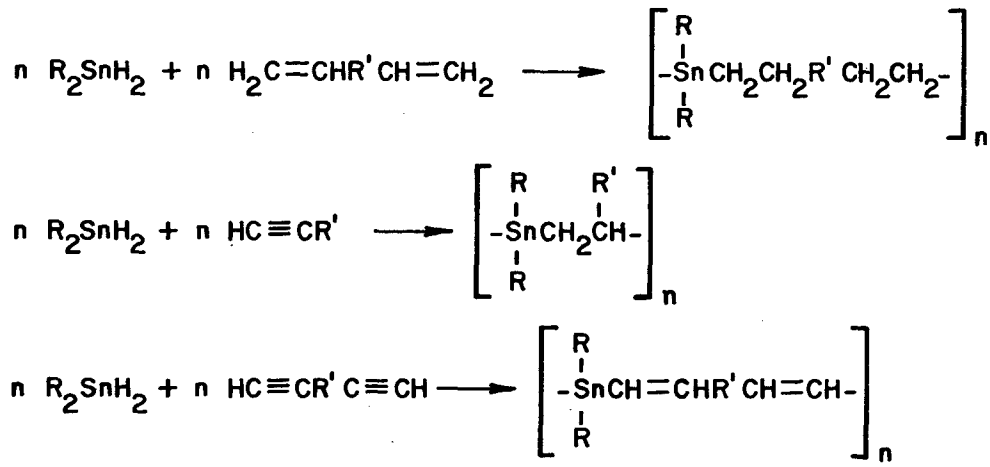
REGION (cm^{-1})	COMPOUND	INFRARED ABSORPTION BANDS[a] (cm^{-1}) Si	Ge	Sn	Pb	ASSIGNMENTS
~ 950	$Ph_3M^{IV}CH{=}CH_2$ (sld.)	958 s	952 s	952 m	942 m	M^{IV}-C)=CH_2 def. vibr. (out-of-plane)
	$Ph_2M^{IV}(CH{=}CH_2)_2$ (sld.)	958 vs	952 vs	951 vs	-	
~ 910	p-Me_3M^{IV}-C_6H_4-CH=CH_2 (liq.)	908 s	907 s	907 s	906 s	(R-C)=CH_2 def. vibr. (out-of-plane)
850-760	p-Me_3M^{IV}-C_6H_4-CH=CH_2 (liq.)	840 vs	826 vs	768 vs	768 s	(M^{IV})-CH_3 rock. vibr.
	p-Me_3M^{IV}-C_6H_4-$M^{IV}Me_3$ (sld.)	836 vs	823 vs	765 vs	-	
830-780	p-Me_3M^{IV}-C_6H_4-CH=CH_2 (liq.)	827 s	826 vs	824 vs	823 vs	C-H def. vibr. (out-of-plane) of -C_6H_4- nucleus
	p-Ph_3M^{IV}-C_6H_4-$M^{IV}Ph_3$ (sld.)	817 w	810 m	798 s	794 m	
	p-Me_3M^{IV}-C_6H_4-$M^{IV}Me_3$ (sld.)	804 s	801 s	789 s	-	
~ 780	 R=Me (sld.)	-	-	781 s	-	vibr. charac. of seven-membered heterocycle
	R=Et (liq.)	-	-	781 vs	-	
	 R=Et (liq.)	-	-	781 vs	-	
	R=Ph (sld.)	-	-	782 s	-	
745-725	Ph_4M^{IV} (sld.)	743 vs	737 vs	731 vs	726 vs	C-H def. vibr. (out-of-plane) of -C_6H_5 nucleus
	p-Ph_3M^{IV}-C_6H_4-$M^{IV}Ph_3$ (sld.)	743 s	735 vs	730 vs	726 vs	
~ 700	Ph_4M^{IV} (sld.)	704 vs	698 vs	698 vs	695 vs	ring def. vibr. (out-of-plane) of -C_6H_5 nucleus
	p-Ph_3M^{IV}-C_6H_4-$M^{IV}Ph_3$ (sld.)	703 vs	698 vs	698 vs	698 vs	

[a]Vw = very weak; w = weak; m = medium; s = strong; vs = very strong; [b]phenyl and vinyl absorption band coincide in this region; [c]no absorption has been observed in the infrared spectra of oligomeric and polymeric p-phenylene dimethylsilanes of the structure p-Me_3Si-$(C_6H_4$-$SiMe_2)_nMe$; see also Reference 28.

SECTION VIII

SUMMARY AND CONCLUSIONS

A great variety of novel Group IV organometallic polymers, having molecular weights up to 150,000, have been prepared by means of poly-addition reactions involving organotin dihydrides and difunctionally unsaturated reactants. Model reactions have been carried out with appropriate combinations of difunctional and monofunctional reactants, affording low-molecular addition products. The polymer-forming reactions studied were of the type:

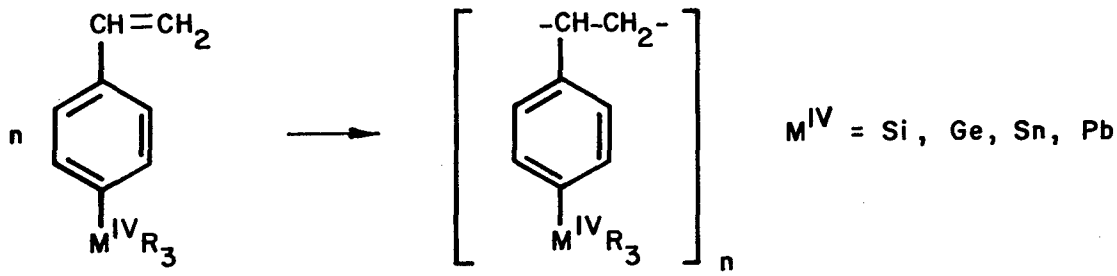


The relation between the nature of the unsaturated reactant and the properties of the resulting polymer has been studied by extensive variation of the first. As another example of an organotin dihydride a p-phenylene-bis(diorganotin monohydride) has been used as well.

The polymers range in appearance from rubbery or thermoplastic solids to viscous oils. A low softening temperature (around 100°C) seems to be an inherent property of the solid linear polymers as a consequence of the presence of the bulky organotin group in the polymer main chain.

The presence of aliphatic carbon-tin bonds and the inevitable presence of β-hydrogen atoms set inherent limitations to the thermal stability of these structures (upper limit found in this investigation at about 575°F).

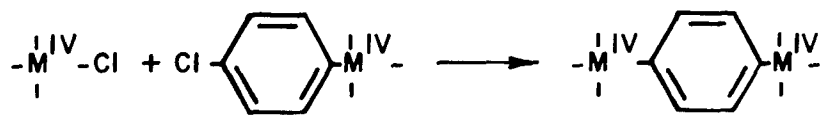
Another approach to the synthesis of Group IV organometallic polymers, viz. polymerization of organometal-substituted vinyl monomers, led to the preparation and polymerization of a series of triphenyl- and trimethylmetal-substituted styrenes:



The thermal stability of this type of polymers is limited by the occurrence of depolymerization at temperatures around 650°F.

A brief investigation has been made of the reactions of bis-cyclopentadienyltitanium diacetate and dichloride with diphenyl- and triphenyl-substituted Group IV metal derivatives with a view to the possibility of preparing polymers with a $-TiCp_2-O-M^{IV}R_2-O$ framework. High-molecular weight products with the proposed structure have not been obtained in this way. Products of the monofunctional reaction of sodium triphenyl-silanolate with bis-cyclopentadienyltitanium dichloride have been isolated and identified.

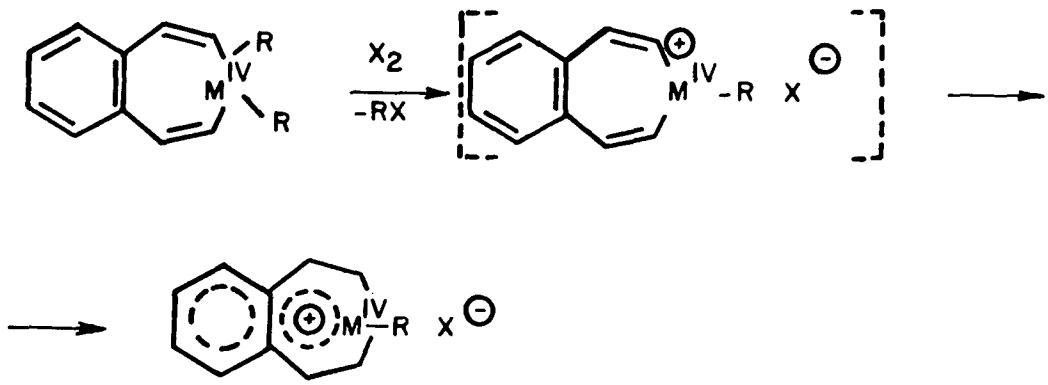
In connection with the search for more thermostable structures the synthesis of polymeric Group IV organometallics containing p-phenylene linkages has been studied. Wurtz-type condensation reactions involving appropriate combinations of p-chlorophenyl- and chlorosilanes or -germanes were applied for polymer formation:



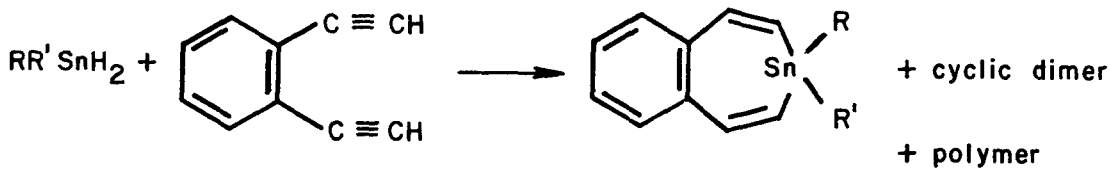
A series of well-defined oligomers as well as polymers having a degree of polymerization of 10-30 resulted from this work. According to expectation the poly-p-phenylenesilanes show considerable thermal stability (weight loss starts at 750°-950°F). The results of thermogravimetric analyses indicate that thermal stability increases with increasing degree of polymerization. However, here the problem of realizing high molecular weights was encountered, a universally limiting problem in the preparation of thermally stable polymers. So far, it has delayed attaining polymers with useful physical and mechanical properties.

Another approach to the synthesis of the above-described type of polymers, viz. the elimination of gaseous products from a high-molecular weight pre-polymer which may be obtained in a preceding step using conventional poly-condensation techniques, led to the synthesis of several Group IV metal model compounds, like benzoates, thiobenzoates, dithiobenzoates, and arylsulphinates. However, attempts at formation of Group IV metal-carbon bonds by elimination of carbon dioxide, carbon oxysulphide, and carbon disulphide have been unsuccessful. Desulphination of organotin arylsulphinates occurred to some extent. This may be a useful route to the preparation of functionally substituted aromatic and aliphatic Group IV organometallic compounds, provided suitable catalysts can be found.

The preparation of cyclic Group IV metal-containing heterocycles have been studied. In particular Group IV metallo-2,4,6-cycloheptatriene derivatives are of interest, because these compounds, in principle, may aromatize to form a tropylium-ion structure:



Of the several routes investigated, leading to the seven-membered Group IV metal-containing heterocycles, the addition reaction of dialkyl- or arylalkyltin dihydrides with o-diethynylbenzene proved to be the most useful. In this way, in addition to other interesting cyclic oligomers and polymers, some 3,3-disubstituted-3-benzostannepins have been obtained:



However, all attempts to establish a positive charge on the tin atom in these 1-stanna-2,4,6-cycloheptatrienes so far have been in vain.

Infrared characteristics in the rocksalt region of the compounds prepared in this study have been presented. Some of these bands show considerable shifts to lower frequencies as the weight of metal atom(s) in the molecule increases.

TABLE 25

Miscellaneous Compounds*

NO.	COMPOUND	FORMULA	MELTING POINT (°C)	BOILING POINT (°C/mm)	n_D^{20}	REFERENCES
1	$CH_2{=}CH$-(C6H4)-$CH{=}CH_2$	$C_{10}H_{10}$	-	50-51/3	-	5, 23
2	$CH_2{=}CMe$-(C6H4)-$CMe{=}CH_2$	$C_{18}H_{18}$	177-179	-	-	5
25	Ph_3Sn-(C5H5)	$C_{23}H_{22}Sn$	82-84	-	-	30
26	CH_3CHBr-(C6H4)-$CHBrCH_3$	$C_{10}H_{12}Br_2$	112	-	-	5, 23
43	$CH{\equiv}CCHOHC{\equiv}CH$	C_5H_4O	51	-	-	6, 24
44	$CH{\equiv}CCPhOHC{\equiv}CH$	$C_{11}H_8O$	66	-	-	6, 8, 24
45	$CH{\equiv}C(CH_2)_5C{\equiv}CH$	C_9H_{12}	-	75-77/33	1.4496	8, 24
49	$CH{\equiv}C$-(C6H4)-$C{\equiv}CH$	$C_{10}H_6$	96.5	-	-	6, 24
50	$CH_2BrCHBr$-(C6H4)-$CHBrCH_2Br$	$C_{10}H_{10}Br_4$	156	-	-	6
51	Bu_2GeBr_2	$C_8H_{18}Br_2Ge$	-	67-71/0.1	1.5110	7, 24
52	Bu_2GePh_2	$C_{20}H_{28}Ge$	-	135-140/0.002	1.5494	7, 24
53	$ClMe_2Si$-(C6H4)-$SiMe_2Cl$	$C_{10}H_{16}Cl_2Si_2$	85-88	150-155/19	-	7, 8, 26

*Part of the compounds compiled in this table have been described in the literature.

TABLE 25 (Continued)

NO.	COMPOUND	FORMULA	MELTING POINT (°C)	BOILING POINT (°C/mm)	n_D^{20}	REFERENCES
54	$ClPh_2Si$-C_6H_4-$SiPh_2Cl$	$C_{30}H_{24}Cl_2Si_2$	195-198	-	-	9, 26
55	$ClMe_2Sn$-C_6H_4-$SnMe_2Cl$	$C_{10}H_{16}Cl_2Sn_2$	160-162	-	-	9, 27
62	HMe_2Sn-C_6H_4-$SnMe_2H$	$C_{10}H_{18}Sn_2$	-	93-94/0.2	1.5732	11, 27
83	$CH_2{=}CHCONHCH_2CH_2NHCOCH{=}CH_2$	$C_8H_{12}N_2O_2$	142-143	-	-	14, 27
84	$CH_2{=}CHCONH(CH_2)_6NHCOCH{=}CH_2$	$C_{12}H_{20}N_2O_2$	142-143	-	-	14, 27
85	$CH_2{=}CHCONH(CH_2)_9NHCOCH{=}CH_2$	$C_{15}H_{26}N_2O_2$	114-118	-	-	14, 27
101	$CH_2{=}CMe$-C_6H_4-Cl	C_9H_9Cl	-	$93\text{-}95/_{20}$	1.5537	22
102	CH_3CHOH-C_6H_4-CMe_3	$C_{12}H_{18}O$	-	$133\text{-}135/_{12}$	-	22
108	$Et_3SnCH{=}CHCMe_2OH$	$C_{11}H_{24}OSn$	-	$118\text{-}124/_{15}$	1.4950	6
109	$Et_3SnCH{=}CHCMe{=}CH_2$[a]	$C_{11}H_{22}Sn$	-	$48\text{-}51/_{0.2}$	1.5021	6
110	$Et_3SnCH{=}CHCHMeCH_2SnEt_3$[b]	$C_{17}H_{38}Sn_2$	-	$105\text{-}112/_{0.015}$	1.5210	6
111	$Et_3SnCH{=}CHCH{=}CHOCH_3$[a]	$C_{11}H_{22}OSn$	-	79-81/0.007	1.5222	6
116	$Et_3SnC{\equiv}CCO_2Me$	$C_{10}H_{18}O_2Sn$	-	83-86/0.1	1.4996	13
117	$CH{\equiv}CCO_2SnMe_3$	$C_6H_{10}O_2Sn$	~ 180	-	-	11, 12
118	$CH{\equiv}CCO_2SnEt_3$	$C_9H_{16}O_2Sn$	~ 150	-	-	12

TABLE 25 (Continued)

NO.	COMPOUND	FORMULA	MELTING POINT (°C)	BOILING POINT (°C / mm)	n_D^{20}	REFERENCES
119	$CH_2{=}C(SiMe_3)CO_2H$	$C_6H_{12}O_2Si$	47	107-110/18	-	11
120	$Ph_3SiOTiCp_2Cl$	$C_{28}H_{25}ClOSiTi$	210-212	-	-	9, 25
121	$Ph_3SiOTiCp_2OSiPh_3$	$C_{46}H_{40}O_2Si_2Ti$	208-210	-	-	5, 9, 25
122	$(Ph_3SiO)_4Ti$	$C_{72}H_{60}O_4Si_4Ti$	> 450[c]	-	-	9, 25
123	$CH_3CO_2TiCp_2O_2CCH_3$	$C_{14}H_{16}O_4Ti$	90 (dec.)	-	-	5
127	$Me_2Si(C_6H_4Cl)_2$	$C_{14}H_{14}Cl_2Si$	44-47	130-133/0.2	-	8, 9, 26
126	$Me_3SiC_6H_4Cl$	$C_9H_{13}ClSi$	-	86-92/17	1.5094	7, 26
128	$Ph_3SiC_6H_4Cl$	$C_{24}H_{19}ClSi$	157-158	-	-	8, 26
129	$Ph_2Si(C_6H_4Cl)_2$	$C_{24}H_{18}Cl_2Si$	138-140	-	-	9, 26
130	$ClMe_2SiC_6H_4Cl$	$C_8H_{10}Cl_2Si$	-	106-109/18	1.5232	8, 26
131	$EtOPh_2SiC_6H_4SiPh_2OEt$	$C_{34}H_{34}O_2Si_2$	158-160	-	-	9, 26
132	$Me_3SiC_6H_4SiMe_2C_6H_4Cl$	$C_{17}H_{23}ClSi_2$	-	129-132/0.1	1.5507	8, 26
147	$Me_3GeC_6H_4Cl$	$C_9H_{13}ClGe$	-	108-114/12	1.5241	15, 28
148	$Me_2Ge(C_6H_4Cl)_2$	$C_{14}H_{14}Cl_2Ge$	45-47	142-144/0.02	-	11, 28

TABLE 25 (Continued)

NO.	COMPOUND	FORMULA	MELTING POINT °C	BOILING POINT °C/mm	n_D^{20}	REFERENCES
149	$ClMe_2Ge$-C6H4-Cl	$C_8H_{10}Cl_2Ge$	-	116-118/12	1.5512	11, 28
150	$ClMe_2Ge$-C6H4-$GeMe_2Cl$	$C_{10}H_{16}Cl_2Ge_2$	97-102	-	-	15, 28
157	Me_3Sn-C6H4-Cl	$C_9H_{13}ClSn$	-	122-126/22	1.5516	7, 28
158	Me_3Sn-C6H4-Br	$C_{19}H_{13}BrSn$	-	132-134/18	1.5704	7
159	Me_2Sn(C6H4-Cl)$_2$	$C_{14}H_{14}Cl_2Sn$	-	135-140/0.15	1.6041	7
160	$ClMe_2Sn$-C6H4-Cl	$C_8H_{10}Cl_2Sn$	~115	88-92/0.03	-	7
161	Me_3Sn-C6H4-$SnMe_3$	$C_{12}H_{22}Sn_2$	123-125	-	-	7, 28
162	Me_3Sn-C6H4-$SnMe_2$-C6H4-$SnMe_3$	$C_{20}H_{32}Sn_3$	94-96	-	-	8
163	$PhMe_2SiCl$	$C_8H_{11}ClSi$	-	97-102/30	1.5115	14
164	HMe_2Si-C6H4-Cl	$C_8H_{11}ClSi$	-	83-88/18	1.5172	15
165	$PhCO_2SiPh_2$-C6H4-$SiPh_2O_2CPh$	$C_{44}H_{34}O_4Si_2$	214-219	-	-	16
166	Ph_3SiO_2CPh	$C_{25}H_{20}O_2Si$	127-129	-	-	16
167	$Ph_3SiO_2CCH_2CN$	$C_{21}H_{17}NO_2Si$	75-95	-	-	16

TABLE 25 (Continued

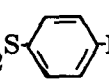
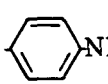
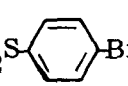
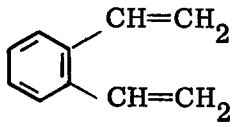
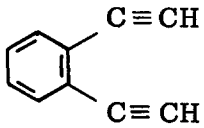
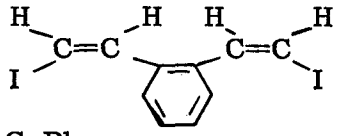
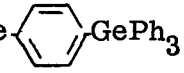
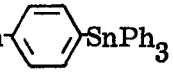
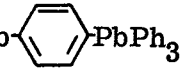
NO.	COMPOUND	FORMULA	MELTING POINT °C	BOILING POINT °C/mm	n_D^{20}	REFERENCES
168	$Ph_3SiSOCPh$	$C_{25}H_{20}OSSi$	84-88	178-200/0.02	-	16
169	$Ph_3SnSOCPh$	$C_{25}H_{20}OSSn$	105-108	-	-	16
170	Ph_3SnS_2CPh	$C_{25}H_{20}S_2Sn$	97-99	-	-	16
171	Ph_3SnSPh	$C_{24}H_{20}SSn$	101-103	-	-	16
172	Ph_3SnO_2SPh	$C_{24}H_{20}O_2SSn$	~ 245[d]	-	-	18
173	$PhSO_2SnPh_2O_2SPh$	$C_{24}H_{20}O_4S_2Sn$	~ 240[d]	-	-	18
174	$ClPh_2SnO_2SPh.Ph_2SnO$	$C_{30}H_{25}ClO_3SSn_2$	~ 200[d]	-	-	18
175	Ph_3SnO_2S-  -Me	$C_{25}H_{22}O_2SSn$	~ 225[d]	-	-	19
176	Ph_3SnO_2S-  -$NHCOCH_3$	$C_{26}H_{23}NO_3SSn$	~ 175[d]	-	-	19
177	Ph_3SnO_2S-  -Br	$C_{24}H_{19}BrO_2SSn$	~ 245[d]	-	-	19
178	$Me_2Si(CH_2I)_2$	$C_4H_{10}I_2Si$	-	107-110/14	-	17
179	$Me_2Si(CH_2PPh_3.I)_2$	$C_{40}H_{40}I_2P_2Si$	~ 280	-	-	17
180	$(BrCH_2)_2SnBr_2$	$C_2H_4Br_4Sn$	84-86	-	-	17
181	$PhSn(CH_2Br)_2Br$	$C_8H_9Br_3Sn$	-	160-166/0.4	-	17
182	$Ph_3SnCH_2SnPh_3$	$C_{37}H_{32}Sn_2$	104-106	-	-	17
183	$Ph_3SnCH_2CH_2CHOHCH_2CH_2SnPh_3$	$C_{41}H_{40}OSn_2$	-	-[e]	-	17
184	$HC \equiv CCH_2CHOHC \equiv CH$	C_6H_6O	-	75-76/26	-[f]	14

TABLE 25 (Continued)

NO.	COMPOUND	FORMULA	MELTING POINT °C	BOILING POINT °C/mm	n_D^{20}	REFERENCES
201	$EtPhSnH_2$	$C_8H_{12}Sn$	-	59-64/0.7	1.5527	19
202		$C_{10}H_{10}$	-	83-86/18	1.5748	10
203		$C_{10}H_6$	-	80-84/15	1.5908	12
204		$C_{10}H_8I_2$	51.5-52.5	-	-	19
205	Ph_3Ge-  -$GePh_3$	$C_{42}H_{34}Ge_2$	349-350	-	-	18, 28
206	Ph_3Sn-  -$SnPh_3$	$C_{42}H_{34}Sn_2$	313-315	-	-	18, 28
207	Ph_3Pb-  -$PbPh_3$	$C_{42}H_{34}Pb_2$	290-292	-	-	18,28

[a]Slightly impure; [b]structure uncertain; [c]Gutmann and Meller (Reference 62) reported m.p. 502° for this compound.

[d]With severe decomposition; these m.p. were determined using a "Kofler" hot bench. [e]Viscous oil;

[f] n_D^{25}: 1.4728.

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13. ABSTRACT

The synthesis and characterization have been described of linear polymers having a carbon chain regularly interrupted by the Group IV elements silicon, germanium, tin or lead. Such polymers have been obtained by means of: (a) poly-addition reactions involving an organotin dihydride and either a dienic, a diynic or a monoynic compound; (b) Wurtz-type poly-condensations involving appropriate combinations of p-chlorophenyl and chloro derivatives of the Group IV elements.

The synthesis and polymerization of vinyl-type IVth group organometallic monomers is dealt with briefly.

Furthermore, interesting IVth group metal-containing heterocycles have been prepared and also a few polymers, containing in addition to Group IV atoms other hetero-elements in their backbone.

All polymer-forming reactions have been studied by carrying out model reactions on a low-molecular weight level.

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Organometallic Compounds						
Silicon Compounds						
Tin Compounds						
Germanium Compounds						
Lead Compounds						

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