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Dialkylammonium *tert*-Butylmethylphosphinites: Stable Intermediates for the Synthesis of P-Stereogenic Ligands

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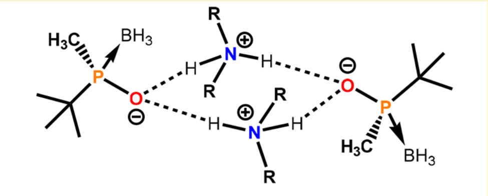
Supporting Information

ABSTRACT: The preparation of shelf-stable crystalline salts of *tert*-butylmethylphosphinous acid borane **1** is described. X-ray analysis of diisopropylammonium *tert*-butylmethylphosphinite borane **6** revealed the presence of a cyclic hydrogen-bond network in the solid state which accounts for an increased melting point and stability. Dialkylammonium phosphinite boranes are convenient precursors of the chiral *tert*-butylmethylphosphine fragment. Compound **6** can be used directly in $S_N2@P$ reactions with various nucleophiles to yield valuable P-stereogenic intermediates and ligands.



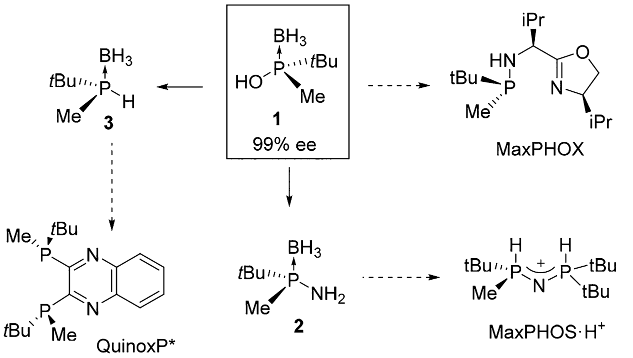
Highly stable surrogate of P-stereogenic phosphinous acid

Since the initial seminal work of Knowles and co-workers,[1] P-stereogenic phosphines have emerged as an important group of ligands that are highly proficient in asymmetric hydrogenation and other relevant industrial catalytic transformations.[2,3] However, the assembly of stereogenic phosphorus centers in an optically pure fashion continues to be a hurdle. In this respect, the development of efficient methods for the rapid assembly of this class of compounds and the availability of key intermediates that facilitate the synthesis of P-stereogenic compounds is highly relevant in this field.

Optically pure P-stereogenic phosphinous acid boranes are attractive synthetic intermediates in the synthesis of compounds with chiral phosphorus; however, they have received little attention. Buono and co-workers described the synthesis of several P-stereogenic phosphinous acid boranes via H-menthylphosphinate or H-adamantylphosphinate technology.[4] Taking advantage of the intrinsic acidity of these compounds, Pietrusiewicz reported the resolution of several P-stereogenic phosphinous acid boranes via diastereomeric cinchonine salt formation.[5]

We have recently achieved the efficient synthesis of optically pure *tert*-butylmethylphosphinous acid-borane **1** (Scheme 1).[6] This compound is a key P-stereogenic intermediate in the synthesis of MaxPHOX and other ligands, which have shown excellent results in iridium- and rhodium-catalyzed asymmetric processes.[7] The transformation of phosphinous acid **1** into optically pure *tert*-butylmethylphosphanamine **2** allows its use in the synthesis of ligands, such as MaxPHOS and SIP.[8] It was also used as starting material for the preparation of optically pure *tert*-butylmethylphosphine-borane **3** which is the precursor of Imamoto's Quinox-P*.[9] We firmly believe that phosphinous acid **1** holds promise to become a key intermediate in the synthesis of new and already known P-stereogenic chiral ligands.

Scheme 1. Applications of Optically Pure *tert*-Butylmethylphosphinous Acid Borane 1



The main drawback that hampers the extensive use of **1** is its limited stability. Phosphinous acid **1** is a gummy-solid with a low melting point (54−56 °C), which upon storage decomposes to yield the corresponding secondary phosphine oxide and borane byproducts. ^1H NMR analysis revealed 35−40% of decomposition when a pure sample of **1** was stored at room temperature for a week. This limited stability made it necessary to use **1** immediately after its preparation. This is clearly a serious drawback for the large-scale utilization of **1**.

With this scenario in mind, we considered that it would be highly desirable to find a derivative of **1** that could circumvent the stability issues associated with pure phosphinous acid **1**. Here we report on dialkylamonium phosphinites, which are stable and convenient surrogates of **1**. These compounds are highly crystalline and can be utilized in the same fashion as **1** in

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