CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE
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# Vinyl Derivatives of Metals. XIV. Reaction of the Trimethylvinyl Compounds of Silicon, Germanium, and Tin with Iodomethylzinc Iodide. Preparation of Cyclopropyltin Compounds by the Grignard Procedure[1]

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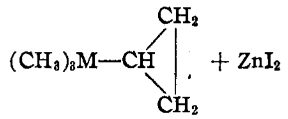
*Received May 28, 1962*

Trimethylvinylsilane and trimethylvinylgermane react with iodomethylzinc iodide to give cyclopropyltrimethylsilane and cyclopropyltrimethylgermane, respectively. The action of iodomethylzinc iodide on trimethylvinyltin also results in formation of cyclopropyltrimethyltin, but in the presence of zinc iodide, which is produced in the reaction, extensive redistribution occurs, and a mixture containing tetramethyltin, cyclopropyldimethylvinyltin, dimethyldivinyltin, and cyclopropylmethyldivinyltin, in addition to the expected product and unreacted starting material, is obtained. The preparation of seven new tetraorganotin compounds containing one or more cyclopropyl groups by the Grignard procedure is described.

The reaction of vinylmetal compounds with electrophilic reagents is well documented.[3] We have continued our study of the reactivity of the carbon–carbon double bond in vinylmetal compounds by examining the reactions of the trimethylvinyl compounds of silicon, germanium, and tin with iodomethylzinc iodide. The action of this reagent on olefins produces cyclopropanes, presumably by direct interaction of the electrophilic zinc compound with the olefin.[4] Trimethylvinylsilane, -germane, and -tin react with this reagent in this manner to give the first cyclopropyl derivatives of these elements to be reported.

$(CH_3)_3MCH{=}CH_2 + ICH_2ZnI \longrightarrow$



$$(CH_3)_3M{-}CH\begin{matrix}CH_2\\ |\\ CH_2\end{matrix} + ZnI_2$$

(M = Si, Ge, Sn)

The yield of the cyclopropyl derivative was highest (50%) in the case of trimethylvinylsilane. Cyclopropyltrimethylgermane was obtained in 29% yield, and conversion of trimethylvinyltin to cyclopropyltin derivatives was effected in *ca.* 27% yield.

The reaction of iodomethylzinc iodide with trimethylvinyltin was complicated by redistribution of organic substituents on tin. Thus, in addition to the expected cyclopropyltrimethyltin (18.8%) and unreacted trimethylvinyltin (21.7%), there were isolated tetramethyltin (42.6%), cyclopropyldimethylvinyltin (8.1%), dimethyldivinyltin (4.4%), and cyclopropylmethyldivinyltin (<1%). Such redistribution is not surprising. Calingaert and co-workers[5] showed that refluxing a pentane solution of tetramethyl- and tetraethyltin for 5 hr. in the presence of a Lewis acid (2.5 mole % of $AlCl_3$) resulted in redistribution, giving ethyltrimethyltin, diethyldimethyltin, and triethylmethyltin in addition to the starting compounds. In our case, zinc iodide, a mild Lewis acid, was being generated during the reaction, and thus redistribution occurred. Furthermore, the vinyl–tin linkage is particularly labile toward attack by electrophilic metal halides of this type.[3] The fact that the tetramethyltin observed was present in a fraction which had not been heated above 30° during subsequent work-up indicates that the redistribution of groups had begun during the reaction period. An independent experiment in which an equimolar mixture of cyclopropyltrimethyltin and trimethylvinyltin in ether solution was heated with an amount of zinc iodide equal to the total moles of tin compounds demonstrated that the zinc iodide indeed was responsible for the observed redistribution reaction; all the organotin

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[1] Part XIII: D. Seyferth, T. Wada, and G. E. Maciel, *Inorg. Chem.*, **1**, 232 (1962).

[2] Allied Chemical Corporation Fellow, 1960–1961.

[3] D. Seyferth, "Vinyl Compounds of Metals," in "Progress in Inorganic Chemistry," Vol. 3, F. A. Cotton, ed., Interscience Publishers, Inc., New York, N. Y., 1962, pp. 130–280.

[4] H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

[5] G. Calingaert, H. A. Beatty, and H. R. Neal, *ibid.*, **61**, 2755 (1939); G. Calingaert, H. Soroos, and V. Hnizda, *ibid.*, **62**, 1107 (1940).

TABLE I

CYCLOPROPYLTIN COMPOUNDS PREPARED BY THE GRIGNARD METHOD

| Compound (R = cyclopropyl) | B.p., °C. (mm.) | $n^{25}D$ | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found |
|---|---|---|---|---|---|---|
| $RSn(CH_3)_3$ | 129–130 (760) | 1.4720 | 35.17 | 35.37 | 6.89 | 7.03 |
| $R_4Sn$ | 67–68 (0.3) | 1.5202 | 50.93 | 50.96 | 7.12 | 6.98 |
| $R_3SnC_4H_9$-*n* | 84–86 (1.0) | 1.5040 | 52.21 | 52.46 | 8.09 | 7.81 |
| $R_2Sn(C_4H_9$-*n*$)_2$ | 79 (0.4) | 1.4912 | 53.37 | 53.70 | 8.96 | 9.03 |
| $RSn(C_4H_9$-*n*$)_3$ | 94–95 (0.65) | 1.4803 | 54.41 | 54.21 | 9.74 | 9.73 |
| $R_3SnC_6H_5$ | 93 (0.23) | 1.5604 | 56.47 | 56.54 | 6.32 | 5.99 |
| $RSn(C_6H_5)_3$ | M.p. 67–68.5 | ... | 64.49 | 64.40 | 5.16 | 5.14 |

products observed in the trimethylvinyltin–iodomethylzinc iodide reaction were found to be present. Such redistribution did not occur when zinc iodide was absent.

The reaction of iodomethylzinc iodide with vinyltin compounds obviously does not constitute a practical synthesis of cyclopropyltin compounds for the reasons cited above. However, the ready availability of cyclopropyl bromide *via* cyclopropanecarboxylic acid[6] and its easily effected conversion to the Grignard reagent in tetrahydrofuran solution provided an alternate route to cyclopropyltin compounds in which the redistribution problem was absent. A number of cyclopropyltin compounds were prepared in good yield by the Grignard procedure, and their physical properties and analytical data are listed in Table I.

A brief discussion of the infrared spectra of cyclopropyl derivatives of the group IV elements is of interest. It has been noted that by using calcium fluoride optics the $CH_2$ vibrations at 3096 and 3012 cm.$^{-1}$ can be used to identify the cyclopropyl ring system.[7] Cyclopropyl bromide shows absorption at 3077 and 2985 cm.$^{-1}$.[8] In all cyclopropylmetal compounds reported here these bands occur at 3060 and 2994 cm.$^{-1}$. A second characteristic band occurs at 1030 cm.$^{-1}$. The most noticeable feature of the infrared spectra of these compounds is the strong absorption near 900 cm.$^{-1}$. In cyclopropyltrimethylsilane this occurs at 902 cm.$^{-1}$; in cyclopropyltrimethylgermane it is shifted to 888 cm.$^{-1}$. In cyclopropyltrimethyltin and in all other cyclopropyltin compounds examined it is found at 875 cm.$^{-1}$. The band at 1030 cm.$^{-1}$ appears to be characteristic of the cyclopropyl ring system itself,[9] whereas that near 900 cm.$^{-1}$ depends on the atom to which the cyclopropyl group is attached. Dicyclopropylmercury has been reported[10] to show absorption at 2990, 1030, and 880 cm.$^{-1}$. Other bands apparently characteristic of the cyclopropyl group occur at 1185–1190 and at 1240–1245 cm.$^{-1}$.

Some results of an investigation of selected reactions of cyclopropyltin compounds will be the subject of later papers.

## Experimental[11]

**Reaction of Trimethylvinylsilane with Iodomethylzinc Iodide.**—To a three-necked flask, fitted with a mechanical stirrer, a water condenser topped with a nitrogen inlet tube, and an addition funnel, was added 16.1 g. of zinc–copper couple[12] (0.24 g.-atom of zinc), 53.5 g. (0.2 mole) of methylene iodide, 0.15 g. of iodine, and 150 ml. of di-*n*-butyl ether. The mixture was heated at 55–65° and stirred for 30 min. To this mixture then was added 22 g. (0.22 mole) of trimethylvinylsilane in an equal volume of di-*n*-butyl ether. The reaction mixture was stirred at 60° for 26 hr., cooled, and filtered. The filtrate was washed with 5% HCl solution, 5% aqueous sodium bicarbonate, and finally with saturated sodium chloride solution. The organic layer was dried and distilled until the lower boiling constituents and a portion of the solvent had been collected. Analysis of the distillate by gas chromatography (30% Dow Corning 710 Silicone fluid on 60–80 mesh Chromosorb P, preheater at 144°, column jacket at 44°, 13 p.s.i. helium) showed that 0.108 mole of trimethylvinylsilane and 0.110 mole of cyclopropyltrimethylsilane were present. The products were identified by their infrared spectra and retention times. Thus this reaction resulted in a 50% conversion of trimethylvinylsilane to cyclopropyltrimethylsilane. A pure sample of the latter was isolated by distillation through a spinning band column, b.p. 91°, $n^{25}D$ 1.4095.

*Anal.* Calcd. for $C_6H_{14}Si$: C, 63.06; H, 12.36. Found: C, 63.07; H, 12.44.

**Reaction of Trimethylvinylgermane with Iodomethylzinc Iodide.**—A mixture of 4.6 g. of zinc–copper couple (0.069

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[6] We are indebted to Professor J. S. Meek, University of Colorado, for communicating to us his excellent synthesis of cyclopropyl bromide prior to publication.

[7] S. E. Wiberly and S. C. Bunce, *Anal. Chem.*, **24**, 623 (1952).

[8] J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5030 (1951).

[9] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., Methuen & Co., Ltd., London, 1958, p. 29.

[10] G. F. Reynolds, R. E. Dessy, and H. H. Jaffé, *J. Org. Chem.*, **23**, 1217 (1958).

[11] Analyses by Dr. S. M. Nagy (M.I.T.) and Dr. I. A. Schoeller (Kronach). All reactions were carried out in an atmosphere of prepurified nitrogen. Ether solvents were dried over lithium aluminum hydride and redistilled before use.

[12] R. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

g.-atom of zinc), 16.6 g. (0.062 mole) of methylene iodide, and a few crystals of iodine in 40 ml. of diethyl ether was stirred at reflux for 40 min. After this time 10.0 g. (0.069 mole) of trimethylvinylgermane[13] in 10 ml. of ether was added, and the mixture was heated gently at reflux for 26 hr. It then was filtered, and the filtrate was distilled at reduced pressure, the distillate being collected in a receiver cooled to −78°. Gas chromatographic analysis of the distillate showed that cyclopropyltrimethylgermane had been formed in 29% yield. An analytical sample, $n^{25}\text{D}$ 1.4321, was isolated by gas chromatography.

*Anal.* Calcd. for $C_6H_{14}Ge$: C, 45.39; H, 8.89. Found: C, 45.39; H, 8.82.

**Reaction of Trimethylvinyltin with Iodomethylzinc Iodide.**—Essentially the same procedure as that described above was used in the reaction of 4.3 g. of zinc–copper couple (0.064 g.-atom of zinc), 16.1 g. (0.06 mole) of methylene iodide, and 12.5 g. (0.066 mole) of trimethylvinyltin in 50 ml. of diethyl ether. The reagent formation was initiated with a few crystals of iodine, and the reaction mixture was heated at reflux for 24 hr. Volatile liquids then were removed at high vacuum by a bulb-to-bulb distillation. Two fractions were collected: (1) 48 ml., bath temperature to 30°; (2) 5.3 ml., bath temperature to 250°. Both were analyzed by gas chromatography using either Dow Corning 710 Silicone fluid or General Electric XF-1150 fluid on Chromosorb P. Details of the gas chromatographic analysis are given in the thesis of H. M. C.[16] The following compounds were identified and are listed in order of increasing retention time.

(1) Tetramethyltin (42.6%), identified by comparing retention time and infrared spectrum with those of an authentic sample, by refractive index, $n^{25}\text{D}$ 1.4381; lit.[17] 1.4386, and by analysis.

*Anal.* Calcd. for $C_4H_{12}Sn$: C, 26.86; H, 6.77. Found: C, 26.65; H, 6.66.

(2) Trimethylvinyltin (21.7%), identified by comparison of its retention time and infrared spectrum with those of authentic material.

(3) Dimethyldivinyltin (4.4%), identified by retention time and infrared spectrum, and by $n^{25}\text{D}$ 1.4715 (lit.[18] $n^{25}\text{D}$ 1.4720).

(4) Cyclopropyltrimethyltin (18.8%), identified by comparison of its retention time and infrared spectrum with those of pure material prepared *via* cyclopropylmagnesium bromide.

(5) Cyclopropyldimethylvinyltin (8.1%), $n^{25}\text{D}$ 1.4844, identified by its infrared spectrum (bands due to $CH_3$, $CH{=}CH_2$, and cyclo-$C_3H_5$ groups) and analysis.

*Anal.* Calcd. for $C_7H_{14}Sn$: C, 38.76; H, 6.51. Found: C, 39.02; H, 6.49.

(6) Cyclopropylmethyldivinyltin (< 1%), identified by its infrared spectrum and by combustion analysis.

*Anal.* Calcd. for $C_8H_{14}Sn$: C, 41.99; H, 6.16. Found: C, 42.07; H, 6.31. The infrared spectrum of this compound was essentially the same as that of cyclopropyldimethylvinyltin, except that the intensity of the absorption due to the cyclopropyl and the vinyl groups differed.

No organotin iodides were found in the reaction mixture. No precipitate was noted when either fraction was shaken with aqueous–alcoholic potassium fluoride solution, nor did the solutions have the sharp odor indicative of the presence of $R_3SnI$ derivatives. However, a compound believed to be cyclopropyl iodide was found as a contaminant of the dimethyldivinyltin fraction as obtained from the Dow Corning 710 Silicone column, which was separated on the General Electric XF-1150 column. Positive identification was not made, but the following suggests that it was cyclopropyl iodide. Pyrolysis of a small sample showed the presence of iodine, but not of tin. Its infrared spectrum is quite similar to that of cyclopropyl bromide. In fact, for every band in the spectrum of this material, a corresponding band can be found in the infrared spectrum of cyclopropyl bromide. Thus bands at 3030 (w), 3000 (m), 2080 (w), 1995 (w), 1785 (w), 1440 (m), 1415 (s), 1195 (vs), 1160 (w), 1085 (w), 1055 (m), 1025 (vs), 855 (s), 800 (vs), and 760 (w) find analogous bands at the same position ±8 cm.$^{-1}$ in the spectrum of cyclopropyl bromide. The only other two bands in the spectrum of this compound are one at 905 cm.$^{-1}$ (at 930 cm.$^{-1}$ in cyclopropyl bromide) and a broad, intense band from 1233 to 1243 cm.$^{-1}$ (centered at 1238 cm.$^{-1}$), found in cyclopropyl bromide at 1258 to 1265 cm.$^{-1}$. Cyclopropyl iodide has been prepared previously,[19] and while its complete infrared spectrum was not tabulated, it was mentioned that a very intense band at 1237 cm.$^{-1}$ was characteristic of this compound.

**Redistribution of Trimethylvinyltin and Cyclopropyltrimethyltin in the Presence of Zinc Iodide.**—A solution containing 6 mmoles each of trimethylvinyltin and cyclopropyltrimethyltin and 12 mmoles of anhydrous zinc iodide (dried under vacuum over $P_2O_5$) in 12 ml. of diethyl ether was heated at reflux for 24.5 hr. Volatile liquids were removed by distillation under high vacuum at as low a temperature as possible. The distillate was analyzed by gas chromatography as before, and the products are given below in order of their elution from a Dow Corning 710 Silicone fluid on Chromosorb P column. Comparison of their retention times and infrared spectra with those of authentic materials in most cases served to identify the products. The redistribution reaction resulted in: (1) tetramethyltin (43.3%), (2) trimethylvinyltin (17.3%), (3) dimethyldivinyltin (1.4%), (4) cyclopropyltrimethyltin (23.2%), (5) cyclopropyldimethylvinyltin (5.4%), (6) trimethyltin iodide (8.1%), (7) dicyclopropylmethylvinyltin (0.04%) (tentative identification), (8) tricyclopropylmethyltin (0.3%) (tentative identification). An equimolar mixture of trimethylvinyltin and cyclopropyltrimethyltin showed only two peaks when subjected to gas chromatography under these conditions. Trimethyltin iodide was characterized further by conversion to the insoluble fluoride by treatment with aqueous–methanolic KF solution. The structures of compounds 7 and 8 were deduced by comparing the relative intensity of bands in their infrared spectra due to the cyclopropyl and vinyl groups with those observed in cyclopropyldimethylvinyltin. Thus in the

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(13) Prepared in 50% yield by the reaction of vinyllithium[14] with trimethylgermanium iodide in ether, b.p. 69–71°, $n^{20}\text{D}$ 1.4168; lit.[15] b.p. 70.6°, $n^{20}\text{D}$ 1.4153.

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

(15) V. F. Mironov, Yu. P. Egorov, and A. D. Petrov, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 1400 (1959).

(16) H. M. Cohen, Ph.D. Thesis, Massachusetts Institute of Technology, in preparation.

(17) H. Korsching, *Z. Naturforsch.*, **1**, 219 (1946).

(18) S. D. Rosenberg, A. J. Gibbons, Jr., and H. E. Ramsden, *J. Am. Chem. Soc.*, **79**, 2137 (1957).

(19) H. Hart and H. Wyman, *ibid.*, **81**, 4891 (1959).

spectrum of compound 7 the cyclopropyl band at 1030 cm.$^{-1}$ is more intense than the vinyl band at 1000 cm.$^{-1}$. Since exactly the reverse is observed in cyclopropyldimethylvinyltin, it is concluded that there are more cyclopropyl groups than vinyl groups in compound 7. Strong absorption at 875 cm.$^{-1}$ indicates the cyclopropyl–tin system, while vinyl attached to tin is suggested by the doublet at 950 and 1000 cm.$^{-1}$. On the basis of this evidence compound 7 could be either dicyclopropylmethylvinyltin or tricyclopropylvinyltin. The spectrum of compound 8 shows no vinyl bands, but does have strong bands indicative of a cyclopropyl group attached to tin at 875 and 1030 cm.$^{-1}$, and is similar to that of tetracyclopropyltin with the exception that a weak band at 1385 cm.$^{-1}$ is present only in the spectrum of compound 8 and that the intensity of the band at *ca.* 2900 cm.$^{-1}$ is much greater relative to the bands at 3000 and 3040 cm.$^{-1}$ than in the spectrum of tetracyclopropyltin. This suggests either tricyclopropylmethyltin or dicyclopropyldimethyltin as the structure of compound 8. Since the retention time of compound 8 is greater than that of compound 7, and since all the compounds appear to be eluted in order of increasing boiling point, it is likely that (7) and (8) are dicyclopropylmethylvinyltin and tricyclopropylmethyltin, respectively. The boiling point sequence, tetramethyltin (78°), trimethylvinyltin (99–100°), cyclopropyltrimethyltin (129–130°), is to be noted in this connection.

The absence of cyclopropyl iodide in this experiment probably is due to the milder distillation conditions employed.

Gas chromatographic analysis showed that no redistribution had occurred after an equimolar mixture of cyclopropyltrimethyltin and trimethylvinyltin in ether had been heated at reflux for 24 hr., thus establishing that zinc iodide was required to effect the redistribution of organic groups on tin.

**Preparation of Cyclopropyltin Compounds by the Grignard Procedure.**—The preparation of di-*n*-butyldicyclopropyltin is described to illustrate the general procedure used.

The Grignard reagent was prepared from 3.16 g. (0.13 g.-atom) of magnesium turnings and 15 g. (0.123 mole) of cyclopropyl bromide in 80 ml. of tetrahydrofuran in the usual manner. The resulting light brown solution was heated at reflux for 1 hr. To this solution was added 13.65 g. (0.045 mole) of di-*n*-butyltin dichloride in 30 ml. of tetrahydrofuran. The reaction mixture was stirred and heated at reflux for 22 hr., cooled, and then hydrolyzed with 20 ml. of saturated aqueous ammonium chloride solution. The organic layer was decanted, and the residual solids were washed with ether. Distillation of the combined organic phase and ether washings gave 10.2 g. (71%) of di-*n*-butyldicyclopropyltin, b.p. 79° at 0.4 mm.

The other compounds in Table I were prepared in this manner from the corresponding organotin chloride in yields of 50–75%. If the initial distillate gave a positive test for halide ion, indicating the presence of organotin halide impurities, it was shaken with aqueous–alcoholic potassium fluoride, and the organic phase was dried and redistilled to give the pure product.

This procedure was varied somewhat in the preparation of cyclopropyltriphenyltin. The Grignard reagent was prepared in tetrahydrofuran from 0.82 mole of cyclopropyl bromide and cooled to 0°. Triphenyltin chloride (0.74 mole) was added through a solids addition funnel. The reaction mixture was heated at reflux for 15 hr. and then was cooled and hydrolyzed with 400 ml. of ice water; subsequently 600 ml. of 10% hydrochloric acid and 400 ml. of pentane were added. The organic layer was dried and evaporated to dryness. To the resulting oil was added 300 ml. of pentane. The solid which formed (20 g., m.p. 165–185°) was filtered, washed with pentane, and recrystallized twice from tetrahydrofuran; m.p. (231–233°) and mixed m.p. established its identity as hexaphenylditin. The pentane solution was poured onto an alumina column and the product eluted with pentane. Triphenylcyclopropyltin, m.p. 66–68°, 207 g. (72%), thus was obtained. Recrystallization from pentane gave an analytical sample, m.p. 67–68.5°.

**Acknowledgment.**—The authors are grateful to the National Science Foundation for support of this work under Grants NSF G-7325 and G-21051 and to the Allied Chemical Corporation for a predoctoral fellowship to H. M. C.