

## Ionene-Bound Borohydrides: Efficient, Selective, and Versatile Polymer-Supported Reducing Agents

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**Summary.** Reduction of structurally different carbonyl compounds, such as aldehydes, ketones,  $\alpha,\beta$ -unsaturated enals and enones, acid chlorides, and imines was accomplished efficiently using high capacity ionene based borohydride reagents. Aldehydes and imines were reduced to the corresponding alcohols and amines in excellent yields in methanol at ambient temperature while ketones and acid chlorides were reduced in *iso*-propanol and *THF-MeOH* at reflux. Chemoselective reduction of aldehydes over ketones was achieved successfully with these reagents. Complete regioselectivity was also observed in the reduction of  $\alpha,\beta$ -unsaturated aldehydes and ketones.

**Keywords.** Ionene; Borohydride; Reduction; Carbonyl compounds; Imines.

### Introduction

Reduction is one of the frequently used reactions in organic synthesis and a vast variety of reducing agents has been introduced for this purpose [1]. Among them, sodium borohydride is the most commonly used reagent for the reduction of variety of functional groups in synthesis. To improve its reducing ability, several substituted borohydrides have been introduced. In fact, the progress in this field has been realized by: (i) substitution of the hydride(s) with other groups [2], (ii) variation in the metal cation [3, 4], (iii) concurrent cation and hydride exchange [5], (iv) complexation with ligands [6], (v) combination of borohydrides with metal, metal salts,

*Lewis* acids, and mixed solvent systems [7, 8], and finally, (vi) use of polymers and solid beds to stabilize the hydride species [9]. Polymer-supported reagents and catalysts have been in use since the 1960s, and the applications of polymer supported borohydride reagents have been recently reviewed [10–12]. Polymer bound borohydrides offer several advantages over the other modified borohydrides. The primary advantage is the convenience of use of these materials and the minimal introduction of ionic species or organic by-product into treated bulk media. Simplified workup of reaction products is another advantage. But, one significant limitation of current polymeric reagents remains their relatively low loading (0.5–2 mmol/g) for most commercial reagents, and practically an excess of polymeric reagents needs to be used to complete reaction. Due to high price, polymer supported reagents are not very economical confining the method to small scale chemistry. High loading resins would increase the efficiency and the atom economy [13] of these reagents considerably. In addition, in high loading reagents, the concentration of the reactant in the polymer is enhanced, thus reducing the amount of polymer backbone employed. However, the important classical ion exchange resins were based on anion exchange resins, which loaded with anionic counter ions show many disadvantages. The classical ion exchange resins prepared from chloromethylated styrene and trimethylamine suffer from low loading because of the weight of polymer backbone, and the

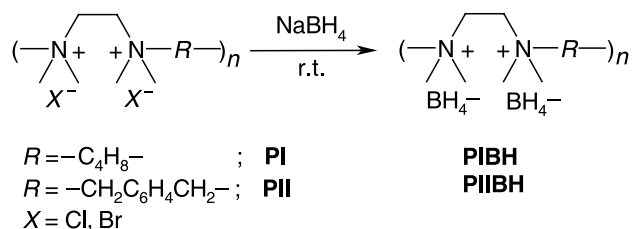
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higher loading is restricted due to *Lewis* acid catalyzed cross-linking of chloromethyl groups within the resin. Furthermore, the molar activity of the supported reagents can decrease considerably during storage and can be significantly lower than the original loading of counter ion because of the chemical lability of the ammonium salt, which releases trimethylamine. Another general problem of polystyrene based resins is their chemical liability under oxidation and strong *Lewis* acidic conditions [14]. In fact, maximum loading of counter ions is obtained by a polymer constructed from low molecular weight functional monomers [15]. Realizing this fact, we studied linear ionene bromide or chloride as poly cationic polymer supports to obtain high capacity linear polymer supported borohydrides, the ionene borohydrides.

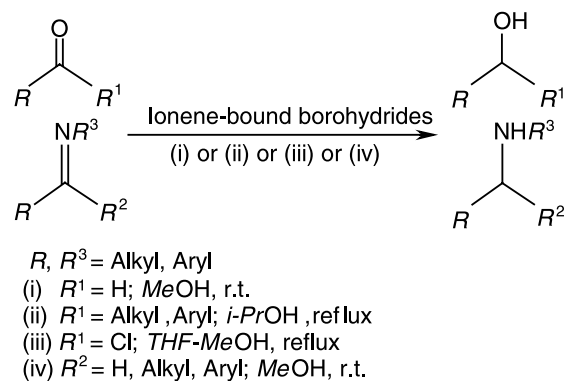
## Results and Discussion

This report describes the results of utilizing linear ionene borohydrides as new polymer-supported reducing agents for the reduction of aromatic, aliphatic, and unsaturated aldehydes, ketones, acid chlorides, and imines. Ionene borohydrides, 2,4-ionene borohydride (**PIBH**) and xylylene-ionene borohydride (**PIIBH**), are stable non-hygroscopic white powders which are insoluble in most organic solvents, including ether, *THF*,  $\text{CHCl}_3$ , *i*-*PrOH*, and *t*-*BuOH*, but slightly soluble in *MeOH*. However, they are quite soluble in water. They are prepared quantitatively by treatment of aqueous solutions of 2,4-ionene bromide (**PI-Br**) [16] or xylylene ionene chloride (**PII-Cl**) [17], with alkaline sodium borohydride solution at room temperature (Scheme 1). The borohydride loading of the ionene borohydrides **PIBH** and **PIIBH** were determined by titration to be 6 and 5 mmol/g of polymer [18].

The synthesis utility of this new polymer supported borohydrides were studied by examining the



Scheme 1



Scheme 2

transformation of aldehydes, ketones, and acid chlorides to the corresponding alcohols, and imines to their amines. In order to find the optimum conditions, we treated benzaldehyde, acetophenone, benzoyl chloride, and *N*-benzylideneaniline as model compounds with ionene borohydrides in different solvents such as *MeOH*, *t*-*BuOH*,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{Cl}$ , and *THF*. Our observation revealed that methanol is the best solvent for reduction of aldehydes and imines, but *iso*-propanol and a mixture of *THF* and methanol (1:1) are the best solvents for the reduction of ketones and acid chlorides (Scheme 2).

Reductions of a variety of structurally different aromatic and aliphatic aldehydes to their corresponding alcohols are performed efficiently using 1:1 molar ratio of reductants to substrate in methanol at room temperature. The reactions proceed within 10–70 min in high to excellent yields (Table 1). Ketones were also reduced with ionene borohydrides in *iso*-propanol at reflux using a 2:1 molar ratio of reducing agents/ketone and the corresponding alcohols formed in excellent yields (Table 2). It is noteworthy that reduction of  $\alpha,\beta$ -unsaturated aldehydes and ketones proceeds in excellent regioselectivity and the corresponding allylic alcohols were obtained exclusively (Table 1, entry 16 and Table 2, entries 7–10).

Conversion of acid chlorides to their alcohols is an important transformation in organic synthesis. In recent years, a few novel reducing agents have been introduced for this purpose [4a, 19]. Ionene borohydrides in a mixture of *THF*-*MeOH* converted both aliphatic and aromatic acid chlorides to the corresponding alcohols in high yields (Table 3).

However, to explore the scope of these polymeric reducing agents, the reduction of a variety of imines was also investigated (Table 4). As listed in Table 4,

**Table 1.** Reduction of Aldehydes with **PIBH** and **PIIBH**<sup>a</sup>

| Entry | Substrate  | Product   | <b>PIBH</b>  |                            | <b>PIIBH</b> |                            | Ref. |
|-------|--|---|--------------|----------------------------|--------------|----------------------------|------|
|       |  |   | Time/<br>min | Yield/<br>% <sup>b,c</sup> | Time/<br>min | Yield/<br>% <sup>b,c</sup> |      |
| 1     | <i>Ph</i> -CHO   | <i>Ph</i> -CH <sub>2</sub> OH   | 30           | 96                         | 30           | 98                         | [23] |
| 2     | 4-HO- <i>Ph</i> -CHO   | 4-HO- <i>Ph</i> -CH <sub>2</sub> OH   | 60           | 93                         | 45           | 95                         | [23] |
| 3     | 4-MeO- <i>Ph</i> -CHO  | 4-MeO- <i>Ph</i> -CH <sub>2</sub> OH  | 50           | 93                         | 40           | 92                         | [23] |
| 4     | 4-Cl- <i>Ph</i> -CHO   | 4-Cl- <i>Ph</i> -CH <sub>2</sub> OH   | 10           | 98                         | 10           | 96                         | [23] |
| 5     | 4-Br- <i>Ph</i> -CHO   | 4-Br- <i>Ph</i> -CH <sub>2</sub> OH   | 15           | 95                         | 10           | 95                         | [23] |
| 6     | 4-NC- <i>Ph</i> -CHO   | 4-NC- <i>Ph</i> -CH <sub>2</sub> OH   | 10           | 92                         | 10           | 95                         | [23] |
| 7     | 4-O <sub>2</sub> N- <i>Ph</i> -CHO   | 4-O <sub>2</sub> N- <i>Ph</i> -CH <sub>2</sub> OH   | 10           | 93                         | 10           | 95                         | [23] |
| 8     | 3-MeO- <i>Ph</i> -CHO  | 3-MeO- <i>Ph</i> -CH <sub>2</sub> OH  | 40           | 93                         | 30           | 90                         | [23] |
| 9     | 3-Cl- <i>Ph</i> -CHO   | 3-Cl- <i>Ph</i> -CH <sub>2</sub> OH   | 10           | 95                         | 10           | 95                         | [24] |
| 10    | 3-O <sub>2</sub> N- <i>Ph</i> -CHO   | 3-O <sub>2</sub> N- <i>Ph</i> -CH <sub>2</sub> OH   | 10           | 96                         | 10           | 93                         | [23] |
| 11    | 2-HO- <i>Ph</i> -CHO   | 2-HO- <i>Ph</i> -CH <sub>2</sub> OH   | 55           | 95                         | 35           | 95                         | [23] |
| 12    | 2-Cl- <i>Ph</i> -CHO   | 2-Cl- <i>Ph</i> -CH <sub>2</sub> OH   | 10           | 97                         | 10           | 96                         | [24] |
| 13    | 2-O <sub>2</sub> N- <i>Ph</i> -CHO   | 2-O <sub>2</sub> N- <i>Ph</i> -CH <sub>2</sub> OH   | 10           | 96                         | 10           | 95                         | [23] |
| 14    | 2,3-HO- <i>Ph</i> -CHO   | 2,3-HO- <i>Ph</i> -CH <sub>2</sub> OH   | 70           | 91                         | 55           | 92                         | –    |
| 15    | 2-(4-Cl- <i>Ph</i> -S)- <i>Ph</i> -CHO   | 2-(4-Cl- <i>Ph</i> -S)- <i>Ph</i> -CH <sub>2</sub> OH   | 40           | 92                         | 30           | 95                         | –    |
| 16    | <i>Ph</i> -CH=CHCHO  | <i>Ph</i> -CH=CHCH <sub>2</sub> OH  | 55           | 90                         | 40           | 92                         | [23] |
| 17    | <i>Ph</i> -CH <sub>2</sub> CHO   | <i>Ph</i> -CH <sub>2</sub> CH <sub>2</sub> OH   | 25           | 95                         | 15           | 96                         | [23] |
| 18    | (CH <sub>3</sub> ) <sub>2</sub> CH(CH <sub>2</sub> ) <sub>3</sub> CH(CH <sub>3</sub> )-CH <sub>2</sub> CHO | (CH <sub>3</sub> ) <sub>2</sub> CH(CH <sub>2</sub> ) <sub>3</sub> CH(CH <sub>3</sub> )-CH <sub>2</sub> CH <sub>2</sub> OH | 35           | 90                         | 30           | 91                         | [23] |
| 19    | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CHO  | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>2</sub> OH  | 25           | 88                         | 20           | 85                         | [23] |

<sup>a</sup> All reactions were carried out in methanol at room temperature using 1/1 molar ratio of BH<sub>4</sub><sup>−</sup>/substrate<sup>b</sup> All products were known compounds and characterized spectroscopically (<sup>1</sup>H NMR and IR) and showed physical and spectral data in accordance with their expected structure and by comparison with authentic samples<sup>c</sup> Yields refer to pure isolated products**Table 2.** Reduction of ketones with **PIBH** and **PIIBH**<sup>a</sup>

| Entry | Substrate                                    | Product  | <b>PIBH</b> |                            | <b>PIIBH</b> |                            | Ref. |
|-------|--|--|-------------|----------------------------|--------------|----------------------------|------|
|       |  |  | Time/<br>h  | Yield/<br>% <sup>b,c</sup> | Time/<br>h   | Yield/<br>% <sup>b,c</sup> |      |
| 1     | <i>Ph</i> -COCH <sub>3</sub>                 | <i>Ph</i> -CH(OH)CH <sub>3</sub>                 | 1.1         | 96                         | 1            | 97                         | [23] |
| 2     | <i>Ph</i> -COCH <sub>2</sub> CH <sub>3</sub> | <i>Ph</i> -CH(OH)CH <sub>2</sub> CH <sub>3</sub> | 1.5         | 95                         | 1.2          | 95                         | [23] |
| 3     | <i>Ph</i> -CH <sub>2</sub> COCH <sub>3</sub> | <i>Ph</i> -CH <sub>2</sub> CH(OH)CH <sub>3</sub> | 1.5         | 98                         | 1.5          | 97                         | [23] |
| 4     | <i>Ph</i> -CO- <i>Ph</i>                     | <i>Ph</i> -CH(OH)- <i>Ph</i>                     | 3           | 96                         | 2.5          | 97                         | [23] |
| 5     | α-tetralone                                  | α-tetralol                                       | 1.8         | 97                         | 1.5          | 96                         | [23] |
| 6     | 9-fluorenone                                 | 9-fluorenol                                      | 3           | 93                         | 2.7          | 93                         | –    |
| 7     | <i>Ph</i> -CH=CHCOCH <sub>3</sub>            | <i>Ph</i> -CH=CHCH(OH)CH <sub>3</sub>            | 2.5         | 92                         | 2            | 92                         | [24] |
| 8     | 4-Me- <i>Ph</i> -CH=CHCO- <i>Ph</i> -4-Me    | 4-Me- <i>Ph</i> -CH=CHCH(OH)- <i>Ph</i> -4-Me    | 3           | 90                         | 2.5          | 90                         | –    |
| 9     | 4-Br- <i>Ph</i> -COCH=CH- <i>Ph</i>          | 4-Br- <i>Ph</i> -CH(OH)CH=CH- <i>Ph</i>          | 2.5         | 92                         | 2.5          | 93                         | –    |
| 10    | 2-cyclohexen-1-one                           | 2-cyclohexen-1-ol                                | 2.2         | 88                         | 2            | 90                         | [23] |
| 11    | 3-acetylpyridine                             | 1-(3-pyridyl)ethanol                             | 0.8         | 97                         | 0.8          | 95                         | [24] |
| 12    | cyclohexanone                                | cyclohexanol                                     | 2           | 88                         | 2            | 90                         | [23] |
| 13    | 2-heptanone                                  | 2-heptanol                                       | 2           | 87                         | 1.5          | 85                         | [23] |

<sup>a</sup> All reactions were carried out in *i*-PrOH at reflux using 2/1 molar ratio of BH<sub>4</sub><sup>−</sup>/substrate<sup>b</sup> All products were characterized spectroscopically (<sup>1</sup>H NMR and IR) and showed physical and spectral data in accordance with their expected structure and by comparison with authentic samples<sup>c</sup> Yields refer to pure isolated products

**Table 3.** Reduction of acid chlorides to alcohols with **PIBH** and **PIIBH**<sup>a</sup>

| Entry | Substrate                       | Product                                       | <b>PIBH</b> |                        | <b>PIIBH</b> |                        | Ref. |
|-------|---------------------------------|---|-------------|------------------------|--------------|------------------------|------|
|       |                                 |   | Time/min    | Yield/% <sup>b,c</sup> | Time/min     | Yield/% <sup>b,c</sup> |      |
| 1     | <i>Ph</i> -COCl                 | <i>Ph</i> -CH <sub>2</sub> OH                 | 30          | 88                     | 20           | 90                     | [23] |
| 2     | 4-Cl- <i>Ph</i> -COCl           | 4-Cl- <i>Ph</i> -CH <sub>2</sub> OH           | 20          | 90                     | 20           | 91                     | [23] |
| 3     | 2-Cl- <i>Ph</i> -COCl           | 2-Cl- <i>Ph</i> -CH <sub>2</sub> OH           | 20          | 95                     | 15           | 94                     | [24] |
| 4     | <i>Ph</i> -CH <sub>2</sub> COCl | <i>Ph</i> -CH <sub>2</sub> CH <sub>2</sub> OH | 60          | 88                     | 45           | 90                     | [23] |
| 5     | <i>Ph</i> -CHClCOCl             | <i>Ph</i> -CHClCH <sub>2</sub> OH             | 40          | 90                     | 30           | 92                     | [24] |

<sup>a</sup> All reactions were carried out in *THF*-*MeOH* at reflux using 4/1 molar ratio of BH<sub>4</sub><sup>-</sup>/substrate<sup>b</sup> All products were characterized spectroscopically (<sup>1</sup>H NMR and IR) and showed physical and spectral data in accordance with their expected structure and by comparison with authentic samples<sup>c</sup> Yields refer to pure isolated products**Table 4.** Reduction of imines to amines with **PIBH** and **PIIBH**<sup>a</sup>

| Entry | Substrate   | Product   | <b>PIBH</b> |                        | <b>PIIBH</b> |                        | Ref. |
|-------|---|---|-------------|------------------------|--------------|------------------------|------|
|       |   |   | Time/h      | Yield/% <sup>b,c</sup> | Time/h       | Yield/% <sup>b,c</sup> |      |
| 1     | <i>Ph</i> -CH=N- <i>Ph</i>                                      | <i>Ph</i> -CH <sub>2</sub> NH- <i>Ph</i>                                      | 4           | 87                     | 3.5          | 88                     | [25] |
| 2     | 4-Cl- <i>Ph</i> -CH=N- <i>Ph</i>                                | 4-Cl- <i>Ph</i> -CH <sub>2</sub> NH- <i>Ph</i>                                | 3.5         | 89                     | 3.2          | 91                     | [26] |
| 3     | 4- <i>MeO</i> - <i>Ph</i> -CH=N- <i>Ph</i>                      | 4- <i>MeO</i> - <i>Ph</i> -CH <sub>2</sub> NH- <i>Ph</i>                      | 5           | 85                     | 4            | 85                     | [26] |
| 4     | 4-NC- <i>Ph</i> -CH=N- <i>Ph</i>                                | 4-NC- <i>Ph</i> -CH <sub>2</sub> NH- <i>Ph</i>                                | 3.5         | 89                     | 3            | 90                     | [27] |
| 5     | 4-O <sub>2</sub> N- <i>Ph</i> -CH=N- <i>Ph</i>                  | 4-O <sub>2</sub> N- <i>Ph</i> -CH <sub>2</sub> NH- <i>Ph</i>                  | 2.7         | 87                     | 2.3          | 88                     | [28] |
| 6     | <i>Ph</i> -CH=NCH <sub>2</sub> - <i>Ph</i>                      | <i>Ph</i> -CH <sub>2</sub> NH-CH <sub>2</sub> <i>Ph</i>                       | 3.5         | 85                     | 3            | 86                     | [23] |
| 7     | CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH=N- <i>Ph</i> | CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH- <i>Ph</i> | 4           | 82                     | 3            | 84                     | [24] |
| 8     | <i>Ph</i> -CH=NC(CH <sub>3</sub> ) <sub>3</sub>                 | <i>Ph</i> -CH <sub>2</sub> NHC(CH <sub>3</sub> ) <sub>3</sub>                 | 4           | 88                     | 4            | 86                     | [29] |
| 9     | <i>Ph</i> -CH=NCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>  | <i>Ph</i> -CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>  | 4           | 85                     | 4            | 86                     | [30] |
| 10    | <i>Ph</i> -(CH <sub>3</sub> )C=N- <i>Ph</i>                     | <i>Ph</i> -(CH <sub>3</sub> )CHNH- <i>Ph</i>                                  | 9           | 84                     | 7            | 82                     | [31] |

<sup>a</sup> All reactions were carried out in *MeOH* at room temperature using 3/1 molar ratio of BH<sub>4</sub><sup>-</sup>/substrate<sup>b</sup> All products were characterized spectroscopically (<sup>1</sup>H NMR and IR) and showed physical and spectral data in accordance with their expected structure and by comparison with authentic samples<sup>c</sup> Yields refer to pure isolated products

ionene borohydride reagents could reduce a variety of imines in high yields. Ketimine was also reduced in excellent yield (entry 10). Imines bearing a chloro, nitro, or a nitrile group were chemoselectively reduced to the corresponding amines (entries 2, 4 and 5).

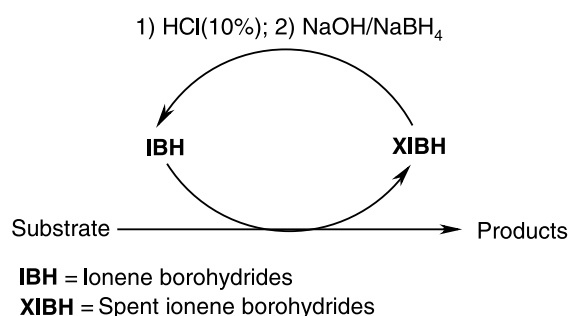
On the other hand, it is often necessary in organic synthesis to reduce one particular carbonyl group without affecting other carbonyl groups in a molecule. In the case of hydride reagents, aldehydes generally are more susceptible to reduction than ketones. The most commonly employed reducing agents are too reactive under normal conditions to differentiate between aldehydes and ketones. A number of modified tetrahydroborate reagents have been reported to show the discrimination ability between aldehydes and ketones [20]. Along the outlined strat-

egy, and to explore the chemoselectivity of ionene borohydrides in reduction of aldehydes over ketones, we carried out competition experiments of a variety of structurally different aldehydes and ketones. In the preceding section, we noticed that reduction of aldehydes and ketones were both temperature and solvent dependent. Therefore, this goal could be easily achieved by selective reduction of aldehyde in the presence of an equimolar amount of ketone using one equivalent of ionene borohydrides at room temperature. The general trend of this discrimination ability for reduction of aldehydes in the presence of ketones is shown in Table 5.

The reduction of the nitro, nitrile, and carboxylate groups by ionene borohydrides does not occur to any appreciable extent under the conditions described above for the reduction of carbonyl compounds and

**Table 5.** Chemoselective reductions of aldehydes versus ketones with (**PIBH** and **PIIBH**) in methanol

| Entry | Substrate                                    | Product  | Time/min | Yield/% <sup>a</sup> |              |
|-------|--|--|----------|----------------------|--------------|
|       |  |  |          | <b>PIBH</b>          | <b>PIIBH</b> |
| 1     | <i>Ph</i> -CHO                               | <i>Ph</i> -CH <sub>2</sub> OH                    | 40       | 96                   | 98           |
|       | <i>Ph</i> -COCH <sub>3</sub>                 | <i>Ph</i> -CH(OH)CH <sub>3</sub>                 |          | 8                    | 8            |
| 2     | <i>Ph</i> -CH=CHCHO                          | <i>Ph</i> -CH=CHCH <sub>2</sub> OH               | 60       | 93                   | 92           |
|       | <i>Ph</i> -CH=CHCOCH <sub>3</sub>            | <i>Ph</i> -CH=CHCH(OH)CH <sub>3</sub>            |          | 5                    | 6            |
| 3     | <i>Ph</i> -CH <sub>2</sub> CHO               | <i>Ph</i> -CH <sub>2</sub> CH <sub>2</sub> OH    | 40       | 96                   | 97           |
|       | <i>Ph</i> -CH <sub>2</sub> COCH <sub>3</sub> | <i>Ph</i> -CH <sub>2</sub> CH(OH)CH <sub>3</sub> |          | 6                    | 9            |
| 4     | <i>Ph</i> -CHO                               | <i>Ph</i> -CH <sub>2</sub> OH                    | 70       | 98                   | 98           |
|       | <i>Ph</i> -CO- <i>Ph</i>                     | <i>Ph</i> -CH(OH)- <i>Ph</i>                     |          | 4                    | 7            |
| 5     | <i>Ph</i> -CH <sub>2</sub> CHO               | <i>Ph</i> -CH <sub>2</sub> CH <sub>2</sub> OH    | 40       | 96                   | 97           |
|       | cyclohexanone                                | cyclohexanol                                     |          | 6                    | 7            |

<sup>a</sup> Yield determined by GC**Scheme 3**

imines. Another interesting feature of this method is that ionene borohydrides could be regenerated to their initial activity. For this purpose, the collected spent polymers were neutralized with HCl (10%) and then treated with a fresh alkaline solution of NaBH<sub>4</sub> (Scheme 3).

In conclusion we developed new and efficient high loading linear polymer-supported reducing agents, 2,4-ionene and xylene ionene borohydrides, for reduction of aromatic and aliphatic aldehydes, ketones, acid chlorides, and imines. The advantages of the present reagent in terms of ease of preparation and reusability of supported polymers, work-up procedure, and high capacity of borohydride make this protocol a valuable alternative to the existing polymeric reductants.

## Experimental

Materials were purchased from Fluka and Merck companies. Aldimines were prepared from stirring a 1:1 mixture of al-

dehydes and amines at ambient temperature under solvent-free conditions [21]. *N*-( $\alpha$ -Methylbenzylidene)benzylamine was prepared from reaction of ketone and amine according to Ref. [22].

The reactions were monitored by TLC using silica gel plates and the products were purified by flash column chromatography on silica gel (Merck; 230–400 mesh) and were identified by comparison of their IR and <sup>1</sup>H NMR spectra and physical data with those of authentic samples. <sup>1</sup>H NMR spectra were measured at 90 MHz with a JEOL JNM-EX 90 spectrometer with tetramethylsilane as an internal reference and CDCl<sub>3</sub> as solvent. IR spectra were recorded with a Pye-unicam SP 1100 spectrophotometer. Gas chromatography was recorded on a Perkin Elmer clarus 500 GC instrument. Elemental analyses were performed on a LECO 250 instrument; their results agreed favorably with the calculated values.

### Preparation of Ionene-Bound Borohydrides

An alkaline solution of sodium borohydride was prepared from 1.51 g NaBH<sub>4</sub> (0.04 mol) in 10 cm<sup>3</sup> 5 M NaOH solution. Then, an aqueous solution of 2,4-ionene bromide [17] (5.00 g in 10 cm<sup>3</sup> H<sub>2</sub>O) or xylene ionene chloride [18] (4.00 g in 20 cm<sup>3</sup> H<sub>2</sub>O) was added drop-wise to the above solution at room temperature and stirred for 2 h. The resulting white solid was filtered off, washed with ethanol:ether (1:1), and dried in a vacuum desiccator over CaCl<sub>2</sub>. The content of active reducing agent BH<sub>4</sub><sup>-</sup> was determined by the titrimetric method [16].

### General Procedure for Reduction of Aldehydes

In a 25 cm<sup>3</sup> round-bottomed flask equipped with a magnetic stirrer, a solution of 1 mmol aldehyde in 10 cm<sup>3</sup> methanol was prepared. The ionene borohydride agent (1 mmol) was added and the mixture was stirred at room temperature. Progress of the reaction was monitored by TLC. On completion of the reaction, the spent polymer was removed by filtration. The solvent was evaporated and the resulting crude material purified by column chromatography on silica gel (*n*-hexane:ethyl acetate = 5:1) to afford the pure alcohol.

### General Procedure for Reduction of Ketones

In a 25 cm<sup>3</sup> round-bottomed flask equipped with a magnetic stirrer and condenser, a solution of 1 mmol ketone in 10 cm<sup>3</sup> *i*-PrOH was prepared. The polymeric reducing agent (2 mmol) was added and the reaction mixture was stirred magnetically under reflux condition for appropriate times (Table 2). Progress of the reaction was monitored by TLC. On completion of the reaction, the spent polymer was removed by filtration. The solvent was evaporated and the resulting crude material purified by column chromatography on silica gel to (*n*-hexane:ethyl acetate = 5:1) to afford the pure alcohol.

### General Procedure for Reduction of Acid Chlorides

Ionene borohydride (4 mmol) was suspended in *THF* in presence of the respective acid chloride (1 mmol) during a period of 15 min under reflux and stirring. Then 8 cm<sup>3</sup> methanol were added and stirred at reflux for specified time (Table 3). The reactions were monitored by TLC using mixtures of ethyl acetate/*n*-hexane as eluent. On completion of the reaction, the spent polymer was removed by filtration. The solvent was evaporated and the resulting crude material was purified by column chromatography on silica gel (*n*-hexane:ethyl acetate = 8:1) to give the pure alcohols in 88–95% yields.

### General Procedure for Reduction of Imines

A mixture of 1 mmol imine, 10 cm<sup>3</sup> methanol, and 3 mmol ionene borohydride was placed in a 25 cm<sup>3</sup> round bottomed flask and stirred at room temperature. After completion of the reaction (monitored by TLC), the spent polymer was removed by filtration. The solvent was evaporated and the resulting crude material was purified by column chromatography on silica gel (*n*-hexane:ethyl acetate = 10:1) to give the pure products.

### General Procedure for Competitive Reduction of Aldehydes and Ketones

In a 25 cm<sup>3</sup> round-bottomed flask, a solution of 1 mmol aldehyde and 1 mmol ketone in 10 cm<sup>3</sup> methanol was prepared. The polymeric reducing agent (1 mmol) was added and the mixture stirred magnetically at room temperature for specified times (Table 5). Progress of the reaction was monitored by TLC. After completion of the reaction, the spent polymer was removed by filtration. The solvent was evaporated and the resulting crude materials were analyzed by GC.

### Regeneration Procedure for Ionene Borohydrides

After completion of the reduction reaction and isolation of the product, the spent polymer was separated and dissolved in water, and neutralized with HCl (10%). Upon addition of freshly prepared alkaline solution of sodium borohydride to this solution at room temperature and stirring for 2 h, ionene borohydride precipitated. The resulting solid was filtered off, washed with ethanol:ether (1:1), and dried in a vacuum desiccator over CaCl<sub>2</sub>.

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