# Chemistry

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1961

SovietRxiv

## Abstract

## Full Text

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## STUDIES IN THE FIELD OF BORON COMPOUNDS

### SYNTHESIS AND PROPERTIES OF TRI-(ω-STYRYL)-BORON

The present work describes the synthesis of tri-(ω-styryl)-boron, which was obtained by the action of the corresponding Grignard reagent (1) on boron trifluoride etherate. A major role in obtaining tri-(ω-styryl)-boron is played by the ratio of the Grignard reagent to boron trifluoride etherate. Tri-(ω-styryl)-boron was obtained in a yield of about 76% in tetrahydrofuran, under a stream of dry argon, at the following molar ratio of reagents: Mg : $C_8H_7Br$ : $(C_2H_5)_2O \cdot BF_3$ = 7 : 3 : 2. It consists of needle-like or columnar crystals with m.p. 64–65°. When the reaction mixture was treated with pyridine, the complex $(\omega\text{-}C_8H_7)_3B \cdot C_5H_5$ was formed—needle-like crystals with a decomposition temperature of 138–140°.

Attempts to synthesize tri-(ω-styryl)-boron at the same ratios in a stream of purified nitrogen led to the formation of the complex compound $[(C_6H_5CH{=}CH_2)_4]$MgBr. It crystallizes from tetrahydrofuran solution with two molecules of solvent, and from ether solution with three molecules of solvent; on heating it loses solvent, and at a temperature of about 300° decomposes with formation of styrene and a carbonaceous precipitate. In air it does not deliquesce, but becomes covered with a white coating. M.p. of the crystals 88–90° (with decomposition). With water the complex compound reacts vigorously, forming styrene, boric acid, and MgBrOH. When the reaction mixture was treated by the method described by V. A. Sazonova and N. Ya. Kronrod (2), followed by drying of the crystals, the anhydride of ω-styrylboronic acid was obtained.

By treating the complex salt with dry hydrogen chloride, tri-(ω-styryl)-boron was isolated.

The temperature of the experiment in obtaining tri-(ω-styryl)-boron and its complex salt was maintained within the range 40–45°. At higher temperatures its yield decreased sharply owing to the occurrence of a side reaction—the reaction of diphenylbutadiene formation.

Analogous results were obtained in the interaction of the Grignard reagent with $BBr_3$.

The different results obtained when the experiments were carried out in nitro-

gen and argon media can be explained by the ability of argon to give coordination compounds with $BF_3$ (3). Argon evidently forms with tri-(styryl)-boron an unstable coordination compound, which under the experimental conditions completely dissociates into its components.

## Experimental Part

**Tri-(ω-styryl)-boron.** To 3.3 g of magnesium turnings in 50 ml of tetrahydrofuran was added a mixture of 10 g of bromostyrene and 5.14 g of boron fluoride etherate. The magnesium turnings had previously been activated with several drops of ethyl bromide. The reaction temperature throughout the entire experiment, and then after completion of the dropwise addition of the mixture for 2 hours, was maintained within 40-45°. After completion of the reaction, the reaction ···

the mixture was filtered under argon pressure from the magnesium salts. On the following day, needle-like crystals of tri-(ω-styryl)-boron precipitated from the reaction mixture; yield 76%, m.p. 64-65°; soluble in benzene and tetrahydrofuran, insoluble in chloroform and petroleum ether.

Found, %: B 3.47; 3.48. $(C_8H_7)_3B$. Calculated, %: B 3.38

**Complex** $(C_8H_7)_3B \cdot C_5H_5N$**.** To the solution, filtered from magnesium salts, of 3.4 g of tri-(ω-styryl)-boron, 0.83 g of pyridine was added dropwise. Crystals of the complex gradually precipitated from the solution; m. dec. 138-140°; soluble in chloroform.

Found, %: B 2.61; 2.58, $(C_8H_7)_3B \cdot C_5H_5N$. Calculated, %: B 2.71

**ω-Styrylboronic acid anhydride.** To the ethereal solution of tri-(ω-styryl)-boron, obtained from 3.3 g of magnesium turnings, 10 g of bromostyrene, and 5.14 g of boron trifluoride etherate, cooled dilute acetic acid (1:10) was added. The ether layer was separated, washed with water, then three times with 2*N* NaOH. The combined alkaline extracts were washed with ether and acidified with concentrated HCl. Styrylboronic acid evidently precipitated; however, after separation of the crystals and drying, styrylboronic acid anhydride was obtained, m.p. 151-152° (yield 43%)—colorless crystals, soluble in acetone and alcohol.

Found, %: B 8.15. $C_{16}H_{14}B_2O_2$. Calculated, %: B 8.32

Received
2 X 1961

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*Note: Figure translations are in progress. See original paper for figures.*