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## Poly(1,4-butyl-bis-vinylpyridinium) borohydride as a new stable and efficient reducing agent in organic synthesis

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## ABSTRACT

The unstable sodium borohydride is stabilized on modified poly(4-vinylpyridinium), and it is used as an efficient and regenerable polymer-supported borohydride reagent for the reduction of a variety of carbonyl compounds, such as aldehydes, ketones,  $\alpha,\beta$ -unsaturated carbonyl compounds,  $\alpha$ -diketones and acylloins, in good to excellent yields.

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## 1. Introduction

Reduction is one of the most fundamental and useful reactions in organic chemistry. There must be few organic syntheses, of any complexity, that do not involve a reduction at some stage. Reduction by hydride transferring agents has been used widely in organic synthesis by the well-known alkali metal borohydrides, NaBH<sub>4</sub>, LiBH<sub>4</sub>, and their modified forms [1–4]. There are few reports in the literature on the use of the covalent transition-metal borohydride complexes as reducing agents because such compounds are volatile unstable solids and as such cannot be used in organic synthesis [5]. The modified stable forms of such compounds were reported as (Ph<sub>3</sub>P)<sub>2</sub>CuBH<sub>4</sub> [6], [(Ph<sub>3</sub>P)<sub>2</sub>CuBH<sub>3</sub>CN]<sub>2</sub> [7], and (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Zr(Cl)BH<sub>4</sub> [8]. Zinc borohydride and the stable modified complex forms of this reagent have been reported as being used frequently in reduction reactions [9].

The immobilization of reagents on the polymeric backbone has been investigated extensively [10,11]. This is primarily because insoluble polymeric reagents expand the range of the applicable solvents, increase the easiness of work-up and product purification and isolation and in most cases provide for recovery and regeneration of the supported reagent.

Pyridine borane has been introduced into organic chemistry years ago [12]. Hallensleben reported the preparation of poly(4-vinylpyridine borane) and its action as a polymeric reducing reagent [13]. Polymer-supported borohydride resins (PSBR) have received considerable attention in recent years and some of them have been used in the mild and selective reduction of organic compounds [14]. These reagents have been used in a number of organic transformations [15]. Tamami et al. reported the stabilization of chloroaluminum borohydride [16,17], zinc borohydride [18,19], and zirconium borohydride [20] on poly(4-vinylpyridine) and their uses as new stable polymeric reducing agents. Very recently, in continuation of our studies on the development of new catalysts and methods for organic transformations [21–24], we wish to report the preparation and characterization of the poly(1,4-butyl-bis-vinylpyridinium) borohydride and the uses of this new polymeric reducing agent for a variety of carbonyl reductive transformations.

## 2. Experimental

## 2.1. General

The chemicals were purchased from Fluka AG, Merck and Synthetic Chemicals Ltd. Poly(4-vinylpyridine)

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cross-linked with 2% divinylbenzene was purchased from Fluka AG. All reduction products were known compounds and they were identified by comparison of their spectra and physical data with those of the authentic samples [25]. Reaction monitoring and purity determination of the products were accomplished by TLC or GC-MS on an Agilent GC-Mass-6890 instrument under 70 eV conditions. IR and FTIR Spectra were obtained using a PerkinElmer spectrometer 781 and a Bruker Equinox 55 using KBr pellets (for solids) or neat liquid samples in the 4000–400  $\text{cm}^{-1}$  range. The UV spectra were recorded with an Agilent 8453 UV-vis spectrophotometer at room temperature. In all cases, the  $^1\text{H}$  NMR spectra were recorded with a Bruker Avance 400 or 300 MHz instrument.  $^{13}\text{C}$  NMR data were collected with a Bruker Avance 100 or 75 MHz instrument. All chemical shifts are quoted in parts per million (ppm) relative to TMS using a deuterated solvent. Microanalyses were performed on a PerkinElmer 240-B microanalyzer. The melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

## 2.2. Preparation of poly(1,4-butyl-bis-vinylpyridinium) chloride

Cross-linked poly(4-vinylpyridine) [poly(4-vinylpyridine) cross-linked with 2% DVB ~ 60 mesh, MW: 60,000; Fluka Chemicals] (5.0 g) was suspended in sulpholane (50 mL) and allowed to swell for about 24 h at room temperature (Scheme 1). To this suspension, freshly distilled 1,4-dichlorobutane (DCB) (4 mL) was slowly added and the reaction mixture was stirred under a stream of  $\text{N}_2$  at 50 °C for 48 h. An additional portion of DCB

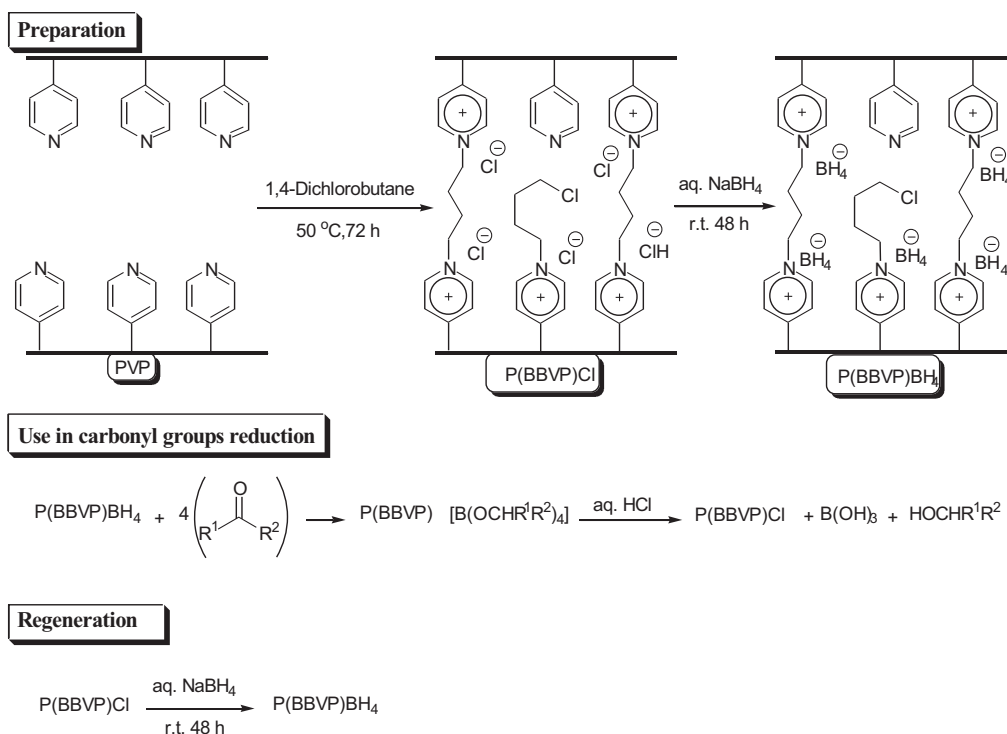
(2 mL) was added and stirred at the same temperature for 24 h. The precipitate was then filtered, washed with distilled water ( $5 \times 10$  mL) and diethyl ether ( $3 \times 5$  mL) to remove the unreacted DCB, and then was dried in the presence of  $\text{P}_4\text{O}_{10}$  under vacuum at 50 °C overnight to give the product (6.88 g). The amount of chloride was determined by gravimetric and potentiometric titration methods [26], and was 5.9 mmol Cl per gram of polymer.

## 2.3. Preparation of poly(1,4-butyl-bis-vinylpyridinium) borohydride $\text{P}(\text{BBVP})\text{BH}_4$ (Scheme 1)

To a solution of  $\text{NaBH}_4$  (4.25 g, 112 mmol) in water (100 mL),  $\text{P}(\text{BBVP})\text{Cl}$  (5.0 g) was added portionwise at room temperature and stirred for 48 h. The resulting material was separated and washed with distilled water ( $5 \times 10$  mL) and diethyl ether ( $2 \times 10$  mL), then dried in a vacuum desiccator in the presence of  $\text{P}_4\text{O}_{10}$  at 50 °C overnight to obtain the powder of  $\text{P}(\text{BBVP})\text{BH}_4$  (4.39 g). The average capacity of the reagent, determined by hydrogen evolution on acidification with 1.0 M hydrochloric acid in a suitable hermetic apparatus, was found to be 5.8 mmol of borohydride per gram of polymeric reagent.

## 2.4. General procedure for the reduction of carbonyl compounds with $\text{P}(\text{BBVP})\text{BH}_4$ (Scheme 1)

To a solution of the substrate (1 mmol) in ethanol as a solvent (5 mL) in a round-bottom flask (25 mL) equipped with a magnetic stirrer,  $\text{P}(\text{BBVP})\text{BH}_4$  (50 mg ~ 0.29 mmol  $\text{BH}_4$ ) was added and stirred at room temperature. The progress of the reaction was monitored by TLC. On



Scheme 1. Preparation, use, and regeneration of poly(1,4-butyl-bis-vinylpyridinium) borohydride.

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