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REACTIONS OF *trans*-CINNAMYLTRIETHYL- AND *trans*-CINNAMYLTRIPHENYLTIN WITH TRIBROMOBORANE. PREFERENTIAL TRANSFER OF THE CINNAMYL GROUP FROM TIN TO BORON

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SUMMARY

The syntheses of *trans*-cinnamyltriethyl- and *trans*-cinnamyltriphenyltin and their reactions with tribromoborane are described. The *trans*-cinnamyl residue on the tin is found to be transferred preferentially to boron, probably through a four-centered transition state or a six-membered cyclic transition state. The double bond in *trans*-cinnamyl group is attacked later by tribromoborane.

INTRODUCTION

Though the reactions of tetrasubstituted organotin compounds (I) with trihaloboranes have been known as a general method for the preparation of organoboranes[1-6], the reaction has been hitherto performed only with organotin compounds of type R_4Sn, in which the tin atom is substituted by four groups of the same kind.

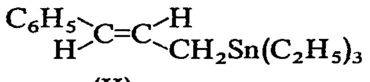
$$R_4Sn + BX_3 \rightarrow R_3SnX + RBX_2 \rightarrow\rightarrow R_3B + RSnX_3$$

(I)

R = Alkyl, aryl, or vinyl

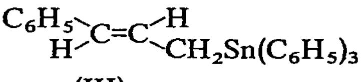
It is thus of considerable interest to investigate this valuable reaction using an unsymmetrically substituted organotin compound to obtain information concerning the reaction mechanism.

In the present investigation, the *trans*-cinnamyl group was selected as the substituent and reactions of *trans*-cinnamyltriethyltin (II) and *trans*-cinnamyltriphenyltin (III) with tribromoborane were investigated.



$$\begin{matrix}C_6H_5 & & & & H\\ & \!\!\searrow C{=}C\swarrow\!\! & & & \\ H & & & & CH_2Sn(C_2H_5)_3\end{matrix}$$

(II)

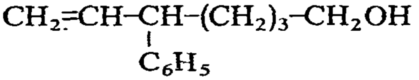


$$\begin{matrix}C_6H_5 & & & & H\\ & \!\!\searrow C{=}C\swarrow\!\! & & & \\ H & & & & CH_2Sn(C_6H_5)_3\end{matrix}$$

(III)

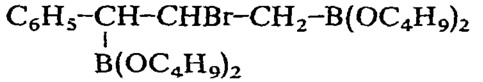
RESULTS AND DISCUSSION

During the course of preparations of (II) and (III), it was found that the cross-coupling reaction between trisubstituted-tin chloride and cinnamyl bromide by magnesium was successful only when the magnesium turnings used in stoichiometric quantity[7]. Thus, (II) and (III) were obtained in 75% and 71% yields, respectively, when an equimolar mixture of the tin chloride and cinnamyl bromide was added to an exactly equivalent amount of magnesium turnings in tetrahydrofuran. When a three-to-five-fold excess of magnesium was used[7], the only product isolated was 5-phenyl-6 hepten-1-ol [(IV), 64% yield].



$$CH_2{=}CH{-}\underset{\displaystyle C_6H_5}{CH}{-}(CH_2)_3{-}CH_2OH$$

(IV)

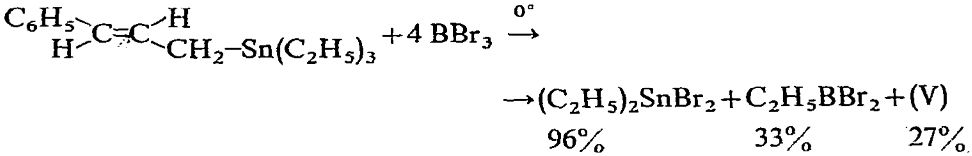


$$C_6H_5{-}\underset{\displaystyle B(OC_4H_9)_2}{CH}{-}CHBr{-}CH_2{-}B(OC_4H_9)_2$$

(V)

This product probably arose from substitution product which would be formed by the reaction of intermediate 1-phenyl-2-propenyl radical with tetrahydrofuran.

A reaction of (II) with a four-fold excess of tribromoborane was carried out at 0° under an argon stream. The volatile products which were obtained were diethyltin dibromide (96%)* and ethyldibromoborane (33%)* (which was characterized further by converting it into di-n-butyl ethylboronate). The residue (V) could not be purified by the distillation but was examined by IR spectroscopy.

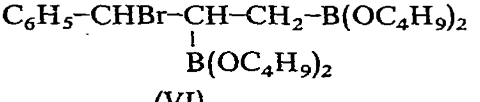


$$\xrightarrow{}(C_2H_5)_2SnBr_2 + C_2H_5BBr_2 + (V)$$

96% 33% 27%

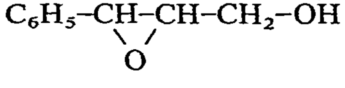
Observed were absorptions due to a monosubstituted phenyl group at 695 and 745 cm^{-1} and a broad peak due to $-BBr_2$ asymmetric stretching at 790–840 cm^{-1} (ref. 9), but characteristic absorptions due to a *trans*-cinnamyl group were absent in the spectrum. Since this product mixture was very sensitive towards oxygen and further purification was impossible, it was treated with n-butanol[8]. The butyl ester of diboronic acid (V) was obtained in 27% yield based on the starting (II)**. The structure of (V) was ascertained by elemental analysis, molecular weight determination and IR and ^1H NMR spectra.

Particularly, the ^1H NMR spectrum is best explained by the structure (V) and not by an alternative, (VI). Moreover, the chemical inertness of C–Br group in (V)



$$C_6H_5{-}CHBr{-}\underset{\displaystyle B(OC_4H_9)_2}{CH}{-}CH_2{-}B(OC_4H_9)_2$$

(VI)



(VII)

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* Yields are all based on the starting (II) or (III) unless otherwise indicated.

** The residue of this butanolysis product was a tarry material which could not be characterized.

under the butanolysis conditions indicates that the bromide does not occupy the benzylic position since benzyl bromide is known to be solvolyzed much more easily than an alkyl bromide[10]. If (VI) were to be the correct structure, the bromide may not survive butanolysis reaction. Thus structure (V) seems indicated. Furthermore, structure (V) was confirmed by the oxidation of this product with alkaline hydrogen peroxide to give 2,3-epoxycinnamyl alcohol, (VII).

The reaction of (III) with a four-fold excess of tribromoborane gave the same results as above. Isolated diphenyltin dibromide (97%), phenyldibromoborane (28%), and an oxygen sensitive material from which diboronic ester (V) was obtained in 36% yield after butanolysis.

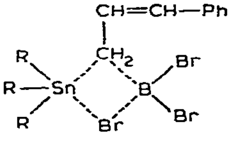
(III) was also reacted with an equivalent amount of diphenylbromoborane at 0°. Triphenyltin bromide was obtained in high yield (90%) and a boron derivative also was present. A careful analysis of its IR spectrum showed the characteristic absorption of the *trans*-cinnamyl group at 1640 and 960 cm^{-1}. Its NMR spectrum also indicated that the group was the *trans*-cinnamyl and not 1-phenyl-2-propenyl.

It was observed in these studies that the formation of diethyltin dibromide, diphenyltin dibromide, and triphenyltin bromide in these reactions was quantitative. Thus the *trans*-cinnamyl group reacts with tribromoborane much more rapidly than do the ethyl or phenyl groups; none of *trans*-cinnamyl residue has remained on the tin after the reaction[*]. The preferential transfer of the *trans*-cinnamyl group in the present reaction may be rationalized by either one of the following two alternatives:

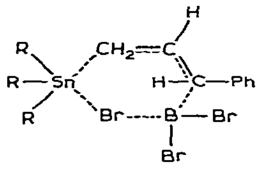
(1). It proceeds through a four-centered cyclic transition state (VIII) as those proposed.

(2). Extended conjugation in the *trans*-cinnamyl group will provide enough stabilization for the transition state of its preferential reaction, so the transfer of the *trans*-cinnamyl group takes place through a six-membered cyclic transition state (IX) which is very favorable in the reactions of carbon analog. A remaining double bond, cinnamyl group in the former and vinyl in the latter, might be easily attacked further by unconverted tribromoborane to afford the products (V) and (VI)[**].

It may be noted that *trans*-cinnamyldibromoborane etherate (X) (prepared in 4% yield reaction of *trans*-cinnamyllithium with a two-fold excess of tribromoborane in ether) reacted with excess tribromoborane to give a product which on treatment with n-butanol at 0° afforded (V) in quantitative yield.



(VIII)



(IX)

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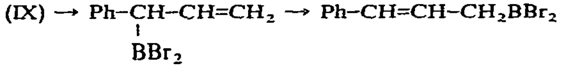
[*] It should be noted that the amount of tribromoborane used in the reaction was 4 times equivalent to that of the tin compound.

[**] Accordingly to referee's suggestion, by analogy with other electrophilic displacements involving allylic organometallics, a six-membered cyclic transition state (IX) may be the initial step to form a product which isomerizes to the cinnamylborane.



$$(IX) \rightarrow \underset{\displaystyle BBr_2}{Ph\text{-}CH}\text{-}CH{=}CH_2 \rightarrow Ph\text{-}CH{=}CH\text{-}CH_2BBr_2$$

CONCLUSIONS

The reaction of *trans*-cinnamyltriethyltin or -triphenyltin with tribromoborane proceeds with the preferential transfer of the *trans*-cinnamyl group from tin to boron. The transformation possibly proceeds through a four-centered cyclic transition state or a six-membered cyclic transition state. The resulting *trans*-cinnamyldibromoborane is attacked further by excess tribromoborane to afford 1-phenyl-2-bromo-1,3-bis(dibromoboryl)propane.

EXPERIMENTAL

The IR spectra were recorded with a Hitachi-S2 spectrophotometer; the NMR spectra were recorded by a Japan Electron Optics JNR-4H-100 or JNM-MH-60 spectrometer; GLC analyses were made by a Yanagimoto GCG gas chromatograph; molecular weight determinations were made by a Mechrolab VPO Model 301A. Diethyl ether and tetrahydrofuran were dried over sodium and distilled from lithium aluminum hydride.

Preparation of trans-cinnamyltriethyltin, (II) and -triphenyltin, (III)

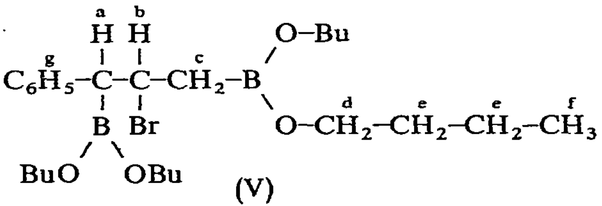
Magnesium turnings (14.7 g, 0.609 g-atom) were placed in a three necked flask equipped with a water condenser, mechanical stirrer, and an addition funnel. Tetrahydrofuran (250 ml) was added, and the reaction was initiated by adding a small amount of *trans*-cinnamyl bromide[11]. The rapidly stirred mixture was then heated to reflux, and a solution of triethyltin chloride[12] (94.0 g, 0.390 mole) and *trans*-cinnamyl bromide (120.0 g, 0.609 mole) in tetrahydrofuran (250 ml) was added slowly over the course of 1½ h. After the addition had been completed, the reaction mixture was heated at reflux overnight, cooled, and hydrolyzed with saturated ammonium chloride solution. After decanting the supernatant organic phase and washing the inorganic salts with ether, the combined organic layers were distilled to remove solvent and then distillation under reduced pressure afforded *trans*-cinnamyltriethyltin (94.0 g, 74.6%), b.p. 145.0–147.0°/4 mm. The IR spectrum showed bands at 1635 cm^{-1} (weak, olefin) and at 966 cm^{-1} (strong, *trans*-olefin). The NMR spectrum (in CCl_4, τ) showed a multiplet at 2.80, 5 H (phenyl protons); a multiplet at 3.75, 2 H (vinyl protons); a doublet at 8.05, $J = 8$Hz, 2 H (allyl protons); a multiplet at 8.80, 6 H (ethyl protons); a multiplet at 9.10, 9 H (methyl protons); [Found: C, 55.72; H, 7.31; mol.wt. (VPO), 311. $C_{15}H_{24}Sn$ calcd.: C, 55.77; H, 7.48%; mol.wt., 323].

trans-Cinnamyltriphenyltin was prepared by a cross-coupling reaction of triphenyltin chloride[13] (100.0 g, 0.260 mole), *trans*-cinnamyl bromide (80.0 g, 0.406 mole) and magnesium turnings (9.8 g, 0.406 g-atom) in tetrahydrofuran as described above. The organic phase was concentrated under reduced pressure and the solid residue was crystallized from petroleum ether. Recrystallization from petroleum ether gave *trans*-cinnamyltriphenyltin (86.4 g, 71.4%), m.p. 73.0–74.0°. The IR spectrum showed bands at 1635 cm^{-1} (weak, olefin) and at 960 cm^{-1} (strong, *trans*-olefin). The NMR spectrum (in CCl_4, τ) showed a multiplet at 2.80, 20 H (phenyl protons); a multiplet at 3.70, 2 H (vinyl protons); a doublet at 7.45, $J = 8$ Hz, 2 H (allyl protons). [Found: C, 69.50; H, 5.21; mol.wt. (VPO), 441. $C_{27}H_{24}Sn$ calcd.: C, 69.41; H, 5.20%; mol.wt., 467.]

When in the attempted preparation of *trans*-cinnamyltriethyltin and -triphenyltin, a tetrahydrofuran solution of an equimolar mixture of triorganotin chloride and *trans*-cinnamyl bromide was added to an excess (3 to 5 times) of magnesium turnings in tetrahydrofuran a different result was obtained[7]. The reaction mixture was heated at reflux overnight, cooled, and treated in the usual manner. Distillation gave high boiling material, GLC analysis of which showed the presence of one major high boiling component which was identified as 5-phenyl-6-hepten-1-ol (IV) (64%). The IR spectrum showed bands at 3350 cm^{-1} (strong, O–H), at 1635 cm^{-1} (weak, olefin), at 1055 cm^{-1} (strong, C–O), at 990 and 910 cm^{-1} (strong, $C{=}CH_2$). The NMR spectrum (in CCl_4, τ) showed a multiplet at 2.90, 5 H (phenyl protons); a multiplet at 5.0, 2 H (vinyl protons); a triplet at 6.50, 2 H ($-CH_2-OH$); a multiplet at 6.75, 1 H (benzyl proton); a singlet at 7.55, 1 H (alcohol proton); a multiplet at 8.50, 6 H [$-(CH_2)_3-CH_2-OH$]. [Found: C, 82.06; H, 9.54; mol.wt. (VPO), 176. $C_{13}H_{18}O$ calcd.: C, 81.51; H, 9.47%; mol.wt., 190.]

The reaction of trans-cinnamyltriethyltin with tribromoborane

Tribromoborane (27.2 g, 0.108 mole) was placed in a three necked flask equipped with a water condenser, mechanical stirrer and an addition funnel, and *trans*-cinnamyltriethyltin (8.8 g, 0.0272 mole) was added slowly at 0°. The color of the reaction mixture changed from colorless to deep red and solid precipitated. After the *trans*-cinnamyltriethyltin had been added, the reaction mixture was treated very slowly with n-butanol (30.0 g, 0.405 mole) at 0°. The reaction was highly exothermic and hydrogen bromide was evolved. The system was warmed to room temperature and freed from hydrogen bromide at 20°/40 mm. All these procedures were performed under an argon atmosphere. Fractional distillation of the mixture in vacuum afforded 1.8 g of dibutoxyethylborane (33%), b.p. 84.5–86.5°/8 mm, reported[14] 70–71°/7 mm, 13.9 g of tributyl borate, b.p. 98–101°/8 mm, reported[15] 103–108°/8 mm, 8.8 g of diethyltin dibromide (96%), b.p. 102–105°/8 mm, m.p. 62.0–63.0°, reported[16] 63.0°, and 3.8 g of 1-phenyl-2-bromo-1,3-bis(dibutoxyboryl)propane (V) (27%), b.p. 105–106°/10^{-3} mm. [Found: C, 58.40; H, 9.27; Br, 15.32; mol.wt. (VPO), 555. $C_{25}H_{45}B_2BrO_4$ calcd.: C, 58.74; H, 8.87; Br, 15.66%; mol.wt., 511]. The IR spectrum: 3060 m, 2960 s, 2900 s (sh), 1605 w, 1495 m, 1455 s, 1415 m, 1375 m, 1360 m (sh), 1340 m, 1315 w, 1250 m, 1230 m, 1070 w, 1030 w, 760 s, 700 s. The NMR spectrum (in CCl_4, τ) showed a multiplet at 2.90, 5 H [proton g in (V)]; a multiplet at 6.30, 2 H [proton d in (V)]; a multiplet at 6.50, 1 H [proton b in (V)]; a multiplet at 8.60, 5 H [proton e and a in (V)]; a multiplet at 9.10, 5 H [proton c and f in (V)]. The residue (5.6 g) was uncharacterised polymeric material.



(V)

Solvolysis of (V)

n-Butanol (1.0 g, 13.5 mmole) was added to (V) (0.0726 g, 0.142 mmole) and heated at 100° for 5 h. After heating, the distillation of the mixture in high vacuum afforded 0.0641 g of (V).

Oxidation of (V) with alkaline hydrogen peroxide

An ether (20 ml) solution of (V) (2.6 g, 5.0 mmoles) was oxidized at room temperature by the addition of 10 ml of a 3 *N* solution of sodium hydroxide, followed by the dropwise addition of 10 ml of 30% hydrogen peroxide. The mixture was stirred an additional 2 h at room temperature. After separating the ether layer and washing the aqueous layer with ether, the combined organic layers were distilled to remove solvent. Distillation of the residue under reduced pressure afforded 2,3-epoxycinnamyl alcohol (VII) (0.63 g, 83.7%), b.p. 159–160°/1.0 mm. The IR spectrum showed at 3350 cm^{-1} s (O–H), 1070 m and 1030 s cm^{-1} (C–O). The NMR spectrum (in CCl_4, τ) showed a multiplet at 2.80, 5 H (phenyl protons); a doublet at 6.48, $J=5.5$ Hz, 1 H (benzyl proton); a multiplet at 6.60, 2 H (methylene protons); a multiplet at 7.15, 1 H (methine proton); a singlet at 7.50, 1 H (alcohol proton). [Found: C, 71.87; H, 6.88; mol.wt. (VPO), 148. $C_9H_{10}O_2$ calcd.: C, 72.000; H, 6.67%; mol.wt., 150.]

The reaction of trans-cinnamyltriphenyltin with tribromoborane

The reaction *trans*-cinnamyltriphenyltin (12.5 g, 0.0270 mole) with tribromoborane (27.2 g, 0.108 mole) was performed as described above. After addition of the *trans*-cinnamyltriphenyltin was complete, the reaction mixture was treated slowly with n-butanol (30.0 g, 0.405 mole) at 0°. Fractional distillation in vacuum gave 15.0 g of tributyl borate, b.p. 97–101°/8 mm, 1.8 g of dibutoxyphenylborane (28%), b.p. 116–118°/4 mm, reported[17] 94°/0.3 mm, 11.3 g of diphenyltin dibromide (97%), b.p. 113–121°/2 mm, m.p. 37.5–38.0°, reported[18] 38°, and 5.0 g of (V) (36%). The residue (6.1 g) was polymeric material.

The reaction of trans-cinnamyltriphenyltin with bromodiphenylborane

Bromodiphenylborane[19] (3.5 g, 0.014 mole) was placed in a three necked flask equipped with a condenser and an argon inlet tube, and *trans*-cinnamyltriphenyltin (6.7 g, 0.014 mole) was added in small portions at room temperature. The reaction was highly exothermic and solid was precipitated. After the filtration of the solid, distillation of the mixture yielded 1.3 g of *trans*-cinnamyldiphenylborane (32%), b.p. 118–120°/10^{-2} mm. The IR spectrum showed bands at 1642 cm^{-1} (olefin), 1275 cm^{-1} (B–C) and 975 cm^{-1} s (*trans*-olefin). The NMR spectrum showed (in CCl_4, τ) a multiplet at 2.85, 15 H (phenyl protons); a multiplet at 3.85, 2 H (vinyl protons); a doublet at 8.80, 2 H (allyl protons). The solid was recrystallized from ether to give 5.8 g of triphenyltin bromide (90%), m.p. 121–122°, reported[20] 120–121°.

Preparation of trans-cinnamyllithium in diethyl ether and its reaction with tribromoborane in diethyl ether

trans-Cinnamyltriphenyltin (25.0 g, 0.0540 mole) in ether (105 ml) was placed in a three necked flask equipped with an addition funnel, mechanical stirrer, and a water condenser topped with an argon inlet tube. A solution of phenyllithium prepared from lithium metal (1.04 g, 0.153 g-atom) and bromobenzene (11.2 g, 0.070 mole) in ether (50 ml) was added at room temperature. A white precipitate formed immediately. The mixture was stirred for 30 min. The solid material was filtered and the filtrate was transferred to an addition funnel under argon. Recrystallization of the precipitate from benzene gave 22.7 g of tetraphenyltin (99%), m.p. 222–223°, reported[20] 225–226°. Carbonation of an aliquot of the filtrate by the usual method afforded 4-phenyl-3-butenoic acid in 78% yield, m.p. 85.5–86.5°, reported[21] 86.0–88.0°. Tribromoborane (25.0 g, 0.100 mole) was added to ether[22] (100 ml) in a three necked flask equipped with a water condenser, mechanical stirrer and an addition funnel. To this solution was added the previously prepared *trans*-cinnamyllithium in ether at 0° during 40 min. Distillation of the reaction mixture afforded 0.8 g of *trans*-cinnamyldibromoborane etherate (X) (4.0%), b.p. 63.0–64.0°/16 mm. The IR spectrum: 3050 m, 3000 m, 2950 s, 2850 m, (sh), 1635 w, 1600 w, 1490 s, 1450 s, 1370 m, 1330 m, 1190 w, 1060 w, 1028 m, 985 m, 960 s, 910 s, 760 s, (sh), 730 s, 695 s. The NMR spectrum showed (in CCl_4, τ) a multiplet at 2.9, 5 H (phenyl protons); a multiplet at 5.2, 2 H (vinyl protons); a quartet at 6.4, 4 H (ethyl protons); a multiplet at 9.1, 6 H (methyl protons); a multiplet at 9.4, 2 H (allyl protons).

Independent preparation of (V)

(X) (0.8 g, 0.0022 mole) was placed in a three necked flask equipped with a water condenser, mechanical stirrer and an addition funnel and tribromoborane (1.1 g, 0.0044 mole) was added at 0°. n-Butanol (0.4 g, 0.054 mole) then was added slowly at 0° under an argon stream. Distillation of the reaction mixture in vacuum afforded 1.1 g of (V) (98%).

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