TABLE I
VINYLTIN COMPOUNDS

Compound	B.p. or m.p. °C.	Mm.	d^{25}_4	n^{25}D	Analyses, % Calcd. Cl	Calcd. Sn	Found Cl	Found Sn
Tetravinyltin	55-57	17	1.267	1.4993		52.32		51.77
Di-*n*-butyldivinyltin	78-80	2	1.127	1.4824		41.36		41.20
Dimethyldivinyltin	120-121	760	1.284	1.4720		58.50		58.29
Diphenyldivinyltin	153-154	5	1.3195	1.5949		36.30		36.30
Tri-*n*-butylvinyltin	114	3	1.085	1.4761		37.44		37.37
Triphenylvinyltin	M. 39-40					31.48		31.11
n-Butylvinyltin dichloride	99-101 M. 27-28	3	1.533	1.5254	25.90	43.36	24.80	42.85
Divinyl-*n*-butyltin chloride	82-84	3	1.370	1.4970	13.36	44.73	13.33	44.51
Di-*n*-butylvinyltin chloride	112-114	4	1.266(20°)	1.4987(20°)	12.00	40.18	11.30	40.31

perature was maintained for 3.0 hr. longer by heating. Then a solution of 663.6 g. (3.5 moles) of tin tetrachloride in 10.8 l. of pentane was added at a rate to maintain reflux.[9] The addition took 4.0 hr. The mixture was refluxed for 5.0 hr.

On cooling, the reaction mixture was partially hydrolyzed by the cautious addition of 2.8 l. of 10% aqueous hydrochloric acid. At this point, a heavy solid[10] dropped out of the organic layer. The organic layer was decanted from the solid into a 22.0-l. flask. The hydrolysis was completed by the addition of 2.0 l. of water to the solid and two liquid phases resulted. The organic layer (*ca.* 300 ml.) was separated and added to the 22.0-l. flask. The solvents, pentane and tetrahydrofuran, were removed by rapid distillation at 1.0 atm. on a steam-bath. The residue was transferred to a 1.0-l. flask and carefully fractionally distilled under reduced pressure to yield: cut 1, b. 25-30° (100-120 mm.), 150 g. of tetrahydrofuran; cut 2, b. 55-57° (17 mm.), 642 g. (82%) of tetravinyltin.

2. **Di-*n*-butyldivinyltin.**—In a 5.0-l. flask equipped as above was placed 303.8 g. (1.0 mole) of di-*n*-butyltin dichloride in 2.0 l. of heptane. To this was added, at reflux, 2.5 moles of vinylmagnesium chloride in tetrahydrofuran over a 2.0-hr. period. The mix was refluxed an additional 4.0 hr. and worked-up as above to yield 254.0 g. (89%) of di-*n*-butyldivinyltin distilling at 78-80° (2.0 mm.).

3. **Triphenylvinyltin.**—In a 3.0-l. flask was placed 385.5 g. (1.0 mole) of triphenyltin chloride in 1.0 l. of heptane. Then 1.2 moles of vinylmagnesium chloride in tetrahydrofuran was added over a 2.0-hr. period at reflux followed by a 3.0-hr. reflux. The mix was hydrolyzed as above. The solvents were distilled at 1.0 atm. with the last traces taken off at water-pump pressure (20 mm.). A solid residue of 362.0 g. (93%) of crude product melting at 31-35° was obtained. This was recrystallized from methanol to yield 298.0 g. (79%) of triphenylvinyltin melting at 39-40°.

4. **Tri-*n*-butylvinyltin.**—In a 5.0-l. flask was placed 592.1 g. (1.0 mole) of bistri-*n*-butyltin oxide in 2.0 l. of heptane. Then 2.2 moles of vinylmagnesium chloride in tetrahydrofuran was added at a temperature of 70-80°. The mix was refluxed for 3.0 hr. and worked-up to yield 541.0 g. (85%) of tri-*n*-butylvinyltin distilling at 114° (3.0 mm.).

5. ***n*-Butylvinyltin Dichloride.**—In a 5.0-l. flask was placed 282.2 g. (1.0 mole) of *n*-butyltin trichloride in 2.5 l. of heptane. Then 1.0 mole of vinylmagnesium chloride in tetrahydrofuran was added over a 2.0-hr. period with the reaction temperature maintained between 25-40°. The mix was stirred for 3.0 hr. and filtered by suction through a Buchner funnel. The solvents were removed at 1.0 atm. and the residue carefully fractionally distilled under reduced pressure to yield 146.0 g. (53.5%) of *n*-butylvinyltin dichloride distilling at 99-101° (3.0 mm.).

6. **Divinyl-*n*-butyltin Chloride.**—In a 5.0-l. flask was placed 339.0 g. (1.2 moles) of *n*-butyltin trichloride in 2.5 l. of heptane. Then 2.4 moles of vinylmagnesium chloride in tetrahydrofuran was added, at reflux, over a 3.0-hr. period with stirring. On completion of addition, the mix was refluxed for 1.0 hr. and allowed to cool. Hydrolysis was accomplished as above. The organic phase was dried on sodium sulfate, freed of solvents at 1.0 atm. and carefully fractionally distilled under reduced pressure to yield 159.0 g. (50%) of divinyl-*n*-butyltin chloride distilling at 82-84° (3.0 mm.).

Acknowledgment.—The authors wish to thank Dr. Marie Farnsworth and her co-workers in the Physical and Analytical Section of this Laboratory for their assistance throughout this work.

RAHWAY, NEW JERSEY

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[9] At this point, two large water condensers were substituted for the thermometer and cold condenser, and the excess vinyl chloride was allowed to vent up the hood. A thorough study of solvent systems has been made and pentane at this relative concentration was found to give maximum yield of product.

[10] The solid is thought to be $MgCl_2 \cdot 6H_2O$.

[CONTRIBUTION FROM THE RAHWAY RESEARCH LABORATORY OF THE METAL AND THERMIT CORPORATION]

The Disproportionation of Tetravinyltin with Tin Tetrachloride and the Cleavage of Some Vinyltin Compounds with Bromine

BY SANDERS D. ROSENBERG AND AMBROSE J. GIBBONS, JR.

RECEIVED OCTOBER 29, 1956

Vinyltin trichloride, divinyltin dichloride and trivinyltin chloride have been prepared in excellent yields by the low temperature disproportionation of tetravinyltin with tin tetrachloride. Dibutyldivinyltin, dimethyldivinyltin and diphenyldivinyltin have been subjected to bromine cleavage, and it has been found that the ease of displacement of these groups from tin is phenyl > vinyl > methyl > butyl. Divinyltin oxide and trivinyltin hydroxide have been prepared by the hydrolysis of divinyltin dichloride and trivinyltin chloride, respectively, with aqueous sodium hydroxide.

The preparation of organotin chlorides by the disproportionation of symmetrical tetrasubstituted organotin compounds with tin tetrachloride has been reported by a number of workers.[1-3] Conditions have been outlined for the synthesis of such compounds as di-*n*-butyltin dichloride,[1,3] di-*n*-hexyltin dichloride[3] and triphenyltin chloride.[2]

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[1] W. J. Jones, W. C. Davies, S. T. Bowden, C. Edwards, V. E. Davies and L. H. Thomas, *J. Chem. Soc.*, 1446 (1947).

[2] H. Gilman and S. D. Rosenberg, THIS JOURNAL, **74**, 5580 (1952).

[3] E. W. Johnson and J. M. Church, U. S. Patent 2,672,471, 1954.

In general the method involves heating the tetrasubstituted organotin compound with tin tetrachloride at 200–240° for 1–3 hr. at 1.0 atmosphere.

$$3R_4Sn + SnCl_4 \longrightarrow 4R_3SnCl$$

$$R_4Sn + SnCl_4 \longrightarrow 2R_2SnCl_2$$

The product is purified by distillation under reduced pressure and/or recrystallization from a suitable solvent.

In the course of research in this Laboratory on the preparation of vinyltin compounds,[4] a need arose for vinyltin chlorides. As it was known that tetravinyltin was not stable at temperatures over 200°, it was decided to investigate the utility of the disproportionation reaction at low temperatures. It was found that vinyltin trichloride, divinyltin dichloride and trivinyltin chloride could be prepared in virtually quantitative yields simply by stirring tetravinyltin with tin tetrachloride, in stoichiometric quantities, for several hours and

$$(CH_2{=}CH)_4Sn + 3SnCl_4 \xrightarrow{75\text{–}90°} 4CH_2{=}CHSnCl_3$$

$$(CH_2{=}CH)_4Sn + SnCl_4 \xrightarrow{0\text{–}10°} 2(CH_2{=}CH)_2SnCl_2$$

$$3(CH_2{=}CH)_4Sn + SnCl_4 \xrightarrow{35\text{–}40°} 4(CH_2{=}CH)_3SnCl$$

isolating the products by distillation under reduced pressure. The disproportionation took place with equal facility over a wide temperature range (0–150°).

Vinyltin trichloride and divinyltin dichloride are stable compounds, but it was found, after a series of vacuum distillations on a 3′-glass helix packed column, that trivinyltin chloride tends to rearrange to form divinyltin dichloride and tetravinyltin. Therefore, it is suggested that the crude trivinyltin chloride be used as such for the preparation of derivatives.

$$2(CH_2{=}CH)_3SnCl \longrightarrow (CH_2{=}CH)_2SnCl_2 + (CH_2{=}CH)_4Sn$$

Cleavage studies on organotin compounds with halogen[5] and halogen acid[6] have shown that the ease of displacement of organic groups from tin is α-thienyl > *p*-tolyl > phenyl > methyl > *n*-butyl > *n*-octyl. It was of interest to ascertain the relative position of the vinyl group in this series. Di-*n*-butyldivinyltin, dimethyldivinyltin and diphenyldivinyltin were allowed to react with bromine at 10–15°. The results are summarized in Table I. It was found that the preferential or-

$$R_2R_2'Sn + Br_2 \begin{array}{l} \nearrow R_2R'SnBr + R'Br \\ \searrow RR'_2SnBr + RBr \end{array}$$

der of cleavage of these groups from tin is phenyl > vinyl > methyl > butyl.

TABLE I

REACTION OF VINYLTIN COMPOUNDS WITH BROMINE

Vinyltin compound	Products isolated
$(n\text{-}C_4H_9)_2Sn(CH{=}CH_2)_2$	$CH_2{=}CHBr$ (60%) $(n\text{-}C_4H_9)_2(CH_2{=}CH)SnBr$ (78%)
$(CH_3)_2Sn(CH{=}CH_2)_2$	$CH_2{=}CHBr$ (69%) $(CH_2{=}CH)(CH_3)_2SnBr$ (88%)[a]
$(C_6H_5)_2Sn(CH{=}CH_2)_2$	C_6H_5Br (90%) $(CH_2{=}CH)_2(C_6H_5)SnBr$[b]

[a] *Anal.* Calcd. for C_4H_9BrSn: Br, 31.25. Found: Br, 30.92; b.p. 72° (21.0 mm.). This compound gave evidence of disproportionation on prolonged distillation under reduced pressure. [b] This compound was not isolated as it apparently disproportionated on distillation under reduced pressure (20 mm.). The main products isolated were diphenyltin dibromide, divinyltin dibromide and trivinyltin bromide.

Experimental

1. **Vinyltin Trichloride.**—In a 500-ml. flask was placed 50.0 g. (0.22 mole) of tetravinyltin. To this was added, with good stirring and over a 2.25-hr. period, 187.6 g. (0.66 mole plus 10%) of tin tetrachloride at a pot temperature of 30°. The solution was then heated to and maintained at 70° for 2.0 hr. and distilled to yield: cut 1, b.p. 115–125° (760 mm.), 32 g. of crude tin tetrachloride; cut 2, b.p. 64–65° (15 mm.), 190.0 g. (86%) of vinyltin trichloride.

Anal. Calcd. for $C_2H_3Cl_3Sn$: Cl, 42.19; Sn, 47.08. Found: Cl, 41.55; Sn, 47.13; $n^{25}D$ 1.5361; d^{25}_4 1.9981.

2. **Divinyltin Dichloride.**—In a 2.0-l. flask was placed 340.5 g. (1.5 moles) of tetravinyltin. To this was added, with good stirring and over a 2.25-hr. period, 390.8 g. (1.5 moles) of tin tetrachloride at a pot temperature of 30°. The solution was then stirred for 2.0 hr. and carefully fractionally distilled under reduced pressure to yield 718.0 g. (98%) of divinyltin dichloride distilling at 54–56° (3.0 mm.).

Anal. Calcd. for $C_4H_6Cl_2Sn$: Cl, 29.10; Sn, 48.71. Found: Cl, 28.81; Sn, 48.71; m.p. 13.2°; $n^{25}D$ 1.5490; d^{20}_4 1.7645.

3. **Trivinyltin Chloride.**—In a 2.0-l. flask was placed 600.0 g. (2.64 moles) of tetravinyltin. To this was added, with good stirring and over a 1.0-hr. period, 229.0 g. (0.88 mole) of tin tetrachloride at a pot temperature of 30°. The solution was stirred for 2.0 hr. and rapidly distilled under reduced pressure to yield 795.0 g. (96%) of trivinyltin chloride distilling at 59–60° (6.0 mm.).

Anal. Calcd. for C_6H_9ClSn: Cl, 15.07; Sn, 50.45. Found: Cl, 14.68; Sn, 50.50; $n^{25}D$ 1.5235; d^{20}_4 1.5139.

4. **Di-*n*-butylvinyltin Bromide.**—In a 500-ml. flask was placed 102.6 g. (0.358 mole) of di-*n*-butyldivinyltin. To this was added, with good stirring and over a 2.0-hr. period, 57.0 g. (0.357 mole) of bromine. Each drop of bromine was decolorized instantly on reaching the solution and the reaction was vigorous.

The solution was then carefully fractionally distilled in an adequately trapped system to yield: cut 1, b.p. 14–17° (760 mm.), 22.7 g. (59.5%) of vinyl bromide; cut 2, b.p. 72–73° (0.03 mm.), 82.7 g. (68.4%) of di-*n*-butylvinyltin bromide; cut 3, pot residue, 13.4 g. (9.1%) of crude di-*n*-butyltin dibromide.

Anal. Calcd. for $C_{10}H_{21}BrSn$: Br, 23.55; Sn, 34.98. Found: Br, 24.28; Sn, 34.63; $n^{25}D$ 1.4970; d^{25}_4 1.3913. Calcd. for $C_8H_{18}Br_2Sn$: Br, 40.60; Sn, 30.18. Found: Br, 39.58; Sn, 30.54.

In a second run 58.6 g. (0.368 mole) of bromine in 184 ml. of CCl_4 was added to 105.3 g. (0.368 mole) of di-*n*-butyldivinyltin in 184 ml. of CCl_4 with good stirring over a 2.0-hr. period at 15°. A total of 99.5 g. (78%) of di-*n*-butylvinyltin bromide and 17.3 g. (12%) of di-*n*-butyltin dibromide was obtained.

5. **Trivinyltin Hydroxide and Divinyltin Oxide.**—In a 500-ml. flask was placed 25.0 g. (0.625 mole) of sodium hydroxide in 300 ml. of water. To this was added, with good stirring and over a 0.5-hr. period, 100.0 g. (0.425 mole) of trivinyltin chloride. A white solid formed immediately. After stirring for 1.0 hr., the solid filtered from the reaction solution under nitrogen was dried under reduced pressure over potassium hydroxide pellets in a vacuum desiccator. A total of 68.0 g. (74%) of trivinyltin hydroxide melting at 67.5–69.0° was obtained.

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(4) S. D. Rosenberg, A. J. Gibbons, Jr., and H. E. Ramsden, THIS JOURNAL, **79**, 2137 (1957).

(5) Z. M. Manulkin, *J. Gen. Chem. (U.S.S.R.)*, **11**, 386 (1941); **13**, 42 (1943); **14**, 1047 (1944); **16**, 235 (1946).

(6) Ch. Bobashinskaya and K. A. Kocheskov, *ibid.*, **8**, 1850 (1938).

Anal. Calcd. for $C_6H_{10}OSn$: Sn, 54.75. Found: Sn, 54.11.

Similarly divinyltin oxide (42%) has been prepared from divinyltin dichloride and aqueous sodium hydroxide.

Anal. Calcd. for C_4H_6OSn: Sn, 62.95. Found: Sn, 62.60.

Acknowledgments.—The authors wish to thank Dr. Marie Farnsworth and her co-workers in the Physical and Analytical Section of this Laboratory for their assistance throughout this work.

RAHWAY, NEW JERSEY

[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORIES OF THE AMERICAN SMELTING AND REFINING COMPANY AND THE RESEARCH LABORATORIES OF E. F. HOUGHTON & CO.]

Arsonosiloxanes[1]

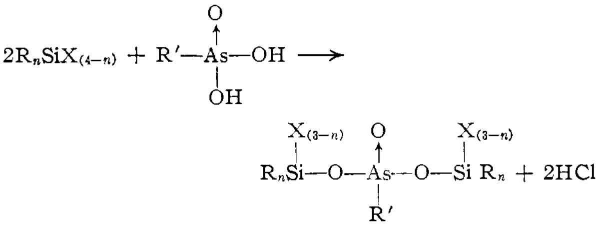
BY ROLAND M. KARY AND KURT C. FRISCH

RECEIVED APRIL 25, 1956

The well-known silicones, such as polymethylsiloxanes, do not exhibit pesticidal properties. Organic arsenical siloxanes could be used to control pest organism in addition to already existing utilities of conventional silicones. It was found that arsenic can be incorporated into siloxane structures by formation of Si–O–As bonds from a novel reaction between organic chlorosilanes and organic arsonic acids. Formation of arsonosiloxane polymers from hydrolysis of chlorosilylarsonates appears to be feasible. Methyl- and phenylchlorosilylarsonates were synthesized and hydrolyzed to the corresponding arsenical siloxane derivatives. Compounds found were identified by chemical analysis and infrared absorption characteristics.

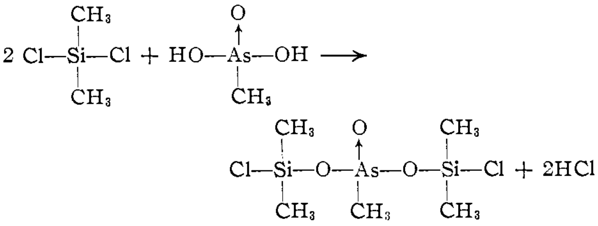
The well-known utilities of silicones, particularly of methylsilicones, do not include action toward pest organisms. Organic arsenical siloxane derivatives could conceivably exhibit pesticidal properties which would add numerous possibilities of applications to those already existing. Therefore, the investigation of organic arsenical silanes and siloxane derivatives was undertaken in order to prepare compounds containing Si–O–As bonds. It was found that methyl- and phenylchlorosilanes react with methyl- and phenylarsonic acids in the presence of an inert solvent such as benzene or carbon tetrachloride, at the temperature of 80° at which these solvents are kept refluxing for about 24 hr. under agitation.

As is shown by the following equation, 2 moles of chlorosilane react with one mole arsonic acid to form a "bis" or neutral chlorosilylarsonate and 2 moles of hydrochloric acid



$$2R_nSiX_{(4-n)} + R'{-}\underset{OH}{\overset{O\,\uparrow}{As}}{-}OH \longrightarrow R_n\overset{X_{(3-n)}}{Si}{-}O{-}\underset{R'}{\overset{O\,\uparrow}{As}}{-}O{-}\overset{X_{(3-n)}}{Si}\,R_n + 2HCl$$

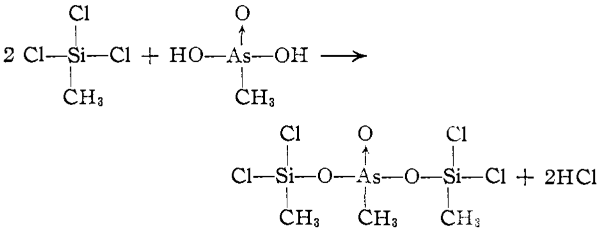
Thus, the reaction between dimethyldichlorosilane and methylarsonic acid resulted in bis-(dimethylchlorosilyl)-methylarsonate (I), shown by the equation



$$2\,Cl{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}Cl + HO{-}\underset{CH_3}{\overset{O\,\uparrow}{As}}{-}OH \longrightarrow Cl{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}\underset{CH_3}{\overset{O\,\uparrow}{As}}{-}O{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}Cl + 2HCl$$

I

In similar manner, bis-(methyldichlorosilyl)-methylarsonate (II) was prepared from methyltrichlorosilane and methylarsonic acid

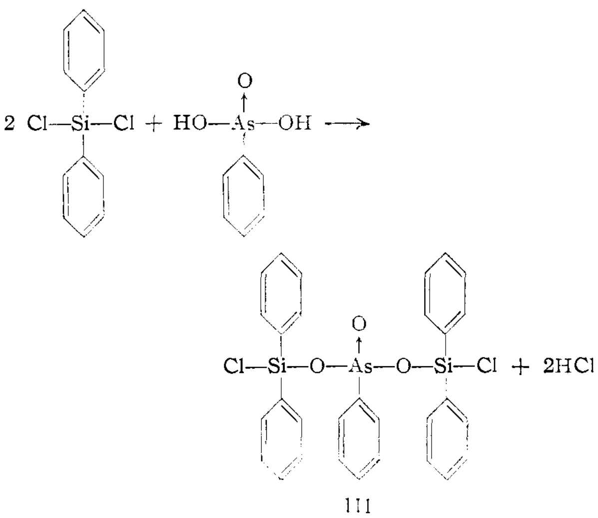


$$2\,Cl{-}\underset{CH_3}{\overset{Cl}{Si}}{-}Cl + HO{-}\underset{CH_3}{\overset{O\,\uparrow}{As}}{-}OH \longrightarrow Cl{-}\underset{CH_3}{\overset{Cl}{Si}}{-}O{-}\underset{CH_3}{\overset{O\,\uparrow}{As}}{-}O{-}\underset{CH_3}{\overset{Cl}{Si}}{-}Cl + 2HCl$$

II

These reactions were carried out in 2:1 molar ratio of chlorosilane and methylarsonic acid. If a 1:1 molar ratio was employed, poor yields of the "bis" compounds were obtained, together with considerable amounts of unreacted starting materials.

Essentially, the same method was used to prepare the corresponding phenyl derivatives. Bis-(diphenylchlorosilyl)-phenylarsonate (III) was synthesized from diphenyldichlorosilane and phenyl arsonic acid



III

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[1] Presented at the 129th Meeting of The American Chemical Society, Dallas, Texas.