Diphenyl-bis-[2′-(triphenylstannyl)]-germane.—Upon mixing 2.81 g. (0.01 mole) of diphenyldivinylgermane and 7.0 g. (0.02 mole) of triphenyltin hydride under nitrogen an exothermal reaction occurred. The reaction mixture became viscous and after two hours had become a solid glass. After heating at 70° for 1 hour, the solid was twice recrystallized from ligroin; white needles with m.p. 139–142°, yield 6.5 g. (66%).

Anal. Calcd. for $C_{52}H_{48}GeSn_2$: C, 63.53; H, 4.92; Ge + Sn, 31.54. Found: C, 63.87; H, 5.01; Ge + Sn, 31.66.

Reaction of Triphenyltin Hydride with Diphenyldivinyltin.—When a mixture of 6.0 g. (0.018 mole) of diphenyldivinyltin and 12.6 g. (0.036 mole) of triphenyltin hydride was heated under nitrogen at 90°, the reaction mixture gradually solidified. Gas was evolved and metallic tin separated. The solid was recrystallized from benzene, acetone and dimethylformamide, respectively. A solid with m.p. 202–203° identified as 1,2-bis-triphenylstannyl ethane was obtained. A mixed m.p. with an authentic sample was not depressed and infrared spectra were superimposable; yield 6.8 g. (52%).

Anal. Calcd. for $C_{38}H_{34}Sn_2$: Sn, 32.61; mol. wt., 728. Found: Sn, 32.73; mol. wt. (Rast), 710.

Reaction of Diphenyltin Dihydride with Triphenylvinylsilane.—A mixture of 3.43 g. (0.012 mole) of triphenylvinylsilane and 1.65 g. (0.006 mole) of diphenyltin dihydride was heated in an atmosphere of nitrogen at 70° for 5 hr. and at 100° for 12 hr. After two hours at the latter temperature evolution of gas set in and metallic tin began to separate. The gas was collected by condensation and shown to be benzene. The reaction mixture was taken up in light petroleum and the insoluble part was filtered (1.7 g. which melted at *ca.* 180°). Solution in hot dimethylformamide and filtration yielded 170 mg. (24%) of metallic tin. Water was added dropwise to the dimethylformamide solution and the precipitated solid, after filtration, recrystallized from benzene–petroleum ether yielding 0.92 g. (24%) of 1-triphenylstannyl-2-triphenylsilylethane with m.p. 201–204°. A mixed m.p. with an authentic sample showed no depression and the infrared spectra were superimposable.

Reaction of Diphenyltin Dihydride with Triphenylvinylgermane.—A mixture of 7.60 g. (0.023 mole) of triphenylgermane and 3.03 g. (0.011 mole) of diphenyltin dihydride was heated under nitrogen at 70° for 5 hr. and at 100° for 12 hr. Gas (identified as benzene) was evolved and metallic tin separated. From the semi-solid reaction product there was isolated 0.26 g. (20%) of metallic tin and 2.7 g. of a solid with m.p. *ca.* 190°. After several recrystallizations from ligroin and dimethylformamide the m.p. was raised to 208–210°. The solid was identified as 1-triphenylstannyl-2-triphenylgermylethane. A mixed m.p. with an authentic sample showed no depression and the infrared spectra were superimposable; yield 1.60 g. (21%).

Reaction of Diphenyltin Dihydride with Triphenylvinyltin.—Gas evolution (benzene) and formation of metallic tin was observed upon heating a mixture of 10.60 g. (0.028 mole) of triphenylvinyltin and 3.85 g. (0.014 mole) of diphenyltin dihydride under nitrogen at 70° for 5 hr. and at 100° for 12 hr. From the semi-solid reaction mixture 2.75 g. (27%) of 1,2-bis-triphenylstannylethane with m.p. 201–204° was isolated. A mixed m.p. with an authentic sample showed no depression and the infrared spectra were superimposable.

Acknowledgments.—The authors are indebted: to Prof. Dr. G. J. M. van der Kerk, Director of this Institute, for encouragement; to Dr. E. S. Hedges, Director of the International Tin Research Council, for his supporting interest; to Miss F. I. van den Hoek Ostende for recording the spectra and to Mr. H. A. Budding for able experimental assistance.

[CONTRIBUTION FROM THE INSTITUTE FOR ORGANIC CHEMISTRY T.N.O., UTRECHT, HOLLAND]

Synthesis of Some New Six-membered Organometallic Ring Systems

BY MALCOLM C. HENRY[1] AND JAN G. NOLTES

RECEIVED APRIL 16, 1959

New organometallic aliphatic heterocycles, *viz.*, the 1-stanna-4-silacyclohexane, the 1-stanna-4-germanacyclohexane and the 1,4-distannacyclohexane ring systems have been synthesized by means of addition reactions involving diphenyltin dihydride and the appropriate unsaturated reactants. Complexes of these compounds with several cyclic solvents were isolated.

Cyclic organotin compounds were described, in 1917, by Grüttner, *et al.*,[2] who prepared cyclopentamethylenedimethyltin and cyclopentamethylenediethyltin by the reaction of pentamethylenedimagnesium bromide with the appropriate dialkyltin dihalide. This method has been applied to the synthesis of cyclopentamethylene derivatives of the other IVth group elements silicon,[3] germanium[4a] and lead.[4b] Although the number of known organotin compounds recently has considerably increased, only one new heterocyclic system containing tin in the ring has been reported since that time. Kuivila, *et al.*,[5] prepared heterocycles in the dibenzocyclo heptadiene series containing tetra- and bivalent tin in the seven-membered ring. This method of synthesis involved the reaction of *o,o′*-dilithiodibenzyl with diphenyltin dichloride or stannic chloride.

In connection with a program involving the synthesis of organometallic compounds containing one of the IVth group elements silicon, germanium or lead in addition to tin,[6] reactions of diphenyltin dihydride with diphenyldivinyl derivatives of silicon, germanium and lead were studied. Since triphenyltin hydride had been found to add to these compounds in good yield,[6] such reactions might be expected to yield organometallic polymers of type II.

Reaction of diphenyltin dihydride with diphenyldivinylsilane afforded a crystalline product (m.p. 134–135°) with molecular weight (Rast determination) and analytical data calculated for the mono-addition product I (M = Si). Examination of the infrared spectrum revealed the presence of C_6H_5Sn and C_6H_5Si in a 1:1 ratio; there appeared to be no absorption bands which could be attributed to Sn–H

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[1] U. S. Army Research and Engineering Command, Natick, Mass.; work done in Utrecht under the auspices of a Secretary of the Army Research Fellowship.

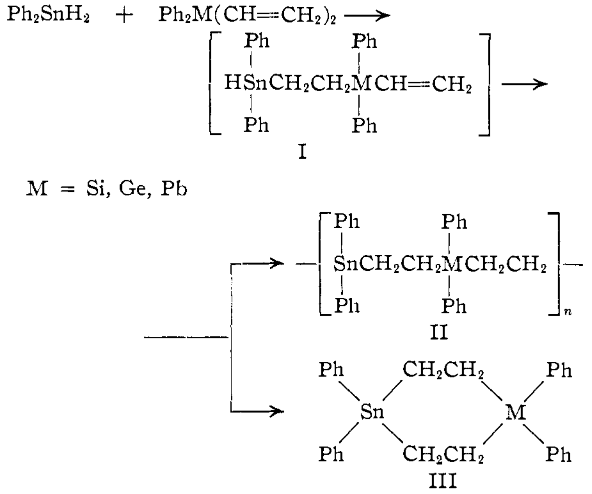
[2] G. Grüttner, E. Krause and M. Wiernik, *Ber.*, **50**, 1549 (1917).

[3] A. Bygden, *ibid.*, **48**, 1236 (1915); G. Grüttner and M. Wiernik, *ibid.*, **48**, 1473 (1915).

[4] (a) R. Schwarz and W. Reinhardt, *ibid.*, **65**, 1743 (1932); (b) G. Grüttner and E. Krause, *ibid.*, **49**, 2666 (1916).

[5] H. G. Kuivila and O. F. Beumel, Jr., THIS JOURNAL, **80**, 3250 (1958).

[6] M. C. Henry and J. G. Noltes, *ibid.*, **82**, 558 (1960).



M = Si, Ge, Pb

or to $SiCH{=}CH_2$.[7] On the basis of the foregoing evidence it is apparent that the product is the cyclic monomer III (M = Si) and as such represents the first example of a 1-stanna-4-silacyclohexane derivative. In addition a small quantity of insoluble, unmeltable material which has not yet been examined in any detail (presumably of structure II) was isolated. Apparently ring closure of the intermediately formed I is the favored reaction.

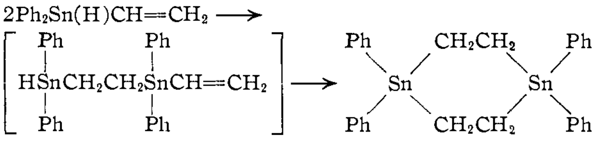
Similarly, reaction of diphenyltin dihydride with diphenyldivinylgermane yielded a crystalline product (m.p. 124–125°). Infrared spectroscopy revealed the presence of C_6H_5Sn and C_6H_5Ge in a 1:1 ratio and the absence of any Sn–H and $Ge{-}CH{=}CH_2$ absorption.[7] This, together with molecular weight and analytical data, identified the product as the cyclic monomer III (M = Ge), a 1-stanna-4-germanacyclohexane derivative. Also here insoluble, unmeltable material was isolated as well.

It appeared that the ring compounds III (M = Si or Ge) when recrystallized from cyclic solvents such as benzene, toluene, pyridine or dioxane formed crystalline complexes in a strict 1:1 ratio. These complexes are quite weak as appears from the fact that they readily decompose on heating. They all show the m.p. of III (M = Si or Ge) which compounds are also obtained upon attempted recrystallization of the complexes from, *e.g.*, ethanol, as appears from the analytical results. Complex formation of this kind has not been previously observed with tetrasubstituted derivatives of silicon, germanium or tin.

Reaction of diphenyltin dihydride with diphenyldivinyllead resulted in formation of metallic lead only (compare ref. 6).

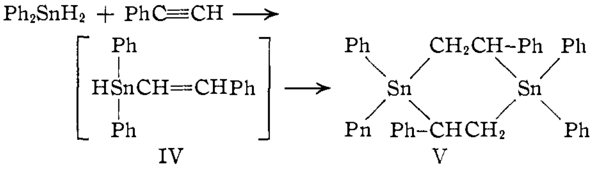
Attempted synthesis of the 1,4-distannacyclohexane system (III, M = Sn) by reaction of diphenyltin dihydride with diphenyldivinyltin proved unsuccessful. Only low-melting products which decomposed on heating with evolution of gas (presumably of structure I, M = Sn) and insoluble, unmeltable material were obtained.

Another possible method of synthesis involves the addition reaction of two molecules of diphenylvinyltin hydride followed by cyclization



The 1,4-disilacyclohexane[8] and the 1,6-disilacyclooctane[9] ring systems have recently been synthesized in this way.

Triphenyltin hydride has been reported to add to phenylacetylene in a 1:1 and 2:1 ratio.[10] Instead of using diphenylvinyltin hydride as the starting material, equimolecular amounts of diphenyltin dihydride and phenylacetylene were allowed to react, the intermediately formed diphenyl-β-styryltin hydride IV not being isolated



The reaction product was a solid which melted at *ca.* 70–90°. Fractional crystallization from 1-butanol afforded fractions melting at 70–72° and at 144–145°, respectively. Comparison of their infrared spectra revealed only very slight differences. In each spectrum there was no evidence for the presence of Sn–H or $SnCH{=}CHPh$ (band at 985 cm.$^{-1}$ [11]). Spectral evidence, together with analytical and molecular weight data, led to the identification of both reaction products as the cyclic dimer of IV, which apparently exists in isomeric forms.

Experimental[12]

Starting Materials.—Diphenyltin dihydride,[13] diphenyldivinylsilane,[14] diphenyldivinylgermane,[7] diphenyldivinyltin[15] and diphenyldivinyllead[7] were obtained by published procedures.

1,1',4,4'-Tetraphenyl-1-stanna-4-silacyclohexane.—A mixture of 5.50 g. (0.02 mole) of diphenyltin dihydride and 4.72 g. (0.02 mole) of diphenyldivinylsilane was heated for 4 hr. at 65° and for 9 hr. at 80°. The solid reaction product was filtered from the adhering oil and recrystallized from dimethylformamide to yield 2.35 g. (23%) of material with m.p. 132–134°. Recrystallization from ethanol raised the m.p. to 134–135°. The infrared spectrum revealed the presence of C_6H_5–Si (band at 1100 cm.$^{-1}$), C_6H_5–Sn (band at 1065 cm.$^{-1}$) and of CH_2 (doublet at 2860 cm.$^{-1}$), but there was no evidence for Sn–H (band at 1825 cm.$^{-1}$), or $SiCH{=}CH_2$ (band at 960 cm.$^{-1}$).

Anal. Calcd. for $C_{28}H_{28}SiSn$: C, 65.77; H, 5.52; Si + Sn, 28.70; mol. wt., 511. Found: C, 65.88; H, 5.77; Si + Sn, 28.86; mol. wt. (Rast), 498.

Complex with Benzene: *Anal.* Calcd. for $C_{28}H_{28}SiSn \cdot C_6H_6$: Si + Sn, 24.89. Found: Si + Sn, 24.54.

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[7] M. C. Henry and J. G. Noltes, THIS JOURNAL, **82**, 555 (1960).

[8] J. W. Curry, *ibid.*, **78**, 1686 (1956).

[9] J. W. Curry and G. W. Harrisson, Jr., *J. Org. Chem.*, **23**, 1219 (1958).

[10] G. J. M. van der Kerk and J. G. Noltes, *J. Appl. Chem.*, **9**, 106 (1959).

[11] M. C. Henry and J. G. Noltes, unpublished results.

[12] All reactions involving diphenyltin dihydride were carried out in an atmosphere of dry oxygen-free nitrogen. Melting points (Kofler block) are uncorrected. Compounds containing different metal atoms were analyzed gravimetrically by determining the total weight of metallic oxides obtained on ignition. Only the total metal content is given.

[13] G. J. M. van der Kerk, J. G. Noltes and J. G. A. Luitjen, *J. Appl. Chem.*, **7**, 366 (1957).

[14] S. D. Rosenberg, *et al.*, *J. Org. Chem.*, **22**, 1200 (1957).

[15] D. Seyferth, THIS JOURNAL, **79**, 2133 (1957).

Complex with Toluene: *Anal.* Calcd. for $C_{28}H_{28}SiSn \cdot C_8H_8$: Si + Sn, 24.32. Found: Si + Sn, 24.56.

Complex with Pyridine: *Anal.* Calcd. for $C_{28}H_{28}SiSn \cdot C_5H_5N$: Si + Sn, 24.85. Found: Si + Sn, 25.03.

Complex with Dioxane: *Anal.* Calcd. for $C_{28}H_{28}SiSn \cdot C_4H_8O_2$: Si + Sn, 24.49. Found: Si + Sn, 24.68.

1,1'4-4'-Tetraphenyl-1-stanna-4-germanacyclohexane.—Equimolecular amounts of diphenyltin dihydride (5.50 g., 0.02 mole) and diphenyldivinylgermane (5.60 g.) were heated together for 4 hr. at 65° and for 8 hr. at 80°. The partly solid reaction mixture was taken up in a small volume of petroleum ether. Filtration yielded 3.45 g. of a solid which melted at 110–115°. Recrystallization from ethanol (twice) raised the m.p. to 124–125°; yield of pure product 1.92 g. (17%). The infrared spectrum revealed the presence of C_6H_5–Ge (band at 1080 cm.$^{-1}$), of C_6H_5–Sn (band at 1065 cm.$^{-1}$) and of $-CH_2-$ (doublet at 2860 cm.$^{-1}$), but there was no evidence for Sn–H (band at 1825 cm.$^{-1}$) or $GeCH=CH_2$ (band at 952 cm.$^{-1}$).

Anal. Calcd. for $C_{28}H_{28}GeSn$: C, 60.42; H, 5.02; Ge + Sn, 34.56; mol. wt., 5.56. Found: C, 60.19; H, 5.19; Ge + Sn, 34.74; mol. wt. (Rast), 545.

Complex with Toluene: *Anal.* Calcd. for $C_{28}H_{28}GeSn \cdot C_7H_8$: Ge + Sn, 29.52. Found: Ge + Sn, 29.59.

1,1',2,4,4',5-Hexaphenyl-1,4-distannacyclohexane.—Phenylacetylene (7.1 g., 0.07 mole) was added dropwise to a rapidly stirred solution of 19.2 g. (0.07 mole) of diphenyltin dihydride in 50 ml. of *n*-pentane. When the spontaneous evolution of heat had ceased the reaction mixture was refluxed for 2 hr. Thereupon the solvent was removed and the residue was heated at 100° for 6 hr. Upon cooling, a brittle product (26.0 g.) was obtained which melted at *ca.* 70–90°.

When a solution of 10.0 g. of this product in 150 ml. of 1-butanol was rapidly cooled, 2.5 g. of a white powder precipitated which melted at 70–72° (sintering at 68°).

Anal. Calcd. for $C_{40}H_{36}Sn_2$: C, 63.71; H, 4.81; Sn, 31.49; mol. wt., 754. Found: C, 63.44; H, 5.05; Sn, 31.79; mol. wt. (Rast), 780.

The mother liquor after 3 days at room temperature had deposited 2.7 g. of a crystalline solid which after recrystallization from acetic acid melted at 144–145°. The infrared spectra of both compounds were very similar in the region of 3500–680 cm.$^{-1}$. There was no evidence of Sn–H (band at 1825 cm.$^{-1}$) or of $SnCH=CHC_6H_5$ (band at 985 cm.$^{-1}$).

Anal. Calcd. for $C_{40}H_{36}Sn_2$: C, 63.71; H, 4.81; Sn, 31.49; mol. wt., 754. Found: C, 63.77; H, 5.08; Sn, 31.69; mol. wt. (Rast), 817.

Acknowledgment.—The authors are indebted: to Prof. G. J. M. van der Kerk, Director of this Institute, for encouragement; to Dr. E. S. Hedges, Director of the International Tin Research Council, for his supporting interest; to Mr. H. A. Budding for able experimental assistance.

[CONTRIBUTION FROM THE ORGANIC CHEMISTRY LABORATORIES, UNIVERSITY OF HEIDELBERG]

The Organometallic Alkylidene Reaction

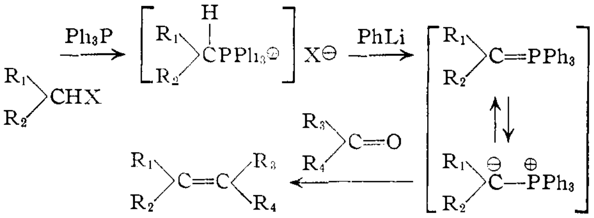
BY MALCOLM C. HENRY[1] AND GEORGE WITTIG

RECEIVED APRIL 25, 1959

The analog of the reaction between triphenylphosphine-methylene and carbonyl compounds to form the corresponding ethylenic compounds has been studied with quaternary compounds of arsenic, antimony and bismuth. The reaction with the arsenic alkylidene, in contrast to the phosphorous alkylidene, yields with benzophenone predominantly the corresponding aldehyde along with smaller amounts of the corresponding ethylenic compound. With the stibonium alkylidene only the corresponding aldehyde is produced. A new reaction has been utilized to produce triaryl-alkyl-quaternary salts of some of the group 5 elements using trimethyloxonium boron tetrafluoride.

The reaction between triarylphosphine alkylidenes and carbonyl compounds has proved to be, because of its specificity and good yields, widely applicable for the conversion of carbonyl compounds into their ethylenic entities.[2,3] Satisfactory results have also been obtained with compounds containing hydroxyl and acetoxy groups in addition to the carbonyl function,[4,5] and in the conversion of different types of saturated and α,β-unsaturated steroidal ketones to the corresponding methylene compounds. The reaction in many instances offers the most accessible route from such carbonyls to the corresponding methylenic compounds. Levine[6] and Wittig[7] have described a modification of the alkylidene reaction whereby aldehydes may be synthesized by way of their enol ethers.

We have attempted to substitute for phosphorus the other members of the group 5A elements, namely arsenic, antimony and bismuth. Benzophenone was selected as the second reactant.



Triphenylmethylarsonium halides have been previously synthesized by Michaelis[8] and Steinkopf[9] using the direct reaction between triphenylarsine and methyl halides. No method was available for the synthesis of triphenylmethylstibonium or bismuthonium salts since methyl halides do not add directly to triphenylstibine and triphenylbismuth. However, trimethyloxonium boron tetrafluoride, $[(CH_3)_3O^+][BF_4^-]$, an active methylating agent described by Meerwein,[10] reacts readily with triphenylstibine to yield the quaternary boron tetrafluoride, which is easily converted to the corresponding iodide. Triphenylbismuth reacts with the reagent, but does not produce the analogous "onium" salt under the conditions used. The

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(1) U. S. Quartermaster Research and Engineering Command, Pioneering Research Division, U. S. Army, Natick, Mass.; work carried out at the University of Heidelberg, Heidelberg, Germany, under the auspices of a Secretary of the Army Research Fellowship.

(2) G. Wittig, *Experientia*, **12**, 41 (1956); *Angew. Chem.*, **68**, 505 (1956).

(3) U. Schöllkopf, *ibid.*, **71**, 260 (1959).

(4) R. Sondheimer and R. Mechoulam, THIS JOURNAL, **79**, 5029 (1957).

(5) G. Wittig, "Festschrift, Prof. Dr. Arthur Stoll," Birkhauser Basel, Switzerland, 1957.

(6) S. Levine, THIS JOURNAL, **80**, 6150 (1958).

(7) G. Wittig and E. Knauss, *Angew. Chem.*, **71**, 127 (1959).

(8) A. Michaelis, *Ann.*, **321**, 141 (1902).

(9) W. Steinkopf and G. Schwen, *Ber.*, **54**, 2973 (1921).

(10) H. Meerwein, *J. prakt. Chem.*, **147**, 257 (1937).