

In view of the above discussion, a detailed commentary on the effect of *para* substituents does not seem warranted. The substituent may affect the protolytic equilibrium as well as the activation parameters for the thermolytic process. The difficulty in interpreting any substituent effect is seen, for example, in the case of the *p*-methoxy group. This compound is a weaker acid than 5-phenyltetrazole⁸ and therefore a higher concentration of the monomeric 5-*p*-anisyltetrazole might be anticipated. At the same time the *p*-methoxy group would be expected to stabilize the incipient *p*-anisonitrile imine. Both effects would lead to a predicted increase in the observed first-order rate constant, whereas the observed value is less.

There is no simple correlation with any of the substituent constants.¹⁸ Changes in the nature of the substituent have little effect on the rate. Although the

(18) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

rate differences are quite small, they reflect rather large variations in activation enthalpies which are apparently offset by compensating activation entropies. This interpretation, however, is open to question.¹⁹

A comparison of the rates in benzonitrile as solvent for 2,5-diphenyltetrazole¹² and 5-phenyltetrazole shows that the former compound undergoes a more facile decomposition. The activation parameters for the latter correspond to a rate constant at 175° of about 1.3×10^{-5} sec.⁻¹, giving $k_{2,5-(C_6H_5)_2}/k_{5-C_6H_5} = 38$.

Acknowledgment.—Exploratory work related to these studies was commenced by one of us in the laboratory of Professor R. Huisgen (Munich). His permission to continue this investigation and his interest in our work are gratefully acknowledged. We are indebted to Dr. S. D. Ross and Dr. R. C. Petersen for many valuable discussions and helpful suggestions.

(19) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, pp. 376-379.

Sterically Hindered Group IVA Organometallics. Preparation and Properties of Certain Neopentyltins¹

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A series of 17 organotin compounds containing the neopentyl group has been prepared in an effort to determine the effect of steric hindrance on the preparation and reactivity of these compounds. The introduction of a fourth neopentyl group around the tin atom required more drastic conditions than necessary for a *n*-alkyl group, and in one instance the attempted preparation led solely to the isolation of the reduction product, hexaneopentyliditin. Once formed, the neopentyl carbon to tin bond strongly resisted cleavage; the bond was broken only slowly at elevated temperatures by bromine and failed to undergo a Kocheshkov reaction below the degradation temperature of the mixture.

The present work was undertaken as part of a study aimed at investigating the formation and reactivity of organotin compounds containing aliphatic groups exerting a steric influence in the final product. Van der Kerk and Luijten³ report that the reaction of isopropylmagnesium bromide and stannic chloride result in the formation of tetraisopropyltin in only 25% yield, accompanied by the formation of a considerable quantity of hexaisopropyliditin. Under similar conditions they observe that tetra-*n*-propyltin is isolated in a 70% yield.⁴ Similarly, the formation of tetracyclohexyltin is reported⁵ to be accompanied by the formation of a considerable quantity of distannane, while the *n*-hexyl compound may be prepared in good yield.⁴

Krause and Weinberg⁶ investigated the reaction of *t*-alkylmagnesium bromides and stannic chloride and found that the addition of the chloride to the Grignard reagent resulted in the formation of a di-*t*-alkyltin, which on treatment with bromine resulted in the formation of the corresponding di-*t*-alkyltin dibromide in al-

most quantitative yield. When the order of addition was reversed, a di-*t*-alkyltin dichloride could be isolated directly. Treatment of the dihalide with a large excess of the Grignard reagent resulted in the formation of a tri-*t*-alkyltin halide, but the authors were unable to obtain a tetra-*t*-alkyltin containing either the *t*-butyl or *t*-amyl group. Working with *t*-butyllithium and stannic chloride, Prince⁷ reported a similar series of results.

Steric effects have also been observed in the attempted formation of tetraaryltins. Tri-1-naphthyltin chloride,⁸ tri-2-biphenyltin chloride,⁸ and tri-2-biphenyltin bromide⁹ result from the reaction of the appropriate Grignard reagent and stannic halide. However, in each instance the tetraaryltin could be prepared by substituting the corresponding organolithium compound for the Grignard reagent. Tris(2-alkoxy-1-naphthyl)tin bromides and trimesityltin bromide were the only products isolated on treatment of stannic bromide with the appropriate Grignard reagent.¹⁰ In the latter case, the authors were unable to prepare the tetraaryltins even with the organolithium, -sodium, or -potassium reagents.

(1) Taken in part from the doctoral degree dissertations of M. D. (1963) and O. A. H. (presumably 1965), University of Cincinnati.

(2) Research Corporation Fellow, 1959-1960.

(3) G. J. M., Van der Kerk, and J. G. A. Luijten, *J. Appl. Chem.* (London), **6**, 49 (1956).

(4) G. J. M., Van der Kerk, and J. G. A. Luijten, "Investigations in the Field of Organotin Chemistry," Tin Research Institute, Middlesex, England, 1955.

(5) E. Krause and R. Pohland, *Ber.*, **57**, 532 (1924).

(6) E. Krause and K. Weinberg, *ibid.*, **63**, 381 (1930).

(7) R. H. Prince, *J. Chem. Soc.*, 1783 (1959).

(8) E. Krause and K. Weinberg, *Ber.*, **62**, 2235 (1929).

(9) G. Bähr and R. Gelius, *ibid.*, **91**, 812 (1958).

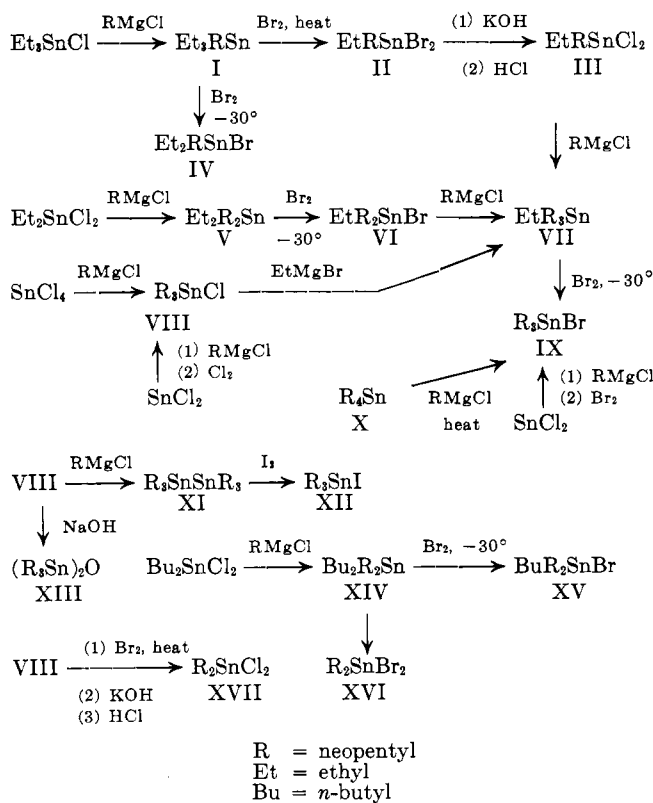
(10) I. I. Lapkin and V. A. Sedel'nikova, *Zh. Obshch. Khim.*, **30**, 2771 (1960); *Chem. Abstr.*, **55**, 14,346b (1960).

The literature contains only two references to the formation of group IV organometallics containing a neopentyl-like group. Rochow and Seyferth¹¹ report the formation of a series of silanes having the general formula $[(\text{CH}_3)_3\text{MCH}_2]\text{CH}_2\text{SiX}_2$, where M may be any element of group IVA and X may be a chloride, methoxide, or ethoxide group. Subsequently, Seyferth¹² reported the preparation of tetrakis(trimethylsilylmethyl) tin in excellent yield.

Results and Discussion

The preparation of neopentylmagnesium chloride was first reported by Whitmore,¹³ who indicated that the reaction of neopentyl chloride and magnesium proceeded very slowly. In the present work it was found that the slow addition of an ethereal solution of neopentyl chloride to magnesium, as in the procedure generally used for the preparation of a Grignard solution, would not maintain a reaction, and that the Grignard reagent was best prepared by adding the halide all at once and heating the resulting mixture under reflux for several hours. That the Grignard reagent did not undergo coupling with the excess halide present was shown by the fact that the magnesium could be completely consumed. (For a compilation of reactions performed and a key to the Roman numerals see Scheme I.)

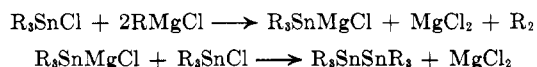
SCHEME I



Neopentylmagnesium chloride reacted with diethyltin dichloride, dibutyltin dichloride, triethyltin chloride, and the alkylneopentyltin halides IV and VI in a straightforward manner and yielded the corresponding

mixed alkyltins in good yield. However, the reaction of the Grignard reagent and stannic chloride resulted in a mixture of VIII, X, and XI, in which the chloride VIII predominated.

The attempted preparation of X by the reaction of VIII and neopentylmagnesium chloride resulted in the formation of the ditin XI. Compound X was finally prepared in good yield by the reaction of the bromide IX and an excess of the neopentyl Grignard reagent in a concentrated benzene solution at 100°. The formation of a distannane during the reaction of VIII and the Grignard reagent could result from an exchange reaction similar to that reported by Morrison¹⁴ for the benzyl halides.



The ethyl and butyl groups of the mixed alkyltins are readily removed by the action of bromine on the tetraalkyltin. The reaction of V or XIV with 1 equiv. of bromine at -30° resulted in the isolation of the corresponding alkylneopentyltin bromide while the reaction with 2 equiv. of bromine in refluxing chloroform resulted in the isolation of the dibromide XVI. II and IV resulted from a similar sequence of reactions between bromine and I.

X reacted only sluggishly with bromide at room temperature and the reaction was completed only by heating the mixture under reflux in chloroform. Similarly, the removal of a second alkyl group from VIII required prolonged refluxing in tetrachloromethane. In the latter case, the product was isolated as the dichloride by first shaking the reaction mixture with dilute sodium hydroxide solution and then treating it with hydrochloric acid.

The results thus place the neopentyl group after the butyl group when the groups are arranged in order of decreasing ease of cleavage, as originally developed by Bullard¹⁵ and subsequently extended by several other authors.¹⁶ The exact position of the neopentyl group with respect to the remaining isomeric pentyl groups and the higher alkyl groups is yet to be determined.

The literature contains numerous references¹⁶ to the ready cleavage of distannanes by halogens. In this laboratory the reaction has been utilized in determining the amount of distannane in tetraalkyltins; a solution of the sample is titrated with 0.1 N iodine in benzene. The reaction has generally been found to be quite rapid, and quantitative. XI reacted with iodine solution, however, only sluggishly at room temperature, necessitating running the titration in boiling benzene, and even under these conditions the reaction appeared incomplete.

When the crude VIII produced by the reaction of neopentylmagnesium chloride and stannic chloride was treated with sufficient stannic chloride to yield XVII in a Kocheshkov-type reaction and heated at 210° , no reaction occurred. Increasing the temperature to 250° resulted in degradation of the reactants.

It therefore becomes apparent from the above described reactions that the neopentyl group shields

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(16) R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).

(11) E. G. Rochow and D. Seyferth, *J. Org. Chem.*, **20**, 250 (1955).

(12) D. Seyferth, *J. Am. Chem. Soc.*, **79**, 5881 (1957).

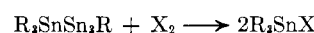
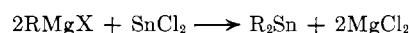
(13) F. C. Whitmore and G. H. Fleming, *ibid.*, **55**, 4161 (1933).

Table I

No.	Compound	M.p., °C.	B.p., °C. (mm.) ^a	n _D ²⁰	d (°C.)	Molar refraction			Formula	Analysis, %						
						Obsd.	Calcd. (West)	Calcd. (Vogel)		C	H	Halogen	C	H	Halogen	Obsd.
I	Et ₂ RSn		106-108 (17)	1.4690	1.1106 (20)	69.34	69.57	69.74	C ₁₁ H ₂₆ Sn	47.69	9.46	48.30	9.65			
V	Et ₂ R ₂ Sn		66 (0.1)	1.4710	1.0680 (24)	83.81	83.73	83.95	C ₁₄ H ₃₂ Sn	52.69	10.11	53.00	9.64			
XIV	Bu ₂ RSn		88 (0.1)	1.4739	1.0303 (27)	102.25	102.50	102.52	C ₁₈ H ₄₀ Sn	57.62	10.75	57.17	10.49			
VII	EtR ₃ Sn		76 (0.1)	1.4754	1.0428 (28)	97.37	98.38	98.13	C ₁₇ H ₃₈ Sn	56.53	10.60	56.82	10.72			
X	R ₄ Sn	134-135.5							C ₂₀ H ₄₄ Sn	59.57	11.00	59.46	10.81			
IV	Et ₂ RSnBr		64 (0.1)	1.5070	1.4341 (25)	68.07	67.81	67.81	C ₉ H ₂₁ BrSn	32.97	6.46	24.37	33.46	6.73	24.10	
VI	EtR ₃ SnBr		75 (0.1)	1.5014	1.3293 (25)	81.98	82.21	82.09	C ₁₂ H ₂₇ BrSn	38.95	7.37	21.60	39.20	7.00	21.39	
XV	BuR ₂ SnBr		94 (0.1)	1.4995	1.2770 (25)	91.59	91.47	91.40	C ₁₄ H ₃₁ BrSn	42.24	7.85	20.08	42.91	7.80	20.02	
IX	R ₃ SnBr	88-91							C ₁₅ H ₃₃ BrSn	43.72	8.07	19.39	43.54	8.04	19.48	
VIII	R ₃ SnCl	112.5-113.5							C ₁₅ H ₃₃ ClSn	49.01	9.05	9.64	49.17	9.04	9.90	
XII	R ₃ SnI	57-58							C ₁₅ H ₃₃ ISn	39.25	7.26	39.46	7.24			
II	EtRSnBr ₂		65 (0.1)	1.5421	1.7820 (22.5)	66.35	66.03	65.97	C ₇ H ₁₆ Br ₂ Sn	22.20	4.26	42.20	22.48	4.36	42.05	
III	EtRSnCl ₂		63 (0.1)	1.5067	1.4410 (25)	59.75	59.61	59.75	C ₇ H ₁₆ Cl ₂ Sn	29.01	5.56	24.47	29.44	5.44	24.35	
XVI	R ₂ SnBr ₂		87 (0.1)	1.5290	1.6141 (25)	80.41	80.44	80.36	C ₁₀ H ₂₂ Br ₂ Sn	28.54	5.27	37.98	28.05	5.06	37.37	
XVII	R ₂ SnCl ₂	43							C ₁₀ H ₂₂ Cl ₂ Sn	36.19	6.68	21.36	35.94	6.58	21.52	
XI	R ₃ SnSnR ₃	275-277							C ₃₃ H ₆₆ Sn ₂	54.24	10.01	54.31	10.29			
XIII	R ₃ SnOSnR ₃	215-217							C ₃₀ H ₆₆ O ₂ Sn ₂	52.98	9.77	53.52	9.76			

through its steric bulk the Sn-C bonds, rendering neopentyltin organics less reactive toward chemical attack than other alkyltin organics. Also, the formation of neopentyltins is markedly influenced by the bulk of this particular group. In an attempt to utilize the steric hindrance of the neopentyl group as a means of forming XVII directly from stannic chloride and neopentylmagnesium chloride, stoichiometric quantities of the reactants were reacted in an acetone-dry ice bath, but only VIII could be isolated from the reaction mixture. Trineopentyltin halides were also the only products isolated when the neopentyl Grignard compound was reacted with stannous chloride, and the resulting ethereal solution was treated with bromine or chlorine.

The formation of a trineopentyltin halide during the latter reaction may result from the disproportionation of the initially formed dialkyltin into a distannane and metallic tin, followed by cleavage of the distannane by the halogen.



This sequence of reactions finds analogy in the phenyl series.¹⁷

Further indications of the steric influence of the neopentyl group on the reactivity of its compounds is shown by the observation that, while VIII reacted readily with ethylmagnesium bromide to yield VII in excellent yield, no phenyltrineopentyltin could be obtained from the reaction of IX with phenylmagnesium bromide under similar conditions, nor could diphenyldineopentyltin be isolated from the analogous reaction. It thus appears that the phenylmagnesium group is too large to get close enough to the trineopentyltin moiety for reaction to occur.

As would be expected from the observation that an increase in the number of carbon atoms in the alkyl group results in an increased tendency to form anhydrides preferentially over hydroxides,⁴ the product isolated from the reaction of IX and aqueous sodium hydroxide proved to be bis(trineopentyltin) oxide, a well-defined crystalline compound with a relatively high melting point (215-217°), compared with those of and straight-chain tributyl, tripropyl-, and trihexyltin oxides, all of which are reported to be oils at room temperature.

This tendency on the part of the neopentyltins to have anomalous physical properties as compared with the straight-chain analogs is exhibited by many of these compounds. Generally, the melting points of the neopentyltins parallel more closely the corresponding aromatic and alicyclic tins than the *n*-alkyltins.^{5,16}

As a means of obtaining an initial identification and indication of purity of the various liquid neopentyltin compounds here prepared, use was made of the molar refractions determined from the density and index of refraction, compared with that calculated from the reported bond refractions. Two series of bond refractions are to be found in the literature. One series, derived by West and Rochow,¹⁸ is based on Denbigh's

(17) J. Bornstein, B. R. LaLiberte, T. M. Andrews, and J. C. Montermose, *J. Org. Chem.*, **24**, 886 (1959).

(18) R. West and E. G. Rochow, *J. Am. Chem. Soc.*, **74**, 2490 (1952).

fundamental bond refractions for C-H and C-C of 1.69 and 1.25, respectively. The authors deduce two values for the Sn-C bond, one for the so-called "primary" bond and second for a "secondary" bond. This work was subsequently augmented by West¹⁹ who derived a value for a "tertiary" Sn-C bond.

The second series of bond refractions is compiled in a publication by Vogel²⁰ and is based on increments for C-H and C-C of 1.676 and 1.296, respectively. In this instance the authors derived only a single value for the Sn-C bond refraction.

In the present work, the molar refraction of ten compounds containing the neopentyl group was determined using the values given in each series. With the figures of West, an average error of -0.52 per neopentyl group was observed, while with the values of Vogel, the error was found to be -0.35 per neopentyl group. Table I contains a tabulation of the observed molar refractions and the calculated molar refractions to which the above corrections have been applied. From the molecular refractions represented here, it appears that both sets of increments give good values and are usable for analytical purposes. In Table I, all of the determined physical properties as well as the analyses of the prepared neopentyltins are compiled.

Experimental

All melting points are uncorrected. Analyses are by A. Bernhardt, Microanalytical Laboratories, Mulheim/Ruhr, Germany, or Galbraith Laboratories, Knoxville, Tenn.

Triethylneopentyltin (I).—A Grignard solution was prepared from 12.1 g. (0.5 g.-atom) of magnesium and 58.6 g. (0.55 mole) of neopentyl chloride in 200 ml. of ether and treated slowly with a solution of 48.3 g. (0.2 mole) of triethyltin chloride in 200 ml. of benzene. The mixture was heated under reflux for 2 hr., cooled, and decomposed with 30 ml. of water and 300 ml. of saturated ammonium chloride solution. The organic layer was separated, filtered, and dried over calcium chloride. The solvent was removed under reduced pressure, the residue was taken up in an equal volume of ether and treated with a slow stream of anhydrous ammonia. After removing the amine complex by filtration, the solvent was removed by stripping under reduced pressure, and the residue was distilled to give 42.4 g. (76.5% yield) of I.

Diethylneopentyltin (V).—A Grignard solution prepared from 12.1 g. (0.5 g.-atom) of magnesium and 58.6 g. (0.55 mole) of neopentyl chloride in 200 ml. of ether was reacted with 24.8 g. (0.1 mole) of diethyltin dichloride in 175 ml. of benzene in a manner similar to that described above for I to yield 25.0 g. (79%) of V.

Dibutylneopentyltin (XIV).—A Grignard solution prepared from 186.4 g. (1.75 moles) of neopentyl chloride and 35.1 g. (1.5 g.-atoms) of magnesium in 600 ml. of ether was treated with 152 g. (0.5 mole) of dibutyltin dichloride in 600 ml. of benzene in the usual manner to give 178 g. (98% yield) of XIV.

Diethylneopentyltin Bromide (IV).—A solution of 13.8 g. (0.05 mole) of I in 25 ml. of chloroform was cooled to -30° in an ice-methanol bath and treated slowly with a solution of 8.0 g. (0.05 mole) of bromine in 25 ml. of chloroform. When the reaction was complete, the solvent and ethyl bromide were removed under reduced pressure and the residue was fractionated to yield 13.8 g. (84%) of IV.

Ethylneopentyltin Dibromide (II).—A solution of 13.8 g. (0.05 mole) of I in 25 ml. of chloroform was treated slowly, without external cooling, with a solution of 16.0 g. (0.1 mole) of bromine in 50 ml. of chloroform. When the addition was complete, the mixture was heated under reflux for 1 hr. to complete the reaction. The reaction mixture was then stripped under reduced pressure and the residue was distilled to yield

16.0 g. (84%) of crude II. After two additional fractionations, a colorless product was obtained.

Ethylneopentyltin Dichloride (III).—An ethereal solution of crude II prepared from 32.0 g. (0.2 mole) of bromine and 27.7 g. (0.1 mole) of I was shaken with a solution of 22.4 g. (0.4 mole) of potassium hydroxide in 45 ml. of water, washed with two 25-ml. portions of distilled water, then shaken with 80 ml. of 1:3 hydrochloric acid, and again washed twice with 25 ml. After drying the ethereal solution over calcium chloride, the solvent was removed under reduced pressure and the residue was distilled to give 18.2 g. (63% yield) of crude III. Two further fractionations gave a colorless product.

Ethylneopentyltin Bromide (VI).—A solution of 16.0 g. (0.05 mole) of V in 25 ml. of chloroform was cooled to -30° in a methanol-ice bath and treated slowly, at such a rate that a bromine color did not develop, with a solution of 8.0 g. (0.05 mole) of bromine. The mixture was stirred for 0.5 hr. after the addition was complete, the solvent was removed under reduced pressure, and the residue was fractionated to yield 15.9 g. (86%) of crude VI. Refractionation yielded a colorless product.

Butylneopentyltin Bromide (XV).—A solution of 9.2 g. (0.025 mole) of XIV in 25 ml. of chloroform was cooled to -30° and treated slowly with a solution of 4.0 g. (0.025 mole) of bromine in an additional 25 ml. of chloroform. When the reaction was complete, the solvent was removed under reduced pressure, and the residue was distilled to yield 8.3 g. (84%) of XV.

Dineopentyltin Dibromide (XVI).—A solution of 132 g. (0.36 mole) of XIV in 100 ml. of carbon tetrachloride was heated under reflux and treated dropwise with a solution of 115 g. (0.72 mole) of bromine in 100 ml. of carbon tetrachloride at such a rate as to maintain reflux without further external heating. When the addition was complete, the mixture was heated under reflux for an additional hour, the solvent was removed under reduced pressure, and the residue was distilled to yield 145 g. (96%) of crude XVI. Refractionation yielded a colorless product.

Ethyltrineopentyltin (VII). A. From VI.—A Grignard solution prepared from 1.2 g. (0.05 g.-atom) of magnesium and 5.9 g. (0.055 mole) of neopentyl chloride in 25 ml. of ether was reacted with 7.4 g. (0.02 mole) of VI in 25 ml. of benzene as previously described to yield 4.5 g. (63%) of VII.

B. From III.—A Grignard solution prepared from 2.4 g. (0.1 g.-atom) of magnesium and 11.8 g. (0.11 mole) of neopentyl chloride in 50 ml. of ether was treated with 5.8 g. (0.02 mole) of III in 50 ml. of benzene in the usual manner to give 4.3 g. (60%) of VII.

Trineopentyltin Bromide (IX). A. From VII.—A solution of 18.0 g. (0.05 mole) of VII in 25 ml. of chloroform was cooled to -30° and treated slowly with a solution of 8.0 g. (0.05 mole) of bromine in 25 ml. of chloroform. When the reaction was complete, as indicated by the absence of a bromine color, the solvent was removed by evaporation to yield 20.8 g. of residue, m.p. 85-90°, which was recrystallized from hexane to give 16.5 g. (81%) of IX.

B. From X.—A solution of 1.6 g. (0.01 mole) of bromine in 50 ml. of chloroform was added dropwise to a rapidly stirred solution of 4.03 g. (0.01 mole) of X in 100 ml. of chloroform. The bromine color in the reaction mixture failed to disappear immediately after the addition of the first few drops. The color resulting from the addition of approximately 1 ml. of the bromine solution required 15 min. at room temperature to discharge, indicating a very slow rate of reaction. The solution was brought to reflux and the remaining bromine solution was added at a moderate rate. Refluxing was continued for 1.5 hr. after the addition was complete, following which the solvent was removed by evaporation and the residue was washed with cold absolute alcohol to yield 3.4 g. (88%) of crude IX, m.p. 78-85°. Recrystallization from alcohol gave a pure product.

Trineopentyltin Chloride (VIII).—A Grignard solution was prepared from 186.4 g. (1.75 moles) of neopentyl chloride and 35.1 g. (1.5 g.-atoms) of magnesium in 600 ml. of ether, and treated with a solution of 65.3 g. (0.25 mole) of stannic chloride in 600 ml. of benzene. After heating under reflux for 2 hr., the mixture was decomposed by pouring onto a mixture of 300 g. of ammonium chloride and 1000 g. of crushed ice. The organic layer was separated, filtered, and dried over anhydrous calcium chloride. After removal of the solvent, the residue was distilled to yield 83 g. of material, b.p. 170-172° (20 mm.), which solidified on cooling, m.p. 82-102°. The product was found to con-

(19) R. West, M. H. Webster, and G. Wilkenson, *J. Am. Chem. Soc.*, **74**, 5794 (1952).

(20) A. T. Vogel, W. T. Cresswell, and J. Leicester, *J. Chem. Phys.*, **58**, 174 (1954).

tain 5.95% of chlorine, indicating that it contained 62% of VIII. Also, a 1.000-g. sample of the product in boiling benzene required 9.10 ml. of 0.102 *N* iodine to titrate, indicating a XI content of 32%.

A 4.0-g. sample of the mixture was taken up in 10 ml. of hexane and cooled slowly to -70° to yield 2.3 g. (93% of expected) of VIII, m.p. 109–111°. Recrystallization from hexane gave a pure product.

The filtrates from above were evaporated to dryness, taken up in ether, and treated with a slow stream of ammonia. After filtering and evaporating almost to dryness, the resulting residue was sucked dry on a Büchner funnel and recrystallized twice from ether to yield a small quantity of X, m.p. 134–137°.

Attempted Disproportionation of Crude VIII.—A mixture of 40 g. of crude VIII and 18.2 g. of stannic chloride was heated at 210° for 1.5 hr., during which time the mixture darkened and formed a black residue. The mixture was cooled to about 70° , taken up in hexane, and filtered; the filtrate was cooled to -20° to yield 24.3 g. of VIII, m.p. 111–112°. As the starting material contained a calculated 24.7 g. of VIII, it was concluded that no reaction had occurred.

In a second attempt at the formation of XVII *via* the disproportionation reaction, 35 g. of the crude VIII and 16.0 g. of stannic chloride were heated rapidly to 210° and then slowly over a 4-hr. period to 255° , at which temperature evolution of a low-boiling material occurred. The mixture was cooled and treated as before to yield 4.6 g. of VIII, m.p. 112–113°. No other identifiable material could be isolated.

Attempted Direct Preparation of Dineopentyltin Dichloride.—A Grignard solution was prepared from 93.2 g. (0.88 mole) of neopentyl chloride and 17.6 g. (0.75 g.-atom) of magnesium in 300 ml. of ether and treated with a benzene solution of 98.0 g. (0.35 mole) of stannic chloride, while cooling in an acetone-dry ice bath. After warming to room temperature, the reaction mixture was decomposed with 50 ml. of concentrated hydrochloric acid and 300 g. of crushed ice; the organic layer was separated, filtered, and dried over calcium chloride. Removal of the solvent gave an 84.0-g. yield of crude VIII, which after crystallization from hexane gave 60.0 g. (65%, based on magnesium) of VIII, m.p. 110–111.5°.

Reaction of Stannous Chloride and Neopentylmagnesium Chloride.—A Grignard solution was prepared from 42.0 g. (0.4 mole) of neopentyl chloride and 8.5 g. (0.37 mole) of magnesium in 150 ml. of ether and treated slowly with 30.5 g. (0.16 mole) of stannous chloride. After heating under reflux for 1 hr., the mixture was decomposed by the addition of 225 ml. of 10% hydrochloric acid, and the organic layer was separated and filtered. The organic layer was then returned to the reaction flask, cooled in an acetone-dry ice bath, and treated with a slow stream of chlorine until the red color had discharged. After warming to room temperature, the mixture was washed with 100 ml. of distilled water, 100 ml. of 1:1 hydrochloric acid, and once again with 100 ml. of distilled water, filtered, and dried over anhydrous calcium chloride. After removal of the solvent, the residue was recrystallized from hexane to yield 15.0 g. of VIII, m.p. 112–113°.

In a second attempt, a Grignard solution was prepared under nitrogen from 12.1 g. (0.5 g.-atom) of magnesium and 58.6 g. (0.55 mole) of neopentyl chloride in 300 ml. of ether. The

etheral solution was cooled to -30° and treated cautiously with 37.9 g. (0.20 mole) of anhydrous stannous chloride. The resulting mixture was stirred for 1 hr., treated with 200 ml. of 10% hydrochloric acid, the organic layer was separated and washed with 100 ml. of 10% hydrochloric acid, followed by 100 ml. of distilled water. The resulting red etheral solution was treated with 32.0 g. (0.2 mole) of bromine and then shaken with a small amount of saturated sodium bisulfite solution to remove the excess bromine. After washing twice with distilled water, the etheral solution was dried over calcium chloride and stripped under reduced pressure. The residue, about 12.0 g., was crystallized from benzene to yield as the only product a small quantity of XI, m.p. 88–91°.

Dineopentyltin Dichloride (XVII).—A mixture of 18.3 g. (0.05 mole) of VIII and 8.0 g. (0.05 mole) of bromine in 60 ml. of carbon tetrachloride was heated under reflux for 1 hr. The solution was cooled, shaken with two 50-ml. portions of 10% sodium hydroxide and once with 100 ml. of water, filtered, and dried over anhydrous calcium chloride. The solvent was removed under reduced pressure and the residue was distilled to yield 14.5 g. (88%) of XVII.

Hexaneopentyliditin (XI).—A Grignard solution was prepared by reacting 3.2 g. (0.13 g.-atom) of magnesium and 14.3 g. (0.14 mole) of neopentyl chloride in 40 ml. of ether and treating the resulting solution with a benzene solution of 18.4 g. (0.05 mole) of VIII. After heating under reflux for 4 hr., the mixture was decomposed with ammonium chloride solution, the organic layer was separated and dried over anhydrous calcium chloride. The solvent was removed by evaporation, and the remaining residue was crystallized from hexane to yield 5.0 g. of XI.

Trineopentyltin Iodide (XII).—A 0.3290-g. sample of XI was titrated in boiling benzene with 9.10 ml. of 0.102 *N* iodine in benzene, indicating an equivalent weight of 354.2 (calcd. 332.1). The solvent was removed and the residue was crystallized from methanol to yield 0.3 g. of XII.

Tetraneopentyltin (X).—A Grignard solution was prepared from 3.2 g. (0.13 g.-atom) of magnesium and 14.3 g. (0.14 mole) of neopentyl chloride in 40 ml. of ether. A solution of 20.6 g. (0.05 mole) of trineopentyltin bromide in 60 ml. of benzene was added, and the mixture was heated under reflux for 2 hr. The solvent was then removed slowly by distillation until the pot temperature had reached 103° and the mixture was heated under reflux for an additional 1.25 hr. The reaction mixture was decomposed by the addition of 100 ml. of 10% hydrochloric acid and the organic layer was separated and dried over calcium chloride. Removal of the solvent gave 21.6 g. of residue, m.p. 130–135°, which was recrystallized from hexane to yield 19.7 g. (99%) of X.

Ethyltrineopentyltin (VII). From VIII.—A Grignard solution prepared from 6.1 g. (0.25 g.-atom) of magnesium and 30.2 g. (0.28 mole) of ethyl bromide in 100 ml. of ether was treated with 36.8 g. (0.1 mole) of VIII in 200 ml. of benzene in the usual manner to yield 28.4 g. (79%) of VII.

Bis(trineopentyltin) Oxide (XIII).—A solution of 3.7 g. (0.01 mole) of VIII in 50 ml. of ether was shaken twice with 5.0-ml. portions of 10% sodium hydroxide, then washed with water and dried over anhydrous sodium sulfate. The solvent was removed and the residue (3.2 g., m.p. 193–207°) was recrystallized twice from ether to yield 1.3 g. of XIII.