# Reduction of Carbonyl Compounds with $NaBH_4$ under Ultrasound Irradiation and Aprotic Condition

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A variety of carbonyl compounds are reduced to their corresponding alcohols with sodium borohydride under ultrasound irradiation and aprotic condition. Reduction reactions are performed in THF at room temperature or under reflux condition. The product alcohols were obtained in good to excellent yields. The chemoselective reduction of aldehydes over ketones was achieved successfully with this system.

*Key words:* Reduction, Sodium borohydride, Ultrasound, Carbonyl Compounds

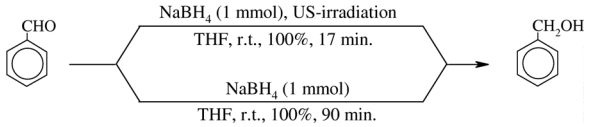
## Introduction

During the past decades, sodium borohydride has had a significant impact on modern organic synthesis [1]. This reagent is a relatively mild reducing agent and mostly used for the reduction of aldehydes and ketones in protic solvents. In order to control the reducing power of $NaBH_4$, hundreds of substituted boron hydrides have been introduced in chemical literature and many of them are now commercially available. In fact, advances in such a field have been realized by: a) Substitution of the hydride(s) with other substituents which may exert marked steric and electronic influences upon the reactivity of the substituted complex ion, *e.g.*, $NaBH_3(OAc)$ [2], $NaBHEt_3$ [3], $NaBH_3CN$ [4] and $NaBH_2S_3$ [5]. b) Variation of alkali-metal cation and metal cation in the hydride complex, *e.g.*, $LiBH_4$ [6], $Cu(BH_4)_2$ [7], $Zn(BH_4)_2$ [8]. c) A concurrent cation and hydride exchange, such as $LiBHEt_3$ (Super Hydride) [9], LiBH(*n*-butyl) [10], LiBH(*sec*-butyl)$_3$ (L-Selectride) [11, 12], KBH(*sec*-butyl)$_3$ (K-Selectride) [12], $Ca(BH_2S_3)_2$ [13a] and $Ba(BH_2S_3)_2$ [13b]. d) Use of the ligands to alter behavior of the metal hydroborates; $(Ph_3P)_2CuBH_4$ [14], $(Ph_3P)_xZn(BH_4)_2$ ($x = 1, 2$) [15], $(i\text{-PrO})_2TiBH_4$ [16], $(dabco)Zn(BH_4)_2$ [17], $(bpy)Zn(BH_4)_2$ [18], and $(py)Zn(BH_4)_2$ [19] are examples in this area. e) Combination of tetrahydroborates with Lewis acids, additives [20] and mixed solvent systems [21]. f) Changing the cation to quaternary ammonium and phosphonium tetrahydroborates, such as $Bu_4NBH_4$ [22], $PhCH_2(Et)_3NBH_4$ [23], 4-aza-*N*-benzylbicyclo[2.2.2]octylammonium tetrahydroborate [24] and $Ph_3PMeBH_4$ [25]. g) Use of the polymers or solid supports to supporting hydride species: amberlyst, zeolite, alumina, silica gel and polyvinylpyridine are usually used as bed supports for different hydride species [26]. Recently, we have extensively reviewed modified hydroborate agents and their applications in organic synthesis [18, 27]. In addition, several recent reports extol the virtues of sonication as a well known tool to facilitate a variety of synthetic methodologies [28].

Along the outlined strategies and our continuous efforts for the preparation and application of modified hydroborate systems in organic synthesis [17 – 19, 29], we decided to investigate the reducing potential of $NaBH_4$ for reduction of carbonyl compounds under ultrasound irradiation and aprotic condition with the hope that this combination system shows a good or excellent selectivity and efficiency. Herein, we describe an efficient and convenient method for the promoted reduction of carbonyl compounds such as aldehydes and ketones to their corresponding alcohols with $NaBH_4$ under ultrasound irradiation.

## Results and Discussion

As mentioned above, sodium borohydride is one of the most widely utilized reducing agents for the reduction of aldehydes and ketones in protic solvents especially methanol or isopropanol [1]. However, it should be pointed out that in spite of its great convenience, this reagent generally suffers from limitations such as:



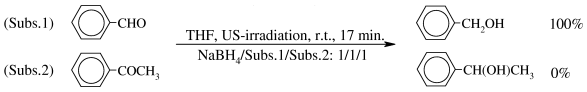

Scheme 1.

a) $NaBH_4$ is a mild reducing agent and reduction reactions are preferentially carried out in protic solvents, b) the number of functional groups which are reduced by this reagent is limited, and c) the rate of reductions is sometimes slow and low chemoselectivity is accompanied with the reductions under protic condition especially between carbonyl compounds or 1,2- *vs.* 1,4-reduction of conjugated enones. This situation made it desirable to develop means to control the reducing properties of sodium borohydride. Combination systems of sodium borohydride have been extensively reviewed in the literature, but, as far as we know, for the use of ultrasound in combination with $NaBH_4$ there is only one report. This report described the reduction of two complex pentacyclic compounds of PCUD-8,11-diones with sodium borohydride under protic condition in MeOH [30].

These facts prompted us to study the reducing potential of $NaBH_4$ for systematic reduction of carbonyl compounds under ultrasound irradiation and aprotic condition. Our preliminarily observations and optimization of solvents reveal that performing of the reduction of benzaldehyde as a model compound with $NaBH_4$ in THF at room temperature is strongly accelerated under ultrasound irradiation (Scheme 1).

This facilitation with ultrasound waves encouraged us to subject a variety of structurally different aromatic and aliphatic aldehydes with sodium borohydride under the same condition. Reduction reactions were performed efficiently in THF at room temperature and completion of the reductions needs to 1 – 2 molar equivalents of sodium borohydride according to the nature of substrates. The sonication of reactions was performed *via* a micro-tip probe. The efficiency of the reactions was excellent and the products were obtained in high to excellent yields. The work-up procedure is simple and addition of water to the reaction mixture, then extracting with $CH_2Cl_2$ affords the corresponding alcohols for further purification with short column chromatography on silica gel (Table 1).

We turned our attention into reduction of ketones with the experiment of benzophenone as a model compound. Low reactivity of ketones relative to aldehydes



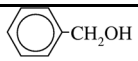
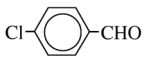
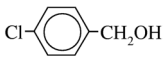
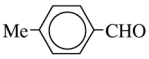
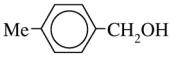
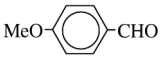
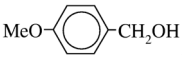
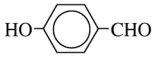
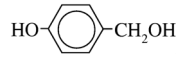
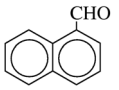
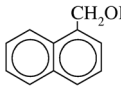
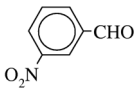
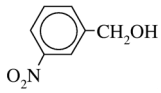
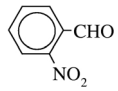
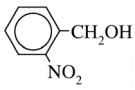
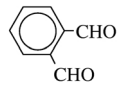
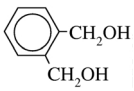
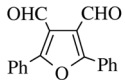
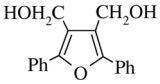
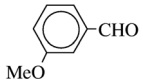
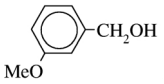
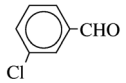
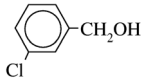
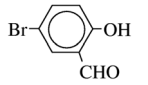
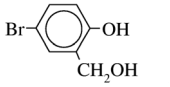
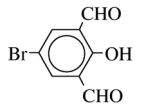
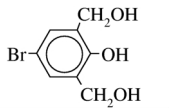
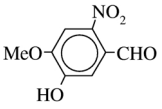
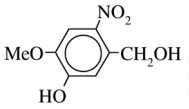
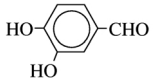
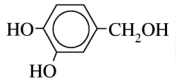
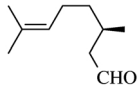
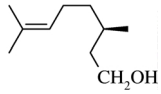
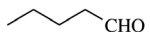

Scheme 2.

led us to perform the reduction reactions under reflux condition in combination with the ultrasound irradiation. THF also is a well suitable solvent for this reaction. To clarify the effect of ultrasound under reflux condition, we performed the reduction of benzophenone with 3 molar equivalents of $NaBH_4$ in absence of ultrasound irradiation under refluxing THF for 24 h. In this case, the progress of reduction was 5 – 8% and unreacted starting material was recovered from the reaction mixture. When we applied ultrasound irradiation, the reduction of benzophenone was completed in 2.4 h. Therefore, to explore the further utility of ultrasound irradiation for the reduction of ketones, we combined a variety of aliphatic and aromatic ketones with 2 – 3 molar equivalents of $NaBH_4$ in refluxing THF. The efficiency of the reactions was good to excellent and only in the reduction of acetophenone, probably due to its tendency to enolization, we observed a low efficiency. The work-up procedure is simple and the same as for aldehydes. This procedure afforded the product secondary alcohols which were purified further by short column chromatography on silica gel (Table 2).

The chemoselective reduction of one functional group without affecting the other one is a well known strategy for the preparation of the molecules with ever-increasing complexity in organic synthesis. This subject is of great interest [31] and numerous modified hydroborate systems have been reported [17 – 19, 24, 32]. Since under conditions described above, reduction of aldehydes and ketones with sodium borohydride and with ultrasound irradiation is temperature-dependent, we thought that this system can have a chemoselectivity towards reduction of aldehydes over ketones. This fact was demonstrated with the selective reduction of benzaldehyde in the presence of an equimolar amount of acetophenone with one equimolar amount of $NaBH_4$ at room temperature for 17 min (Scheme 2).

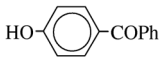
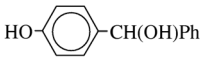
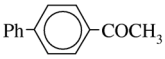
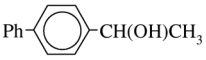
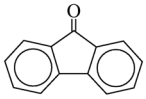
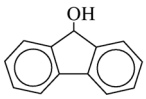
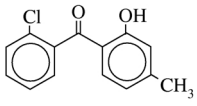
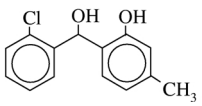
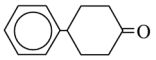
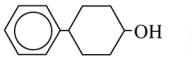
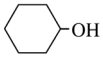
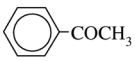
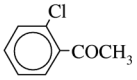
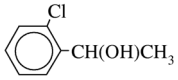
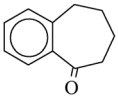
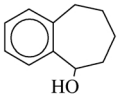
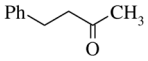
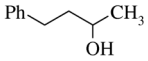
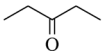
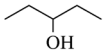
The obtained chemoselectivity was excellent and benzyl alcohol was detected as the sole product of reduction besides unchanged acetophenone as an intact material (Table 3). To further explore the utility, we examined reduction of benzaldehyde in the presence of other ketones such as benzophenone or cyclohexanone. We observed that the aldehyde was reduced exclusively or nearly so. In another attempt, we applied

Table 1. Reduction of aldehydes to their alcohols with $NaBH_4$ under ultrasound irradiation[a].

| Entry | Substrate | Product | Molar ratio $NaBH_4$/Subs. | Time (min) | Yield (%)[b] | M.p. or B.p. (°C) found | calcd. |
|---|---|---|---|---|---|---|---|
| 1 |  |  | 1:1 | 17 | 97 | 204 – 205 | 205 [33a] |
| 2 |  |  | 1:1 | 22 | 98 | 70 – 71 | 70 – 72 [33a] |
| 3 |  |  | 1.7:1 | 60 | 98 | 60 – 61 | 59 – 61 [33a] |
| 4 |  |  | 1.7:1 | 94 | 96 | 23 – 25 | 23 – 25 [33a] |
| 5 |  |  | 2:1 | 25 | 95 | 119 – 121 | 118 – 122 [33a] |
| 6 |  |  | 1:1 | 20 | 99 | 62 – 63 | 61 – 63 [33a] |
| 7 |  |  | 1:1 | 24 | 95 | 30 – 31 | 30 – 32 [33a] |
| 8 |  |  | 1:1 | 15 | 94 | 70 – 71 | 70 – 72 [33a] |
| 9 |  |  | 1:1 | 30 | 95 | 64 – 65 | 63 – 65 [33a] |
| 10 |  |  | 1:5:1 | 22 | 97 | – | – |
| 11 |  |  | 1:1 | 35 | 96 | 250/723 | 250/723 [33a] |
| 12 |  |  | 1:1 | 18 | 99 | 236 | 237 [33a] |
| 13 |  |  | 1:1 | 6 | 94 | 109 – 111 | 110 – 112 [33a] |
| 14 |  |  | 1.2:1 | 8 | 94 | – | – |
| 15 |  |  | 1:1 | 5 | 97 | – | – |
| 16 |  |  | 2:1 | 30 | 93 | 115 – 116 | 114 – 115 [33b] |
| 17 |  |  | 1:1 | 15 | 93 | 113/12 | 113/12 [33a] |
| 18 |  |  | 1:1 | 22 | 92 | 135 – 137 | 136 – 138 [33a] |

[a] All reactions were irradiated with ultrasound waves in THF at room temperature; [b] yields refer to isolated pure products.

Table 2. Reduction of ketones to their alcohols with $NaBH_4$ under ultrasound irradiation[a].

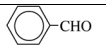
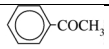
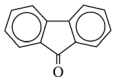
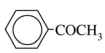
| Entry | Substrate | Product | Molar ratio $NaBH_4$/Subs. | Time (h) | Yield (%)[b] | M.p. or B.p. (°C) found | calcd. |
|---|---|---|---|---|---|---|---|
| 1 |  |  | 3:1 | 2.4 | 99 | 66 – 67 | 65 – 67 [33a] |
| 2 |  |  | 3:1 | 3 | 97 | – | – |
| 3 |  |  | 3:1 | 1.8 | 99 | – | – |
| 4 |  |  | 2:1 | 1.5 | 98 | 154 – 155 | 153 – 154 [33a] |
| 5 |  |  | 2:1 | 2 | 95 | – | – |
| 6 |  |  | 2:1 | 0.4 | 96 | 116 – 118 | 118 – 119 [33b,c] |
| 7 |  |  | 2:1 | 0.9 | 93 | 161 | 160 – 161 [33a] |
| 8 |  |  | 3:1 | 6 | 30 | 203/745 | 204/745 [33a] |
| 9 |  |  | 2:1 | 2 | 99 | 122/14 | 121 – 123/14 [33d] |
| 10 |  |  | 3:1 | 4 | 80 | – | – |
| 11 |  |  | 2:1 | 3 | 97 | 129/16 | 128 – 130/16 [33e] |
| 12 |  |  | 2:1 | 0.6 | 92 | 114/749 | 115/749 [33a] |

[a] All reactions were irradiated with ultrasound waves in refluxing THF; [b] yields refer to isolated pure products.

this procedure to the reduction of two ketones such as 9-fluorenone and acetophenone and it was found that 9-fluorenone was reduced exclusively (Table 3).

In order to highlight and showing the advantages and limitations of our system, we compared our results with those achieved by other systems such as $NaBH_4$/Dowex1-x8 [29], $(bpy)Zn(BH_4)_2$ [18], $(py)Zn(BH_4)_2$ [19a], $(Ph_3P)_2Zn(BH_4)_2$ [15], $Ph_3PMeBH_4$ [25], and 4-aza-*N*-benzylbicyclo[2.2.2] octylammonium tetrahydroborate [24] (Table 4). The comparison shows that in most cases our system is comparable or more efficient.

Table 3. Competitive reduction of aldehydes and ketones with $NaBH_4$ under ultrasound irradiation[a].

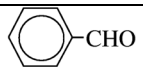
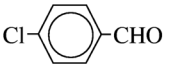
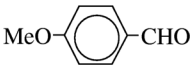
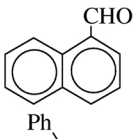
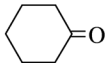
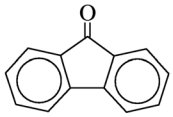
| Entry | Substrate 1 | Substrate 2 | Condition | Molar ratio[b] | Time (min) | Conv.1/ Conv.2 (%)[c] |
|---|---|---|---|---|---|---|
| 1 |  |  | RT | 1:1:1 | 17 | 100:0 |
| 2 |  |  | RT | 1:1:1 | 18 | 100:0 |
| 3 |  |  | RT | 1:1:1 | 20 | 100:5 |
| 4 |  |  | Reflux | 2:1:1 | 1.5 h | 100:0 |

[a] All reactions were irradiated with ultrasound waves in THF; [b] molar ratio as: $NaBH_4$/Subs.1/Subs.2; [c] conversions refer to TLC monitoring and isolated pure products.

## Conclusion

Under the defined conditions, we observed that irradiation with ultrasound waves efficiently promoted the reduction of a variety of aromatic and aliphatic carbonyl compounds with $NaBH_4$. Reduction reactions

Table 4. Comparison of reductions of aldehydes an ketones with $NaBH_4$/ultrasound system and other reported reagents.

| Entry | Substrate | Molar ratio (reag./subs.), Time (h), Yield (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | I | II [29] | III [18] | IV [19a] | V [15] | VI [25] | VII [24] |
| 1 |  | 1(0.28)(97) | 1[a](0.05)(96) | 0.25(0.02)(95) | 1(0.5)(91) | – | 1(*c*)(90) | 1(0.25)(90) |
| 2 |  | 1(0.36)(98) | 1[a](0.15)(99) | 0.25(0.08)(98) | 1(0.2)(99) | 1(*c*)(88) | 1(*c*)(86) | 1(0.23)(90) |
| 3 |  | 1.7(1.56)(96) | 1.5[a](3)(99) | 0.35(0.17)(99) | 1(1.3)(96) | 1(0.17)(89) | 1(*c*)(83) | 2(0.8)(85) |
| 4 |  | 1(0.33)(99) | – | 0.25(0.13)(99) | 1(0.8)(95) | 1.5(*c*)(100) | 1(*c*)(100) | 1(0.25)(90) |
| 5 |  | 3(2.4)(99) | 3[b](3.2)(98) | 1(0.75)(99) | 2(4.3)(97) | – | – | 2(21.5)(90) |
| 6 |  | 2(0.9)(93) | 1.5[b](1.25)(90) | 0.5(0.15)(88) | 2(2)(89) | 1(1)(95) | 1(10)(95) | – |
| 7 |  | 2(1.5)(99) | 2[b](1.8)(94) | 1(1.5)(94) | 2(5.3)(98) | 2(0.33)(85) | 1.6(18)(80) | – |

[I] $NaBH_4$/Ultrasound; [II] $NaBH_4$/Dowex1-x8; [III] $[(bpy)Zn(BH_4)_2]$; [IV] $[(py)Zn(BH_4)_2]$; [V] $[(Ph_3P)_2Zn(BH_4)_2]$; [VI] $Ph_3PMeBH_4$; [VII] $[PhCH_2$-(dabco)$]BH_4$; [a,b] referred to using of 10 and 20 mg of Dowex1-x8 per one mmol of substrate respectively;[c] immediately.

were performed in THF at room temperature or under reflux condition. The product alcohols were obtained in good to excellent yields. The chemoselective reduction of aldehydes over ketones was achieved successfully with this system. In addition to these advantages, the simple work-up procedure and convenient reduction reactions under aprotic condition are the reasons that could be making this system an attractive and additional bench-top reducing system to the present methodologies.

## Experimental Section

*General:* Sonication was performed by using a Cole Palmer high intensity ultrasonic processor (600 W, 20 KHz) *via* a micro-tip probe and 30% amplitude. All reagents and substrates were obtained from commercial sources and used without further purification. THF was dried prior to use by a standard method. The products were characterized by a comparison with authentic samples (melting or boiling points) and their $^1H$ NMR or IR spectra. Organic layers were dried with anhydrous sodium sulfate before concentration *in vacuo*. All yields refer to isolated pure products. The purity determination of the substrates, products and reactions was accomplished by TLC on silica gel PolyGram SILG/UV 254 plates. Products were purified by column chromatography packed with silica gel.

*A typical procedure for reduction of aldehydes to alcohols with $NaBH_4$ under ultrasound irradiation:* In a round-bottom flask (10 ml) equipped with magnetic stirrer, $NaBH_4$ (0.037 g, 1 mmol) was added, to the solution of benzaldehyde (0.106 g, 1 mmol) in THF (5 ml). The stirring reaction mixture was irradiated with ultrasound waves at room temperature. Sonication was continued for 17 min and the progress of the reaction (eluent: $CCl_4/Et_2O$ = 5/2) was monitored by TLC. At the end of the reaction, distilled water (5 ml) was added and the reaction mixture was stirred for additional 5 min. The mixture was extracted with $CH_2Cl_2$ ($3 \times 10$ ml) and dried over anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel (elution with $CCl_4/Et_2O = 5/2$) afforded pure liquid benzyl alcohol (0.l05 g, 97% yield, Table 1).

*A typical procedure for reduction of ketones to alcohols with $NaBH_4$ under ultrasound irradiation:* In a two necked round-bottom flask (10 ml) equipped with a magnetic stirrer and condenser, to the solution of benzophenone (0.182 g, l mmol) in THF (5 ml), $NaBH_4$ (0.113 g, 3 mmol) was added. The reaction mixture was stirred and irradiated with ultrasound waves under reflux condition. Sonication was continued for 2.4 h and TLC monitored the progress of the reaction (eluent: $CCl_4/Et_2O = 5/2$). After completion of the reaction, distilled water (5 ml) was added and the reaction mixture was stirred for additional 5 min. The mixture was extracted with

$CH_2Cl_2$ ($3 \times 10$ ml) and dried over anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel (elution with $CCl_4/Et_2O = 5/2$) afforded pure crystals of benzhydrol (0.l82 g, 99% yield, Table 2).

*Acknowledgement*

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