analogously to those described above. At some point a N–B bond is formed and either halogen migration or methyl migration occurs to give the products, $(CH_3)_2NBY_2$ and $(CH_3)_xPY_{3-x}$.

In the aminophosphine reactions with $B(CH_3)_3$ 1:1 adducts may serve as initial steps. Studies at −46° showed that such adducts were isolatable with additional reaction proceeding very slowly; however, no adducts were obtained with the boron halides apparently due to the much higher reactivity encountered.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASSACHUSETTS]

The Preparation of Organolithium Compounds by the Transmetalation Reaction. IV. Some Factors Affecting the Transmetalation Reaction[1]

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Evidence is presented to show that the exchange reaction occurring between organolithium compounds and allyl- and vinyltin compounds is an equilibrium reaction. The position of the C=C bond in olefinic organotin compounds is an important factor with regard to the transmetalation reaction, since 3-butenyl- and 4-pentenyltin compounds were found not to react with *n*-butyllithium in ether. The action of phenyllithium on triphenylvinyllead gave vinyllithium and tetraphenyllead; on the other hand, phenyllithium added across the C=C bond of triphenylvinylgermane.

In previous papers of this series practical laboratory directions were given for the preparation of vinyllithium allyllithium and methallyllithium by the exchange reactions occurring between vinyl-, allyl- and methallyltin compounds and phenyl- and *n*-butyllithium

$$R_4Sn + 4\ C_6H_5Li \longrightarrow (C_6H_5)_4Sn + 4\ RLi\ (R = CH_2{=}CH\text{–}\ \text{and}\ CH_2{=}CHCH_2\text{–})$$

Transmetalations of this type are of value, since they make available organolithium reagents, the preparation of which either is difficult or impossible by the more conventional procedures. In order to make the most efficient use possible of the transmetalation reaction for this purpose, we have studied in greater detail the factors which affect this reaction. The results of some of our studies are discussed below.

Equilibria in Transmetalation Reactions.—It has been reported[2] that some transmetalation reactions represent equilibrium situations. This raised the question as to whether or not the exchange reaction between vinyltin and allyltin compounds and organolithium compounds might also involve an equilibrium reaction. As was shown in Part I,[3] the reaction

$$(CH_2{=}CH)_4Sn + 4\ C_6H_5Li \longrightarrow (C_6H_5)_4Sn + 4\ CH_2{=}CHLi$$

went to completion for all practical purposes, tetraphenyltin being formed in virtually quantitative yield. The insolubility of tetraphenyltin in ether[4] might possibly have been the factor which made this reaction proceed to near completion, and the possibility existed that in a system where both products were soluble the equilibrium (if one existed) might be such as to make the transmetalation of no preparative value. For this reason the solubility factor was examined. In the systems

$$n\text{-}Bu_3SnCH{=}CH_2 + C_6H_5Li \xrightarrow{Et_2O} n\text{-}Bu_3SnC_6H_5 + CH_2{=}CHLi \quad (a)$$

$$n\text{-}Bu_3SnCH{=}CH_2 + n\text{-}BuLi \xrightarrow{Et_2O} n\text{-}Bu_4Sn + CH_2{=}CHLi \quad (b)$$

all components are soluble in the ether medium. Tri-*n*-butylvinyltin and phenyllithium were allowed to react in ether solution during 2 hr.; the mixture then was treated with acetone and hydrolyzed. The products isolated included dimethylvinylcarbinol (63%), tri-*n*-butylphenyltin (73%) and tri-*n*-butylvinyltin (12%). Similarly, reaction b, in which the vinyllithium produced was characterized by its reaction with triethylbromosilane, gave tetra-*n*-butyltin in 87% yield, as well as triethylvinylsilane in 65% yield. Similar observations were made when the reaction of allyltri-*n*-butyltin with phenyllithium was studied; tri-*n*-butylphenyltin was isolated in 78% yield. Obviously the insolubility of tetraphenyltin is not the most important factor, since good conversions are obtained even when the organotin products are soluble in the reaction medium. The presence of the starting material, tri-*n*-butylvinyltin, has been noted among the products of the reaction between phenyllithium and tri-*n*-butylvinyltin. In order to ascertain whether this represents an equilibrium situation, the reverse reaction, that between vinyllithium and tri-*n*-butylphenyltin, was examined. In addition to tri-*n*-butylphenyltin (75%), a liquid representing *ca.* 5% yield of crude tri-*n*-butylvinyltin was obtained. This material was purified and identified positively as tri-*n*-butylvinyltin. To substantiate further this evidence, the forward reaction was carried out again, using the same reaction conditions. In this case tri-*n*-butylphenyltin and tri-*n*-butylvinyltin were isolated in yields of 76% and 10%, respectively.

An indirect, though substantial, piece of evidence in favor of an equilibrium situation was observed

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[1] Part III, D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **26**, 4797 (1961).

[2] R. G. Jones and H. Gilman, *Chem. Revs.*, **54**, 863 (1954).

[3] D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **83**, 3583 (1961).

[4] W. Strohmeier and K. Miltenberger, *Chem. Ber.*, **91**, 1357 (1958).

when the reaction of vinyllithium with triphenylvinyltin was examined. A 62% conversion of triphenylvinyltin to tetraphenyltin resulted when this reaction was carried out. Addition of phenyllithium to the liquid residue remaining after filtration, hydrolysis and distillation of the solvent converted another 36% of the tin compound to tetraphenyltin. The formation of these products can be explained by assuming the equilibria

$$\mathrm{CH_2{=}CHLi + (C_6H_5)_3SnCH{=}CH_2 \rightleftarrows (C_6H_5)_2Sn(CH{=}CH_2)_2 + C_6H_5Li}$$

$$\mathrm{CH_2{=}CHLi + (C_6H_5)_2Sn(CH{=}CH_2)_2 \rightleftarrows C_6H_5Sn(CH{=}CH_2)_3 + C_6H_5Li}$$

$$\mathrm{CH_2{=}CHLi + C_6H_5Sn(CH{=}CH_2)_3 \rightleftarrows (CH_2{=}CH)_4Sn + C_6H_5Li}$$

The position of the equilibrium in each case would be expected to favor greatly the reactants, but any phenyllithium formed could react with triphenylvinyltin to form the ether-insoluble tetraphenyltin. Thus the equilibria would be displaced continually to the right. This then theoretically is a disproportionation of triphenylvinyltin, catalyzed by vinyllithium

$$\mathrm{4\ (C_6H_5)_3SnCH{=}CH_2 \xrightarrow{CH_2{=}CHLi} 3\ (C_6H_5)_4Sn + (CH_2{=}CH)_4Sn}$$

The yield of tetraphenyltin isolated from the initial reaction, based on this equation, is 83%. Actually, a situation seems to obtain in which disproportionation is not complete, since tetravinyltin could not be isolated. The infrared spectrum of the liquid organotin product resembles that of phenylvinyltin compounds, and the equation

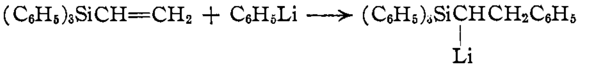
$$\mathrm{3\ (C_6H_5)_3SnCH{=}CH_2 \xrightarrow{CH_2{=}CHLi} 2\ (C_6H_5)_4Sn + C_6H_5Sn(CH{=}CH_2)_3}$$

is more in line with the experimental results. Based on this equation, the yield of tetraphenyltin then is 92.5%. It is of interest to note that when triphenylvinyltin and vinyllithium were allowed to react in 2:1 molar ratio, a 60% conversion to tetraphenyltin was realized. It would be of interest to investigate the effect of increasing the triphenylvinyltin/vinyllithium ratio still further and to see if truly catalytic quantities of vinyllithium are sufficient to cause this disproportionation reaction to occur.

Since the vinyllithium solutions used in the above experiments were prepared by the phenyllithium–triphenylvinyltin exchange reaction in ether, they were saturated with respect to tetraphenyltin. For this reason another vinyllithium–triphenylvinyltin reaction was carried out using a vinyllithium solution prepared by dissolving the solid reagent (*cf.* Part I[3]) in ether, thus insuring the absence of tetraphenyltin. In this case a 57% conversion to tetraphenyltin was observed when the two solutions were mixed.

Effect of the Nature of the Olefinic Group.—It was of theoretical and of practical interest to determine the scope of this reaction as a preparative method for olefinic organolithium reagents. The transmetalation reaction also is applicable to the synthesis of substituted vinylic and allylic lithium compounds (for instance, methallyllithium,[1] 1-propenyl-, isopropenyl- and β-styryllithium[5]). However, this procedure is not applicable when the carbon–carbon double bond is separated from the tin atom by more than one methylene group. Thus 3-butenyltri-*n*-butyltin and di-*n*-butyldi-4-pentenyltin did not undergo transmetalation with *n*-butyllithium in ether. A discussion of this observation is premature in absence of knowledge concerning the mechanism of the transmetalation reaction. In soluble systems, in which the added complication of the insolubility of one of the products is not present, the tendency is for that organolithium compound to predominate which contains the more polarizable potential anion. Thus *n*-butyllithium will react with phenyl- and vinyltin compounds to form phenyl- and vinyllithium in good yield. Allyllithium, which also is formed readily in reactions of this type, apparently represents a different type of system in which stabilization is conferred by rapid intra- or intermolecular lithium exchange.[6] Neither type of stabilization should be available in 3-butenyl or in 4-pentenyllithium. Furthermore, the starting organolithium compound and the lithium compound formed in the exchange reaction (when it occurs) may differ in their degree of association in ether solution, and this also may be an important factor. However, since no reaction at all was found to occur between *n*-butyllithium and 3-butenyl- and 4-pentenyltin compounds, not only the relative stability of the lithium compounds in these systems but also the transition state of the reaction must be considered. It is hoped that studies presently in progress will shed some light on this question.

Effect of the Group IV Metal Atom.—It was known through the work of Cason and Brooks[7] that triphenylvinylsilane undergoes an addition reaction with phenyllithium



$$\mathrm{(C_6H_5)_3SiCH{=}CH_2 + C_6H_5Li \longrightarrow (C_6H_5)_3Si\underset{\displaystyle Li}{\underset{|}{C}}HCH_2C_6H_5}$$

whereas the present study demonstrated the exchange reaction occurring between triphenylvinyl tin and phenyllithium. It was of interest to this study to determine which of these two possible reactions would be observed with the analogous germanium and lead compounds. The results of these experiments—transmetalation between phenyllithium and triphenylvinyllead and nucleophilic addition of phenyllithium to triphenylvinylgermane—were in line with the close similarities of the organic chemistry of tin and lead in contrast to that of silicon and germanium. It should be emphasized that in this case this is a difference in degree, not in kind. Organosilicon compounds of suitable structure (*e.g.*, $(C_6H_5)_3SiCH{=}CHC_6H_5$[8]) will undergo an exchange reaction with phenyllithium, and some preliminary evidence was obtained in this

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(8) H. Gilman, T. C. Wu and D. Wittenberg, *J. Org. Chem.*, **25**, 596 (1960).

study that addition of suitable organolithium reagents to vinyltin compounds can occur (*cf.* the reactions of vinyllithium with allyltin compounds in the Experimental Section). This then, in the absence of more detailed knowledge, seems to be a problem of relative rates of the two possible competing reactions.

Effect of the Solvent.—It has been pointed out[1,3] that diethyl ether is the solvent of choice in the transmetalation reactions which have been reported in this study. Complete exchange of all four groups in tetravinyltin and tetraallyltin with *n*-butyllithium or phenyllithium is possible in ether. In pentane, however, this is not the case, no exchange being detectable when tri-*n*-butylvinyltin was treated with one equivalent of *n*-butyllithium in this solvent. Only partial exchange occurred when tetravinyltin or tetraallyltin was treated with four equivalents of *n*-butyllithium in pentane, but the fact that both vinyllithium and allyllithium are relatively insoluble in pentane and can be isolated in the solid form from these reactions makes the use of this solvent of value in certain cases.[1,3]

In summary, enough appears to be known at the present writing about the factors which influence the transmetalation reaction so that it can be used as a versatile preparative method for novel organolithium reagents. However, it is readily apparent that further studies are required before our understanding of this reaction can be considered satisfactory. Studies are in progress which should yield information concerning the stereochemistry and mechanism of the transmetalation reaction.

Experimental[9]

Preparation of Starting Materials. Preparation of 3-Butenyl-tri-*n*-butyltin.—To 0.168 mole of $CH_2{=}CHCH_2CH_2MgBr$ in tetrahydrofuran, prepared by addition of 23 g. of 4-bromo-1-butene[10] to 4.0 g. of magnesium turnings, was added 37 g. (0.115 mole) of tri-*n*-butyltin chloride (Metal & Thermit Corp., redistilled before use). The resulting mixture was refluxed overnight and hydrolyzed with saturated ammonium chloride solution. The organic layer was separated from the inorganic salts, and the latter were washed with ether. The combined organic phase was distilled to give 32 g. (81%) of 3-butenyltri-*n*-butyltin, $(C_4H_9)_3SnCH_2CH_2CH{=}CH_2$, b.p. 91–93° (0.35 mm.), $n^{25}\mathrm{D}$ 1.4792, d^{25}_4 1.062, $\nu_{C=C}$ at 1640 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{34}Sn$: C, 55.68; H, 9.93; MRD, 92.05. Found: C, 55.87; H, 9.81; MRD, 92.19.

Preparation of Di-*n*-butyl-di-4-pentenyltin.—To the Grignard reagent prepared from 25 g. (0.168 mole) of 5-bromo-1-pentene (Peninsular Chem. Research, Inc.) and 4.0 g. (0.168 g. atom) of magnesium turnings in tetrahydrofuran was added 16.7 g. (0.055 mole) of di-*n*-butyltin dichloride (Metal & Thermit Corp.). The mixture was refluxed overnight. The work-up procedure described above gave 13.5 g. (66%) of di-*n*-butyldi-4-pentenyltin, $(C_4H_9)_2Sn(CH_2CH_2CH_2CH{=}CH_2)_2$, b.p. 117–118° (0.5 mm.), $n^{25}\mathrm{D}$ 1.4842, d^{25}_4 1.050, $\nu_{C=C}$ at 1641 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{36}Sn$: C, 58.24; H, 9.78; MRD, 100.87. Found: C, 58.4; H, 9.8; MRD, 101.17.

Preparation of Triphenylvinyllead.—Triphenyllead bromide[11] was converted to triphenylvinyllead by treatment with vinylmagnesium chloride, following the procedure of Henry and Noltes.[12] The crude oil obtained could be crystallized from hexane without prior distillation, so that the yield was greatly improved: 52% *vs.* 19%[12] and 23%.[13] The material showed a m.p. of 33–34.5° (lit.[12] m.p. 35–36°).

Reaction of Phenyl- and *n*-Butyllithium with Allyltri-*n*-butyltin and Tri-*n*-butylvinyltin.—(1) A solution of 1.16 *M* phenyllithium in ether (310 ml., 0.36 mole) was added to 114 g. (0.36 mole) of tri-*n*-butylvinyltin in a one-liter, three-necked flask equipped with a mechanical stirrer, an addition funnel and a water condenser topped with a nitrogen inlet tube. After the homogeneous solution had been stirred at room temperature for one hr., 17.5 g. (0.3 mole) of acetone in an equal volume of ether was added. Following a two hr. reflux period, the mixture was hydrolyzed with distilled water, and the organic layer was separated, dried and distilled. A 63% yield (16.2 g.) of dimethylvinylcarbinol was obtained at 93–96°, $n^{25}\mathrm{D}$ 1.4161 (lit.[14] b.p. 96°, $n^{25}\mathrm{D}$ 1.4153). Distillation of the residue gave a 12% recovery of crude tri-*n*-butylvinyltin and a 73% yield (93 g.) of tri-*n*-butylphenyltin, b.p. 116–118° (0.15 mm.), $n^{20}\mathrm{D}$ 1.5152 (lit.[15] b.p. 139° (0.6 mm.), $n^{20}\mathrm{D}$ 1.5155).

(2) A similar procedure was used in the reaction of *n*-butyllithium in ether with tri-*n*-butylvinyltin on a 0.065 mole scale. The organolithium compound present was characterized using triethylbromosilane. Fractional distillation gave 5.5 g. (65%) of triethylvinylsilane, b.p. 43–44° (17 mm.), $n^{20}\mathrm{D}$ 1.4333 (lit.[16] b.p. 140° (740 mm.), $n^{20}\mathrm{D}$ 1.4340). Distillation of the organotin residue produced 19.5 g. (87%) of tetra-*n*-butyltin, b.p. 82–85° (0.1 mm.), $n^{20}\mathrm{D}$ 1.4715 (lit.[17] b.p. 145° (10 mm.), $n^{20}\mathrm{D}$ 1.4730). The infrared spectrum of this material showed the absence of the C=C bond.

(3) Similar reactions between allyltri-*n*-butyltin and phenyl- and *n*-butyllithium, both on a 0.098 mole scale, were carried out. In both cases the organolithium reagent was characterized by means of its reaction with 4-methyl-2-pentanone; 4,6-dimethylhept-1-en-4-ol, b.p. 69–71° (19 mm.), $n^{20}\mathrm{D}$ 1.4400 (lit.[18] b.p. 68–69° (20 mm.), $n^{20}\mathrm{D}$ 1.4402), was isolated in yields of 70 and 73%, respectively. The organotin products, tri-*n*-butylphenyltin and tetra-*n*-butyltin, were isolated in yields of 78% and 88%.

Reaction of Vinyllithium with Tri-*n*-butylphenyltin, and the Reverse Reaction.—A solution of *ca.* 0.055 mole of vinyllithium was prepared in ether from 0.055 mole of phenyllithium in 52 ml. of ether and 20.7 g. (0.055 mole) of triphenylvinyltin in *ca.* 100 ml. of ether. The tetraphenyltin (95%) was filtered off and washed twice with ether. To the clear vinyllithium solution was added 20 g. (0.055 mole) of tri-*n*-butylphenyltin. The mixture was stirred at room temperature, under nitrogen, for 40 hr. and then hydrolyzed with distilled water. The organic layer was separated and distilled to give 0.8 g. of liquid at 75–90° (0.35 mm.), representing a maximum yield of 5% of tri-*n*-butylvinyltin. From the residue 15 g. (75%) of tri-*n*-butylphenyltin was obtained at 121–124° (0.35 mm.), $n^{20}\mathrm{D}$ 1.5163. The first fraction was purified by passing it twice through an alumina-filled chromatography column, using pentane as the eluant. A liquid was obtained with $n^{25}\mathrm{D}$ 1.4783 (reported for tri-*n*-butylvinyltin: $n^{25}\mathrm{D}$ 1.4761[19]). Its infrared spectrum was identical with the spectrum of an authentic sample of tri-*n*-butylvinyltin except for a small band at 725 cm.$^{-1}$, due to a small amount of tri-*n*-butylphenyltin impurity. On passing the liquid once again through the alumina column, a liquid was obtained with $n^{25}\mathrm{D}$ 1.4770 and an infrared spectrum whose 725 cm.$^{-1}$ band had all but disappeared.

The reaction of phenyllithium with tri-*n*-butylvinyltin was carried out on the same scale under the same conditions. A liquid weighing 1.7 g. (representing a maximum yield of 9.7% of tri-*n*-butylvinyltin) was obtained at 72–87° (0.25 mm.). In addition, 15.2 g. (76%) of tri-*n*-butylphenyl

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(9) All reactions involving use of organolithium reagents were carried out under an atmosphere of prepurified nitrogen. Analyses were performed by Dr. S. M. Nagy, M.I.T.; the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.; Dr. Carol Fitz, Needham Heights, Mass. Melting points were determined using a Mel-Temp apparatus and are uncorrected.

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tin, n^{20}D 1.5157, was obtained. The crude tri-*n*-butylvinyltin was purified and characterized as described above.

Reaction of Vinyllithium with Triphenylvinyltin.—A solution of 0.025 mole of vinyllithium in about 300 ml. of ether was prepared by the usual procedure from triphenylvinyltin and phenyllithium. To this clear solution of vinyllithium was added 9.4 g. (0.025 mole) of triphenylvinyltin dissolved in a small amount of ether. A white solid precipitated immediately. The mixture was stirred at room temperature under nitrogen for 18 hr. and then hydrolyzed. The precipitate was filtered and dried; 6.4 g., m.p. 224–227°. Upon concentrating the organic phase of the filtrate, an additional 0.2 g. was obtained. The total conversion was 62%, assuming the material to be tetraphenyltin. A sample of this material was recrystallized from dioxane to give a solid, m.p. 227–228°, which showed no depression of melting point when mixed with an authentic sample of tetraphenyltin. The concentrated filtrate was dried and distilled under reduced pressure to remove solvent. The oily residue was dissolved in ether, and 35 ml. (0.04 mole) of a phenyllithium solution in ether was added. A precipitate appeared immediately. The mixture was stirred overnight, and the precipitate then was filtered and dried; 3.8 g. (36% conversion) of tetraphenyltin, m.p. 221–224°, was isolated. Recrystallization gave pure tetraphenyltin, identified by mixed m.p.

The reaction was repeated using 0.05 mole of vinyllithium and 0.1 mole of triphenylvinyltin. Essentially the same results were obtained: an original 60% conversion to tetraphenyltin, with an additional 25% conversion obtained upon addition of phenyllithium to the residue dissolved in ether. Another reaction, in which the vinyllithium solution (*ca.* 0.025 mole), prepared from solid vinyllithium and hence free of tetraphenyltin, was added to 0.025 mole of triphenylvinyltin, gave a 57% conversion to tetraphenyltin. In this reaction the concentrated filtrate was dried and distilled to give 0.6 g. of liquid at 70–90° (0.4 mm.) and another 0.7 g. at *ca.* 140–175° (0.4 mm.). One g. of viscous oil remained as residue. The infrared spectra of all three fractions were essentially the same as the published spectra of phenylvinyltin compounds.[12]

Reaction of *n*-Butyllithium with 3-Butenyltri-*n*-butyltin.—A mixture of 22.5 g. (0.065 mole) of 3-butenyltri-*n*-butyltin and 53 ml. of a solution of *n*-butyllithium in ether (0.068 mole) was stirred under nitrogen for 1.5 hr. Triethylbromosilane (11.7 g., 0.06 mole) was added, and the resulting mixture was refluxed for 3 hr. The usual work-up gave 7.5 g. (73%) of *n*-butyltriethylsilane, b.p. 67–68° (8 mm.), n^{25}D 1.4322 (lit.[20] b.p. 190–191°, n^{25}D 1.4323). The infrared spectrum of this product showed the absence of an olefinic double bond. From the organotin residue 19.5 g. (87% recovery) of 3-butenyl-tri-*n*-butyltin, b.p. 93–95° (0.3 mm.), n^{25}D 1.4780, was obtained.

Reaction of *n*-Butyllithium with Di-*n*-butyldi-4-pentenyltin.—Using the procedure described above, the reaction of 11.7 g. (0.06 mole) of triethylbromosilane with a mixture of 12.3 g. (0.033 mole) of di-*n*-butyldi-4-pentenyltin and 0.07 mole of *n*-butyllithium in ether produced 7.5 g. (73%) of *n*-butyltriethylsilane, n^{25}D 1.4324, and 8.5 g. (70% recovery) of the starting tin compound, b.p. 116–118° (0.45 mm.), n^{25}D 1.4841. The infrared spectrum of the product silane showed no absorption in the C=C bond region.

Reaction of Phenyllithium with Triphenylvinylgermane.—A 1.13 *N* solution of phenyllithium (40 ml., 0.045 mole) was added to 1.2 g. (0.0036 mole) of triphenylvinylgermane dissolved in ether. The mixture was stirred overnight and then added slowly to a 10% hydrochloric acid solution. The organic layer was separated and the ether removed under reduced pressure. The residue consisted of a mixture of a solid and an oil. Ethanol was added; the oil went into solution, and the ethanol-insoluble solid was filtered to give 1.0 g. (68%) of crude product, m.p. 139–142°. On concentration of the ethanol solution an additional 0.05 g. of crude product was obtained. The crude material was purified by elution from an alumina-filled chromatography column with pentane. Pure material weighing 0.6 g., m.p. 146–148° (reported for β-phenylethyltriphenylgermane: m.p. 147–149°[21]), as well as 0.28 g. of less pure solid, was obtained. The total yield was 60%.

An authentic sample of β-phenylethyltriphenylgermane, prepared in 82% yield by the reaction of β-phenylethylmagnesium bromide in tetrahydrofuran with triphenylgermanium bromide, m.p. 147–149°, showed no depression of m.p. when mixed with a sample from the phenyllithium-triphenylvinylgermane reaction. Also, the infrared spectra of the two solids were identical.

Reaction of Phenyllithium with Triphenylvinyllead.—A solution of 0.018 mole of phenyllithium in ether was added to 8.35 g. (0.018 mole) of triphenylvinyllead dissolved in ether. A precipitate appeared immediately. After the mixture had been stirred under nitrogen for 45 min., 5.0 g. (0.017 mole) of triphenylchlorosilane was added. The resulting mixture was refluxed for 4 hr., hydrolyzed and the solid filtered. Crude tetraphenyllead, m.p. 215–222°, 8.4 g. (91%), thus was obtained. The organic layer of the filtrate was separated, the solvent removed at reduced pressure and the residue crystallized from an ethanol–water mixture to give 4.2 g. (86%) of crude triphenylvinylsilane, m.p. 60–64°. Several recrystallizations from ethanol and hexane were required to give 3.0 g. (60%) of pure product, m.p. 69–70° (lit.[7] m.p. 67–68°). The crude tetraphenyllead was recrystallized from dioxane to give 7.2 g. (78%) of pure material, m.p. 226–227.5°, which showed no depression of its m.p. when mixed with an authentic sample of tetraphenyllead. The spectrum of this product was identical with that of tetraphenyllead.

Reaction of Vinyllithium with Diallyldi-*n*-butyltin.—A solution of 0.1 mole of vinyllithium in ether was prepared by the usual method from triphenylvinyltin. To this clear, filtered solution was added 15.7 g. (0.05 mole) of diallyldi-*n*-butyltin. The resulting mixture was stirred for one hr., and then 9.0 g. (0.09 mole) of 4-methyl-2-pentanone was added. After a 40 min. reflux period, hydrolysis was effected with distilled water and the organic phase separated, dried and distilled. A 55% yield of 4,6-dimethylhept-1-en-4-ol (7.0 g.) was obtained at 69–72° (19 mm.), n^{20}D 1.4394. The organotin residue consisted of 5.6 g. of a mixture of liquids distilling over the range 58–110° (0.65 mm.), the temperature range at which compounds of the type $Bu_2Sn(CH_2CH{=}CH_2)_n(CH{=}CH_2)_{2\ n}$ would be expected to distil. In addition, 9.3 g. of an orange oil remained.

Reaction of Allyllithium with Di-*n*-butyldivinyltin.—A solution of 0.1 mole of allyllithium was prepared in ether from allyltriphenyltin. The solution was filtered to remove tetraphenyltin (94%), and 14.3 g. (0.05 mole) of di-*n*-butyldivinyltin was added and the mixture stirred for one hr. Subsequent to the addition of 9.0 g. (0.09 mole) of 4-methyl-2-pentanone, the procedure described in the preceding experiment was followed. Distillation gave, after a large forecut (b.p. 58–68° at 19 mm.), 5.5 g. (43%) of 4,6-dimethylhept-1-en-4-ol at 68–71° (19 mm.), n^{20}D 1.4401. The organotin residue consisted of a mixture similar to that described above.

Reaction of Vinyllithium with Allyltrimethyltin.—A solution of 0.06 mole of vinyllithium in ether was prepared from triphenylvinyltin and filtered. To this solution was added 12.3 g. (0.06 mole) of allyltrimethyltin, and the resulting mixture was refluxed for 3.5 hr. After hydrolysis and separation of the organic layer, the organotin mixture was distilled at 0.4 mm., and 1.5 g. of liquid (a mixture of allyltrimethyltin and trimethylvinyltin) was collected in a receiver cooled to −78°. The distillation residue was distilled without using a column, and the following cuts were taken: 58–65° (0.4 mm.), 1.7 g., mol. wt. (Rast) 266; 160–175° (0.5 mm.), 1.2 g., mol. wt. 502; 200–210° (0.5 mm.), 1.2 g., mol. wt. 561. The infrared spectra of all three fractions showed a band at 1640 cm.$^{-1}$, attributable to the stretching frequency of an olefinic double bond further removed from the tin atom than the allylic position.

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