

Synthesis of Dimethyl (*m*-Carboran-9-yl)phosphonate and Dimethyl (*p*-Carboran-2-yl) Phosphonate by Palladium-catalyzed Cross Coupling of 9-I-*m*- and 2-I-*p*-Carboranes with Dimethyl Hydrogen Phosphite

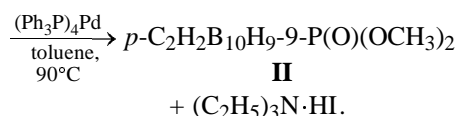
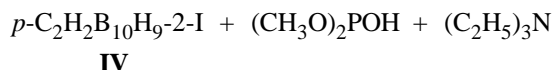
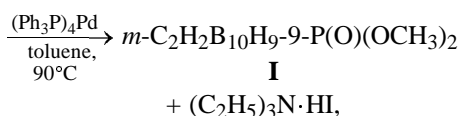
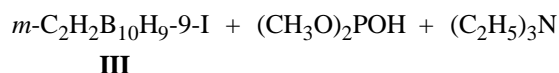
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Abstract—Dimethyl (*m*-carboran-9-yl)- and (*p*-carboran-2-yl)phosphonates were prepared by $(\text{Ph}_3\text{P})_4\text{Pd}$ -catalyzed cross coupling of 9-I-*m*- and 2-I-*p*-carboranes with dimethyl hydrogen phosphite in the presence of triethylamine.

Carborane derivatives containing a boron–phosphorus σ bond have received insufficient study, evidently because they are difficult to prepare. At the same time, carborane derivatives with boron–arsenic σ bond are readily available [1]. The only reported synthesis of B–P carborane derivatives is rather complicated [2] and includes photolysis of a mixture of bis(*m*-carboran-9-yl)mercury and bis(*p*-carboran-2-yl)mercury with trimethyl phosphite to obtain 5% of dimethyl (*m*-carboran-9-yl)phosphonate (**I**) and 60% of dimethyl (*p*-carboran-2-yl)phosphonate (**II**), respectively. Bis(*o*-carboran-9-yl)mercury does not react under these conditions. We propose a new synthetic approach to compounds **I** and **II**, based on the palladium-catalyzed cross coupling of 9-iodo-*m*-carborane (**III**) and 2-iodo-*p*-carborane (**IV**) with dimethyl hydrogen phosphite according to the procedure in [3]. Compounds **I** and **II** were prepared by the following scheme:



A mixture of carborane **III** and dimethyl hydrogen

phosphite in the presence of 1 mol of triethylamine and catalytic amounts of $(\text{Ph}_3\text{P})_4\text{Pd}$ was heated under argon in toluene solution at 85–90°C for 20 h until compound **III** had been consumed completely (by TLC). The yield of phosphonate **I** was 60%. Phosphonate **II** was obtained from carborane **IV** in a similar way (yield 63%). Products **I** and **II** are crystalline substances, their composition was confirmed by elemental analysis.

Regretfully, dimethyl (*o*-carboran-9-yl)phosphonate could not be prepared by this method, because 9-iodo-*o*-carborane, as well as other *o*-carborane derivatives, are cleaved with triethylamine in toluene at 85–90°C.

EXPERIMENTAL

2-Iodo-*p*-carborane was prepared according to [4].

Dimethyl (*m*-carboran-9-yl)phosphonate (I**).** To a stirred mixture of 2 g of dimethyl hydrogen phosphite, 1.4 ml of triethylamine, and 250 mg of $(\text{Ph}_3\text{P})_4\text{Pd}$ in 5 ml of dry toluene, 2.4 g of 9-iodo-*m*-carborane was added. The resulting solution was heated under argon at 90°C for 20°C until 9-iodo-*m*-carborane had been consumed completely. Most toluene was removed in a vacuum, and the residue was treated with 50 ml of ether. The triethylamine hydroiodide precipitate was filtered off, the solvent was removed, and the residue was passed through a column of silica gel (75 × 1.2 cm), filled with benzene, eluent CHCl_3 . The solvent was removed to obtain 1.36 g (60%) of compound **I**, mp 98–99°C (from toluene) (see [2]). Found, %: C 19.10, H 6.71, B 42.66, P 12.40. $\text{C}_4\text{H}_{17}\text{B}_{10}\text{O}_3\text{P}$. Calculated, %: C 19.03, H 6.74, B 42.90, P 12.01.

Dimethyl (*p*-carboran-2-yl)phosphonate (II) was obtained by the above procedure from 2-iodo-*p*-carborane (dry toluene, 30 h). Yield 1.4 g (63%), mp 73–74.5% (from benzene) (see [2]). Found, %: C 19.30, H 6.54, B 42.60, P 12.46. $C_4H_{17}B_{10}O_3P$. Calculated, %: C 19.03, H 6.74, B 42.90, P 12.01.

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