ORGANIC AND BIOLOGICAL CHEMISTRY

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

The Preparation of Some Vinyltin Compounds with Vinylmagnesium Chloride

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Tetravinyltin, dibutyldivinyltin, dimethyldivinyltin, diphenyldivinyltin, tributylvinyltin, triphenylvinyltin, butylvinyltin dichloride, dibutylvinyltin chloride and divinylbutyltin chloride have been prepared by the reaction of vinylmagnesium chloride with appropriate tin chlorides. In addition, dibutyldivinyltin and tributylvinyltin have been synthesized from vinylmagnesium chloride and dibutyltin oxide and bistributyltin oxide, respectively.

The development of vinylmagnesium chloride in this Laboratory[1] has made possible the synthesis of vinyltin compounds by classical Grignard techniques. The only vinyltin compounds previously reported in the literature are vinyltin tribromide[2] and several 2-chlorovinyltin compounds.[3,4]

Four general methods have been developed for the synthesis of organotin compounds: 1, the complete replacement of the halogen of tin tetrachloride or organotin halides by use of an active organometallic compound; 2, the stepwise partial replacement of the halogen of organotin halides by use of an active organometallic compound; 3, the disproportionation of symmetrical tetrasubstituted organotin compounds with tin tetrachloride; 4, the cleavage of organotin compounds with halogen or halogen acid. The use of the first two methods in the preparation of vinyltin compounds will be reported here and of the last two in a subsequent article.

Tetravinyltin (82%), di-*n*-butyldivinyltin (89%), dimethyldivinyltin (75%), diphenyldivinyltin (73%), tri-*n*-butylvinyltin (82%) and triphenylvinyltin (79%) have been prepared by the reaction of vinylmagnesium chloride in tetrahydrofuran solution with the appropriate tin halide in a hydrocarbon solvent. These compounds, with the exception of triphenylvinyltin, were purified by distillation under reduced pressure to give colorless liquids. Triphenylvinyltin, a colorless solid, was crystallized from ethanol.

$$4CH_2{=}CHMgCl + SnCl_4 \longrightarrow (CH_2{=}CH)_4Sn + 4MgCl_2$$

$$2CH_2{=}CHMgCl + (n\text{-}C_4H_9)_2SnCl_2 \longrightarrow (n\text{-}C_4H_9)_2Sn(CH{=}CH_2)_2 + 2MgCl_2$$

$$CH_2{=}CHMgCl + (C_6H_5)_3SnCl \longrightarrow (C_6H_5)_3SnCH{=}CH_2 + MgCl_2$$

n-Butylvinyltin dichloride (54%), divinyl-*n*-butyltin chloride (50%) and di-*n*-butylvinyltin chloride (56%) have been synthesized by the stepwise substitution of *n*-butyltin trichloride and di-*n*-butyltin dichloride, respectively, with vinylmagnesium chloride. The problem in this approach was one of limiting the substitution to a stepwise vinylation. Failure to do this led to a separation step in which the product had to be won from unreacted starting material and/or the completely substituted vinyltin compound. It was this difficult separation that caused the yield of desired product to be lower than in the preparation of completely substituted compounds.

$$CH_2{=}CHMgCl + n\text{-}C_4H_9SnCl_3 \longrightarrow (n\text{-}C_4H_9)(CH_2{=}CH)SnCl_2 + MgCl_2$$

$$2CH_2{=}CHMgCl + n\text{-}C_4H_9SnCl_3 \longrightarrow (CH_2{=}CH)_2(n\text{-}C_4H_9)SnCl + 2MgCl_2$$

$$CH_2{=}CHMgCl + (n\text{-}C_4H_9)_2SnCl_2 \longrightarrow (n\text{-}C_4H_9)_2(CH_2{=}CH)SnCl + MgCl_2$$

In a search for a shorter preparative method, it was found that di-*n*-butyldivinyltin could be prepared in a 58% yield from di-*n*-butyltin oxide[5] and vinylmagnesium chloride. Similarly tri-*n*-butylvinyltin (85%) was synthesized from bistri-*n*-butyltin oxide[5] and vinylmagnesium chloride.

$$2CH_2{=}CHMgCl + (n\text{-}C_4H_9)_2SnO \longrightarrow (n\text{-}C_4H_9)_2Sn(CH{=}CH_2)_2 + (MgCl)_2O$$

$$2CH_2{=}CHMgCl + (n\text{-}C_4H_9)_6Sn_2O \longrightarrow 2(n\text{-}C_4H_9)_3SnCH{=}CH_2 + (MgCl)_2O$$

These results demonstrate that the oxide bond in organotin compounds, and most likely in other similar organometallic compounds, is very different from those encountered in the chemistry of carbon. These oxides behave like the halides and esters of silicon and tin and undergo similar nucleophilic substitution reactions.

Experimental

Starting Materials.—Commercial tin tetrachloride was redistilled through a short column. Du Pont tetrahydrofuran and Matheson vinyl chloride were used without additional purification. Dow Grignard grade magnesium turnings were used. Triphenyltin chloride, diphenyltin dichloride, butyl trichloride, dibutyltin dichloride, tributyltin chloride and dimethyltin dichloride were obtained by disproportionation of the corresponding tetrasubstituted compounds.[6,7]

1. Tetravinyltin.—In a 22.0-l. flask[8] was placed 394.0 g. (16.2 g. atoms) of magnesium turnings. To this was added 100 ml. of a solution of 1212 g. (19.4 moles) of vinyl chloride in 3460 g. (48 moles) of tetrahydrofuran. The reaction was initiated by heating the flask to cause reflux, followed by the addition of 2.0 ml. of ethyl bromide. Once thoroughly initiated, the heating was stopped and the remainder of the mix added at a rate to maintain a pot temperature of 48–56°. The addition took 6.0 hr. The tem-

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[1] H. E. Ramsden, J. R. Leebrick, S. D. Rosenberg, E. H. Miller, J. J. Walburn, A. E. Balint and R. Cserr, unpublished.

[2] A. Solerio, *Gazz. chim. ital.*, **85**, 61 (1955).

[3] A. N. Nesmeyanov, A. E. Borisov and A. N. Abramova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 647 (1946).

[4] We have learned in a private communication from Dr. D. Seyferth of the Chemistry Department of Harvard University that several vinyltin compounds have been synthesized recently by his group utilizing vinylmagnesium bromide, THIS JOURNAL, **79**, 2133 (1957).

[5] This compound is commercially available at the Rahway Chemical Plant of the Metal and Thermit Corporation.

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

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

[8] The flask was equipped with a swivel anchor stirrer ($^3/_8$" blade on $^3/_8$" shaft, stainless steel), a 2.0-l. dropping funnel, an extra large Dry Ice–acetone cold condenser and a thermometer.

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	3	1.533	1.5254	25.90	43.36	24.80	42.85
	M. 27–28							
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.).

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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 $MgCl_2 \cdot 6H_2O$.

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

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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.