

# POLYMER SUPPORTED ZINC BOROHYDRIDE: A STABLE, EFFICIENT, SELECTIVE, AND REGENERABLE REDUCING AGENT FOR VARIETY OF ORGANIC COMPOUNDS<sup>☆</sup>

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**ABSTRACT:** *The difficult to handle and store zinc borohydride,  $Zn(BH_4)_2$ , is stabilized by supporting it on polyvinylpyridine. This new mild, efficient, selective, and regenerable polymer supported borohydride reducing agent reduces a variety of organic compounds such as, aldehydes,  $\alpha, \beta$ -unsaturated carbonyl compounds, acid chlorides, epoxides, disulfides, as well as reductive acetylation of carbonyl compounds. It absolutely discriminates aldehydes from ketones.*

**KEY WORDS:** *Reduction, Polymer supported, Reducing agent, Zinc borohydride.*

## INTRODUCTION

Reduction is one of the most fundamental and useful reactions in organic chemistry. There must be few organic synthesis of any complexity which do not involve a reduction at some stage. Reduction by hydride transferring agents has widely been used in organic synthesis by well known alkali metal borohydrides,  $NaBH_4$ ,  $LiAlH_4$ , and their modified forms [1-4]. However, there are few reports in the literature

on the use of covalent transition-metal borohydride complexes as reducing agents. This is primarily because almost all of them are volatile unstable solids [5] and as such cannot be used in organic synthesis without modification. A few modified forms of these compounds such as  $(Ph_3P)_2CuBH_4$  [6],  $[(Ph_3P)_2CuBH_3CN]_2$  [7] and  $(C_5H_5)_2Zr(Cl)BH_4$  [8] have been used as reducing agents.

<sup>☆</sup> *This paper is dedicated to Professor Ali Akbar Moshfegh the founder of the chemistry department of Shiraz University on the occasion of his 70th birthday.*

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Zinc borohydride,  $Zn(BH_4)_2$ , a white insoluble solid which decomposes slowly and hydrolyzes vigorously when allowed to contact with water [5], is the only reported transition-metal borohydride which has been used frequently in reduction reactions [9,10]. However, because of its instability it should always be used freshly and in the form of cold ethereal solutions, and even when it is supported on silica gel, it should be used on the same day of its preparation [11].

Immobilization of the reagents on polymeric supports has been investigated extensively [12,13]. This is primarily because insoluble polymeric reagents expand the range of applicable solvents, facilitate the ease of work-up and product purification, and in most cases provide the recovery and regeneration of the polymeric support. Polymer supported reducing agents have received considerable attention in recent years and a variety of them, while exhibiting the advantages of polymeric reagents, have been used in the mild and selective reduction of organic compounds [12]. The only reported polymer supported borohydride reagents are Amberlyst anion exchange resin supported borohydride and cyanoborohydride [14]. These reagents have been used in a number of organic transformations [15].

Recently, in a short communication, we reported preparation and use of polyvinylpyridine supported zinc borohydride as a stable chemoselective polymeric transition-metal borohydride reducing agent for reduction of carbonyl compounds [16]. In this paper, we describe fully the preparation and application of this mild, efficient and selective borohydride reducing agent in reduction of a variety of organic functional groups such as aldehydes and ketones,  $\alpha$ - $\beta$  unsaturated carbonyl compounds, acid chlorides, epoxides, disulfides, as well as reductive acetylation of carbonyl compounds.

## EXPERIMENTAL

### General

Crosslinked poly(4-vinylpyridine) (2% divinylbenzene) was commercial product (*Fhuka*). All reduction products were known compounds and were identified by comparison of their spectra and physical data with those of authentic samples. Reaction

monitoring and the purity of the products were accomplished by GLC or TLC. Separation of the products, if needed, was conducted on a silica gel plate or column. IR and NMR spectra were recorded on *Perkin-Elmer* IR 157 G and *Hitachi* R-2413, 60 MHz spectrophotometer. The capacity of the reagent was determined by idometric titration method [17] and atomic absorption technique.

### Preparation of crosslinked poly(4-vinylpyridine) supported zinc borohydride [ $PVP-Zn(BH_4)_2$ ]

Crosslinked poly(4-vinylpyridine) (1.0 g) suspended in methanol/water (50 mL, 4/1), was added to a warm solution of zinc chloride (5.4 g, 40 mmol) in methanol (50 mL). The mixture stirred and kept warm for 12 hours. The precipitate was filtered off, washed with methanol and dried under vacuum. The resulting polyvinylpyridine supported zinc chloride was suspended in ethanol (50 mL) and was added to a cold solution of excess sodium borohydride (3.8 g) in ethanol (100 mL). The mixture was stirred magnetically at room temperature for 4 hours. The resulting supported reagent was separated, washed several times with ethanol and ether, and dried in vacuum overnight to produce a white, stable and nonhygroscopic powder in a quantitative yield. The capacity of [ $PVP-Zn(BH_4)_2$ ] determined by iodometric titration method was 3.04 mmol  $BH_4^-$  per gram of reagent which was in good agreement with the Zn content of the reagent determined by atomic absorption technique.

### General procedure for reduction of carbonyl compounds with [ $PVP-Zn(BH_4)_2$ ]

To a solution of the carbonyl compound (3 mmol) in ethanol (20 mL) in a 50 mL round bottomed flask equipped with a condenser and a magnetic stirrer, polymeric reducing agent (1.2 g) was added. The reaction mixture was stirred magnetically while being refluxed. Progress of the reaction was monitored by TLC (eluent:  $CCl_4$ /ether, 6/1) or GLC. On completion of the reaction, the mixture was cooled to room temperature and filtered. The filter cake was washed several times with ethanol and finally with dichloromethane. The combined filtrates were evaporated on a rotary evaporator and the pure

product was obtained in 0-95% yield. When necessary the product was separated from the starting material by a silica gel plate or column using an appropriate eluent. Representative examples are given in Table 1.

To study the effect of Lewis acid catalyst,  $\text{FeCl}_3$ , on the efficiency of  $[\text{PVP-Zn}(\text{BH}_4)_2]$ , the same procedure as above was followed while the catalyst (0.3 mmol) was added together with the reagent performing the reaction in THF. On completion of the

Table 1: Reduction of different carbonyl compounds with  $[\text{PVP-Zn}(\text{BH}_4)_2]^a$

No.	Substrate	Product <sup>b</sup>	Time (hr)	Yield (%) <sup>c</sup>
1	Benzaldehyde	Benzyl alcohol	8 5 <sup>d</sup>	80 98 <sup>e</sup>
2	<i>p</i> -Chlorobenzaldehyde	<i>p</i> -Chlorobenzyl alcohol	5 3 <sup>d</sup>	95 97
3	<i>p</i> -Methoxybenzaldehyde	<i>p</i> -Methoxybenzyl alcohol	12 10 <sup>d</sup>	75 95
4	Piperonal	Piperonol	8 6 <sup>d</sup>	65 95
5	Furfural	Furfuryl alcohol	8 6 <sup>d</sup>	83 95
6	2-Phenylethanal	2-Phenylethanol	15 10 <sup>d</sup>	75 93
7	Acetophenone	1-Phenylethanol	15 11 <sup>d</sup>	0 70
8	Benzophenone	Benzhydrol	24 24 <sup>d</sup>	0 20
9	Cyclohexanone	Cyclohexanol	24 12 <sup>d</sup>	0 75 <sup>e</sup>
10	$\text{PhCH}=\text{CHCHO}$	$\text{PhCH}=\text{CHCH}_2\text{OH}$	9	90 <sup>e</sup>
11	$\text{CH}_3\text{CH}=\text{CHCHO}$	$\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$	15	85 <sup>e</sup>
12	$(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}(\text{CH}_3)=\text{CHCOH}$	$(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}(\text{CH}_3)=\text{CHCH}_2\text{OH}$	18 10 <sup>d</sup>	80 <sup>e</sup> 85 <sup>e</sup>
13	$\text{PhCH}=\text{CHCOPh}$	$\text{PhCH}=\text{CHCH}(\text{OH})\text{Ph}$	24 20 <sup>d</sup>	0 20 <sup>e</sup>
14	$\text{PhCH}=\text{CHCOCH}_3$	$\text{PhCH}=\text{CHCH}(\text{OH})\text{CH}_3$	15	0

a) Reactions performed in refluxed ethanol unless otherwise indicated

b) Identified by comparing with the authentic samples TLC, GC, IR, NMR

c) Isolated yields unless otherwise indicated

d) Reaction performed in THF under refluxed condition using  $\text{FeCl}_3$  as catalyst

e) GC yield

reaction, methanol (15 mL) was added and stirred for a few hours before working up the reaction mixture.

**General procedure for reduction of acid chlorides to the corresponding aldehydes and alcohols with [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>]**

Polymeric reagent (0.7 g) was added to a stirred solution of acid chloride (2 mmol) in THF/CH<sub>3</sub>CN (20 mL, 10/1) and the mixture was refluxed. Progress of the reaction was followed by TLC (eluent: CCl<sub>4</sub>/ether, 6/1). On completion of the reaction methanol (10 mL) was added and stirred for 4 hours. It was then filtered and washed several times with methanol and ether. The combined filterates was evaporated under reduced pressure and the resulting material was purified on a silica gel column. On evaporation of the solvent the pure alcohol was obtained as the major product in 50-85% yield.

When this same reaction was performed in (CH<sub>2</sub>Cl<sub>2</sub>/CHCl<sub>3</sub>, 4/1) solvent at room temperature

the major product was the corresponding aldehyde in 60-90% yield. Representative examples are given in Table 2.

**General procedure for reduction of epoxides, and disulfides with [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>]**

To a solution of the substrate (2 mmol) in THF (20 mL), polymeric reagent (0.7-1.5 g) was added and refluxed. progress of the reaction was followed by TLC or GLC. After 5-24 hours methanol (15 mL) was added to the suspension, stirred for 4 hours at room temperature, and filtered. The filter cake was washed several times with methanol and dichloro-methane. The combined filterates was evaporated on a rotary evaporator and the resulting alcohols, in the case of epoxides, were separated by column chromatography to give the more substituted alcohol as the major product. In the case of disulfides, evaporation of the combined filterates afforded the pure thiol in 40-100% yield. Representative examples are given in Tables 3 and 5.

Table 2: Reduction of acid chloride to the corresponding aldehydes and alcohols with [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>]

No.	Substrate	Product <sup>d</sup>	Time <sup>a</sup>	Time <sup>b</sup>	Yield (%) <sup>a</sup>	Yield (%) <sup>b</sup>
1	PhCH=CHCOCl	PhCH=CHCOH	12	7	5 <sup>c</sup>	7
		PhCH=CHCH <sub>2</sub> OH	12	7	85	20 <sup>c</sup>
2	<i>p</i> -NO <sub>2</sub> PhCOCl	<i>p</i> -NO <sub>2</sub> PhCHO	10	5	15 <sup>c</sup>	87
		<i>p</i> -NO <sub>2</sub> PhCH <sub>2</sub> OH	10	5	70	10 <sup>c</sup>
3	3,5-Dinitrobenzoyl chloride	3,5-Dinitrobenzaldehyde	10	5	25 <sup>c</sup>	90
		3,5-Dinitrobenzylalcohol	10	5	70	5 <sup>c</sup>
4	PhCH <sub>2</sub> COCl	PhCH <sub>2</sub> CHO	20	10	20 <sup>c</sup>	65
		PhCH <sub>2</sub> CH <sub>2</sub> OH	20	10	70	25 <sup>c</sup>
5	<i>p</i> -BrPhCOCl	<i>p</i> -BrPhCHO	16	12	15 <sup>c</sup>	75
		<i>p</i> -BrPhCH <sub>2</sub> OH	16	12	78	15 <sup>c</sup>
6	<i>p</i> -MeOPhCOCl	<i>p</i> -MeOPhCHO	24	18	35 <sup>c</sup>	60
		<i>p</i> -MeOPhCH <sub>2</sub> OH	24	18	50	30 <sup>c</sup>

a) Reactions performed in THF/CH<sub>3</sub>CN (10/1) under reflux

b) Reactions performed in CH<sub>2</sub>Cl<sub>2</sub>/CHCl<sub>3</sub>, 4/1 at room temperature

c) Estimated by GC

d) Identified by comparing with the authentic samples (TLC, GC, IR, NMR)

### General procedure for reduction of azides with [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>]

Polymeric reagent (0.7-3 g) was added to a stirred solution of azide (2 mmol) in isopropanol (50 mL) and the mixture was heated under reflux condition. Progress of the reaction was followed by TLC. The reaction mixture was filtered and washed twice with

methanol (10 mL). The filtrates were combined and solvent evaporated. The resulting material was purified, if necessary, on a silicagel plate (eluent: petroleum benzene). Evaporation of the solvent afforded the pure amine or sulfanamide in 0-95% yield. The representative examples are given in Table 4.

Table 3: Reduction of epoxides with [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>]<sup>a</sup>

No.	Substrate	Product <sup>b</sup>	Time (hr)	Yield (%) <sup>c</sup>
1	Propylene oxide	CH <sub>3</sub> CH(OH)CH <sub>3</sub>	8	51 <sup>b</sup>
		CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	8	15 <sup>b</sup>
2	Styrene oxide	PhCH(OH)CH <sub>3</sub>	7	54
		PhCH <sub>2</sub> CH <sub>2</sub> OH	7	18
3	Cyclohexene oxide	Cyclohexanol	7.5	77 <sup>b</sup>
4	PhOCH <sub>2</sub> CH-CH <sub>2</sub>   O	PhOCH <sub>2</sub> CH <sub>2</sub> (OH)CH <sub>3</sub>	5	85
		PhOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	5	<5
5	<i>trans</i> -stilbene oxide	PhCH(OH)CH <sub>2</sub> Ph	7	85

a) Reactions performed in THF under reflux

b) GC yield

c) Identified by comparing with the authentic samples (TLC, GC, IR, NMR)

Table 4: Reduction of azides to the corresponding amines and sulfonamides with [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>]<sup>a,d</sup>

No.	Substrate	red./Sub. <sup>b</sup>	Time (hr)	Yield (%) <sup>c</sup>
1	PhN <sub>3</sub>	2	8	90
2	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> N <sub>3</sub>	1	10	85
3	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> N <sub>3</sub>	1	7	85
4	PhCH <sub>2</sub> N <sub>3</sub>	3	18	64
5	<i>p</i> -C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> N <sub>3</sub>	3	11	65
6	1-Naphthyl azide	2	8	80
7	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> N <sub>3</sub>	1	6	95
8	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> N <sub>3</sub>	2	9	80
9	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> N <sub>3</sub>	4	24	0
10	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH <sub>2</sub> N <sub>3</sub>	4	24	0

a) Reactions performed in isopropanol under reflux

b) Approximate molar ratio of reducing agents/substrate

c) Isolated yield

d) Products were identified by comparing with the authentic samples (TLC, GC, IR, NMR)

Table 5: Reduction of disulfides to the corresponding thiols with [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>]<sup>a,d</sup>

No.	Substrate	Red./Sub. <sup>b</sup>	Time (hr)	Yield (%) <sup>c</sup>
1	Benzyl disulfide	1	18	100 <sup>c</sup>
2	Phenyl disulfide	2	15	100 <sup>c</sup>
3	Cyclohexyl disulfide	2	15	75 <sup>c</sup>
4	Furfuryl disulfide	1	24	80
5	<i>n</i> -Butyl disulfide	2	24	40 <sup>c</sup>
6	2,2'-Dipyridyl disulfide	1	12	95
7	2,2'-Dipyrimidinyl disulfide	2	18	78
8	HOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> S <sub>2</sub>	1	15	96

a) Reactions performed in THF under reflux

b) Approximate molar ratio of reducing agents/substrate

c) GC yield

d) Products were identified by comparing with the authentic samples (TLC, GC, IR, NMR)

### General procedure for reductive acetylation of aldehydes and ketones with [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>]

To a solution of carbonyl compound (2 mmol) in ethylacetate (20 mL), polymeric reagent (0.7 g) was added and the suspension stirred under refluxed condition. Progress of the reaction was followed by TLC. After 12-24 hours, the mixture was cooled to room temperature and filtered. The resulting product was purified if necessary, by column chromatography. Evaporation of the solvent afforded the pure product in 0-87% yield. Representative examples are given in Table 6.

### Regeneration of the reagent

Polymeric spent reagent, originally prepared from poly (4-vinylpyridine) (0.69 g), was treated with hydrochloric acid (20 mL, 3N). The resulting light brown suspension was poured onto a solution of sodium hydroxide (40 mL, 3N). The solid resin was filtered and washed several times with distilled water and dried in vacuum at 40-50°C overnight to give the recovered polymer (0.67 g), which could be used successively for the preparation of the reducing agent by the same procedure described in the preceding section.

## RESULTS AND DISCUSSION

Crosslinked poly(4-vinylpyridine) supported zinc borohydride, [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>] was prepared by adding polymer supported zinc chloride complex to an excess alcoholic solution of NaBH<sub>4</sub>, while the exchange reaction occurred rapidly. The capacity as mmol of BH<sub>4</sub><sup>-</sup> per gram of [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>] was obtained by iodometric titration method and was in good agreement with the amount of zinc on the polymer determined by atomic absorption technique. This white powder polymeric reducing agent, unlike its monomeric analogue, was very stable at room temperature and could be stored as a bench top reagent for months without appreciable change in its capacity.

It is known that solvent can play an important role in the stability, reducing power, and selectivity of borohydride reagents in reduction reactions [4,18]. It is also well known that for using a polymeric reagent in an organic reaction a solvent should be chosen in which the polymeric reagent can swell to a considerable extent. Considering these facts, solvent optimization reaction for each organic functional group reduction was performed using different solvents and the best solvent was chosen on the base

Table 6: Reduction acetylation of aldehyde and ketones with [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>]<sup>a</sup>

No.	Substrate	Product	Time (hr)	Yield (%)
1	1-Octanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>2</sub> OCOCH <sub>3</sub>	18	80 <sup>b</sup>
2	PhCH <sub>2</sub> CHO	PhCH <sub>2</sub> CH <sub>2</sub> OCOCH <sub>3</sub>	15	85
3	PhCHO	PhCH <sub>2</sub> OCOCH <sub>3</sub>	15	83
4	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OCOCH <sub>3</sub>	24	87
5	Citral	(CH <sub>3</sub> ) <sub>2</sub> C=CH(CH <sub>2</sub> ) <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> OCOCH <sub>3</sub>	18	80 <sup>b</sup>
6	PhCH=CHCHO	PhCH=CHCH <sub>2</sub> OCOCH <sub>3</sub>	15	60
7	Cyclohexanone	C <sub>6</sub> H <sub>11</sub> OCOCH <sub>3</sub>	12	35 <sup>b</sup>
8	2-Octanone	C <sub>6</sub> H <sub>13</sub> (CH <sub>3</sub> )CH <sub>2</sub> OCOCH <sub>3</sub>	24	30 <sup>b</sup>
9	PhCOCOPh	—	24	0
10	PhCOPh	—	24	0
11	PhCOCH <sub>3</sub>	Ph(CH <sub>3</sub> )CHOCOCH <sub>3</sub>	24	25

a) Reactions performed in ethylacetate under reflux.

b) GC yield

c) Identified by comparison with the authentic samples (TLC, GC, IR, NMR)

of the efficiency of the polymeric reducing agent in that solvent. The solvents of choice were those mentioned in the Tables. In these solvents the polymeric reagent was completely insoluble and zinc and boron moieties before and after the reduction reactions remained firmly bound to the insoluble polymeric support. The product isolation and purification were performed simply by filtration of the reaction mixture, evaporation of the solvent, and if necessary further separation of the starting material by column chromatography.

Chemoselective reduction of aldehydes in the presence of ketones and other reducible groups is a very useful reaction in organic synthesis. A wide range of reagents have been reported for this purpose, but only few have proved very general in scope [19]. [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>] proved to be an excellent chemoselective reducing agent for aldehydes with respect to ketones. As seen in Table 1 aldehydes are reduced to their corresponding alcohols in moderate to high yields, but ketones remained largely intact. Selective reduction of  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds without disturbing the carbon-carbon double bond was also achieved by this reagent (entries 10-14). In these compounds, again, the reagent discriminates between aldehydes and ketones.

It is known that the reducing power of borohydride reagents can be modified by the use of catalytic amounts, of Lewis acids [20]. In order to see this effect on the efficiency of [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>] in reduction of carbonyl compounds catalytic amount of FeCl<sub>3</sub>, which proved to be the best among other Lewis acids, was used in several reduction reactions. As shown in the table, efficiency of the polymeric reagent was improved considerably to the extent that even ketones could be reduced with low to moderate yields.

Direct conversion of readily available acid chlorides into aldehydes, without further reduction to alcohols, is a useful reaction in organic synthesis and many reducing agents have been developed for this purpose [4,7,21]. With [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>] it was noticed that by changing the solvent system and reaction condition acid chlorides could be reduced to the corresponding aldehydes or alcohols as major products in moderate to high yields. As shown in Table

2, [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>] could reduce acid chlorides to aldehydes at room temperature using CH<sub>2</sub>Cl<sub>2</sub>/CHCl<sub>3</sub> (4/1) as a solvent. However, using THF/CH<sub>3</sub>CN (10/1) system under reflux condition gave the corresponding alcohols as major products.

Regioselective reduction of epoxides to the corresponding less or more substituted alcohols is of great importance and for this many hydride transferring agents have been developed [4,22]. However, in most cases more substituted alcohols are easily obtained whereas access to the less substituted alcohols is not so simple and mixture of alcohols usually results. Only, recently reductive cleavage of epoxides to the less substituted alcohols was achieved using zinc borohydride supported on silica gel [11,23]. As seen in Table 3, [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>] reduced epoxides to the mixture of their corresponding alcohols with the more substituted alcohols being the major products.

There are several reports in the literature on reduction of azides to amines using different types of reducing agents [24]. Some of these reducing agents normally give poor yields of amines. [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>] could successfully be utilized in reduction of aryl azides and arylsulfonyl azides to the corresponding amines and sulfonamides respectively, Table 4. Aliphatic azides were not reduced by this reagent even after long reaction time.

Reduction of disulfides to the corresponding thiols with different reagents has been subjected to considerable study [25]. As shown in Table 5, [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>] proved to be a very good reducing agent for conversion of aryl and aliphatic disulfides to their corresponding thiols in moderate to high yields.

Generally, aldehydes and ketones are converted to acetates via reduction followed by acetylation. A few methods of direct reductive acetylation of such compounds have been reported [26]. Table 5, summarizes reductive acetylation of aldehydes and ketones with [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>] in ethylacetate under reflux condition. As expected this reagent is chemoselective for reductive acetylation of aldehydes with respect to ketones.

One of the most important advantages of the polymeric reagents over their monomeric analogues

is that in most cases the spent reagent can be regenerated and recycled [12]. Regeneration of [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>] was accomplished by simple washing-reactivation procedure in which the spent reagent was first washed with an acid to remove the metal complexes and then with a base to obtain original polymer followed by activation reactions. No change in the capacity of the regenerated reagent was observed and loss of the original polymer during this process was negligible.

Attempts to reduce other organic functional groups such as, acids, esters, amides, alkenes, nitriles, oximes and nitro groups with [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>] was unsuccessful.

In conclusion, [PVP-Zn(BH<sub>4</sub>)<sub>2</sub>] unlike its unsupported analogue Zn(BH<sub>4</sub>)<sub>2</sub>, is stable and can be kept for a long time. It is a regenerable polymeric reducing agent. The mildness, chemo and regioselectivity, easy reaction work-up with no boron moiety in the final product solution, and high reaction yields make this stabilized transition-metal borohydride reagent useful in the field of organic synthesis.

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