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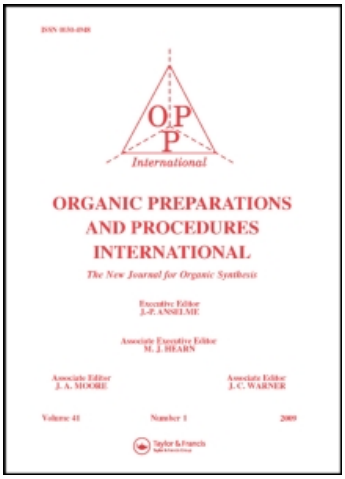

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ARYLBORON DICHLORIDES

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ARYLBORON DICHLORIDES

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Organoboron dihalides are useful synthetic intermediates[1,2,3] and have been prepared by the reaction of boron trichloride with a variety of organometallics (Al,[4] B,[5] Hg[6]). Apart from its use for the preparation of phenylboron dichloride, however, tetraaryltin precursors appear not to have been employed for this purpose. When solvents (benzene,[7] methylene chloride or carbon tetrachloride[8]) are used, incomplete reaction occurs and only two, or at most, three of the phenyl groups are efficiently replaced, according to the equations:

$$(C_6H_5)_4Sn + 2BCl_3 \longrightarrow 2C_6H_5BCl_2 + (C_6H_5)_2SnCl_2$$

$$(C_6H_5)_4Sn + 3BCl_3 \longrightarrow 3C_6H_5BCl_2 + C_6H_5SnCl_3$$

We thought the organotin route to be worthy of further investigation since tetraaryltin derivatives are invariably solids, and are easily prepared in good yields from readily available materials by conventional Grignard techniques.[9,10]

$$4ArMgBr + SnCl_4 \longrightarrow Ar_4Sn + Mg(Br)Cl$$

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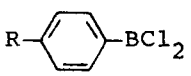
In the absence of solvents (modified Gerrard method[2,8]), boron trichloride reacts with a variety of tetraaryltin species to give the corresponding arylboron dichlorides, and all aryl groups are efficiently utilized. Using this simple procedure,

$$Ar_4Sn + 4BCl_3 \longrightarrow 4ArBCl_2 + SnCl_4$$

compounds I, II, and III were conveniently prepared in isolated yields of 70%, 85%, and 78%, respectively.



I, R = CH_3

II, R = Cl

III, R = C_6H_5

This preparative method simply involves admixture of the reagents at -78° and gradually warming - at ca. 0°-5° a vigorous reaction occurs. The product is directly isolated by fractional distillation.

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EXPERIMENTAL

All boiling points are uncorrected. Mass spectra were measured by Dr. A.M. Hogg and his associates using an A.E.I. MS-9 spectrometer at an ionization potential of 70eV. Elemental analyses were performed by the Microanalytical Laboratory at the University of Alberta.

All arylboron dichlorides were prepared by the procedure described in detail for the preparation of p-chlorophenylboron dichloride, except where otherwise indicated.

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p-Chlorophenylboron dichloride (II).

A 250-ml. three-necked flask, fitted with a nitrogen inlet, a magnetic stirring bar, and a Kjeldahl connecting bulb[11] attached to a Dry Ice-condenser (connected to a mercury bubbler) was charged with 33.3 g. (0.06 mole) of tetrakis(p-chlorophenyl) tin[12], then cooled (Dry Ice acetone bath). Boron trichloride (21.4 ml., 0.26 mole) was added. No apparent reaction occurred at -78°. The cooling bath was allowed to gradually warm, and at ca. 0°-5° a vigorous reaction occurred which was moderated by addition of several pieces of Dry Ice. This process was repeated until no exotherm occurred upon warming. The mixture was then refluxed (5 hr.). The Kjeldahl bulb and Dry Ice condenser was replaced by a short-path condenser. Distillation under nitrogen afforded 38.4 g. (85%) of p-chlorophenylboron dichloride, b.p. 104°-105°/21 mm. (lit.[13] b.p. 106°-107°/24 mm.).

p-Diphenylboron dichloride (III).

No exotherm was observed at ca. 5° from the reaction mixture of boron trichloride (16.5 ml., 0.20 mole) and tetrakis(p-diphenyl) tin[14] (32.3 g., 0.044 mole). After a reflux period of 4 hr., distillation afforded 32.1 g. (78%) of p-diphenylboron dichloride, b.p. 136-137°/0.6 mm.; mass spectrum, M^+ 234.0117 (calcd. 234.0115).

Anal. Calcd for $C_{12}H_9BCl_2$; C, 61.35; H, 3.86; Cl, 30.18.

Found: C, 61.11; H, 4.20; Cl, 29.76.

p-Tolylboron dichloride (I).

The reaction between boron trichloride (21.4 ml., 0.06 mole) and tetrakis(p-tolyl)tin[15] (29.0 g., 0.06 mole), after a reflux period of 30 min., afforded 28.4 g. (70%) p-tolylboron dichloride, b.p. 88°-90°/11 mm. (lit.[6] b.p. 92°/10 mm.).

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