ϵ_{247} 8,100, $\epsilon_{271.5}$ 1,230; ϵ_{306} 3,560. These values correspond to a mixture of 96% of *o*-methoxyacetophenone and 4% of the *p*-isomer. The presence of the *p*-isomer was confirmed by vapor phase chromatography.

The Reaction of Acetic Anhydride with Di-(*m*-methoxyphenyl)-cadmium.—The cadmium reagent prepared from 28.0 g. (0.15 mole) of *m*-bromoanisole was allowed to react n benzene solution with 7.54 g. (0.074 mole) of acetic anhydride (freshly distilled) for two hours and the reaction mixture processed in the usual manner. Upon distillation there was obtained 3.95 g. of material containing 0.87% Br and thus the yield of ketone is 3.87 g. (35%), b.p. 118–125° (16 mm.). The ultraviolet spectrum showed the values: ϵ_{217} 19,000, ϵ_{249} 7,420, $\epsilon_{271.5}$ 5,540, ϵ_{306} 2,080. These values correspond to a mixture of 68% of *m*-methoxyacetophenone and 32% of the *p*-isomer.

The Reaction of Succinic Anhydride with Di-(*m*-methoxyphenyl)-cadmium.—The cadmium reagent from 13.2 g. (0.07 mole) of *m*-bromoanisole in 100 ml. of dry benzene was allowed to react for one hour with 3.02 g. (0.03 mole) of succinic anhydride. The reaction mixture was decomposed with 50 ml. of 5% hydrochloric acid, the organic material extracted with ether, the ether solution washed with water and then extracted with 10% sodium bicarbonate solution. Acidification of the alkaline extract followed by ether extraction and evaporation of the solvent yielded 2.55 g. of a semi-solid. The material was dissolved again in sodium bicarbonate, extracted with ether and reprecipitated, yield 2.02 g. of yellow solid. The acid (1.82 g.) was chromatographed on 90 g. of Florex XXS and after elution with benzene and benzene–ether (4:1) to remove oily material, benzene–ether (1:1) and ether yielded a total of 0.992 g. of solid. These latter fractions were dissolved in ether, extracted into sodium bicarbonate and precipitated with concentrated hydrochloric acid, yield 0.697 g.; ultraviolet spectrum: ϵ_{217} 22,400, ϵ_{249} 8,000, $\epsilon_{271.5}$ 1,000, ϵ_{306} 2,560. These values correspond to 94–98% of β-(*m*-methoxybenzoyl)-propionic acid and 2–6% of the *p*-isomer.

Anal. Calcd. for $C_{11}H_{12}O_4$ (208.21): C, 63.45; H, 5.81; neut. equiv., 208. Found: C, 63.68; H, 6.09; neut. equiv., 206.

β-(*m*-Methoxybenzoyl)-propionic Acid.—The keto-acid was prepared following the procedures of Thompson and of Martin,[19] m.p. 107–108° (lit.[19] m.p. 107–108°); $\lambda_{\text{mxx}}^{\text{alc}}$ 217 mμ (ε 23,400), 249 mμ (ε 8,200), 306 mμ (ε 2,600). The methyl ester was prepared with diazomethane, $\lambda_{\max}^{\text{alc}}$ 217 mμ (ε 25,800), 249 mμ (ε 8,560), 307 mμ (ε 2,600). The semicarbazone was prepared, m.p. 173–174° (lit.[19] 177–178°), $\lambda_{\max}^{\text{alc}}$ 275 mμ (ε 11,100).

Anal. Calcd. for $C_{12}H_{14}O_4$ (222.23): C, 64.85; H, 6.35; OMe, 27.94. Found: C, 64.44; H, 6.43; OMe, 28.20.

β-(*p*-Methoxybenzoyl)-propionic Acid.—The keto-acid was prepared following the procedure of Fieser and Hershberg,[20] m.p. 146.0–147.5° (lit.[20] 146–147°), $\lambda_{\max}^{\text{alc}}$ 217 mμ (ε 11,900), 271 mμ (ε 17,000). The methyl ester was prepared with dizomethane, m.p. 48.6–49.5° (lit.[21] 7.5–49.5°); $\lambda_{\max}^{\text{alc}}$ 217 mμ (ε 11,500), 271.5 mμ (ε 16,900). The semicarbazone was prepared, m.p. 175–176° dec. (lit.[22] 185–186°), $\lambda_{\max}^{\text{alc}}$ 281 mμ (ε 17,000). The semicarbazones of the *m*- and *p*-isomers when mixed showed a melting point depression of only 1–2°.

The Product from the Reaction of Di-(*m*-methoxyphenyl)-cadmium with β-Carbomethoxypropionyl Chloride.[6]—The infrared spectrum of the resulting keto-ester was essentially identical with that of methyl β-(*p*-methoxybenzoyl)-propionate. The ultraviolet spectrum had maxima at 217 mμ (ε 13,600) and 271 mμ (ε 17,200). The keto-acid, derived by saponification of the ester, had a m.p. of 147.5–148.5° and was not depressed upon admixture with authentic *p*-isomer. The semicarbazone was prepared from the acid and had a m.p. of 174–175° and a maximum at 281 mμ (ε 16,900).

***o*-Methoxyacetophenone** was prepared by allowing dimethylcadmium to react with *o*-methoxybenzoyl chloride. The material had the properties: b.p. 127° (15 mm.), $n^{20}D$ 1.5395 (lit.[23] b.p. 126.5° (15 mm.), $n^{20}D$ 1.5395); $\lambda_{\max}^{\text{alc}}$ 211 mμ (ε 20,800), 247 mμ (ε 8,350), 306 mμ (ε 3,780); $\epsilon_{271.5}$ 650; $\lambda_{\max}^{\text{liq}}$ 6.00, 12.40, 13.15 μ.

***m*-Methoxyacetophenone** was prepared by allowing dimethylcadmium to react with *m*-methoxybenzoyl chloride; b.p. 129–132° (19 mm.), $n^{20}D$ 1.5408 (lit.[23] b.p. 125–126° (12 mm.), $n^{20}D$ 1.5410); $\lambda_{\max}^{\text{alc}}$ 217 mμ (ε 22,600), 249 mμ (ε 8,800), 306 mμ (ε 2,450); $\epsilon_{271.5}$ 700; $\lambda_{\max}^{\text{liq}}$ 5.98, 12.70, 14.35, 14.60 μ.

***p*-Methoxyacetophenone.**—The commercial material (Eastman Organic Chemicals) was recrystallized twice from ether, m.p. 37–38° (lit.[24] m.p. 37.5–38.5°); spectral properties: $\lambda_{\max}^{\text{alc}}$ 217 mμ (ε 11,700), 271.5 mμ (ε 16,600); ϵ_{247} 4,270, ϵ_{249} 5,200, ϵ_{306} 780; $\lambda_{\max}^{\text{Nujol}}$ 6.00, 11.95, 12.05, 12.25 μ.

Pertinent Spectral Properties of Isomeric Bromoanisoles: (a) *ortho:* $\lambda_{\max}$ 13.35 μ, ϵ_{306} 0, $\epsilon_{271.5}$ 2,480, ϵ_{247} 100; (b) *meta:* $\lambda_{\max}$ 13.00 μ, 14.72 μ, $\epsilon_{271.5}$ 1,640, ϵ_{249} 400; (c) *para:* $\lambda_{\max}$ 12.15 μ.

Method of Analysis.—Infrared analyses were carried out by comparison of the spectrum of the mixture to that of a mixture of known composition. Ultraviolet analyses were carried out by measurement of the spectrum from 210 μ to 400 mμ using a model 14 Cary spectrophotometer. If any starting bromoanisole was present, as indicated by bromine analysis, the concentration of the solution and the observed optical density were corrected. The extinction coefficients due to the ketones then were calculated at several wave lengths and the proportion of *p*-isomer determined by simultaneous equations. When the amount of *p*-isomer present was appreciable, this value was checked by merely dividing the extinction at 271.5 mμ by 16,000.

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[19] H. W. Thompson, *J. Chem. Soc.*, 2310 (1932); E. L. Martin, THIS JOURNAL, **58**, 1438 (1936).

[20] L. F. Fieser and E. B. Hershberg, *ibid.*, **58**, 2314 (1936).

[21] M. D. Soffer and M. C. Hunt, *ibid.*, **67**, 692 (1945).

[22] P. C. Mitter and S. De, *J. Indian Chem. Soc.*, **16**, 35 (1939)

[23] K. von Auwers, *Ann.*, **408**, 220 (1915).

[24] F. Straus and H. Grindel, *ibid.*, **439**, 276 (1924).

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

The Preparation of Some Unsymmetrical Organotin Bromides and Acetates

BY SANDERS D. ROSENBERG,[1] EUGENE DEBRECZENI AND ELLIOTT L. WEINBERG

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A series of unsymmetrical organotin bromides has been prepared by the stepwise cleavage of appropriate organotin compounds with bromine in carbon tetrachloride or chloroform at −50, 0 or 40°. The bromides have been converted to acetates by treatment with aqueous potassium hydroxide to form bisorganotin oxides, followed by reaction of these intermediate compounds with glacial acetic acid at 100°.

As part of a systematic investigation on the biological properties of triorganotin halides, hydroxides, oxides and esters, a series of new unsymmetrical triorganotin compounds of the type $R_2R'SnX$ has been prepared for microbiological testing. Evaluation of compounds of the type R_3SnX has shown that there is little or no difference in activity, on a tin-contained basis, where X is chloride, bromide, hydroxide, oxide or acetate.

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Table I

Unsymmetrical Organotin Compounds

Compound	B.p. °C.	B.p. Mm.	$n^{25}D$	d^{25}_4	Yield, %	Tin, % Calcd.	Tin, % Found
Diallyldi-*n*-butyltin[a]	93	0.1	1.4986	1.0999	52	37.70	37.59
Diallyldiphenyltin[b]	120–124	.005	1.6013	1.2688	60	33.40	33.68
Dimethyldi-2-ethylhexyltin	101–102	.2	1.4715	1.0307	73	31.61	31.86
Dimethyldi-*n*-octyltin	121–122	.2	1.4659	1.0168	72	31.61	31.48
Triallyl-*n*-butyltin	116–119	10.0	1.5162	1.1335	83	39.70	39.42
Trimethyl-*n*-decyltin	67	0.05	1.4602	1.0487	73	38.90	38.93
Trimethyl-*n*-dodecyltin[c]	93–98	.15	1.4610	1.0285	73	35.64	35.45
Trimethyl-*n*-octyltin[c]	56–58	.03	1.4587	1.0802	74	42.88	42.59
Triphenyl-*n*-hexyltin	M.p. 54				83	27.30	27.47
Trivinyl-*n*-decyltin	90–94	0.05	1.4820	1.0672	83	34.80	34.67
Trivinyl-*n*-hexyltin	57–61	.03	1.4851	1.1266	80	41.64	41.86
Trivinyl-*n*-octyltin	90–93	.2	1.4819	1.0865	86	37.91	37.98

[a] W. J. Jones, W. C. Davies, S. T. Bowden, C. Edwards, V. E. Davies and L. H. Thomas, *J. Chem. Soc.*, 1446 (1947). [b] H. Gilman and J. Eisch, *J. Org. Chem.*, **20**, 763 (1955); M. M. Koton and T. M. Kiseleva, *Zhur. Obshchei Khim.*, **27**, 2553 (1957) [*C. A.*, **52**, 7136 (1958)]. [c] J. G. A. Luijten and G. J. M. van der Kerk, "Investigations in the Field of Organotin Chemistry," Tin Research Institute, Greenford, Middlesex, England; 1955; G. J. M. van der Kerk and J. G. A. Luijten, *J. Appl. Chem.*, **6**, 56 (1956).

For ease of synthesis it was decided to prepare representative bromides and acetates for testing. This report deals with the synthetic chemical research required by this project. The results of the microbiological evaluation of these compounds will be reported at a later date.

Discussion

One of the more direct methods available for the synthesis of organotin compounds of the type $R_2R'SnX$ (where X = Cl, Br or I) is the stepwise, controlled substitution of R_2SnX_2 with $R'MgX$ to form $R_2R'SnX$. Unfortunately this stepwise, controlled substitution is very difficult, if not impossible, to obtain when stoichiometric amounts of reactants are used.[2] This fact is dramatically pointed out by two experiments that were carried out in an attempt to prepare unsymmetrical triorganotin halides by this method.

In one reaction, 1.0 equivalent of *n*-octylmagnesium chloride in tetrahydrofuran solution was added to 1.0 equivalent of dimethyltin dichloride in heptane under mild controlled conditions. In a second reaction, under analogous conditions and stoichiometry, 2-ethylhexylmagnesium chloride was added to dimethyltin dichloride. In each case, the only tin-containing compounds isolated were unreacted dimethyltin dichloride and the bis-substituted organotin compound.

$$n\text{-}C_8H_{17}MgCl + (CH_3)_2SnCl_2 \longrightarrow \underset{\text{none isolated}}{(CH_3)_2(n\text{-}C_8H_{17})SnCl} + \underset{72\%\ \text{yield}}{(CH_3)_2Sn(n\text{-}C_8H_{17})_2}$$

$$2\text{-}C_2H_5C_6H_{12}MgCl + (CH_3)_2SnCl_2 \longrightarrow \underset{\text{none isolated}}{(CH_3)_2(2\text{-}C_2H_5C_6H_{12})SnCl} + \underset{73\%\ \text{yield}}{(CH_3)_2Sn(2\text{-}C_2H_5C_6H_{12})_2}$$

These results, coupled with those obtained in an earlier study in vinyltin chemistry,[2] led to the conclusion that a two-step synthesis system would produce the desired $R_2R'SnX$ compounds in a shorter time and in higher over-all yields.

$$R_2SnX_2 + 2R'MgX \longrightarrow R_2R'_2Sn + 2MgX_2$$

$$R_2R'_2Sn + X_2 \longrightarrow R_2R'SnX + R'X$$

The appropriate unsymmetrical organotin compounds required for halogen cleavage were synthesized in good yields (52–86%) by well known methods. The physical properties of these organotin compounds are listed in Table I.

The cleavage of organic groups from tin by halogen has been investigated by several workers[3–8] and the preferential removal of groups can be predicted accurately. In this work bromine was chosen as the cleavage halogen as it reacts more promptly than iodine and is more easily handled than chlorine on a laboratory scale. The yields (63–99%) of these new organotin bromides are shown in Table II. The purity of the compounds was satisfactory and even those compounds that had to be isolated as pot residues, due to their thermal instability,[6] were obtained as reasonably pure materials. Note that the allyl group is promptly cleaved from tin by bromine at −50°, the phenyl and vinyl groups at 0°, and the methyl and butyl groups at 40°. Vijayaraghavan[4] reported in an attempt to prepare triallyltin bromide by reaction of tetraallyltin with bromine at −15° that an inseparable mixture of diallyltin dibromide and triallyltin bromide was obtained. Apparently the lowering of the reaction temperature to −50° results in the stepwise cleavage of the allyl group from these unsymmetrical organotin compounds.

Since most of the organotin bromides to be converted into acetates contained organic groups which are easily cleaved from tin by acidic reagents a mild conversion method was sought. An attempt to convert a bromide to an acetate using sodium acetate failed. The method used by Luijten and van der Kerk[8] to convert organotin iodides to acetates was used with slight modification. The satisfactory conversions are listed in

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(2) S. D. Rosenberg, A. J. Gibbons, Jr., and H. E. Ramsden, This Journal, **79**, 2137 (1957).

(3) Z. M. Manulkin, *J. Gen. Chem.* (*U.S.S.R.*), **11**, 386 (1941); **13**, 42 (1943); **14**, 1047 (1944); **16**, 235 (1946) [*Chem. Zentr.*, **112** (**2**), 1845 (1941); *C.A.*, **38**, 331 (1944); **41**, 89 (1947); **41**, 90 (1947)].

(4) K. V. Vijayaraghavan, *J. Indian Chem. Soc.*, **22**, 135 (1945).

(5) H. Gilman and C. E. Arntzen, *J. Org. Chem.*, **15**, 994 (1950).

(6) S. D. Rosenberg and A. J. Gibbons, Jr., This Journal, **79**, 2138 (1957).

(7) D. Seyferth, *ibid.*, **79**, 2133 (1957); *J. Org. Chem.*, **22**, 1599 (1957).

(8) Table I, footnote *c*.

TABLE II

ORGANOTIN BROMIDES

Compound, bromide	B.p. °C.	B.p. Mm.	Yield, %	Bromine, % Calcd.	Bromine, % Found	Tin, % Calcd.	Tin, % Found
Diallyl-*n*-butyltin	[a]		99	23.65	23.24	35.10	35.34
Di-*n*-butylallyltin	85–89	0.03	87	22.58	22.99	33.54	33.45
Di-*n*-butylphenyltin	120–124	.001	76	20.49	19.68	30.44	30.40
Dimethyl-*n*-decyltin	110–114	.2	80	21.52	21.63	32.19	31.40
Dimethyl-*n*-dodecyltin	124–128	.05	80	20.13	20.01	29.90	29.19
Dimethyl-*n*-octyltin	77–81	.01	86	23.37	23.96	34.72	34.38
Diphenylallyltin	[a]		93	20.13	19.56	29.90	30.14
Diphenyl-*n*-butyltin	155–159	.2	63	19.50	19.69	28.99	29.23
Diphenyl-*n*-hexyltin	[a]		91	18.24	17.11	27.10	26.25[b]
Diphenylvinyltin	[a]		95	21.00	18.35	31.20	27.93[c]
Divinyl-*n*-decyltin	96–100	.01	75	20.28	19.38	30.13	30.26
Divinyl-*n*-hexyltin	70–74	.05	90	23.65	23.17	35.13	34.63
Divinyl-*n*-octyltin	82–86	.01	80	21.84	22.29	32.44	32.74

[a] Isolated as a pot residue after solvent strip at 0.5 mm. These materials were not vacuum distilled due to their thermal instability. [b] Estimated purity is 95.5%; impurity is bromobenzene. [c] Estimated purity is 88.5%; impurity is bromobenzene.

TABLE III

ORGANOTIN ACETATES

Compound, acetate	Physical form	M.p., °C.	Yield, %	Tin, % Calcd.	Tin, % Found
Di-*n*-butylvinyltin	Colorless liq.		84	37.21	37.34
Dimethyl-*n*-decyltin	Amorphous solid	96–98	98	34.00	33.85
Dimethyl-*n*-dodecyltin[a]	Amorphous solid	97–98.6	96	31.21	31.02
Dimethyl-*n*-octyltin[a]	Amorphous solid	96–97.8	98	36.98	36.91
Diphenylallyltin	Amorphous solid	Dec. 260	92	31.82	32.32

[a] Table I, footnote *c*.

Table III. In spite of the changes made it is doubtful that this method will produce the desired acetate if very easily cleaved groups are present in the molecule. In the attempted conversion of di-*n*-butylallyltin bromide to di-*n*-butylallyltin acetate, the analyses indicated that bisdi-*n*-butylacetoxytin oxide was formed as the major product. The same result was obtained with

$$(n\text{-}C_4H_9)_2(CH_2{=}CHCH_2)SnBr \xrightarrow[\text{aq}]{\text{KOH}}$$

$$[(n\text{-}C_4H_9)_2(CH_2{=}CHCH_2)Sn]_2O \xrightarrow{CH_3CO_2H}$$

$$[(n\text{-}C_4H_9)_2(CH_3CO_2)Sn]_2O + CH_2{=}CHCH_3$$

diphenyl-*n*-butyltin bromide. The tin analyses for other acetates prepared in this manner indicated that the compounds were not pure. The competing reaction, acid cleavage, may have taken place in all of the reactions that were run.

Experimental

Diallyldiphenyltin.—A refluxing solution of diphenyltin dichloride (343.8 g., 1.0 mole) in 2.0 l. of heptane was treated with 2.2 moles of allylmagnesium chloride in tetrahydrofuran solution over a 2.0-hr. period. The mixture was refluxed an additional 4.0 hr.

On cooling, the reaction mixture was hydrolyzed by the cautious addition of 2% aqueous hydrochloric acid until two clear liquid layers formed. The organic layer was separated, dried on sodium carbonate, and filtered. The solvents were removed by distillation at 1.0 atm. The residue was carefully fractionally distilled under reduced pressure to yield 213.0 g. (60%) of diallyldiphenyltin distilling at 120–124° (0.005 mm.).

In an analogous manner diallyldi-*n*-butyltin and triallyl-*n*-butyltin were prepared from allylmagnesium chloride and di-*n*-butyltin dichloride and *n*-butyltin trichloride, respectively; trimethyl-*n*-decyltin, -dodecyltin and -octyltin from trimethyltin chloride and *n*-decyl-, *n*-dodecyl- and *n*-octylmagnesium chloride, respectively; trivinyl-*n*-decyltin, -hexyltin and -octyltin from trivinyltin chloride[6] and *n*-decyl-, *n*-hexyl- and *n*-octylmagnesium chloride, respectively; triphenyl-*n*-hexyltin from triphenyltin chloride and *n*-hexylmagnesium chloride. The latter compound was purified by crystallization from a methanol–benzene solvent pair after the 1.0-atm. solvent strip.

Divinyl-*n*-octyltin Bromide.—A solution of 115.2 g. (0.368 mole) of trivinyl-*n*-octyltin in 184 ml. of carbon tetrachloride was cooled externally to 0° and treated with 58.6 g. (0.368 mole) of bromine in 184 ml. of carbon tetrachloride over a 2-hr. period with stirring. The bromine solution was decolorized instantly on reaching the reaction solution and the reaction was vigorous.

The carbon tetrachloride was removed by distillation under reduced pressure (water-pump) to a pot temperature of 60°. The residue was carefully fractionally distilled under reduced pressure to yield 107.6 g. (80%) of divinyl-*n*-octyltin bromide distilling at 82–86° (0.01 mm.).

In an analogous manner diphenylvinyl-, divinyl-*n*-decyl- and divinyl-*n*-hexyltin bromide were prepared from bromine and triphenylvinyl-,[2,9] trivinyl-*n*-decyl- and trivinyl-*n*-hexyltin, respectively; di-*n*-butylphenyl-, diphenyl-*n*-butyl- and diphenyl-*n*-hexyltin bromide were prepared from bromine and di-*n*-butyldiphenyl-, triphenyl-*n*-butyl- and triphenyl-*n*-hexyltin, respectively.

In similar reactions at 40°, dimethyl-*n*-decyl-, dimethyl-*n*-dodecyl- and dimethyl-*n*-octyltin bromide were prepared from bromine and trimethyl-*n*-decyl-, trimethyl-*n*-dodecyl- and trimethyl-*n*-octyltin, respectively. Likewise, at −50°, diallyl-*n*-butyl-, di-*n*-butylallyl- and diphenylallyltin bromide were prepared from bromine and triallyl-*n*-butyl-, diallyldi-*n*-butyl- and diallyldiphenyltin, respectively. Chloroform was the solvent used in the allyl cleavage reactions.

Diphenyl-*n*-hexyltin Acetate.—A solution of 34.0 g. (0.1 mole) of di-*n*-butylvinyltin bromide in 150 ml. of diethyl ether was shaken with 25.2 ml. (0.1 mole) of 20% aqueous potassium hydroxide solution for 10 minutes. The aqueous phase was drawn off and the process repeated with 12.6 ml. (0.05 mole) of the potassium hydroxide solution. The ethereal solution was concentrated and the residue was stored under reduced pressure (*ca.* 25 mm.) for 18-hr. over concd. sulfuric acid to yield 25.0 g. (95%) of bis di-*n*-butylvinyltin oxide.

To the oxide was added 9.0 g. (0.105 mole) of glacial acetic acid. The solution was warmed on a boiling water-bath for 0.5 hr. with occasional stirring. The mixture was then

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(9) D. Seyferth and F. G. A. Stone, THIS JOURNAL, **79**, 515 (1957).

stored in a vacuum desiccator over potassium hydroxide pellets and maintained under reduced pressure (25 mm.) for 18 hr. In this manner 26.8 g. (84% over-all) of di-*n*-butylvinyltin acetate was obtained. In an analogous manner the other organotin acetates listed in Table III were prepared and crude samples, suitable for testing, of di-*n*-butylvinyl-, diphenyl-*n*-hexyl-, divinyl-*n*-decyl-, divinyl-*n*-hexyl- and divinyl-*n*-octyltin acetate were obtained.

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RAHWAY, N. J.

[CONTRIBUTION FROM THE MELLON INSTITUTE]

The Preparation and Properties of Some Silylmethyl and Silylpropyl Substituted Tin Compounds

BY ROBERT L. MERKER AND MARY JANE SCOTT[1]

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The preparation and properties of compounds possessing the structures $[XMe_2Si(CH_2)_m]_2SnR_2$ and $XMe_2SiCH_2SnR_3$, where X is hydrogen, ethoxyl or oxygen ($O_{1/2}$), are described. The two six-membered cyclic siloxanes, $Me_2\underline{SiCH_2SnMe_2CH_2SiMe_2O}$ and $Me_2\underline{SiCH_2SnBu_2CH_2SiMe_2O}$ are the first reported compounds containing both tin and silicon in the same ring system. The addition of dimethylhydrogensilylmethyltributyltin to vinyldimethylchlorosilane using chloroplatinic acid as a catalyst proceeded smoothly resulting in a fair yield of the β-adduct.

Introduction

A number of hybrid organotin–organosilicon compounds have been previously reported in the literature by Rochow and Seyferth[2,3] and Post and Papetti.[4] The compounds reported by Rochow and Seyferth were of the type, ($X_2SiMeCH_2SnR_3$) and, therefore, were capable of forming polymeric materials containing organotin substituents in the side chains. The other compounds reported by Seyferth[3] and Post and Papetti[4] were all trimethylsilylmethyl substituted tin compounds and hence did not possess a reactive functional group on the silicon which could lead to the formation of polymers.

The intent of this present investigation was the preparation of hybrid organotin–organosiloxane monomers (preferably as siloxane cyclics) which could on polymerization yield polymers having both tin and silicon in the backbone chain. One of the more promising classes of compounds falling into this category possessed the structures $[XMe_2Si(CH_2)_m]_2SnR_2$ (chain extending species) and ($XMe_2SiCH_2SnR_3$) (end-blocking species). This paper, however, is restricted to a discussion of the preparation, the properties and a few of the reactions of such compounds. The results of polymerization studies will be reported at a later date.

Discussion

The dimethylhydrogensilylmethyl and dimethylhydrogensilylpropyl tin compounds were prepared utilizing the reaction

$$nHMe_2Si(CH_2)_mMgCl + (R_{(4-n)})\ SnCl_n \xrightarrow[\text{ether}]{\text{ethyl}} [HMe_2Si(CH_2)_m]_nSnR_{(4-n)} + nMgCl_2 \quad (1)$$

where m = 1 or 3, n = 1 or 2, and R was methyl or butyl. The dimethylhydrogensilylmethyl- and dimethylhydrogensilylpropylalkyl tin compounds so prepared were found to be quite stable to cleavage under basic conditions in either absolute ethanol or aqueous ethanol at reflux temperatures. Thus it was possible to convert them to the corresponding ethoxyl derivatives in nearly quantitative yields

$$[HMe_2Si(CH_2)_m]_nSnR_{(4-n)} + nEtOH(\text{abs.}) \xrightarrow{\text{NaOEt}} [EtOMe_2Si(CH_2)_m]_nSnR_{(4-n)} + nH_2 \quad (2)$$

The compounds in which m = 1 and n = 2 were smoothly converted to the six-membered cyclic siloxanes on hydrolysis in moderately dilute solution in aqueous ethanol.

$$(HMe_2SiCH_2)_2SnR_2 + HOH \xrightarrow[\text{EtOH}]{\text{NaOH}} Me_2\underline{SiCH_2SnR_2CH_2SiMe_2O} + 2H_2 \quad (3)$$

These are the first well characterized compounds reported which contain both tin and silicon in a cyclic ring system.

It is of interest that under the reaction conditions employed (reaction 3), nearly quantitative yields of the six-membered cyclic siloxanes were obtained. Attempts to prepare the ten-membered cyclic from the propyl derivative (m = 3) under identical conditions were unsuccessful and yielded

$$[HMe_2Si(CH_2)_3]_2SnMe_2 + HOH \xrightarrow[\text{EtOH}]{\text{NaOH}} (Me_2\underset{|}{Si}(CH_2)_3SnMe_2(CH_2)_3SiMe_2O\text{–})_x + 2H_2 \quad (4)$$

only linear polysiloxanes. A small yield of the ten-membered cyclic, however, was obtained by thermally cracking the linear polysiloxanes under alkaline conditions.

$$(Me_2Si(CH_2)_3SnMe_2(CH_2)_3SiMe_2O\text{–})_x \xrightarrow[\Delta]{\text{KOH}} Me_2\underline{Si(CH_2)_3SnMe_2(CH_2)_3SiMe_2O} \quad (5)$$

A compound in which m = 1 and n = 1, dimethylhydrogensilylmethyltributyl tin or its ethoxy

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[1] Multiple Fellowship on Silicones sustained by the Dow-Corning Corporation and Corning Glass Works.

(2) D. Seyferth and E. G. Rochow, *J. Polymer Sci.*, **18**, 543 (1955).

(3) D. Seyferth, THIS JOURNAL, **79**, 5881 (1957).

(4) H. W. Post and S. Papetti, *J. Org. Chem.*, **22**, 526 (1957).