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Vinyl Derivatives of the Metals. I. Synthesis of Vinyltin Compounds

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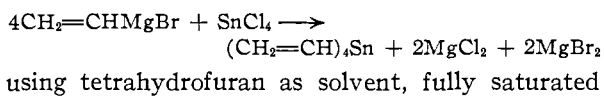
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The synthesis of alkyl- and arylvinyltin compounds and of allyltrimethyltin by the Grignard method, and of the vinyltin chlorides by the Kocheshkov procedure is described. Solid derivatives of divinyltin dichloride and dimethyltin dichloride have been prepared. The vinyltin compounds show good thermal stability.

A brief consideration of some of the properties of vinylsilicon compounds led to the suggestion that there may be d_{π} - p_{π} bonding between the π -electrons of the vinyl group and the vacant 3d orbitals of the silicon atoms in compounds such as triphenylvinylsilane and trimethylvinylsilane.¹ Similarly, it has been found² that in molecules where a vinyl group is adjacent to a boron atom having sp^2 -hybridization, the properties of the resulting molecule may best be understood if it is assumed that π -bonding arises through p_{π} -electrons of the vinyl group entering the vacant boron p_{π} -orbital. It would seem, therefore, from what is thus far known of the vinyl chemistry of silicon and boron, that when a vinyl group is bonded to a metal possessing a vacant p_{π} - or d_{π} -orbital, the organometallic compound may possibly display interesting physical and chemical properties.

For this reason, we are undertaking a wide study of vinyl derivatives of metals and metalloids of Groups III, IV and V, as well as of vinyl derivatives of some sub-group metals. We have begun our work with a study of the preparation, properties and some reactions of vinyltin compounds.

Although a number of allyltin compounds have been reported,³⁻⁶ only one vinyl derivative, vinyltin tribromide,⁶ and a few 2-chlorovinyltin compounds⁷ have been prepared. Vinyltin tribromide was prepared by the reaction of vinyl bromide with a sodium stannite solution, followed by treatment of the resulting crude vinylstannonic acid with concentrated hydrobromic acid. This method is suitable only for preparing monovinyl compounds. We have found that vinyltin compounds of the types $(\text{Vinyl})_n\text{Sn}(\text{Alkyl})_{4-n}$ and $(\text{Vinyl})_n\text{Sn}(\text{Aryl})_{4-n}$ ($n = 1-3$) may be prepared by treating organotin halides with excess of vinylmagnesium bromide,⁸ using the relatively basic ether tetrahydrofuran as solvent. The method was applied to a variety of tin compounds, and the yields of desired product ranged from 70-85%. When tin(IV) chloride was treated with the vinyl Grignard reagent the interesting compound tetravinyltin was obtained. Our work with the vinyl derivatives led to the discovery that by



(1) (a) F. G. A. Stone and D. Seyferth, *J. Inorg. Nuclear Chem.*, **1**, 112 (1955); (b) M. Kanazashi, *Bull. Chem. Soc. Japan*, **28**, 44 (1955).

(2) T. D. Parsons and D. M. Ritter, *This Journal*, **76**, 1710 (1954).

(3) K. V. Vijayaraghavan, *J. Ind. Chem. Soc.*, **22**, 135 (1945).

(4) W. J. Jones, *et al.*, *J. Chem. Soc.*, 1446 (1947).

(5) H. Gilman and J. Eisch, *J. Org. Chem.*, **20**, 763 (1955).

(6) A. Solerio, *Gazz. chim. ital.*, **85**, 61 (1955).

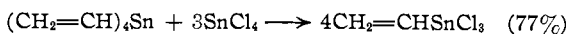
(7) A. N. Nesmeyanov, A. E. Borisov and A. N. Abramova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 647 (1946); 570 (1949).

(8) H. Normant, *Compt. rend.*, **239**, 1510 (1954).

tetralkyltin compounds, such as tetraethyltin or dimethyldiethyltin, also could be prepared by the Grignard method with less trouble than when diethyl ether is used as a solvent, and comparable yields are obtained.

With the exception of triphenylvinyltin, the vinyl compounds are colorless liquids with pleasant odors. They all show good thermal stability. Indeed, it was found that tetravinyltin could be distilled at atmospheric pressure in the absence of any polymerization inhibitor. Some decomposition occurred, however, when the still-pot temperature approached 200°. Other vinyltin compounds were similarly found to be completely stable in air, and in water or dilute acid solution. This is in striking contrast to the instability of allyltin compounds. The latter must be distilled under reduced pressure in an inert atmosphere.⁴ Similarly, when we prepared the hitherto unreported compound allyltrimethyltin, distillation in air at atmospheric pressure resulted in a yield of only 14%. However, once this compound had been distilled, it appeared to be quite stable in air at room temperature, no change in refractive index being detected over a period of several months.

Because of the realization that the Grignard method is unsuitable for preparing alkyltin chlorides,⁹ the preparation of vinyltin compounds, $(\text{CH}_2=\text{CH})_n\text{SnCl}_{4-n}$ (where $n = 1-3$) was accomplished using the method developed by Kocheshkov¹⁰ for the synthesis of alkyltin chlorides. For the latter synthesis it is necessary to heat the tetraalkyltin compound with tin(IV) chloride for a prolonged period at temperatures from 185 to 200°. However, when tetravinyltin was heated with tin(IV) chloride at these temperatures, the major reaction product was a grey solid,¹¹ and only low yields of the desired vinyltin chlorides were obtained. Nevertheless, it was found that by using a much shorter heating time and temperatures of from 90 to 100° tetravinyltin and tin(IV) chloride reacted smoothly, giving good yields of the desired products, as in



Of the three vinyltin chlorides only divinyltin dichloride is a crystalline solid. Vinyltin trichloride is a heavy liquid that fumes strongly in moist air, while trivinyltin chloride, also a liquid, has the strong lachrymatory properties associated with all

(9) E. Krause and A. von Grosse, "Die Chemie der metallorganischen Verbindungen," Borntraeger, Berlin, 1937, pp. 335-342.

(10) K. A. Kocheshkov, *Ber.*, **66**, 1661 (1933).

(11) The grey solid is probably a mixture of tin metal and tin(II) chloride. See J. G. A. Luitjen and G. J. M. van der Kerk, "Investigations in the Field of Organotin Chemistry," Tin Research Institute, Greenford, England, 1955, p. 106.

TABLE I

VINYL TIN COMPOUNDS PREPARED BY THE GRIGNARD METHOD TOGETHER WITH SOME OF THEIR DERIVATIVES

Compound	Boiling range		M.p., °C.	d_{25}^4	n_{25}^D	$M R_D^b$		Carbon, % ^c		Hydrogen, %	
	°C.	Mm.				Calcd.	Found	Calcd.	Found	Calcd.	Found
$\text{CH}_2=\text{CH})_2\text{Sn}$	{ 160-163 67-70 }	{ 766 28 }		1.246	1.4914	53.43	52.77	42.35	42.45	5.33	5.62
$(\text{CH}_3)_3\text{SnCH}=\text{CH}_2$	99-100	760		1.265	1.4544	40.92	40.89	31.46	31.13	6.34	6.35
$(\text{CH}_3)_2\text{Sn}(\text{CH}=\text{CH}_2)_2$	118.5-120	759		1.265	1.4701	45.09	44.75	35.52	35.02	5.97	5.99
$(\text{C}_2\text{H}_5)_2\text{SnCH}=\text{CH}_2$	60-62	13-12		1.198	1.4738	54.86	54.63	41.25	41.49	7.79	7.98
$\text{CH}_3(\text{C}_2\text{H}_5)_2\text{SnCH}=\text{CH}_2$	56-59	26		1.222	1.4697	50.22	49.97	38.41	38.68	7.37	7.44
$(n\text{-C}_4\text{H}_9)_2\text{SnCH}=\text{CH}_2$	95	1.5		1.081	1.4751	82.75	82.62	53.03	52.85	9.54	9.48
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{CH}=\text{CH}_2)_2$	54-55	0.35		1.122	1.4797	72.98	72.64	50.21	50.03	8.43	8.18
$n\text{-C}_4\text{H}_9\text{Sn}(\text{CH}=\text{CH}_2)_3$	77-78	8.6-8.5		1.174	1.4851	63.20	62.76	46.74	46.97	7.06	7.27
$(\text{C}_6\text{H}_5)_2\text{SnCH}=\text{CH}_2$			45.2-45.4					63.71	63.94	4.81	4.85
$\text{C}_6\text{H}_5\text{Sn}(\text{CH}=\text{CH}_2)_3$	73-75	0.45		1.282	1.5478	68.74	68.58	52.04	51.92	5.10	5.25
$(\text{CH}_3)_3\text{SnCH}_2\text{CH}=\text{CH}_2$	128-129	767		1.248	1.4741	45.57	46.13	35.17	35.52	6.89	7.04
$(\text{CH}_2=\text{CH})_2\text{SnCl}$	90-96	26			1.5237			30.63	30.87	3.86	4.14
$(\text{CH}_2=\text{CH})_2\text{SnCl}_2^g$			74.5-75.5					19.71	19.66	2.48	2.74
$\text{CH}_2=\text{CHSnCl}_2^f$	48-50	5.2-5.3						9.53	9.71	1.20	1.29
$(\text{CH}_2=\text{CH})_2\text{Sn}(\text{SCN})_2$			163.6-165 dec.					24.94	24.77	2.09	2.18
$(\text{CH}_2=\text{CH})_2\text{SnO}$			>345 ^d					25.45	25.68	3.20	3.22
$(\text{CH}_2=\text{CH})_2\text{Sn}[\text{C}_6\text{H}_4(\text{CO}_2)_2\text{-}o]$			283 dec.					42.78	42.91	2.99	2.97
$(\text{CH}_2=\text{CH})_2\text{SnO}_2\text{PC}_6\text{H}_5$			>355					36.52	36.71	3.37	3.43
$\text{CH}_3(\text{C}_2\text{H}_5)_2\text{SnBr}$	95-98	11						22.10	21.86	4.82	4.87

^a All melting points were determined using a Hershberg melting point apparatus. ^b Bond refraction values from A. I. Vogel, *et al.*, *J. Phys. Chem.*, 58, 174 (1954). ^c Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, New York. ^d Color change from white to yellow to tan above 310°. ^e % Cl: calcd., 29.10; found, 29.04. ^f % Cl: calcd., 42.19; found, 42.00.

the lower trialkyltin halides. Vinyltin trichloride and divinyltin dichloride are readily soluble in water, as well as in organic solvents.

Several derivatives of divinyltin dichloride have been prepared by metathetical reactions in aqueous solution, using techniques similar to those applied to the preparation of dimethyltin compounds.¹² In addition, several new dimethyltin compounds containing phosphorus in the anion, as well as the compound di-*n*-butyltin di-*p*-toluenesulfonate, are reported here for the first time.

All the new vinyltin compounds prepared in this work, as well as the new compound diethylmethyltin bromide are listed, with their physical properties and analytical data, in Table I.

The reactions that occur between vinyltin compounds and the halogens, metal salts, hydrogen halides and organic acids, as well as addition and polymerization reactions, will be published shortly.

Experimental

1. **Starting Materials.**—Trimethyltin bromide, triethyltin bromide and diethylmethyltin bromide were prepared by bromination of tetramethyltin, tetraethyltin and dimethyldiethyltin, respectively, at -40° .⁹ Triphenyltin chloride was prepared¹³ from tetraphenyltin and tin(IV) chloride, and dimethyltin dichloride by the direct reaction between methyl chloride and tin metal.¹⁴ Grossly impure phenyltin trichloride was obtained from the reaction of triphenylvinyltin with tin(IV) chloride.

2. **Vinylation by the Grignard Method.**—As an example the preparation of an alkyl(vinyl)tin compound the method used for vinyl-tri-*n*-butyltin is given here.

Vinylmagnesium bromide was prepared by the usual procedure for Grignard reagents. Thus 61 g. (0.61 mole) of vinyl bromide was added to 14.6 g. (0.61 g. atom) of magnesium turnings in 500 ml. of tetrahydrofuran, the latter having been distilled from lithium aluminum hydride to remove water and peroxides. A Dry Ice condenser was used, and addition of a few drops of methyl iodide sufficed to initiate the reaction. When the Grignard preparation was completed, the condenser, at -78° , was replaced with a water condenser, and 107.5 g. (0.33 mole) of tri-*n*-butyltin chloride, dissolved in an equal volume of tetrahydrofuran,

was added at such a rate that a gentle reflux was maintained. After the addition was completed, the reaction mixture was refluxed for 19 hours. It subsequently was cooled to room temperature, and hydrolyzed by addition of 100 ml. of a saturated aqueous solution of ammonium chloride.

The orange organic layer was decanted, and the residual salts washed with several portions of diethyl ether. The ether washings were combined with the organic layer and the mixture was distilled at atmospheric pressure to remove solvents. The residue was fractionally distilled at reduced pressure. In this manner, 88.4 g. (yield 84.5%) of vinyltri-*n*-butyltin was obtained.

All other liquid vinyltin compounds were prepared using the method described above. Experimental results are presented in Table II.

TABLE II

VINYLATION BY THE GRIGNARD METHOD, EXPERIMENTAL

Tin halide, moles	$\text{CH}_2=\text{CHMgBr}$, moles	Reflux time, hr.	Yield, %
SnCl_4	0.4	22	74
$(\text{CH}_3)_3\text{SnBr}$.413	18	68
$(\text{CH}_3)_2\text{SnCl}_2$.33	20	79
$(\text{C}_2\text{H}_5)_2\text{SnBr}$.28	20	85
$\text{CH}_3(\text{C}_2\text{H}_5)_2\text{SnBr}$.213	20	77
$(n\text{-C}_4\text{H}_9)_2\text{SnCl}$.33	19	85
$(n\text{-C}_4\text{H}_9)_2\text{SnCl}_2$.214	20	85
$n\text{-C}_4\text{H}_9\text{SnCl}_3$.21	20	84
$(\text{C}_6\text{H}_5)_2\text{SnCl}$.25	27	82
$\text{C}_6\text{H}_5\text{SnCl}_3$.116	20	38

Triphenylvinyltin was isolated by chilling to -78° the oil which remained after the solvents had been removed, and recrystallizing the waxy solid so obtained from an ethanol-methanol mixture at -78° .

3. **Preparation of Vinyltin Chlorides.** (a) **Vinyltin Trichloride.**—A 35.7-g. (0.157 mole) sample of tetravinyltin was added to a flask containing 123.0 g. (0.471 mole) of tin(IV) chloride. The flask was immediately fitted with an air condenser, to the exit of which a drying tube, filled with Drierite, was attached. A vigorous reaction commenced immediately after the addition. The temperature rose rapidly to 120° , and the whole mixture turned from colorless to brown. Subsequently the reaction mixture was heated on a steam-bath for 3.5 hours. Filtration through a sintered-glass funnel removed the small amount of grey solid which formed. Fractional distillation at reduced pressure yielded first a small quantity of white crystals; then 122.2 g. (yield 77%) of vinyltin trichloride boiling from 48° (5.2 mm.) to 55° (5.1 mm.) was obtained.

(12) E. G. Rochow, D. Seyferth and A. C. Smith, *THIS JOURNAL*, 75, 3099 (1953).

(13) H. Gilman and S. D. Rosenberg, *ibid.*, 74, 5580 (1952).

(14) A. C. Smith and E. G. Rochow, *ibid.*, 75, 4103 (1953).

(b) **Divinylytin Dichloride.**—To 30 g. (0.134 mole) of tetravinylytin in a flask equipped as described above was added 34.4 g. (0.134 mole) of tin(IV) chloride. The temperature rose rapidly to ca. 110° and the mixture turned brown. The reaction mixture was then heated on the steam-bath for 3.5 hours. After the heating period it was cooled in an ice-bath. A brown semi-solid slush resulted. Addition of a little 30–60° petroleum ether, cooling to 0° and filtration gave 45 g. of crude vinylytin dichloride, a yield of 70%. Three recrystallizations from 30–60° petroleum ether of a small quantity of the product gave fluffy, white needles, which melted at 74.5 to 75.5°.

(c) **Trivinylytin Chloride.**—To a 32.7-g. (0.144 mole) sample of tetravinylytin was added 12.5 g. (0.048 mole) of tin(IV) chloride. The temperature immediately rose to 80° and the mixture turned yellow. After heating the mixture for 3.5 hours at 90–100°, fractional distillation gave 19.7 g. of crude trivinylytin chloride, b.p. 86–97° at 26 mm., a yield of 43.6%. The still-pot residue (11.0 g.) solidified on cooling. Recrystallization from 30–60° petroleum ether gave a 22% yield of pure divinylytin dichloride.

(d) **High Temperature Redistribution.**—As an example the attempted preparation of trivinylytin chloride at 200° is described. To 30 g. (0.134 mole) of tetravinylytin was added 11.65 g. (0.045 mole) of tin(IV) chloride. A vigorous reaction began immediately. The mixture was heated at 180 to 205° for 1.5 hours. During this time decomposition became apparent; the reaction mixture began to fume strongly and grey insoluble matter began to form. After the mixture had cooled it was filtered to give a heavy yellow oil. Attempted distillation at reduced pressure gave only a small amount of liquid boiling from 66 to 69° at 5.8 mm. Further decomposition occurred during the distillation. Treatment of the distillate with a large excess of aqueous-alcoholic potassium fluoride solution gave impure trivinylytin fluoride, the purification of which was not attempted.

Anal. Calcd. for C_8H_8FSn : C, 32.93; H, 4.15. Found: C, 31.02; H, 4.41.

4. **Preparation of Divinylytin Derivatives.** (a) **Divinylytin Dithiocyanate.**—The method used¹⁵ for the preparation of dimethyl- and di-*n*-butyltin dithiocyanates was used. To 2.0 g. (0.0082 mole) of divinylytin dichloride dissolved in absolute ethanol was added a solution of 1.33 g. (0.0164 mole) of sodium thiocyanate in ethanol. The mixture was heated briefly on the steam-bath, the precipitated sodium chloride was filtered off, and the filtrate was concentrated under reduced pressure. The residue was recrystallized from benzene to give 1.8 g. (76% yield) of pure divinylytin dithiocyanate.

(b) **Divinylytin Oxide.**—To 2.0 g. (0.0082 mole) of divinylytin dichloride dissolved in 30 ml. of ethanol was added enough aqueous ammonia to make the solution weakly alkaline. The white amorphous oxide precipitated immediately, and was washed successively with water, acetone and ether. It was dried in the steam-oven to give 12.4 g. of pure material, a yield of 80%.

(c) **Divinylytin Phthalate.**—To 2.0 g. (0.0082 mole) of divinylytin dichloride dissolved in water was added an aqueous solution containing 2.0 g. (0.01 mole) of potassium acid phthalate. Divinylytin phthalate precipitated immediately; the fine crystals were digested in distilled water on the steam-bath, filtered and washed with water and acetone and were subsequently dried in the steam-oven to give 2.6 g. (95% yield) of pure compound.

(d) **Divinylytin Benzenephosphonate.**—To 2.0 g. (0.0082 mole) of divinylytin dichloride in 30 ml. of water was added 1.6 g. (0.01 mole) of benzenephosphonic acid dissolved in water. A white precipitate was formed immediately; this was then filtered, washed repeatedly with water and dried in the steam-oven to give 2.13 g. (79% yield) of pure divinylytin benzenephosphonate. This compound is soluble in acetone.

(15) D. Seyferth and E. G. Rochow, *THIS JOURNAL*, **77**, 1302 (1955).

5. **Preparation of Dimethyltin Derivatives.** (a) **Dimethyltin Benzenephosphonate**, $(CH_3)_2SnO_2(O)PC_6H_5$.—The addition of a solution of 4.4 g. (0.02 mole) of dimethyltin dichloride in 20 ml. of water to 6.32 g. (0.04 mole) of benzenephosphonic acid dissolved in 100 ml. of water resulted in immediate precipitation of this compound. Washing with water and acetone and drying at 50° gave 5.65 g. (92.5% yield) of the pure compound, which remained unmelted and undecomposed at 350°.

Anal. Calcd. for $C_8H_{11}O_4PSn$: C, 31.5; H, 3.64. Found: C, 31.33; H, 3.34.

(b) **Dimethyltin Dibenzenephosphinate**, $(CH_3)_2Sn[O(O)HPC_6H_5]_2$.—By a similar procedure this compound was obtained in 89% yield (7.53 g.) from 4.4 g. (0.02 mole) of dimethyltin dichloride and 5.68 g. (0.04 mole) of benzenephosphonic acid. This derivative melted at 159° with decomposition (frothing and solidification of the froth at 162°).

Anal. Calcd. for $C_{14}H_{19}O_4P_2Sn$: C, 39.02; H, 4.21. Found: C, 39.00; H, 4.04.

(c) **Dimethyltin Phosphate**, $(CH_3)_2SnHPO_4$.—No precipitate formed when a solution of 2.2 g. (0.01 mole) of dimethyltin dichloride in 20 ml. of water was added to 3.58 g. (0.01 mole) of $Na_2HPO_4 \cdot 12H_2O$ dissolved in 90 ml. of water. However, the dimethyltin phosphate came out of solution after the mixture had been left to stand overnight. The filtered precipitate was washed with water and methanol and dried at 50° to give 2.0 g. (82% yield) of pure compound, which remained unmelted and undecomposed at 345°.

Anal. Calcd. for $C_2H_7O_4PSn$: C, 9.81; H, 2.88. Found: C, 9.71; H, 2.57.

(d) **Dimethyltin Dihypophosphite**, $(CH_3)_2Sn(H_2PO_2)_2 \cdot 2H_2O$.—No immediate precipitate was obtained when aqueous solutions of 2.2 g. (0.01 mole) of dimethyltin dichloride and 2.12 g. (0.02 mole) of sodium hypophosphite monohydrate were mixed. However, on shaking the solution a few minutes the first fine crystals formed, and then precipitation of the dimethyltin hypophosphite was rapid. The fine crystals were washed with water and methanol and dried at 50° to yield 2.8 g. (89% yield) of pure material, m.p. 213° (decomposition with vigorous frothing).

Anal. Calcd. for $C_2H_{14}O_8P_2Sn$: C, 7.63; H, 4.48. Found: C, 7.72; H, 4.25.

(e) **Di-*n*-butyltin Di-*p*-toluenesulfonate**, $(n-C_4H_9)_2Sn(O_2SC_6H_4CH_3-p)_2$.—A solution of 21.3 g. (0.112 mole) of *p*-toluenesulfonic acid monohydrate in 125 ml. of methanol was added to 14 g. (0.056 mole) of di-*n*-butyltin oxide. The mixture was heated on the steam-bath until all of the oxide had dissolved, was treated with charcoal and filtered. Concentration of the clear solution on the steam-bath gave a yellow semi-solid slush. Extraction with ether resulted in 22.5 g. of di-*n*-butyltin di-*p*-toluenesulfonate. The compound did not melt below 320°.

Anal. Calcd. for $C_{22}H_{32}O_6S_2Sn$: Sn, 20.63. Found: Sn, 20.50.

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