



THE EXPEDITIOUS OXIDATION OF ARYLBORONIC ACIDS TO PHENOLS BY TERTIARY BUTYL HYDROPEROXIDE IN GREEN AQUEOUS ETHANOL

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An efficient protocol for the synthesis of phenols from arylboronic acids has been developed by using t-butyl hydroperoxide (TBHP) as oxidant in water-ethanol as a binary reaction medium. The reaction is metal and additive free and does not require strong basic conditions. The developed protocol has a broad substrate scope and functional group compatibility. Notably the mild conditions, shorter reaction time, good to excellent yields and eco-friendly reaction medium are some important features of the developed method.

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environmentally benign and mild synthetic procedure for the synthesis of phenols is still desirable. In our previous communication, we report ipso-hydroxylation of phenyl boronic acids,¹⁷ therefore, in continuation of our previous research endeavors for the development of green and more efficient synthetic methods,¹⁸⁻²⁰ herein we wish to report a rapid, base-free ipso-hydroxylation of arylboronic acids to phenols at room temperature in a green binary reaction medium (water-ethanol) and TBHP as an oxidant/catalyst.

INTRODUCTION

Phenols and their derivatives are found in numerous bioactive natural products and serve as well-known precursors for the synthesis of pharmaceuticals and natural product analogs of therapeutic importance.¹ Consequently, the synthesis of phenols has attracted a considerable impetus and numerous methods have been developed over the years. Among these, copper-catalyzed conversion of diazoarenes, benzynes and aromatic nucleophilic substitutions of aryl halides are the main routes for the synthesis of phenols.² Some other strategies utilize palladium-based catalysts using phosphine ligands and copper catalyst using non-phosphine ligands at elevated temperature for the conversion of aryl halides into phenols.^{3,4} However, these methods involve prefunctionalization–defunctionalization strategies, rely upon the use of hazardous metal catalysts and harsh reaction conditions which limit their utility due to functional group compatibility problems.

An alternative easy accessible route utilizes arylboronic acids/esters for the synthesis of phenols. The harmless nature of arylboronic acids, their thermal, air and moisture stability make them useful and readily available precursors for the synthesis of phenols.^{5,6} In this direction, numerous methods are known for arylboronic acid/ester hydroxylation which include CuSO₄-phenanthroline,⁷ H₂O₂-poly (N-vinylpyrrolidone),⁸ NH₂OH,⁹ potassium per-oxy sulfate,¹⁰ H₂O/H₂O₂,¹¹ I₂/H₂O₂,¹² PEG400/H₂O₂,¹³ Cu₂O NPs,¹⁴ m-CPBA/KOH,¹⁵ TBPH/KOH.¹⁶ These strategies, however, have some demerits such as long reaction times,^{9,11} use of strong basic conditions⁷ and toxic chlorinated organic solvents.⁸ Thus, development of more efficient and

EXPERIMENTAL

All the melting points were determined on a Kofler apparatus and are uncorrected. The IR spectra were recorded on KBr pellets with Perkin Elmer RXI Spectrophotometer and values are given in cm⁻¹. ¹H and ¹³C NMR spectra were run in CDCl₃ on a JEOL Eclipse (400 MHz) instrument with TMS as internal standard and values are given in ppm (δ). Mass spectra were recorded on a JEOL SX 102/DA-6000 Mass Spectrometer. Thin layer chromatography (TLC) plates were coated with silica gel G and exposed to iodine vapours to check the homogeneity as well as the progress of reaction. Petroleum ether refers to a fraction of boiling point 60-80 °C. Sodium sulfate (anhydrous) was used as a drying agent. All the chemicals were purchased from Merck India and were used after distillation.

Procedure for ipso-hydroxylation of arylboronic Acid

A reaction flask was charged with 1.0 mmol of arylboronic acid and TBPH (2.0 mmol) in 2 mL of H₂O-C₂H₅OH solvent (1:1) and stirred at room temperature for 8-18 min. The reaction progress and completion was monitored by TLC. After completion, the crude reaction mixture was extracted with ethyl acetate and dried over sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by SiO₂ column chromatography (ethyl acetate: hexane) to afford the desired product. The prepared phenols were characterized by comparing the observed spectral data¹⁷ and physical properties.