(44%) of 2,1,3-benzothiadiazole, m.p. 41.5–42.5°. A mixed melting point with an authentic sample of 2,1,3-benzothiadiazole was 41.5–43°.

e. **Reaction with Anisole.**—Phenyliminosulfur difluoride (16 g., 0.1 mole) was added to a mixture of 30 ml. of anisole and 2.5 g. of fused zinc chloride at 0°. The dark mixture was allowed to warm to room temperature and was stirred for 15 hr. The mixture then was heated on a steam-bath for 1 hr., cooled and poured onto a mixture of ice and concentrated hydrochloric acid. Separation of the product from tarry material was effected by extraction with benzene. The benzene solution was washed with 10% sodium hydroxide solution and water, and next was dried over anhydrous magnesium sulfate. Removal of solvent and excess anisole, with subsequent distillation of the residue, yielded 9.16 g. (37%) of 4,4'-dimethoxydiphenyl sulfide as a viscous liquid, b.p. 158–161° (0.5 mm.), which soon solidified. Crystallization from petroleum ether at −78° gave colorless plates, m.p. 44–45° (lit.[7] m.p. 45–46°).

In order to confirm the structure of the product as 4,4'-dimethoxydiphenyl sulfide, 1.0 g. was dissolved in 20 ml. of glacial acetic acid, and a solution of 1.0 g. of potassium permanganate in 15 ml. of water was added. After 1 hr. at room temperature, the mixture was poured onto ice, and the solid was collected by filtration. Crystallization from ethanol gave 0.73 g. of 4,4'-dimethoxydiphenyl sulfone, m.p. 129.5–130.5° (lit.[10] m.p. 129–130°).

f. **Reduction by Lithium Aluminum Hydride.**—A solution of 4 g. (0.025 mole) of phenyliminosulfur difluoride in 25 ml. of dry ethyl ether was added dropwise during 2.5 hr. to a stirred mixture of 6 g. of lithium aluminum hydride in 75 ml. of ether. An extremely vigorous reaction occurred. The excess lithium aluminum hydride was decomposed by adding ethyl acetate; then 200 ml. of 20% sodium hydroxide solution was added, and the mixture was extracted with ether. After the ether solution had been washed with water and dried over anhydrous magnesium sulfate, the ether was distilled. To the residual brown oil was added 50 ml. of 10% sodium hydroxide solution and 7 ml. of benzoyl chloride. The mixture was shaken for 30 minutes, and the solid was collected by filtration. Crystallization of the solid from ethanol gave 0.31 g. of benzanilide, m.p. 160–161°. A mixed melting point with an authentic sample of benzanilide was 162–163°.

Acknowledgments.—The authors are particularly indebted to Dr. W. D. Phillips for the nuclear magnetic resonance studies and to Miss Naomi Schlicter and Mr. W. B. Askew for the spectral analyses which contributed so significantly to this work.

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WILMINGTON, DELAWARE

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

Infrared Absorption Spectra of Some IVth Group Organometallic Compounds

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

RECEIVED APRIL 16, 1959

The infrared absorption spectra of compounds of the type $(C_6H_5)_4M$, $(C_6H_5)_3MCH{=}CH_2$, $(C_6H_5)_2M(CH{=}CH_2)_2$, $(C_6H_5)_3MCH_2CH{=}CH_2$ and $(C_6H_5)_2M(CH_2CH{=}CH_2)_2$ in which M = Si, Ge, Sn and Pb have been recorded in the region of 3500–680 cm.$^{-1}$. Empirical assignments have been made for specific vibrations. Comparison of the spectra revealed a shift of some characteristic band frequencies to longer wave lengths in the series M = Si, Ge, Sn and Pb. The preparation of triphenylallylsilane, triphenylvinyl-, diphenyldivinyl- and diphenyldiallylgermane, triphenylvinyl- and diphenyldivinyllead, compounds not previously described, is given.[2]

Although considerable work has been done in the field of infrared spectroscopy of organosilicon compounds, there have been relatively few reports in the literature of the spectra of organometallic compounds of the other IVth main group elements. In connection with a program involving the reactions of organotin hydrides with vinyl- and allyl-substituted IVth group phenylmetal compounds,[3] infrared spectra of organometallic derivatives of the type $(C_6H_5)_4M$, $(C_6H_5)_3MCH{=}CH_2$, $(C_6H_5)_2M(CH{=}CH_2)_2$, $(C_6H_5)_3MCH_2CH{=}CH_2$ and $(C_6H_5)_2M(CH_2CH{=}CH_2)$ in which M = Si, Ge, Sn and Pb in the region of 3500–680 cm.$^{-1}$ were recorded. This paper deals with tentative band assignments and with characteristic differences in the spectra when passing from Si to Pb as the central metal atom.

Experimental

Preparation of Compounds.—Tetraphenylsilane[4] was prepared by a Wurtz reaction, tetraphenylgermane,[5a] tetraphenyltin[5b] and tetraphenyllead[6] were prepared by a Grignard reaction, phenylmagnesium chloride in tetrahydrofuran (THF) being used as the phenylating agent.[7]

These compounds were converted into the corresponding triphenylmetal monohalides $(C_6H_5)_3MX$ and diphenylmetal dihalides $(C_6H_5)_2MX_2$ by published procedures. Triphenylbromosilane $(C_6H_5)_3SiBr$, prepared by Ladenburg[8] by heating equimolecular amounts of tetraphenylsilane and bromine in a sealed tube, was obtained in an appreciably higher yield (76%) by carrying out the reaction in a high-boiling solvent (ethylene bromide).

The phenylmetal halides were converted into the corresponding vinyl and allyl derivatives by reaction with vinylmagnesium bromide in THF[9] and with allylmagnesium bromide in diethyl ether.[10] Stock solutions of these reagents were stored in calibrated flasks under nitrogen. Molarities were determined by titrating a hydrolyzed aliquot with standard acid.[11] Storage for considerable time did not result in appreciable decrease in reactivity. All reactions were carried out in an atmosphere of dry nitrogen.

Triphenylvinylsilane,[12,13] triphenylvinyltin,[14] diphenyldivinylsilane,[13] diphenyldivinyltin,[15] triphenylallylgermane,[16] triphenylallyltin,[17] triphenylallyllead,[18] diphenyldi-

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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) Juenge and Cook have reported the preparation of triphenylvinyllead and diphenyldivinyllead at the 135th Meeting of the American Chemical Society, April, 1959, Boston, Mass.

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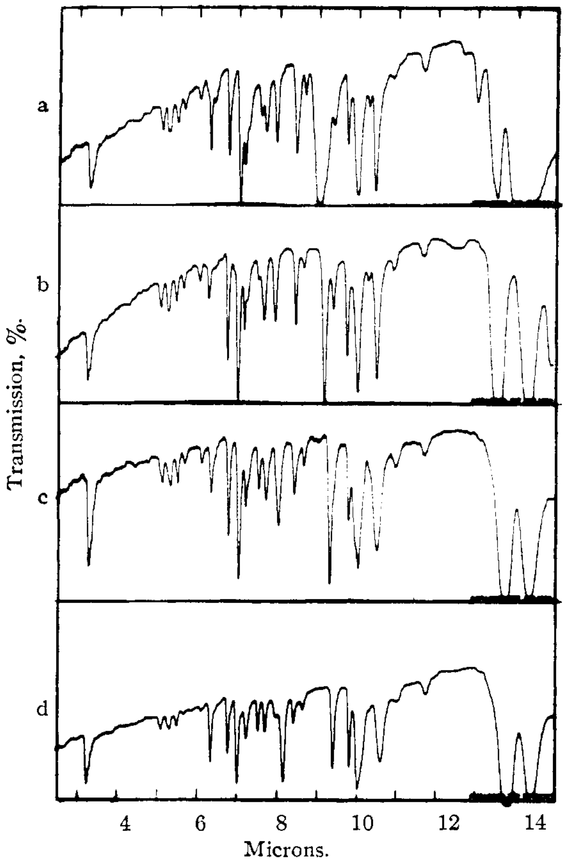

Fig. 1.—Infrared spectra from 3500–680 cm.$^{-1}$ of: a, triphenylvinylsilane; b, triphenylvinylgermane; c, triphenylvinyltin; d, triphenylvinyllead.

allylsilane[19] and diphenyldiallyltin[17] have been previously prepared. Triphenylallylsilane, triphenylvinylgermane, diphenyldivinylgermane, diphenyldiallylgermane, triphenylvinyllead and diphenyldivinyllead are new compounds. The attempted isolation of pure diphenyldiallyllead was unsuccessful (compare ref. 17).

Triphenylallylsilane.—Triphenylbromosilane (33.9 g., 0.10 mole) dissolved in 50 ml. of THF was added dropwise to 0.10 mole of allylmagnesium bromide in 120 ml. of ether. After being held at room temperature for 4 hours the reaction mixture was decomposed by pouring into cold ammonium chloride solution. The separated ether layer was dried over sodium sulfate and the ether was removed. The residue was recrystallized from ligroin to give 22.0 g. (74%) of colorless crystals with m.p. 84–86°.

Anal. Calcd. for $C_{21}H_{20}Si$: Si, 9.35. Found: Si, 9.43.

Triphenylvinylgermane.—Triphenylbromogermane (11.7 g., 0.03 mole) dissolved in 30 ml. of benzene was added dropwise to 0.07 mole of vinylmagnesium bromide dissolved in 70 ml. of THF. After heating at reflux temperature for 1 hour, the mixture was hydrolyzed in the usual way. Evaporation of the organic layer yielded an oil, a solution of which in hot 96% ethanol upon cooling yielded 8.3 g. (84%) of colorless crystals with m.p. 62–64°.

Anal. Calcd. for $C_{20}H_{18}Ge$: Ge, 21.94. Found: Ge, 21.71.

Diphenyldivinylgermane.—A mixture of 0.09 mole of vinylmagnesium bromide, in 120 ml. of THF and 15.4 g. (0.04 mole) of diphenyldibromosilane was refluxed for 4 hours and thereupon worked up in the usual way. Distillation of the reaction product yielded a colorless liquid with b.p. 111–113° at 0.003 mm., yield 7.3 g. (67%).

Anal. Calcd. for $C_{16}H_{16}Ge$: Ge, 25.85. Found: Ge, 25.92.

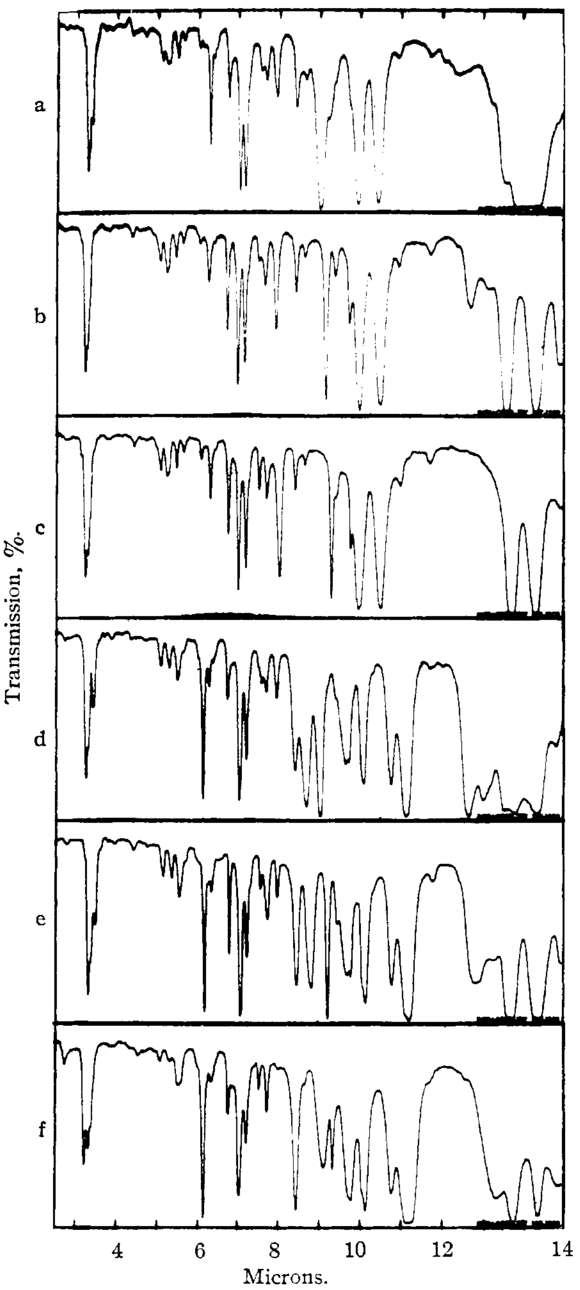

Fig. 2.—Infrared spectra from 3500–680 cm.$^{-1}$ of: a, diphenyldivinylsilane; b, diphenyldivinylgermane; c, diphenyldivinyltin; d, diphenyldiallylsilane; e, diphenyldiallylgermane; f, diphenyldiallyltin.

Diphenyldiallylgermane.—The mixture obtained on dropwise addition of 15.4 g. (0.04 mole) of diphenyldibromogermane to 0.08 mole of allylmagnesium bromide in 100 ml. of ether was refluxed for 4 hours and thereupon worked up in the usual way. Distillation of the reaction product yielded a colorless liquid with b.p. 117–120° at 0.007 mm., yield 9.4 g. (77%).

Anal. Calcd. for $C_{18}H_{20}Ge$: Ge, 23.50. Found: Ge, 23.64.

Triphenylvinyllead.—A suspension of 19.0 g. (0.04 mole) of triphenyllead chloride in 50 ml. of THF was added dropwise to 0.052 mole of vinylmagnesium bromide in 75 ml. of THF. After heating at 50° for 15 minutes the reaction mixture was worked up in the usual way. Evaporation of the dried organic layer yielded an oil which failed to crystallize. Distillation was accompanied by considerable decom-

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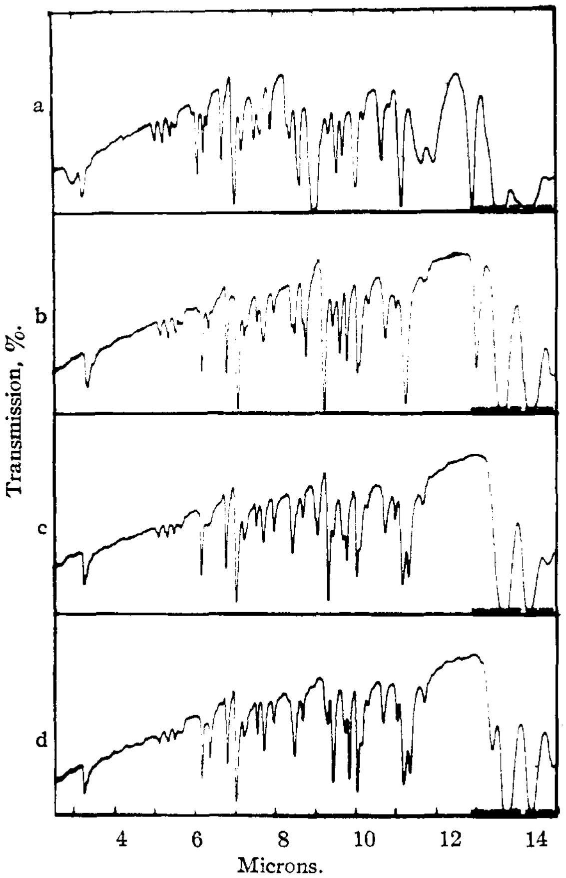

Fig. 3.—Infrared spectra from 3500–680 cm.$^{-1}$ of: a, triphenylallylsilane; b, triphenylallylgermane; c, triphenylallyltin; d, triphenylallyllead.

position and gave a fraction with b.p. 150–154° at 0.002 mm. which solidified on cooling, m.p. 32–35°, yield 2.7 g. (14%). An analytical sample recrystallized from ethanol melted at 35–36°.

Anal. Calcd. for $C_{20}H_{18}Pb$: Pb, 44.51. Found: Pb, 44.58.

Diphenyldivinyllead.—When 25.0 g. (0.058 mole) of diphenyllead dichloride was added portionwise to 0.117 mole of vinylmagnesium bromide in 150 ml. of THF the solid went gradually into solution and a muddy-green color developed. Warming the mixture at 50° resulted in deposition of metallic lead. Working up of the reaction mixture in the usual way yielded a yellow oil which was distilled with much decomposition. A colorless liquid with b.p. 111–114° at 0.002 mm., 9.8 g. (41%), was collected. Once pure, this compound can be kept for considerable time without decomposition.

Anal. Calcd. for $C_{16}H_{16}Pb$: Pb, 49.87. Found: Pb, 49.61, 49.82.

Apparatus and Technique.—The infrared spectra were obtained with a Perkin-Elmer Infracord spectrophotometer equipped with a sodium chloride prism. The solid samples were recorded using the potassium bromide pressed disk method; the liquid samples were recorded in a 0.025-mm. cell with sodium chloride windows.

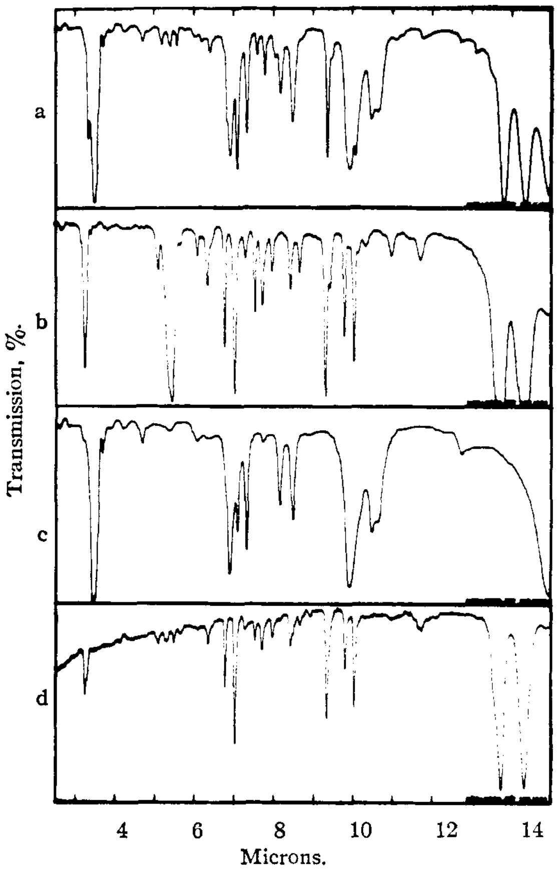

Fig. 4.—Infrared spectra from 3500–680 cm.$^{-1}$ of: a, phenyltriethyltin; b, triphenyltin hydride; c, tetraethyltin; d, hexaphenyldistannane.

Results and Discussion

The spectra of the phenylmetal compounds presented in Figs. 1, 2 and 3 show the usual absorptions associated with aromatic compounds at 3058, at 1075, in the region of 730–750 and at 690 cm.$^{-1}$.[20] The latter vibrations are all evidence for the presence of monosubstituted phenyl groups as are the absorption frequencies between 1600 and 2000 cm.$^{-1}$. These above-mentioned absorptions show no shift as the central metal atom changes and are absent in the spectra of molecules containing only aliphatic groups (see, *e.g.*, the spectrum of tetraethyltin, Fig. 4).

One of the most interesting areas of the spectra occurs in the region 1050 to 1120 cm.$^{-1}$. In a preliminary communication[21] the occurrence of a sizable band shift in the spectra of a series of IVth group tetraphenylmetal compounds has been noted. The following band shift was observed: tetraphenylsilane 1100 cm.$^{-1}$, tetraphenylgermane 1080 cm.$^{-1}$, tetraphenyltin 1065 cm.$^{-1}$ and tetraphenyllead 1052 cm.$^{-1}$. A corresponding band is absent in the spectrum of tetraphenylmethane. The same shift also occurs in each series of the mixed phenyl compounds, *i.e.*, the monovinyl, the divinyl, the monoallyl and the diallyl series (Figs. 1, 2 and 3). The band at 1065 cm.$^{-1}$ is also present in the spectrum of hexaphenyldistannane, triphenyltin hydride and phenyltriethyltin, while it is noticeably absent in the spectrum of tetraethyltin (Fig. 4). As it is clear that frequencies of vibrations directly involving metal atoms are well beyond the rock salt region, this band is believed to be a perturbed phenyl vibrational absorption, probably a C–H

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[21] J. G. Noltes, M. C. Henry and M. J. Janssen, *Chemistry & Industry*, 298 (1959).

in plane deformation vibration,[22] which shifts to lower frequencies as the weight of the metal atom increases. As this shift is relative to the central metal atom, this band is useful as a characteristic vibration frequency. A corresponding band shift has been observed in the infrared spectra of the phenyl halides.[23]

Young, *et al.*,[24] have described phenyl–silicon vibrations at 1429 and 1110 cm.$^{-1}$. These authors regard the absorption at 1429 cm.$^{-1}$ to be characteristic of the phenyl–silicon structure. This band, which is also present in phenyl compounds of the other IVth group elements, does, however, not shift as it should were it indeed characteristic of a specific phenyl–metal structure. Moreover, the band at 1429 cm.$^{-1}$ is situated in the region where aliphatic vibrations occur, which is apparent upon comparison of the spectra of tetraethyltin and phenyltriethyltin (Fig. 4). Since there are no interfering vibrations around 1100 cm.$^{-1}$ and as has already been noted the frequency of the absorption in this region is specifically dependent on the nature of the metal atom, the perturbed phenyl vibrations in the area between 1050 and 1120 cm.$^{-1}$ may be successfully used for the characterization of molecules containing different phenyl–IVth group metal bonds.[1,2]

A corresponding picture is presented by the compounds containing vinyl groups where the $=CH_2$ out-of-plane bending vibration is perturbed by the adjacent metal atom. This results in a characteristic band shift in the region of 940 to 960 cm.$^{-1}$ (Figs. 1 and 2). The following values are tabulated: triphenylvinylsilane 960 cm.$^{-1}$, diphenyldivinylsilane 960 cm.$^{-1}$, triphenylvinylgermane 952 cm.$^{-1}$, diphenyldivinylgermane 952 cm.$^{-1}$, triphenylvinyltin 950 cm.$^{-1}$, diphenyldivinyltin 950 cm.$^{-1}$ and triphenylvinyllead 942 cm.$^{-1}$. Since the position of this band is relative to the central metal atom it is useful as a characteristic vibration frequency.

In the compounds containing allyl groups the out-of-plane hydrogen deformation absorptions are noticed at 894 and 930 cm.$^{-1}$ characteristic of $CH_2{=}CHR$ where R must contain at least one carbon. No shift is noticed going from one metal atom to another.

The C–H stretching vibration for triphenylmethane has been proposed by Fox and Martin[25] to occur at 2890 cm.$^{-1}$, that of Si–H in the case of triphenylsilane has been reported at about 2135 cm.$^{-1}$,[26] a shift of 755 cm.$^{-1}$. The corresponding Ge–H frequency is reported to be about 2040 cm.$^{-1}$ [27] while the Sn–H frequency as observed in aliphatic tin hydrides is about 1820 cm.$^{-1}$.[28] The spectrum of triphenyltin hydride which shows the tin–hydrogen absorption occurring at 1825 cm.$^{-1}$ is presented in Fig. 4. In all cases the absorption is strong. Because the hydrogen atom is so light relative to the attached atom, it is obvious that as the weight of the adjacent atom increases the vibrational shift should decrease markedly.

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

Reactions of Phenyltin Hydrides with Vinyl and Allyl Derivatives of the IVth Main Group Elements

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

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The reactions of triphenyltin hydride and diphenyltin dihydride with vinyl and allyl derivatives of silicon, germanium, tin and lead have been studied. Organometallic compounds containing two and three metal atoms, these being various combinations of tin and silicon or germanium, have been obtained. Vinyl and allyl compounds of lead appeared to be reductively cleaved by phenyltin hydrides with formation of metallic lead. The infrared spectra of the addition compounds are presented and discussed. Separate absorption bands characteristic of each different metal atom present are shown to be useful for identification of these types of compounds.

The formation of tin-carbon bonds by the addition of organotin hydrides to compounds containing olefinic double bonds was first reported in 1956[2] and has been the subject of considerable study at our Institute since that time.[3a,b] Such addition reactions proceed in excellent yield in the absence of any added solvent or catalyst, especially when the double bond is activated by the presence of neighboring electron-attracting substituents. It is noteworthy that attempts at synthesis of organotin adducts using hydrocarbon solvents and peroxides or ultraviolet irradiation as a catalyst were unsuccessful,[4] whereas with the same react-

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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.

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