lithium aluminum hydride in 300 ml. of anhydrous ether. The suspension was stirred overnight, refluxed for 1 hr. and the excess hydride was decomposed with methanol in ether solution. Water was added slowly and the pasty mass was acidified with hydrochloric acid. The aqueous layer was removed and extracted twice with ether. The combined ether extract was washed with dilute sodium hydroxide solution and water. The ether layer was dried over magnesium sulfate, filtered, and evaporated. The yield of product (64.2 g., n_D^{20} 1.4385) was 99%.

Anal. Calcd. for $C_{11}H_{24}O$: C, 76.67; H, 14.04. Found: C, 76.39; H, 13.99.

4,8-Dimethylnonyl chloride. A mixture of 94.0 g. (0.546 mole) of 4,8-dimethylnonanol-1 and 41.0 g. (0.519 mole) of pyridine was added slowly to 130 g. (1.09 mole) of thionyl chloride during cooling and shaking in an ice bath. The mixture was refluxed 1.5 hr., cooled, and the upper layer was separated and poured onto crushed ice. The aqueous layer was separated and the product layer was diluted with benzene, washed with water several times, 10% sodium carbonate solution twice and was dried over potassium carbonate. After filtration, the benzene was evaporated and the product was distilled in vacuum at 92–93°/7.5 mm; wt. 98.8 g. (95%). The product was redistilled in a packed column. The major portion boiled at 99°/10 mm., n_D^{20} 1.4396.

Anal. Calcd. for $C_{11}H_{23}Cl$: C, 69.26; H, 12.15; Cl, 18.6. Found: C, 69.29; H, 12.17; Cl, 18.8.

2,7-Octanedione. A Grignard reagent was prepared from 88.7 g. (0.62 mole) of methyl iodide, 15.2 g. (0.63 mole) of magnesium and 250 ml. of ether. The solution was cooled under nitrogen and treated with 62.5 g. of anhydrous cadmium chloride during stirring. A negative Gilman test was obtained after 0.5 hr. The ether was replaced with benzene by distillation until the distillate began to leave a deposit on evaporation.

The dimethylcadmium suspension was cooled and added slowly during stirring to a cooled solution of 49 g. (0.27 mole) of adipyl chloride (Distillation Products Inc.) in 300 ml. of benzene. The mixture was refluxed for 1 hr., cooled and treated with 500 ml. of saturated ammonium chloride. The benzene layer was separated and the aqueous residue was extracted twice with ether. The combined extract was washed with dilute sodium bicarbonate and water and dried over magnesium sulfate. After filtration, the benzene was evaporated and the product was crystallized from benzene-petroleum ether (30–60°). Fractional crystallization from benzene-petroleum ether gave 20.1 g., (53%) m.p. 39.5–40.5.

2,6,10,15,19,23-Hexamethyl-10,15-tetracosanediol. A Grignard reagent was prepared from 57.2 g. (0.3 mole) of 4,8-dimethylnonyl chloride and 7.3 g. (0.3 mole) of magnesium in about 250 ml. of ether at reflux. The solution was assayed by titration of an aliquot and 0.273 mole of Grignard reagent was found. A solution of 14.2 g. (0.1 mole) of 2,7-octanedione in 100 ml. of benzene was added to the ethereal Grignard solution during stirring under nitrogen. The mixture was placed on a steam bath and the ether was replaced with benzene by distillation over an hour's time. The mixture was allowed to stand under nitrogen for 2 days and 500 ml. of 20% sulfuric acid was added during cooling and stirring. The benzene layer was separated and washed with water and sodium bicarbonate until neutral. The aqueous layers were washed with benzene and the combined benzene extract was dried over magnesium sulfate, filtered, and concentrated in vacuum. The infrared absorption spectrum of the residue, 42 g. (92% based on diketone) indicated the presence of tertiary hydroxyl groups.

Anal. Calcd. for $C_{30}H_{62}O_2$: C, 79.22; H, 13.74. Found: C, 78.95; H, 13.65.

Octahydrosqualene. A solution of 30 g. of the above diol in 350 ml. of xylene was treated with 0.1 g. of iodine and was distilled slowly for 1 hr. Another 0.1 g. portion of iodine was added each hour for 12 hr. as the distillation was continued. The xylene was removed by distillation in vacuum and the residue was dissolved in petroleum ether and passed through a 170 × 66 mm. alumina column. A total of 29.0 g. was isolated in the first 500 ml. of petroleum ether eluate; a colored zone remained on the column. The product was heated at 100°/4 mm. for 0.5 hr. and 26.1 g. of product (94%) was obtained.

Anal. Calcd. for $C_{30}H_{58}$: C, 86.04; H, 13.96. Found: C, 86.0; H, 13.9.

Squalane. A mixture of 23.0 g. of octahydrosqualene was placed in a hydrogenation bottle with 0.5 g. of platinum oxide. The mixture was shaken under hydrogen until the theoretical amount of hydrogen was absorbed. Shaking was continued for several hours without further hydrogen uptake. The product was diluted with benzene and filtered. Evaporation of the benzene gave a residue of 17.5 g., n_D^{20} 1.45200. It was passed through a 20 × 200 mm. silica gel column with isopentane; 17.0 g., n_D^{20} 1.45195. Distillation in a molecular still gave about 1.0 g. of forerun, n_D^{20} 1.4511 and a main fraction, n_D^{20} 1.4520, viscosity at 100°F., 20.21 cs. The ultraviolet and infrared absorption spectra showed traces of a monosubstituted benzene. The product was passed through a twelve-foot column of silica gel with isopentane and the eluate was examined in an ultraviolet spectrophotometer. No absorption was noted. The cuts were combined and evaporated. The product, 7.0 g., n_D^{20} 1.45189 gave an infrared absorption spectrum identical with the reference curve. The viscosity was essentially unchanged.

Anal. Calcd. for $C_{30}H_{62}$: C, 85.22; H, 14.78. Found: C, 85.26; H, 14.76.

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Vinyl Derivatives of the Metals. V. Free Radical Addition Reactions of Triethylvinyltin[1]

DIETMAR SEYFERTH

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In Part II of this series[2] it was shown that hydrogen bromide and mercaptans, which undergo free radical, peroxide-catalyzed addition to vinylsilicon compounds, cleave the vinyl-tin bond. The fact that even mercaptans reacted in this manner seemed to indicate that any reagent capable of electrophilic attack on the *alpha*-carbon atom of the vinyl group attached to tin would undergo this reaction in preference to the double bond addition reaction. Thus a rather severe limit was set on the types of compounds that could conceivably add to the vinyl-tin system.

The polyhalomethanes[3] and hydrogenchlorosilanes[4] are known to add to vinylsilanes. It would

(1) Part IV, D. Seyferth, *J. Am. Chem. Soc.*, **79**, 2738 (1957).

(2) D. Seyferth, *J. Am. Chem. Soc.*, **79**, 2133 (1957).

(3) (a) P. Tarrant, WADC Technical Report 55-220, August 1955; (b) A. F. Gordon, U. S. Patent 2,715,113 (August 1955); *Chem. Abstr.*, **50**, 7131 (1956); (c) A. D. Petrov, E. A. Chernyshev and M. Bisku, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1445 (1956).

(4) (a) C. A. Burkhard and R. H. Krieble, *J. Am. Chem. Soc.*, **69**, 2687 (1947); (b) M. Kanazashi, *Bull. Chem. Soc. Japan*, **26**, 493 (1953); (c) D. Seyferth and E. G. Rochow, *J. Org. Chem.*, **20**, 250 (1955).

not be expected that these reagents would cause vinyltin bond cleavage, hence a study of their action on vinyltin compounds was undertaken.

We have found that polyhalomethanes do indeed add to triethylvinyltin in the presence of benzoyl peroxide at about 90–95° to give moderate yields of adduct

$$(C_2H_5)_3SnCH{:}CH_2 + CCl_3Z \xrightarrow{Bz_2O_2} (C_2H_5)_3SnCHZCH_2CCl_3$$
$$(Z = H, Cl \text{ or } Br)$$

No proof was obtained that this is the structure of the addition product. However, in the case of vinylsilanes,[3a] it was shown by chemical means that addition of the trichloromethyl radical to the β-carbon atom of the vinyl group had occurred.

Triethylvinyltin was found to be considerably less reactive toward trichlorosilane than was trimethylvinylsilane. Thus only a 31% yield of adduct could be obtained in the case of the tin compound at 95° for 17 days. A yield of 71% was reported for the addition of trichlorosilane to trimethylvinylsilane.[4c] The adduct, β-trichlorosilylethyltriethyltin, could not be isolated in analytical purity, even after several fractional distillations. Pure β-trimethoxysilylethyltriethyltin was obtained, however, by treating the crude chlorosilane with a slurry of sodium methoxide in diethyl ether.[4c]

The platinum-on-charcoal–catalyzed addition of hydrogensilanes to olefins has been used extensively as a preparative method since its original disclosure by Wagner.[5] It was found that this catalyst system is not effective in promoting the reaction of triethylvinyltin with trichlorosilane or methyldichlorosilane. It is interesting to note that the attempted platinum-catalyzed hydrogenation of trialkylvinyltin compounds was also unsuccessful. It is thus possible that organotin compounds function as platinum catalyst poisons.

EXPERIMENTAL

Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

Starting materials. Triethylvinyltin was prepared by the method described in Part I of this series.[6] The organic halides and hydrogensilanes were commercial materials.

Reaction of triethylvinyltin with polyhalomethanes. (a) 3,3,3-Trichloropropyltriethyltin. A mixture of 23.4 g. (0.1 mole) of triethylvinyltin, 24 g. (0.2 mole) of $CHCl_3$, and 1.2 g. of benzoyl peroxide was sealed in a Carius tube and heated for 24 hr. in a steam bath. The tube was then cooled in liquid nitrogen and opened. Distillation of the contents gave 17.5 g. of unreacted $CHCl_3$, a small fraction apparently consisting of a mixture of triethylvinyltin and Et_3SnCl, and finally, 9.1 g. of $Et_3SnCH_2CH_2CCl_3$, b.p. 74° at 0.25 mm., n_D^{25} 1.5086, a yield of 25.8%.

Anal. Calcd. for $C_9H_{19}Cl_3Sn$: C, 30.68; H, 5.44; Cl, 30.19. Found: C, 30.70; H, 5.47; Cl, 30.05.

(b) 1,3,3,3-Tetrachloropropyltriethyltin. A procedure similar to that described in (*a*) was used in the reaction of 22.4 g. (0.096 mole) of triethylvinyltin, 30.8 g. (0.2 mole) of CCl_4, and 1.2 g. of benzoyl peroxide. Fractional distillation gave a small forerun boiling from 35° at 2 mm. to 90° at 0.35 mm. and then 22.0 g. (59%) of $Et_3SnCHClCH_2CCl_3$, b.p. 100° at 0.3 mm., n_D^{25} 1.5230.

Anal. Calcd. for $C_9H_{18}Cl_4Sn$: C, 27.95; H, 4.69; Cl, 36.67. Found: C, 28.18; H, 4.40; Cl, 36.78.

(c) 1-Bromo-3,3,3-trichloropropyltriethyltin. A mixture of 23.4 g. (0.1 mole) of triethylvinyltin and 20 g. of $CBrCl_3$ was heated to 90°, and then a solution of 1.2 g. of benzoyl peroxide in 20 g. of $CBrCl_3$ was added slowly in small portions. A very vigorous reaction commenced and the pot temperature quickly rose to 160°. After this initial exotherm, the pot temperature dropped to 120° during the addition of the remainder of the peroxide solution. Upon completion of the addition the reaction mixture was heated on the steam bath for 2 hr.

Distillation gave first a mixture of volatiles boiling from 32° at 1.3 mm. to 115° at 0.6 mm. This fraction smelled of trialkyltin halides, indicating some cleavage had taken place. The desired adduct, $Et_3SnCHBrCH_2CCl_3$, 15 g. (34.8%), b.p. 115° at 0.65 mm. to 119° at 0.9 mm., n_D^{25} 1.5425, followed.

Anal. Calcd. for $C_9H_{18}Cl_3BrSn$: C, 25.07; H, 4.21; Cl, 24.67; Br, 18.53. Found: C, 25.00; H, 4.08; Cl, 24.93; Br, 18.29.

Reaction of triethylvinyltin with trichlorosilane. A mixture of 23.4 g. (0.1 mole) of triethylvinyltin, 27 g. (0.2 mole) of $HSiCl_3$ and 2 g. of benzoyl peroxide was heated in a Carius tube in a steam bath for 17 days. Fractional distillation of the reaction mixture gave 14 g. of unreacted trichlorosilane, a forerun boiling from 25–72° at 0.6 mm., and 11.5 g. (31.2%) of crude $Et_3SnCH_2CH_2SiCl_3$, b.p. 85° at 0.6 mm.

Anal. Calcd. for $C_8H_{19}Cl_3SiSn$: C, 26.08; H, 5.20; Cl, 28.87. Found: C, 27.07; H, 5.70; Cl, 29.64.

Two further fractional distillations did not improve the analytical values.

β-Trimethoxysilylethyltriethyltin. A slurry of 7 g. (0.128 mole) of sodium methoxide in 100 ml. of diethyl ether was cooled to 0°. A solution of 15.6 g. (0.0424 mole) of crude $Et_3SnCH_2CH_2SiCl_3$ in an equal volume of ether was added slowly with vigorous stirring. The mixture then was refluxed for 2 hr., filtered, and the salts were washed with ether, the ether washings being added to the filtrate. Fractional distillation of the ether solution gave 9.9 g. (65.8%) of $Et_3SnCH_2CH_2Si(OMe)_3$, b.p. 78° at 0.4 mm., n_D^{25} 1.4638, d_4^{25} 1.209.

Anal. Calcd. for $C_{11}H_{28}O_3SiSn$: C, 37.20; H, 7.95; MR_D 80.0. Found: C, 37.37; H, 7.94; MR_D 81.0.

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MALLINCKRODT CHEMICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASS.

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