

HYDROSTANNATION OF 2-VINYL-4,4,6-TRIMETHYL-1,3,2-DIOXABORINANE

RICHARD H. FISH*

U.S. Borax Research Corporation, Anaheim, California 92801 (U.S.A.)

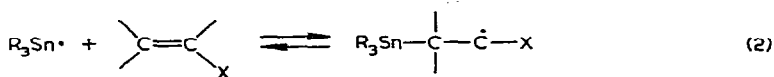
(Received March 14th, 1972)

SUMMARY

The hydrostannation of 2-vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane (VTDB) with trimethyl-, triethyl-, tripropyl-, tributyl-, and triphenyltin hydrides has been studied. The hydrostannation reactions, in all the cases studied, provided adducts with the organotin moiety at the β -carbon position; there was no indication of adducts with the organotin moiety at the α -carbon position. The reaction rate of tributyltin hydride with VTDB was accelerated by azobis(isobutyronitrile) (AIBN), retarded by galvinoxyl radical, and unaffected by change in solvent polarity. These observations confirm a free radical process for the hydrostannation of VTDB with triorganotin hydrides.

INTRODUCTION

The addition of organotin hydrides to substituted olefins (hydrostannation) has been recently summarized by Kuivila¹. Kuivila has pointed out that the majority of the hydrostannation reactions studied can be accommodated by a free radical chain mechanism (eqns. 1-3).



This free radical mechanism has been proven in several examples particularly by Neumann and Sommer². Recently, however, this mechanism for the hydrostannation of olefins substituted with electron-withdrawing groups has come under scrutiny by Leusink and Noltes³. They studied the hydrostannation of acrylonitrile with several organotin hydrides and found that α -adducts, as well as the usual β -

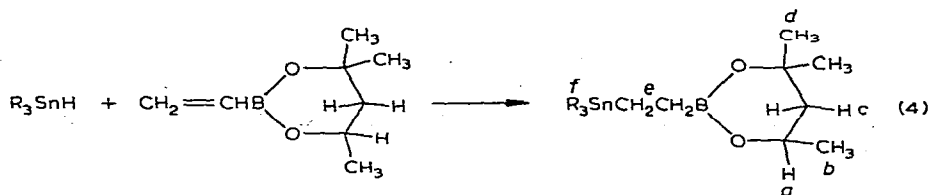
* Western Regional Research Lab., U.S. Department of Agriculture, Berkeley, California 94710 (U.S.A.)

adducts, were formed. In this example, both a radical mechanism (β -organotin substituent) and an ionic mechanism (α -organotin substituent) were in operation. There has been relatively little work done on the hydrostannation of vinylboron compounds. Seyferth and Takamizawa⁴ added triphenyl- and triethyltin hydrides to *B*-trivinyl-*N*-triphenylborazine and obtained definitive structure proof for the triphenyltin analog. They found that the triphenyltin group was attached to the carbon β to the boron atom. In a paper more related to the present work, Braun⁵ studied the addition of triethyltin hydride to 2-propenyl-1,3,2-dioxaborinane and found only the β -substituted organotin compound and none of the α -adduct.

In view of the fact that no mechanistic studies have been done on the hydrostannation of vinylboron compounds, we have studied the hydrostannation of 2-vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane (VTDB) with five organotin hydrides in order to establish the mode of addition and the structure of the adducts. We have utilized a free radical initiator (AIBN), an inhibitor (galvinoxyl), and the effect of solvent polarity (cyclohexane/butyronitrile) on the rate of hydrostannation of VTDB by tributyltin hydride to prove the free radical nature of this hydrostannation reaction.

RESULTS AND DISCUSSION

The hydrostannation reactions were carried out in sealed glass ampoules and the adducts (I)–(V) were identified by infrared and nuclear magnetic resonance (NMR) spectroscopy, as well as chemical degradation studies. The preparative, physical, and analytical data are tabulated in Table 1, while the NMR data are shown in Table 2 for adducts (I)–(V). The results indicate that the hydrostannation reactions (eqn. 4) proceed to place the triorganotin moieties on the β carbon in all the cases studied.



I, R = Me; II, R = Et; III, R = Pr; IV, R = Bu; V, R = C₆H₅

STRUCTURE ANALYSIS

The structure of (I) was ascertained from its NMR spectrum, which notably gave a triplet at τ 9.16 (4 protons). This is consistent with two methylene groups flanked on one side with a boron atom and on the other side with a tin atom having similar chemical shifts. Gas-liquid chromatography (GLC) showed (I) to be homogeneous on several columns. The reaction of (I) with bromine gave the expected methyl bromide, and no trimethyltin-bromide was detected (GLC). This is consistent with the trimethyltin group being on the carbon atom that is β to the functional group⁶ (*i.e.* dioxaborinane ring). We also attempted to oxidize the boron-carbon bond with alkaline hydrogen peroxide to obtain the trimethylstannylethanol; however, the

TABLE I
 PREPARATIVE, PHYSICAL AND ANALYTICAL DATA ON THE 2-VINYL-4,4,6-TRIMETHYL-1,3,2-DIOXABORINANE-ORGANOTIN HYDRIDE ADDUCTS

Organotin hydride	Compound	Conditions ^{a,b}		b.p. (°C/mm)	Yield	n_D^{20} (°C)	Formula	Analysis (%)		Prominent infrared bands
		Temp. (°C)	Time (h)					Found (calcd.)	C H	
(CH ₃) ₃ SnH	(I)	110 ^a	30	59/0.1	70	1.4671 (25)	C ₁₁ H ₂₃ O ₂ SnB	41.28 (41.56)	7.97 (7.87)	3050 s, 1400 s, 1325 s, 765 s
(CH ₃ CH ₂) ₃ SnH	(II)	100 ^a	5	110-112/0.15	69	1.4779 (25)	C ₁₄ H ₃₁ O ₂ SnB	46.12 (46.40)	8.52 (8.66)	3000 s, 1400 s, 1359 s, 1225 s
(CH ₃ CH ₂ CH ₂) ₃ SnH	(III)	100 ^a	5	136-137/0.5	58	1.4791 (21)	C ₁₇ H ₃₉ O ₂ SnB	50.65 (50.78)	9.25 (9.21)	2900 s, 1440 s, 1300 s, 1100 s
[CH ₃ (CH ₂) ₂ CH ₂] ₃ SnH	(IV)	110 ^a	23	135-137/0.3	78.5	1.4750 (25)	C ₂₀ H ₄₃ O ₂ SnB	53.78 (54.01)	9.60 (9.75)	2950 s, 1375 s, 1210 s
Ph ₃ Sn	(V)	70 ^{a,c}	8	205-215/0.7	38	—	C ₂₆ H ₃₁ O ₂ SnB	61.75 (61.83)	6.13 (6.19)	3100 s, 3000 s, 1425 s, 1390 s, 1300 s, 1200 s, 725 s, 689 s

^a Catalyzed with 2 mole percent AIBN. ^b Unanalyzed reaction. ^c Reaction run in hexane, all others neat.

TABLE 2

NMR SPECTRAL DATA ON THE 2-VINYL-4,4,6-TRIMETHYL-1,3,2-DIOXABORINANE-ORGANOTIN HYDRIDE ADDUCTS^{a,b}

Adduct	Conc. in CCl ₄ (%)	a	b	c	d	e	f
(I)	50	6.05 m ^{c,d}	8.83 d	8.3 m	8.75 s	9.16 t	9.97 s
(II)	35	5.85 m	8.93 d	7.9–8.4 m	8.75 s	9.17 m	8.93–9.4 m
(III)	35	5.83 m	8.81 d	7.85–8.5 m	8.71 s	8.8–9.25 m	8.8–9.25 m
(IV)	35	5.81 m			7.8–9.3 m		
(V)	25	6.15 m	9.02 d	8.51 m	8.90 s	9.05 m	2.2–2.9 m

^a See Eqn. 4 for structure and proton designation.

^b Center of each multiplet. Spectra recorded on a Varian A60-A instrument with TMS as internal standard.

^c m = multiplet, s = singlet, d = doublet, t = triplet.

^d Integrated ratios for I (a–f) were 1/3/2/6/4/9. Those for II–IV were difficult to integrate, while V had values of 1/3/2/6/4/15.

hexylene glycol which formed interfered with the isolation of the tin alcohols (GLC).

The adducts (II), (III), and (IV) had NMR spectra which were difficult to interpret, hence we resorted to their GLC purity and their reaction with bromine to resolve their structures. All the adducts (II), (III), and (IV) were homogeneous (GLC) using several columns, while reaction with bromine produced ethyl bromide, n-propyl bromide, and n-butyl bromide respectively. In all cases no corresponding trialkyltin bromide could be detected (GLC). Again, alkaline hydrogen peroxide produced mixtures which were inseparable via GLC. Hence none of the tin ethanols could be identified. The triphenyltin analog (V) was, however, quite smoothly oxidized to β -triphenylstannylethanol (VI).

MECHANISM OF ADDITION

It was of interest to prove that indeed a free radical mechanism for the addition of triorganotin hydrides to VTDB was in effect. In this regard, the reaction rate of tributyltin hydride with VTDB was conveniently followed using the absorption of the Sn–H stretch at 1835 cm⁻¹ in the infrared². Figure 1 shows the results. AIBN, a well known free radical initiator, dramatically increased the rate of reaction while galvinoxyl radical, a well known free radical inhibitor, dramatically inhibited the reaction rate. This substantiates a free radical chain mechanism for the hydrostannation of VTDB. We also ran the reaction in cyclohexane, 80/20 cyclohexane/butyronitrile, and 50/50 cyclohexane/butyronitrile without any substantial rate increase (Fig. 2). The point made in this experiment is that if an ionic mechanism were in operation, increasing the solvent polarity (*i.e.* cyclohexane to 50/50 cyclohexane/butyronitrile) should have increased the rate of reaction. This obviously did not happen and further substantiates a free radical mechanism for the hydrostannation of VTDB (eqns. 2 and 3).

The free radical mechanism for the hydrostannation of VTDB is consistent with the fact that boron has the ability to stabilize a radical on an α carbon through its vacant 2p orbital⁷. Together with the fact that only extremely powerful electron-with-

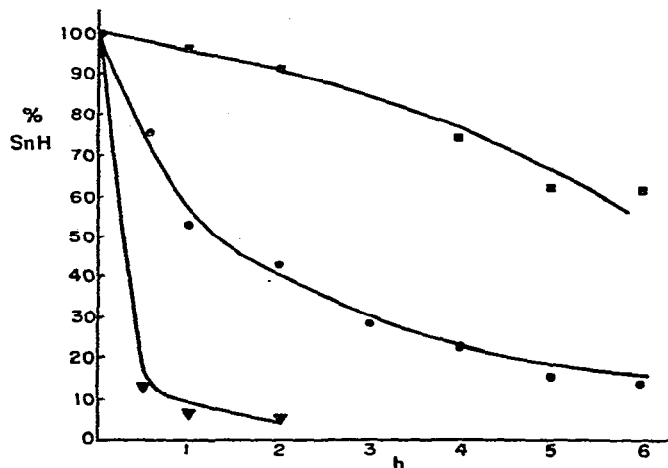


Fig. 1. Plot of % Bu_3SnH vs. time in the addition of Bu_3SnH to VTDB. ●, uncatalyzed reaction at 100° 1/1 mole ratio; ▼, catalyzed with 2 M % AIBN; ■, galvinoxyl 2 M % as an inhibitor.

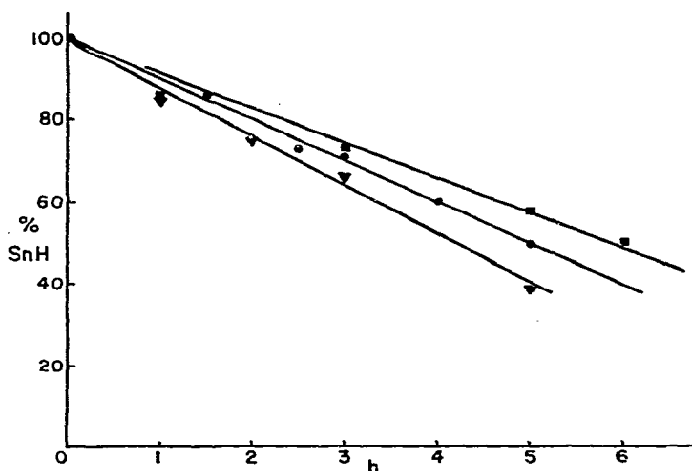


Fig. 2. Solvent effect in the addition of Bu_3SnH to VTDB. Plot of % Bu_3SnH vs. time. ▼, thermal reaction at 100° 0.01 mole in each reactant in 20 ml of cyclohexane; ●, 20 ml of 50/50 cyclohexane/butyronitrile; ■, 20 ml of 80/20 cyclohexane/butyronitrile.

drawing groups (e.g. CN) attached to olefins are capable of ionic hydride additions to give α -substituted triorganotin adducts³, this leads one to conclude that the $-\text{BO}_2$ group attached to an olefin is, as Matteson⁸ points out, weakly electron-withdrawing.

EXPERIMENTAL

Materials

The VTDB was generously supplied by Dr. William G. Woods of these laboratories. The trimethyltin, triethyltin, tripropyltin, and triphenyltin hydrides were prepared by reducing the corresponding chloride with lithium aluminum hydride.

Tributyltin hydride was prepared by reducing bis(tributyltin) oxide with lithium aluminum hydride. The GLC was done on a Varian Aerograph 1520-B with XF-1150 (silicon nitrile on Chrom W), SE-30, and Carbowax 20M columns.

A typical hydrostannation reaction

To 6.8 g (0.041 mole) trimethyltin hydride was added 12.4 g (0.082 mole) 2-vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane (VTDB) in a glass ampoule. The ampoule was sealed at -78° and then heated in a bath at 110° for 30 h. Distillation gave 9.12 g (70%) b.p. $59^{\circ}/0.1$ mm n_D^{25} 1.4671 of adduct (I). The adducts, (I)–(IV) were examined on three different GLC columns (XF-1150, SE-30, and Carbowax 20M on Chrom W) and were all found to be homogeneous. See Table 1 for analytical and physical data for all the adducts (I)–(V).

Reaction of 2-(tributylstannylethyl)-4,4,6-trimethyl-1,3,2-dioxaborinane with bromine

In a flask equipped with a magnetic stirring bar, reflux condenser and a serum cap was placed 1.0 g ($2.2 \cdot 10^{-3}$ mole) 2-(tributylstannylethyl)-4,4,6-trimethyl-1,3,2-dioxaborinane. To the neat solution was added dropwise 0.3515 g ($2.2 \cdot 10^{-3}$ mole) bromine. The reaction was followed by GLC (5 ft. \times 0.25 in. silicone nitrile (XF-1150) column at 60°). As compound (IV) disappeared, butyl bromide appeared. We also looked for tributyltin bromide but, however, none was observed. Attempts to isolate the 2-(bromodibutylstannylethyl)trimethyl-1,3,2-dioxaborinane by distillation were unsuccessful, since reaction of this product with bromine competes with compound (IV). Then a mixture of bromo compounds were obtained as evidenced by elemental analysis and NMR spectroscopy.

Reaction of (I), (II), and (III) with bromine

In a similar manner as with compound (IV), (I), (II), and (III) were reacted with bromine and then analyzed by GLC to give methyl, ethyl and n-propyl bromides, respectively.

Oxidation of (V)

In a three-necked flask equipped with a magnetic stirrer, reflux condenser and addition funnel was placed 4.05 g of (V), 0.8 g of sodium hydroxide in 5 ml of 95% ethanol and 10 ml of ether. The reaction mixture was brought to reflux and then 4.8 g of 30% hydrogen peroxide was slowly added. The reaction mixture, after addition of hydrogen peroxide, was cooled to room temperature and then water (24 ml) and ether (24 ml) were added. The ether layer was separated and dried and then evaporated to give a white solid. The solid was recrystallized from 20– 40° ligroin to give 1.6 g (51%) m.p. 66 – 68° (lit.⁴ 67 – 68°) of β -triphenyltinethanol.

Oxidation of (II), (III), and (IV)

Oxidation of (II), (III), and (IV) was carried out by the same method as with (V), however, attempts to separate the triorganostannylethanols from hexylene glycol by distillation or preparative GLC were unsuccessful.

Rate studies on the tributyltin hydride addition to 2-vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane

Tributyltin hydride, which has a strong Sn–H stretching band at 1835 cm^{-1} in

the infrared spectrum, was used in these rate studies, since its disappearance could be followed conveniently. The reactions were run neat at $100 \pm 2^\circ$ (each reactant was 0.01 mole) in a flask equipped with a magnetic stirring bar and a rubber septum for ease of sampling. The reactions were run under an atmosphere of prepurified nitrogen, and at appropriate intervals samples were removed via a syringe and placed in an IR cell (0.1 mm path length with a volume of 8 μ l) and the spectrum recorded. The disappearance of the Sn-H band at 1835 cm^{-1} was followed at intervals for 6 h. The reactions run in solvents were as follows: The reactants (0.01 mole) were dissolved in 20 ml of solvent or cosolvent and analyzed as described above.

REFERENCES

- 1 H. G. Kuivila, *Advan. Organometal. Chem.*, 1 (1964) 47.
- 2 W. P. Neumann and R. Sommer, *Ann.*, 675 (1964) 10.
- 3 A. J. Leusink and J. G. Noltes, *Tetrahedron Lett.*, (1966) 335.
- 4 D. Seyferth and M. Takamizawa, *Inorg. Chem.*, 2 (1963) 731.
- 5 J. Braun, *C.R. Acad. Sci. Paris*, 260 (1965) 218.
- 6 G. J. M. van der Kerk and J. G. Noltes, *J. Appl. Chem.*, 9 (1959) 179.
- 7 W. G. Woods, I. S. Benglesdorf and D. L. Hunter, *J. Org. Chem.*, 31 (1966) 2766.
- 8 D. S. Matteson, *Organometal. Chem. Rev.*, 1 (1966) 1.

J. Organometal. Chem., 42 (1972)