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Synthesis, characterization and X-ray studies of new six–seven membered rings [4.5.0] heterobicyclic system of monomeric boronates

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ABSTRACT

Different tridentate ligands derived from ethanolamines and 2-hydroxyacetophenone, 2-hydroxybenzophenone and salicylaldehyde were reacted with two equivalents of phenylboronic acid to obtain compounds ***6a–6f*** which are [4.5.0] heterobicyclic systems with a B—O—B structural unit. The boronates were fully characterized and two heterobicyclic [4.5.0] structures have been analyzed by X-ray crystallography, where a series of parameters such as bond distances, bond angles, torsion angles, tetrahedral character at the boron atom and deviation of the boron atom from the mean plane have been evaluated.

1. Introduction

Recently, there has been a considerable interest in the synthesis, characterization and study of organoboron compounds, due to a great variety of applications derived from these complexes in different areas such as supramolecular chemistry [1,2]; boron complexes have found application in medicinal chemistry, as anticancer agents in boron neutron capture therapy [3,4]; as bioactive materials, ^{10}B is employed in the control of nuclear reactors as a shield against the nuclear radiation [5]. Moreover, they also display a wide range of applications in organic synthesis [6], for example, in the synthesis of polyolefins, styrene, and substituted biphenyls by the Suzuki reaction [7–10]; as materials with fluorescence [11], electro optical and nonlinear optical properties which are areas recently explored using boron chemistry [12,13]. In this context, the synthesis and characterization of boron complexes obtained from the condensation of 3-amino-phenylboronic acid and 1,3-diketones [14] and recently the synthesis, characterization and X-ray studies of new fused five–six-membered rings, [4.3.0.] heterobicyclic systems of monomeric boronates derived from optically active tridentate ligands [15] have been reported. Our previous studies have shown that fused five–six membered rings compounds are obtained under strong reaction conditions such as reflux of toluene for 24 h. In turn, dimeric compounds were formed when the ligands have zero, two, five or six methylene units between the imino and hydroxyl group, using mild reactions conditions such as reflux of THF for approximately 30 min [16] (Scheme 1). In this work, tridentate ligands ***5a–5f*** were allowed to react with two equivalents of phenylboronic acid to give six new [4.5.0] heterobicyclic boronates which possess two boron atoms in the structure. The results from X-ray diffraction indicated low strain present in the seven membered rings of the molecules as well as the chair conformation and the tetrahedral character of the boron atoms which is directly associated to the geometry [17,18] and shows deviation from ideal values. The presence of two different boron atoms in the structures suggests that these molecules are intermediates in the reaction. One of the boron atoms (B1) is tetrasubstituted forming a coordination bond to the nitrogen and the other boron atom (B2) is trisubstituted with an empty p orbital. These boronate units are connected by two covalent B–O and a coordinative N → B bond, which are responsible for hydrolytic stability of these molecules [19] (Scheme 2).

2. Experimental

2.1. Instrumentation

NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 solutions on Bruker Avance 300 spectrometer. Chemical shifts (ppm) are

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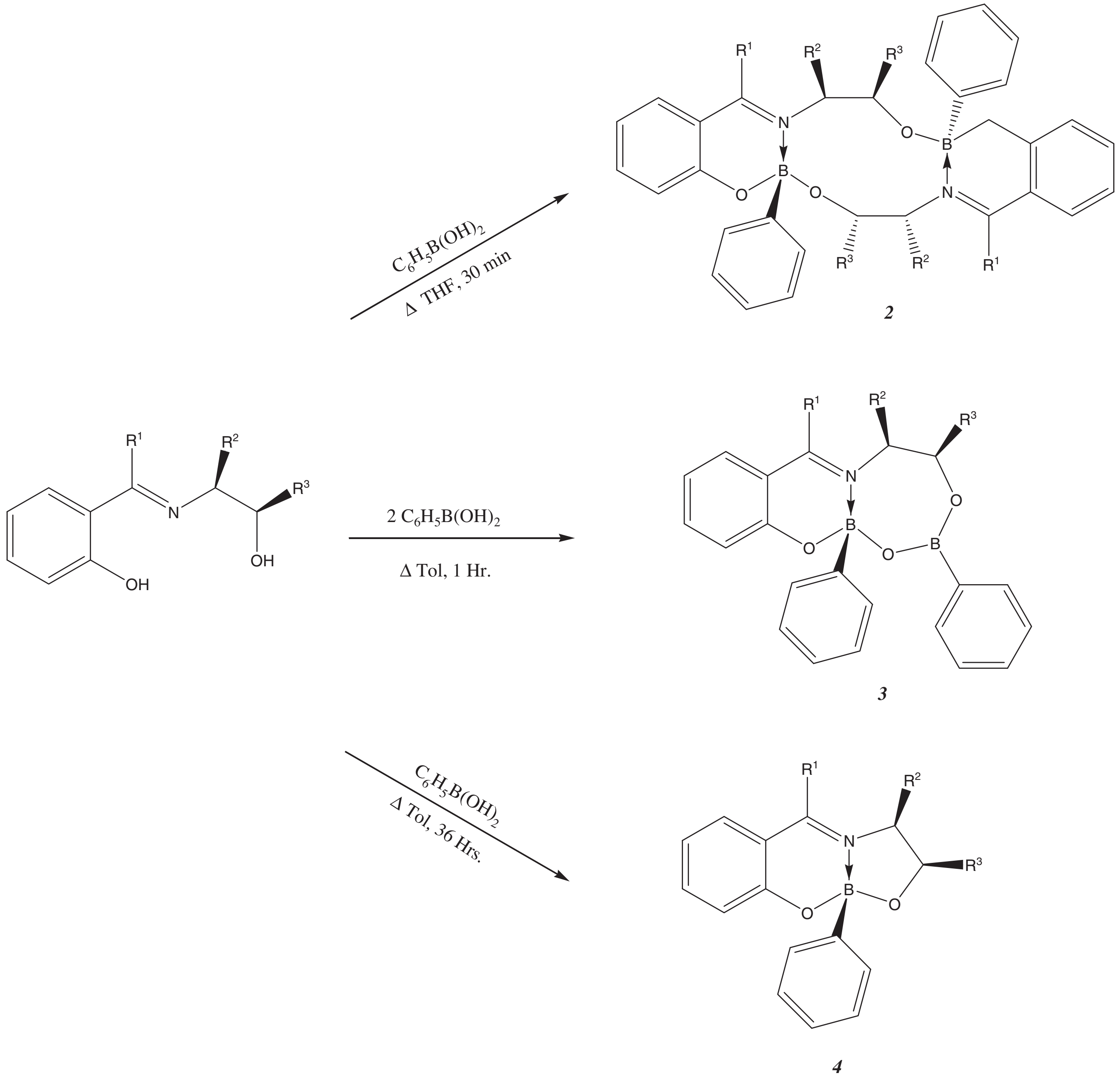

Scheme 1. Monomeric and dimeric boronates obtained using different reactions conditions.

relative to $(CH_3)_4Si$ for ^1H and ^{13}C and $BF_3{\cdot}OEt_2$ for ^{11}B. Coupling constants are reported in Hz. Infrared spectra were recorded on a Perkin–Elmer 16F-PC FT-IR spectrometer. Mass spectra were recorded on a Hewlett–Packard model 5989 engine, coupled to a GC 5890 series II. Melting points were obtained on a Gallenkamp MFB-595 apparatus and are uncorrected. Elemental analyses were carried out on a FLASH (EA) 1112 series, thermo Finnigan apparatus. The X-ray diffraction study was determined on an Enraf–Nonius-Fr590 Kappa-CCD ($\lambda_{Mo\ K\alpha} = 0.71073$ Å, graphite monochromator, $T = 293$ K, CCD rotating images scan mode) and the crystals were mounted on a LINDEMANN tube. Absorption correction was not necessary. All reflections data set were corrected for Lorentz and Polarizations effects. Structure solution and refinement were performed using the SHELX-S-97 program and then SHELX-L-97 program was applied for refinement and output data [20,21]. All software manipulations were done under the WINGX environment program set [22]. Single crystal structure validation was done with PLATON [23]. Molecular perspectives were drawn under ORTEP-3 [24], and DIAMOND 2.1e drawing applications.

2.2. Reagents

All reactants and solvents were purchased from Aldrich chemical Co. and solvents were dried previous to use [25]. Single crystals were grown using spectroscopic grade solvents.

2.3. Synthesis

2.3.1. General method for the preparation of tridentate ligands ***5a–5f***

In order to prepare the tridentate ligands ***5a–5f***, equimolecular quantities of the corresponding aminoalcohol and 2-hydroxyacetophenone, 2-hydroxybenzophenone or salicylaldehyde, respectively, were refluxed in ethanol for 1 h. The solvent and water formed during the reaction were eliminated with a Dean–Stark