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VINYLATION OF TRI-n-BUTYLTIN HYDRIDE

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During the course of an investigation of the reactions of acetylene with various reagents which are capable of generating free radicals, it was observed that tri-n-butyltin hydride added smoothly to acetylene. The product was tri-n-butylvinyltin, obtained in 75-80% yields (1). The reaction was conducted in benzene in an autoclave under 150-200 p.s.i.g. pressure of acetylene. A relatively mild reaction temperature of 75-80° was sufficient to initiate the reaction.

$$(n\text{-}C_4H_9)_3SnH + C_2H_2 \xrightarrow{\text{AIBN}} (n\text{-}C_4H_9)_3SnCH = CH_2 \qquad (1)$$

Tri-n-butylvinyltin has been prepared [1,2] by treating tri-n-butyltin chloride with excess vinylmagnesium bromide and by treating bis-tributyltin oxide with vinylmagnesium chloride. However, the present method has not been previously reported. It constitutes one of the few successful additions to unsubstituted acetylene to produce a vinyl derivati rather than a bis adduct.

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1. D. Seyferth and F. G. Stone, *J. Am. Chem. Soc.* **79**,515 (1957)
2. S. D. Rosenberg, A. J. Gibbons and H. E. Ramsden, *J. Am. Chem. Soc.* **79**, 2137 (1957).

The structure of tri-n-butylvinyltin was shown by boiling point, infra-red spectrum, nuclear magnetic resonance spectrum and elemental analysis.

A typical experiment was carried out in the following manner: A solution of 0.076 mole of tri-n-butyltin hydride, prepared from the chloride according to the procedure of van der Kerk[4], in 57 ml of dry, thiophene-free benzene, was placed in a standard, 300 ml stainless steel Aminco autoclave and 0.21 g of azobisisobutyronitrile was added. The autoclave was sealed, evacuated and purged three times with dry nitrogen and pressured to 155 p.s.i.g. with acetylene. It was heated to 80° with rocking for 30 minutes, cooled, the pressure released, and the contents charged to a distillation flask. The benzene was removed under vacuum, 1% hydroquinone was added to the residue, and 0.0615 mole of tri-n-butylvinyltin was collected as a colorless liquid, b.p. 88°/0.8 mm (literature[1,2] b.p. is 98°/1.5 mm and 114°/3 mm). The tin hydride absorbed strongly at 1810 $cm.^{-1}$ in the infra-red; the vinyl derivative had no absorption in this region, but showed absorption peaks at 943, 1007, 1900 and 3070 cm^{-1} and weak absorption at 1650, all characteristic of a vinyl group. The NMR spectrum unequivocally identified the protons from the three butyl groups and differentiated them from those of the vinyl group. Peak areas were in the correct ratio of 9:1.

Anal. Calcd. for $C_{14}H_{30}Sn$: C, 53.03; H, 9.54.

Found: C, 53.13; H, 9.49.

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[3] G. Gruettner, Ber. 50, 1812 (1917).

[4] G. J. M van der Kerk, J. G. Noltes and J. G. A. Luijten, J. Applied Chem. 7, 366 (1957).

There was obtained as by-product in the reaction a clear mobile liquid which could not be distilled. It was at first believed to be the hexakis tin compound that would arise from coupling of two tri-n-butyltin radicals (2).

$$2(n\text{-}C_4H_9)_3Sn\cdot \longrightarrow (n\text{-}C_4H_9)_3SnSn(n\text{-}C_4H_9)_3 \qquad (2)$$

However, the corresponding hexaisobutylbistannane boils[3] at 179°/3.5 mm without decomposition. The n-butyl compound should boil close to the iso derivative. Several attempts were made to distill the high boilers, but no distillate could be collected at 200° and 0.05 mm. Higher temperatures caused decomposition. When the azo initiator concentration was raised from 1% to 2%, the yield of vinyl monomer dropped from 81% to 55% with a corresponding increase in the undistillable high boilers The latter are therefore believed to consist of polymers of the vinyl tin derivative.

Investigation of other trisubstituted tin compounds with acetylene and a variety of catalysts and conditions is in progress.