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Preliminary communication

SYNTHESES OF (*E*,*E*)-1,4-DIARYL-1,3-BUTADIENES

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Summary

trans-β-Phenylethenylboronic acid, *trans*-β-*p*-methylphenylethenylboronic acid and *trans*-β-*p*-methoxyphenylethenylboronic acid on treatment with catalytic amounts of palladium chloride in presence of excess of lithium chloride and triethylamine give the corresponding (*E*,*E*)-1,4-diaryl-1,3-butadienes in virtually quantitative yield.

Brown and coworkers showed some time ago that the reaction of trialkylboranes with silver nitrate provides a convenient synthesis of symmetrical and unsymmetrical hydrocarbons [1]. Murphy and Prager have recently extended this reaction to cyclization of a variety of dienes [2], while Yamamoto and coworkers have synthesized symmetrical (*E*,*E*)-1,3-dienes from dialkenylchloroboranes using a three molar equivalent of methylcopper as the coupling reagent [3].

Our interest in the chemistry of organoboranes prompted us to examine the synthesis of dienes from vinylboronic acids, which are easily obtained by hydroboration of acetylenes with catecholborane followed by hydrolysis [4]. Contrary to our expectation, treatment of *trans*-β-phenylethenylboronic acid with silver nitrate gave styrene as the exclusive product. Further studies showed that catalytic amounts of palladium chloride with excess of lithium chloride and triethylamine, provide the best conditions for the desired coupling of *trans*-β-phenylethenylboronic acid and (*E*,*E*)-1,4-diphenyl-1,3-butadiene is obtained in excellent yield. The results with various *trans*-β-arylethenylboronic acids are summarized in Table 1.

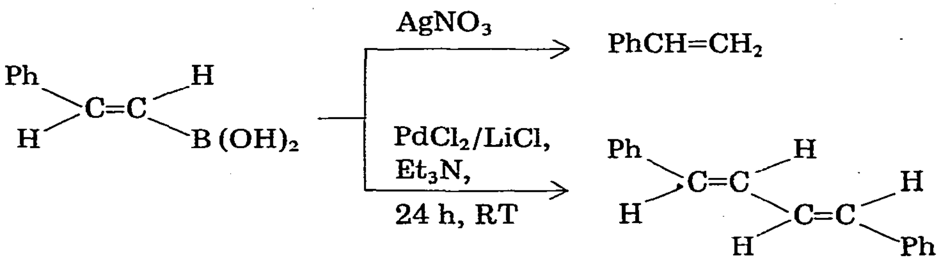

TABLE 1

SYNTHESES OF (*E,E*)-1,4-DIARYL-1,3-BUTADIENES FROM *trans*-β-ARYLETHENYLBORONIC ACIDS

Boronic acid[a]	M.p. (°C)	Product[a]	M.p. (°C)	Yield[b]
trans-β-Phenylethenylboronic acid	163—164	(*E,E*)-1,4-Diphenyl-1,3-butadiene	152—153	94
trans-β-*p*-Methylphenylethenylboronic acid	126—127	(*E,E*)-1,4-Bis(*p*-methylphenyl)-1,3-butadiene	198	94
trans-β-*p*-Methoxyphenylethenylboronic acid	173—174	(*E,E*)-1,4-Bis(*p*-methoxyphenyl)-1,3-butadiene	223	94

[a] Characterized by spectral and analytical data. [b] Isolated yield.

The simplicity of the present procedure is illustrated by the following example. A mixture of *trans*-β-phenylethenylboronic acid (148 mg, 1 mmol), palladium chloride (18 mg, 0.1 mmol), lithium chloride (850 mg, 20 mmol) and triethylamine (5 ml) in tetrahydrofuran (50 ml) was stirred at room temperature for 24 h, diluted with petroleum ether, and centrifuged. The supernatant liquid was washed with diluted HCl (5%) and then water, and filtered through a short layer of silica-gel. Evaporation of the solvent left (*E,E*)-1,4-diphenyl-1,3-butadiene (97 mg, 0.47 mmol) as colourless crystals in 94% yield, m.p. 152—153°C.

Further work is in progress to explore the mechanism and synthetic utility of this stereospecific coupling reaction, with special reference to the synthesis of bicyclic hydrocarbons from bicyclic organoboranes [5].

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