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# Reductive Amination of Aldehydes and Ketones in a Heterogeneous System in *THF* and under Solvent-Free Conditions Using Sodium Borohydride-Silica Phosphoric Acid

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**Summary.** A chemoselective, fast, efficient, and high yielding method for the preparation of amines by reductive amination of aldehydes and ketones using sodium borohydride in the presence of silica phosphoric acid in *THF* and under solvent-free conditions at room temperature is described.

**Keywords.** Silica phosphoric acid; Reductive amination; Aldehydes; Ketones; $NaBH_4$.

## Introduction

Reductive amination of aldehydes and ketones is one of the most useful methods to prepare amines in biological and chemical systems [1]. Amines are very important industrial organic compounds that have found wide-spread applications as solvents, intermediates for pharmaceuticals, raw materials for resins, textile additives, disinfectants, rubber stabilizers, corrosion inhibitors, and in the manufacture of detergents and plastics [2]. The reaction involves the initial formation of an intermediate carbinol amine, which dehydrates to form an imine under the reaction conditions. The imine is then protonated to form an iminium ion. Subsequent reduction of this iminium ion produces the alkylated amine [3]. Catalytic hydrogenation is an effective method for this conversion that has limited uses with compounds containing reducible functional groups, such as nitro, cyano, and C–C multiple bonds. For reductive amination, a variety of reducing agents, such as $NaBH_3CN$ [4], $NaBH(OAc)_3$ [5], borane-pyridine [6], tetrahydroborate exchange resin [7], $Zn(BH_4)_2$ [8], $Zn(BH_4)_2$–$ZnCl_2$ [9], $Zn(BH_4)_2$–$SiO_2$ [10], Ti(O-*iPr*)$_4$–$NaBH_4$ [11], decaborane [12], $NaBH_4$ wet clay-microwave [13], *Ph*$SiH_3$–*Bu*$_2$$SnCl_2$ [14], *Bu*$_3$SnH [15], *Bu*$_3$SnH–$SiO_2$ [16], $Zr(BH_4)_2Cl_2$(*dabco*)$_2$ [17], picolineborane [18], *Hantzsch* dihydropyridine [19], $NaBH_4$ in micellar media [20], and solid acid-activated $NaBH_4$ under solvent-free conditions [21] have been developed. However, most of these reagents may have one or another drawback. For example, the use of expensive and highly toxic $NaBH_3CN$ that carries the risk of having residual cyanide in the products as well as in the work-up stream makes this procedure less attractive. Clearly the use of $NaBH_3CN$ is not acceptable in the context of green synthesis, especially in industry [22]. Tin hydride reagents are also highly toxic [23].

Recently, we reported reductive amination of aldehydes and ketones with *N*-methylpiperidine zinc borohydride [19] and $NaBH_4$ [24] in a micellar media. Sodium borohydride is a cheap, safe to handle, and environmentally friendly reducing agent which rapidly reduces aldehydes, ketones, and acid chlorides [25]. This reagent is commonly employed in hydroxylic solvents, such as methanol, ethanol, and 2-propanol, although it is unstable in both methanol and ethanol due to solvolysis [26].

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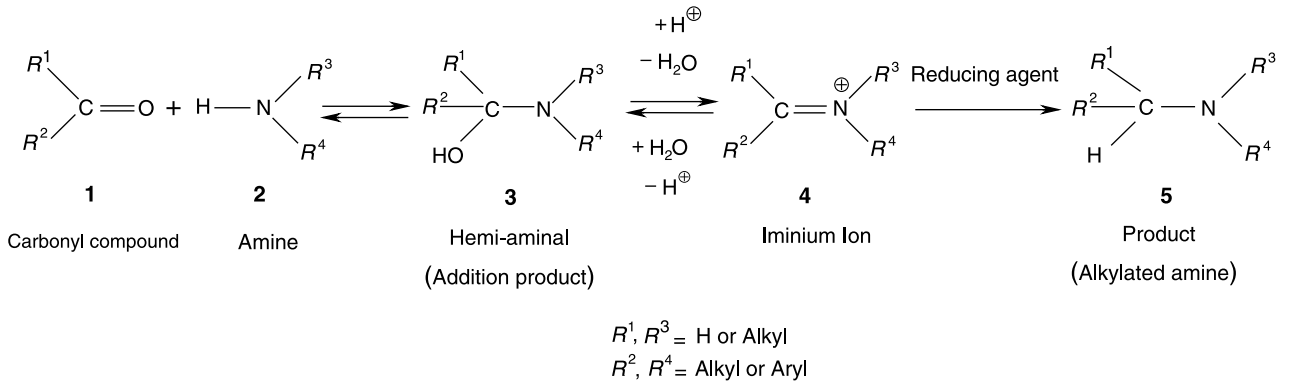


**Scheme 1**

Acids are widely used as catalysts in industry, producing more than $1 \times 10^8$ Mt/year of products. The most commonly used acids are HF, $H_2SO_4$, $HClO_4$, and $H_3PO_4$ (in liquid form or supported on kieselguhr). Solid acids have many advantages such as simplicity in handling, decreased reactor and plant corrosion problems, and environmentally safe disposal. There is much current research and general interest in heterogeneous systems because of the importance of such systems in industry and in developing technologies. Silica phosphoric acid is prepared *via* reaction of silica chloride and phosphoric acid. The application of silica phosphoric acid as a stable and efficient heterogeneous catalyst in organic synthesis has been widely studied [27]. On the other hand, solvent-free reactions are not only of interest from an ecological point of view, but in many cases offer considerable synthetic advantages in terms of yield, selectivity, and simplicity of the reaction procedure [26] (Scheme 1).

We report here a method for the efficient reductive amination of a series of aldehydes and ketones using $NaBH_4$ in the presence of silica phosphoric acid. This reaction is of significance because of its versatility and wide application in industry. Silica phosphoric acid is a cheap and readily available solid acid which enables the synthesis of a series of amines with unprecedented reaction time and yields.

## Results and Discussion

We initially examined the reductive anilation of benzaldehyde with sodium borohydride in the presence of silica phosphoric acid in *THF* as the solvent (method I) and under solvent-free conditions (method II). In both methods the reaction was carried out with an equimolar ratio of benzaldehyde, aniline, and sodium borohydride, and the *pH* of the mixture was adjusted to neutrality by addition of silica phosphoric acid at room temperature. In method I after 15 min, TLC showed complete disappearance of imine and in method II the reaction took place within 2 min. After work-up of the reaction mixture, *N*-benzylaniline was obtained in excellent isolated yield (93 and 95%). We then applied these optimal conditions for the reductive amination of various aldehydes and ketones with aliphatic and aromatic amines and these transformations were successful and gave the desired products in good to excellent yields (85–95%) as shown in Table 1.

We also examined chemoselective reductive amination of functionalized benzaldehydes bearing other reducible functional groups employing the same methodologies. As shown in Table 1, aromatic aldehydes having nitro and cyano groups underwent reductive amination to give the corresponding *N*-phenylamines in good yields without reduction of any other functional groups (entries 4 and 6). In the case of $\alpha,\beta$-unsaturated aldehydes, such as cinnamaldehyde, reductive amination was successfully achieved in excellent yield without reduction of the carbon-carbon double bond (entry 24). Similarly, aliphatic and cyclic ketones underwent reductive amination successfully to give the corresponding amines in excellent yields (entries 15 and 22). Weakly acidic anilines like nitro- and chloroanilines do not usually undergo clean reductive amination reactions. The most widely used reagent for this purpose, $NaBH_3CN$, is an inefficient and sluggish reagent for the transformation. Both 4-nitro- and 4-chloroaniline react

**Table 1.** Reductive amination of aldehydes and ketones using $NaBH_4$–silica phosphoric acid[a]

| Entry | Carbonyl compound | Amine | Product[b] | Method I[c] | | Method II[d] | | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | | | Time/min | Yield/% | Time/min | Yield/% | |
| 1 | *Ph*–CHO | *Ph*–$NH_2$ | *Ph*–$CH_2$NH–*Ph* | 10 | 93 | 4 | 95 | [28] |
| 2 | 4-Cl–*Ph*–CHO | *Ph*–$NH_2$ | 4-Cl–*Ph*–$CH_2$NH–*Ph* | 22 | 90 | 19 | 90 | [13] |
| 3 | 2-Cl–*Ph*–CHO | *Ph*–$NH_2$ | 2-Cl–*Ph*–$CH_2$NH–*Ph* | 25 | 87 | 22 | 88 | [41] |
| 4 | 4-CN–*Ph*–CHO | *Ph*–$NH_2$ | 4-CN–*Ph*–$CH_2$NH–*Ph* | 30 | 90 | 25 | 86 | [29] |
| 5 | 4-O*Me*–*Ph*–CHO | *Ph*–$NH_2$ | 4-O*Me*–*Ph*–$CH_2$NH–*Ph* | 16 | 90 | 10 | 90 | [13] |
| 6 | 4-$NO_2$–*Ph*–CHO | *Ph*–$NH_2$ | 4-$NO_2$–*Ph*–$CH_2$NH–*Ph* | 28 | 94 | 18 | 90 | [29] |
| 7 | *Ph*–CHO | 4-Cl–*Ph*–$NH_2$ | *Ph*–$CH_2$NH–*Ph*–Cl | 25 | 85 | 15 | 85[f] | [36] |
| 8 | *Ph*–CHO | 4-O*Me*–*Ph*–$NH_2$ | *Ph*–$CH_2$NH–*Ph*–O*Me* | 20 | 85 | 15 | 85 | [13] |
| 9 | *Ph*–CHO | 4-$NO_2$–*Ph*–$NH_2$ | *Ph*–$CH_2$NH–*Ph*–$NO_2$ | 19 | 94 | 12 | 92 | [30] |
| 10 | *Ph*–CHO | *Ph*–NH*Me* | *Ph*–$CH_2$N(*Me*)–*Ph* | 12 | 92 | 8 | 92 | [31] |
| 11 | *Ph*–CHO | $CH_2$=$CHCH_2NH_2$ | *Ph*–$NHCH_2CH$=$CH_2$ | 13 | 90 | 6 | 90 | [32] |
| 12 | *Ph*–CHO | Piperidine | *Ph*–$CH_2$–N-pip | 5 | 90 | 2 | 92 | [28] |
| 13 | *Ph*–CHO | Pyrrolidine | *Ph*–$CH_2$–N-pyr | 4 | 92 | 2 | 90 | [33] |
| 14 | *Ph*–CHO | Morpholine | *Ph*–$CH_2$–N-morph | 10 | 94 | 8 | 93 | [28] |
| 15 | $CH_3$–$(CH_2)_4$–CO–$CH_3$ | *Ph*–$NH_2$ | $CH_3$–$(CH_2)_4$–C(*Me*)HNH–*Ph* | 13 | 94 | 5 | 92 | [34] |
| 16 | $CH_3$–$(CH_2)_4$–CO–$CH_3$ | Pyrrolidine | $CH_3$–$(CH_2)_4$–C(*Me*)H–N–pyr | 12 | 94 | 2 | 93 | [42] |
| 17 | $CH_3$–$(CH_2)_4$–CO–$CH_3$ | Piperidine | $CH_3$–$(CH_2)_4$–C(*Me*)H–N–pip | 10 | 90 | 5 | 94 | [38] |
| 18 | Cyclohexanone | *Ph*–$NH_2$ | *Ph*–HN–cyclohex | 2 | 95 | 1 | 95 | [28] |
| 19 | Cyclohexanone | $CH_2$=$CHCH_2NH_2$ | cyclohex–NH–$CH_2$–CH–$CH_2$ | 10 | 90 | 7 | 92 | [28] |
| 20 | Cyclohexanone | Piperidine | cyclohex–N–pip | 2 | 92 | 1 | 92 | [28] |
| 21 | Cyclohexanone | Pyrrolidine | cyclohex–N–pyr | 2 | 94 | 2 | 92 | [33] |
| 22 | Cyclohexanone | Morpholine | cyclohex–N–morph | 15 | 90 | 8 | 92 | [35] |
| 23 | $CH_3CH_2CH_2CHO$ | *Ph*–$NH_2$ | $CH_3CH_2CH_2CH_2$–NH–*Ph* | 5 | 88 | 2 | 88 | [32] |
| 24 | *Ph*–CH=CHCHO | *Ph*–$NH_2$ | *Ph*–CH=$CHCH_2$NH–*Ph* | 5 | 90 | 2 | 87 | [29] |
| 25 | *p*–$CH_3$O–CO–*Ph*–CHO | *Ph*–$NH_2$ | *p*–$CH_3$O–CO–*Ph*–$CH_2$NH–*Ph* | 31 | 81 | 22 | 89 | [21] |

[a] All reactions were carried out at room temperature and molar ratio of reagent/carbonyl compound/amine was 1/1/1 and 0.2 g, 0.5 mmol silica phosphoric acid were used

[b] All products were characterized spectroscopically ($^1$H NMR and IR) and showed physical and spectral data in accordance with their expected structure by comparison with authentic samples

[c] Method I: Reaction was carried out in *THF*

[d] Method II: Reaction was carried out under solvent-free condition

[e] Yields refer to pure isolated products

[f] 4-Chloroaniline under similar reaction conditions with 1 mmol excess of $NaBH_4$ afforded 85% of *N*-benzyl-4-chloroaniline within 15 min (entry 7)

efficiently with benzaldehyde within 12–25 min (entries 7 and 9). However, in order to examine a wider range of amines to better illustrate the scope and limitation of these methods, we investigated the reaction with both primary and secondary amines, such as allyl amine, piperidine, pyrrolidine, and morpholine using *Ph*CHO as a representative aldehyde, and cyclohexanone and 2-heptanone as representative ketones (entries 10–22). Reductive amination of aliphatic aldehyde, such as butanal with aniline also gives excellent yield of the corresponding amine (entry 23).

In order to show the drawbacks and advantages of our method we have compared some of our results with those reported in the literature in Table 2: As shown in this table reductive amination employing $NaBH_4$ and silica phosphoric acid is as good as or better than comparable reported results. However, in many cases our results were superior to others. For example, we compared the reductive amination of cyclohexanone with morpholine using $NaBH_3CN$ and $NaBH(OAc)_3$ *vs*. $NaBH_4$–silica phosphoric acid (Table 2, entry 6). The reaction with $NaBH_3CN$ in methanol and in the absence of *Ac*OH was only 34% complete after 23 h with the formation of about 10% of the corresponding enamine. The conversion improved to 50% in 23 h with *Ac*OH (1 equiv) with no enamine formation. The reaction using $NaBH(OAc)_3$

**Table 2.** Comparison of silica phosphoric acid and the other reducing agents in reductive amination of aldehydes and ketones

| Entry | Carbonyl compound | Amine | $NaBH_4$–silica phosphoric acid | | | | Other reducing agents | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Method I[a] | | Method II[b] | | Method I[a] | | Method II[b] | |
| | | | Time/min | Yield/% | Time/min | Yield/% | Time/min | Yield/% | Time/min | Yield/% |
| 1 | *Ph*–CHO | *Ph*–$NH_2$ | 10 | 93 | 4 | 95 | 15 | 92[c] | 15 | 94[d] |
| 2 | *Ph*–CHO | 4-$NO_2$–*Ph*–$NH_2$ | 19 | 94 | 12 | 92 | 90 | 85[e] | 40 | 86[f] |
| 3 | *Ph*–CHO | Morpholine | 10 | 94 | 8 | 93 | 60 | 83[g] | 30 | 99[d] |
| 4 | *Ph*–CHO | $CH_2$=$CHCH_2NH_2$ | 13 | 90 | 6 | 90 | 50 | 92[f] | 15 | 94[f] |
| 5 | Cyclohexanone | *Ph*–$NH_2$ | 2 | 95 | 1 | 95 | 60 | 42[i] | 10 | 93[d] |
| 6 | Cyclohexanone | Morpholine | 15 | 90 | 8 | 92 | 23[h] | 34[j] | 20 | 35[d] |
| 7 | Cyclohexanone | Morpholine | 15 | 90 | 8 | 92 | 180 | 96[e] | – | – |
| 8 | $CH_3$–$(CH_2)_4$–CO–$CH_3$ | *Ph*–$NH_2$ | 13 | 94 | 5 | 92 | 110 | 92[h] | 25 | 92[f] |

[a] Method I: Reaction was carried out in solvent
[b] Method II: Reaction was carried out under solvent-free condition
[c] $NaBH_4$–*PTSA* (*p*-toluenesulfonic acid monohydrate) [35]
[d] $NaBH_4$–$H_3BO_3$ (in entry 3, benzyl alcohol and in entry 6, cyclohexanol were obtained as a major product) [35]
[e] $Na[BH(OAc)_3]$ [30]
[f] *N*-Methylpiperidine zinc borohydride (*ZBNMPP*) [24]
[g] Zinc-modified cyanotrihydroborate [37]
[h] $[Zr(BH_4)_2Cl_2(dabco)_2]$(Zr*BDC*) [17]
[i] Tetrahydroborate exchange resin [39]
[j] $Na[BH_3CN]$ [40, 38]

completed in 3 h. This reaction with $NaBH_4$–silica phosphoric acid whether in *THF* or under solvent-free conditions completed after 8–15 min.

In another comparison the reductive amination of benzaldehyde with morpholine, in the reaction with $NaBH_4$–$H_3BO_3$ under solvent-free conditions, benzyl alcohol was obtained in 99% yield after 30 min as a major product. While in our method, using $NaBH_4$–silica phosphoric acid, corresponding alcohol was not obtained, and reaction completed in 8–10 min with the high yield of *N*-benzylmorpholine (Table 2, entry 3). Similarly, the reaction of cyclohexanone with morpholine led to only 35% *N*-cyclohexylmorpholine and cyclohexanol formed as major product (Table 2, entry 6). This reaction with silica phosphoric acid took only 8–15 min and gave a high yield of the corresponding amine (Table 2, entry 6).

## *Conclusion*

We have established a direct reductive amination of aldehydes and ketones using sodium borohydride activated by silica phosphoric acid in *THF* and solvent-free conditions. Solvent-free conditions can offer a great opportunity for green chemistry. The use of inexpensive reducing agent requiring no special handling techniques is the notable advantage of this method. Moreover, easy reaction work-up, high reaction rates and yields, and neutral condition make this method a useful addition to the category of procedures used for the reductive preparation of amines.

Furthermore, due to compatibility of this reagent system with a variety of otherwise reducible functional groups, this method can provide an easy access to analogous amines bearing functionalized pendant chains.

## Experimental

Materials were purchased from Fluka and Merck companies. 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 spectra ($^1$H NMR and FTIR) and physical data with those of the authentic samples. $^1$H NMR spectra were measured at 270 and 300 MHz on a JEOL spectrometer with tetramethylsilane (*TMS*) as the internal reference and $CDCl_3$ as the solvent. IR spectra were recorded on a Pye-unicam SP 1100 spectrophotometer. Elemental analysis was performed with a CHN-600 Elemental Analyzer for macro samples, system 785-500, 1988 LECO Corporation; results agreed within standard errors with calculated values. Silica phosphoric acid was prepared according to the reported procedure [27].

*General Procedure for the Reductive Amination of Carbonyl Compounds in THF (Method I)*

Carbonyl compound (1 mmol) and 1 mmol amine were mixed in 5 $cm^3$ *THF* and then treated with 1 mmol $NaBH_4$ and the *pH* was adjusted to neutral by addition of 0.2 g silica phosphoric acid (0.5 mmol $H^+$). The mixture was stirred at room temperature. After completion of the reaction, as indicated by TLC, the mixture was filtered and the residue was washed with $2 \times 15\,cm^3$ $CH_2Cl_2$ or ether. The solvent was evaporated and a pure product was obtained. If necessary, the crude product was purified by column chromatography on silica gel (eluent: *n*-hexane/*EtOAc* = 20/1).

*General Procedure for the Reductive Amination of Carbonyl Compounds Under Solvent Free Condition (Method II)*

Carbonyl compound (1 mmol) and 1 mmol amine was ground with 1 mmol $NaBH_4$ in the presence of 0.2 g silica phosphoric acid (0.5 mmol $H^+$) under solvent-free condition at room temperature. After complete transformation of the aldehyde or ketone as monitored by TLC, the mixture was washed with $3 \times 25\,cm^3$ $CH_2Cl_2$ or ether and the combined washing solvents were dried ($Na_2SO_4$). Evaporation of the solvent and a short-column chromatography of the product on silica gel (eluent: *n*-hexane/*EtOAc* = 20/1) gave the pure product. After work-up all products were characterized spectroscopically ($^1$H NMR and IR) and showed physical and spectral data in accordance with their expected structure and by comparison with authentic samples. Yield refers to pure isolated products.

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