

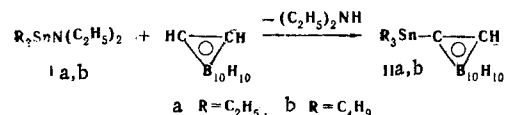
REACTION OF N-STANNYLAMINES WITH CARBORANES

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Until recently, stannyl-substituted carboranes could be obtained exclusively by the condensation of lithium derivatives of carboranes with halostannanes [1-3].

We have detected another unique route to the synthesis of these compounds – the reaction of o-, m-, and p-carboranes with organic tin compounds that have Sn-N bonds; for example:



The temperature required for this reaction is lowered on passing from p- to m- and o-carboranes; this is associated with the increased degree of protonation of the hydrogen in them [4]. Substitution of a second hydrogen atom of carborane does not occur under the reaction conditions, even when there is a twofold excess of aminostannane; however, the reaction does occur under more severe conditions.

EXPERIMENTAL

Triethylstannyl-o-carborane (IIa). A 1.75 g (0.0122 mole) sample of o-carborane was added to 6.8 g (0.0245 mole) of Ia. The reaction mixture warmed spontaneously to 35°. The mixture was then held at 120-140° for 2 h, the diethylamine was removed by distillation, and the residue was vacuum distilled to give 3.2 g (75%) of IIa with bp 125-130° (1.5 mm), n_D^{20} 1.5601, and d_4^{20} 1.2102. Found %: C 28.0; H 7.5; B 30.9. $C_8H_{28}B_{10}Sn$. Calculated %: C 27.5; H 7.5; B 31.0.

Tributylstannyl-o-carborane (IIb). A 2 g (0.0139 mole) sample of o-carborane, which dissolved immediately, was added to 7.8 g (0.02 mole) of Ic. No spontaneous warming was observed. The usual workup gave 4.2 g (70%) of IIb with bp 175-178° (0.5 mm) and mp 38-39.5° (from heptane). Found %: C 39.8; H 8.94; B 24.1. $C_{14}H_{38}B_{10}Sn$. Calculated %: C 38.8; H 8.8; B 24.9.

Triethylstannyl-m-carborane (III). A 2.8 g (0.0194 mole) sample of m-carborane was added to 6.1 g (0.022 mole) of Ia. No spontaneous warming was observed. The m-carborane dissolves, and diethylamine is evolved only above 100°. The reaction mixture was heated at 140° for 2 h with simultaneous distillation of diethylamine. Distillation of the mixture gave 4.2 g (60%) of III with bp 115-117° (1.5 mm), n_D^{20} 1.5519, and d_4^{20} 1.1914. Found %: C 27.4; H 7.5; B 32.2. $C_8H_{28}B_{10}Sn$. Calculated %: C 27.5; H 7.5; B 31.0.

Absorption bands at 3070 (C-H) and 2600 cm^{-1} (B-H), characteristic for carborane, were found in the IR spectra of IIa,b and III.

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