

One-Pot Self-Condensation of Phenylboronic Acid with Phenols and Aldehydes

ALI SHARIFI*, M. SAEED ABAEE, MOJTABA MIRZAEI and M. REZA NAIMI-JAMAL†
Chemistry and Chemical Engineering Research Center of Iran, P.O. Box 14335-186, Tehran, Iran
Fax: (98)(21)44580762; Tel: (98)(21)44580720; E-mail: sharifi@ccerci.ac.ir

An efficient procedure is developed for additive-free condensation of boronic acid with phenols and various aromatic and aliphatic aldehydes under solvent-free conditions.

Key Words: Benzodioxaborinine, Boronic acid, Phenols, Aldehydes, Solvent-free.

INTRODUCTION

Condensation of phenols and aldehydes with boronic acid is a well-known method for the synthesis of dioxaborins. The products are precursors for facile *ortho* substitution of phenols¹, preparation of quinone methides for Diels-Alder cycloadditions² and protection of diols^{3,4}. The usefulness of the reaction also arises from the application of the dioxaborins as key intermediates for preparation of a variety of natural and synthetic products such as saligenol derivatives⁵, polycyclic chromans^{6,7}, cannabinoids⁸, precocene and robustadiol derivatives⁹, decaline portion of (+)-compactin¹⁰, (+) decursinol¹¹ and thielocin¹².

The scope of the process, primarily reported by Peer under acid catalysis for formaldehyde in refluxing benzene¹³, was later improved by Nagata using optimized reaction conditions and employing other aldehydes⁵. Dufresne *et al.* also offered a more efficient synthetic procedure by using dichlorophenylborane¹⁴. However, the available methods are either conducted under environmentally unsafe conditions^{1,5}, are limited to the condensation of phenols with more reactive aldehydes¹⁴, or needs labor and time consuming procedures to make the starting reagents¹⁵⁻¹⁷. Due to environmental and economic reasons, solvent-free reactions have been of huge interest in synthetic organic chemistry in the last two decades¹⁸⁻²¹. In the framework of our investigations on the development of environmentally friendly procedures²²⁻²⁵, we recently communicated a solid supported synthesis of dioxaborines under microwave irradiation²⁶. We now wish to report a general procedure for the title reaction applicable to the condensation of both aliphatic and various aromatic aldehydes with different phenols in absence of solvent, additive, or external stimulant (**Scheme-I**).

†Organic Chemistry Research Laboratory, Faculty of Chemistry, Iran University of Science and Technology, Narmak, Tehran, Iran.