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Fast and convenient method for reduction of carbonyl compounds with $NaBH_4/Cu(dmg)_2$ in aprotic and protic solvents

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ABSTRACT

During the past decades, sodium borohydride as a key reagent has played an important role in the reduction of organofunctional groups in modern organic synthesis. This reagent is a relatively mild reducing agent and mostly used for the reduction of aldehydes and ketones in protic solvents. It is also know that the reducing capability of $NaBH_4$ greatly could be accelerated by using many of additives. Therefore, controlling the reducing power of sodium borohydride has been one of the main interests for organic chemists in many years. In this context, we wish to introduce a new combination system of $NaBH_4$ and $Cu(dmg)_2$ for fast and efficient readuction of carbonyl compounds such as aldehydes, ketones, α-diketones and conjugated enones to their corresponding alcohols in high to excellent yields.

KEYWORDS

Reduction;
Sodium borohydride;
(dimethylglyoximato) Copper(II);
Carbonyl compounds;
Alcohol.

INTRODUCTION

During the past decades, sodium borohydride as a key reagent has played an important role in the reduction of organofunctional groups in modern organic synthesis. This reagent is a relatively mild reducing agent and mostly used for the reduction of aldehydes and ketones in proticsolvents[1-4]. In order to control the reducing power of $NaBH_4$, hundreds of substituted boron hydrides have been made and introduced in chemical literature and many of them are now commercially available[5-10]. In fact, advances in such field have been realized by: a) substitution of the hydride(s) with other constituents which may exert marked steric or electronic influences upon the reactivity of substituted complex ion[11], b) variation of alkali-metal cation and metal cation in the hydride complex[12], c) a concurrent cation and hydride exchange, d) use of amin or phosphin ligands to alter behaviour of the metal hydroborates[13], e) combination of tetrahydroborates with Lewis acids, additives and mixed solvent systems[14], f) changing the cation to quaternary ammonium and phosphonium tetrahydroborates[15], g) and finally use of polymers or solid supports for supporting the hydride species[16]. Modification of borohydride agents and their applications in organic synthesis have been extensively reviewed.

In line of the outlined strategies, although the reducing properties of sodium borohydride in the presence of metal borides have been intensively investigated[17-19], in our literature survey we could not find any report for the combination of $NaBH_4$ with $Cu(dmg)_2$. Therefore, in continuation of our efforts towards the development of new borohydride systems[20,21], we decided to investigate the reducing properties of $NaBH_4$

in the presence of $Cu(dmg)_2$ for the reduction of a variety of carbonyl compounds with the hope that this system shows efficiencies. Now we wish to report a mild and efficient method for reduction of aldehydes, ketones, α-diketones, acyloinsand α,β-unsaturated carbonyl compounds to the corresponding alcohols with a $NaBH_4/Cu(dmg)_2$ system.

EXPERIMENTAL

General

All reagents and substrates were purchased from commercial sources with the best quality and were used without further purification. IR and ^1H NMR spectra were recorded on Thermo Nicolet Nexus 670 FT–IR and 300 MHz BrukerAvance spectrometers, respectively. The products were characterized by a comparison with authentic samples (melting or boiling points) and their ^1H NMR or IR spectra. All yields refer to isolated pure products. TLC was applied for the purity determination of substrates, products and reaction monitoring over silica gel 60 F254 aluminum sheet.

Preparation of catalyst (dimethylglyoximato) copper (II)

Dimethylglyoxime and $Cu(OAc)_2.H_2O$ were added into absolute ethanol to get brown precipitates of $Cu(dmg)_2$[4].

A typical procedure for reduction of aldehydes to alcohols with $NaBH_4/Cu(dmg)_2$ system

In a round-bottom flask (15 mL) equipped with magnetic stirrer, charged with a solution of benzaldehyde (0.106 g, 1 mmol) in CH_3CN (2mL), $NaBH_4$ (0.038 g, 1mmol) was added. To this mixture, $Cu(dmg)_2$ (0.058 g, 0.02mmol) was added immediately and the resulting brown mixture was stirred at room temperature for 5 min. 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 to the mixture and stirred for additional 5 min. The mixture was extracted with CH_2Cl_2(3 × 10 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel by eluent of CCl_4/Et_2O : 5/2 affords the pure liquid benzyl alcohol (0.104 g, 95% yield, TABLE 2).

A typical procedure for reduction of ketones to alcohols with $NaBH_4/Cu(dmg)_2$ system

In a round-bottom flask (15 mL) equipped with a magnetic stirrer and a condenser, to a solution of acetophenone (0.12 g, l mmol) in CH_3CN (2 mL), $NaBH_4$ (0.076 g, 2 mmol) was added. To this mixture, $Cu(dmg)_2$ (0.029 g, 0.01 mmol) was added immediately and the resulting brown mixture was heated to gentle reflux with stirring. 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 to the reaction mixture and stirred for additional 5 min. The mixture was extracted with CH_2Cl_2 (3 × 10 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel by eluent of CCl_4/Et_2O : 5/2 affords the pure crystals of 1-phenyletanol (0.l22 g, 97% yield, TABLE 4).

A typical procedure for reduction of α-diketonesand acyloins with $NaBH_4/Cu(dmg)_2$ system

In a round-bottom flask (15 mL) equipped with magnetic stirrer, to a solution of benzil (0.21 g, l mmol) in CH_3CN (2 mL), $NaBH_4$ (0.076 g, 2 mmol) was added. To this mixture, $Cu(dmg)_2$ (0.029 g, 0.01 mmol) was added immediately and the resulting brown mixture was stirred at refluxcondition for 8 min. 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 to the mixture and stirred foradditional 5 min. The mixture was extracted with CH_2Cl_2(3 × 10 mL) and dried over anhydrous sodium sulfate. Evaporation of all the volatile materials and short column chromatography of the resulting crude material over silica gel by eluent of CCl_4/Et_2O : 5/3 affords the pure crystals of hydrobenzoin (0.212 g, 91% yield, TABLE 6).

A typical procedure for regioselective 1,2-reduction of conjugated enones with $NaBH_4/Cu(dmg)_2$

In a round-bottom flask (15 mL) equipped with a magnetic stirrer and a condenser, to a solution of cinnamaldehyde (0.132 g, 1 mmol) in CH_3CN (5 mL), $NaBH_4$(0.038 g, 1mmol) was added. To this mixture, $Cu(dmg)_2$(0.058 g, 0.02mmol) was added immediately

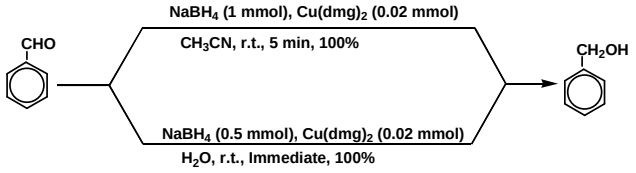
and the resulting brown mixture was wasstirred at room temperature for 7 min. TLC monitored the progress of the reaction (eluent; CCl_4/Et_2O : 5/2). After the completion of the reaction, distilled water (5 mL) was added to the reaction mixture and stirred for additional 5 min. The mixture was extracted with CH_2Cl_2 (3 × 10 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel by eluent of CCl_4/ Et_2O : 5/2 affords the pure cinnamylalcohol (0.l34 g, 97% yield, TABLE 8).

RESULT AND DISCUTION

Reduction of aldehydes and ketones

Sodium borohydride is usually used for the reduction of aldehydes and ketones to their corresponding alcohols in protic solvents, especially ethanol or isopropyl alcohol. In our preliminary experiment we observed that by $NaBH_4$ in the presence of catalytic amount of $Cu(dmg)_2$ accelerated remarkably the rate of reduction of benzaldehyde under aprotic condition at room temperature (Scheme 1). Although $NaBH_4$ alone is very slightly soluble in CH_3CN, but in the presence of $Cu(dmg)_2$ its solubility increases tremendously accompanied by the color change to deep brown.

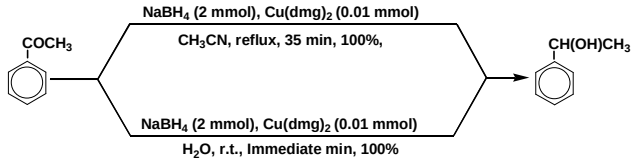
These results prompted us to investigate the optimumreaction conditions for the reduction of a variety of carbonyl compounds. For the selection of appropriate solvents in such reactions, we examined Et_2O, $CHCl_3$, CH_2Cl_2, CH_3CN and THF in which 3-chlorobenzaldehyde and benzophenonewere adopted as model compounds. Our observations reveal that THF and CH_3CN are suitable for the reduction, but the reductions in CH_3CN provides faster and more efficient than in THF. In addition, we found that addition order of reaction components plays a role in these reactions.



Scheme 1

Reduction of a variety of structurally different aromaticand aliphatic aldehydes to their corresponding alcohols is performed efficiently with this reducing system (TABLE 2). Aldehydes are reduced rapidly with 1 molar equivalent of $NaBH_4$ and in the presence of 0.02 mole % of $Cu(dmg)_2$ in CH_3CN and 0.5 molar equivalent of $NaBH_4$ and in the presence of 0.02 mole % of $Cu(dmg)_2$ in H_2O at room temperature. The yields are high to excellent (91-99%). In general, the reduction of aromatic aldehydes bearing an electron-withdrawing group is fasterthan that of bearing an electron-releasing group. The reduction of ketones requires more drastic conditions: a larger amount of $NaBH_4$(2 molar equivalents) in refluxing acetonitrile or at room temperature are required (TABLE 4). The yields are generally higher than 90%. The work-up procedure is simple: distilled water was added to the reaction mixture and the resulting mixture was extracted with CH_2Cl_2. The crude products were further purified by a short column chromatography on silica gel.

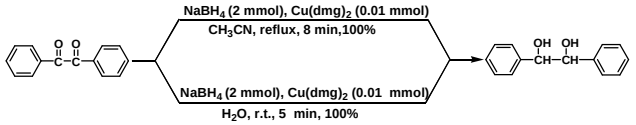
As shown in TABLES 1 and 2, aldehydes are generally much reactive than ketones with $NaBH_4/Cu(dmg)_2$ system and we investigated a chemoselective reduction of aldehydes over ketones.



Scheme 2

Reduction of α-diketones and acyloins

Reduction of α-hydroxy ketones and α-diketones to vicinal diols and/or acyloins has attracted a great deal of attention in organic synthesis. Reduction of α-diketones usually gives a mixture of α-hydroxy ketones and vicinal diols. Selective reduction of α-diketones to acyloins or vicinal diols can undergo with some chemical or biochemical reagents. Reduction of α-diketones with modified borohydride agents is also the subject of interests and can be easily achieved by $NaBH_4$/ $Cu(dmg)_2$ system. Sodium borohydride in the presence of catalytic amount of $Cu(dmg)_2$ reduces readily α-



Scheme 3

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TABLE 1 : Reduction of aldehydes with $NaBH_4/Cu(dmg)_2/H2O$ system[a]

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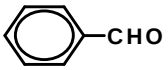
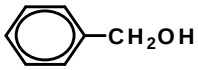
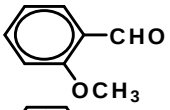
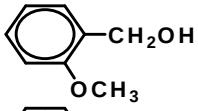
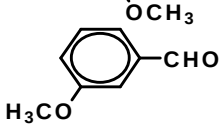
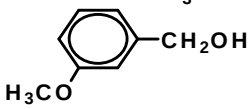
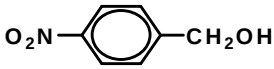
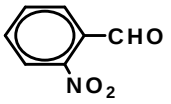
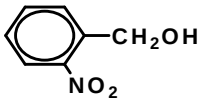
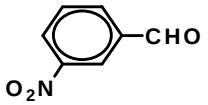
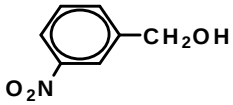
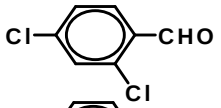
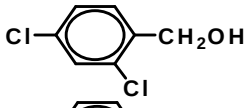
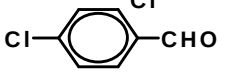
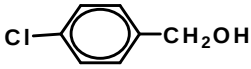
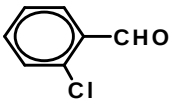
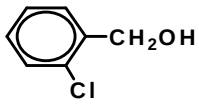
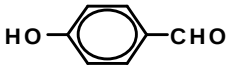
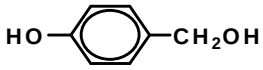
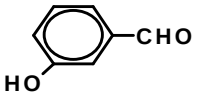
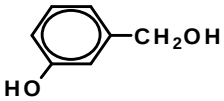
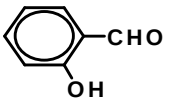
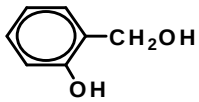
1			1:0.5:0.02	Immediate	93
2			1:0.5:0.02	2	94
3			1:0.5:0.02	Immediate	93
4			1:0.5:0.02	4	91
5			1:0.5:0.02	Immediate	96
6			1:0.5:0.02	2	98
7			1:0.5:0.02	2	98
8			1:0.5:0.02	2	94
9			1:0.5:0.02	Immediate	97
10			1:0.5:0.02	Immediate	91
11			1:0.5:0.02	Immediate	94
12			1:0.5:0.02	Immediate	91
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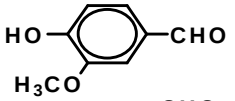
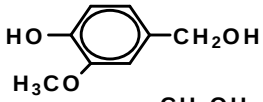
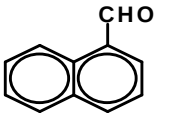
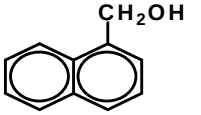
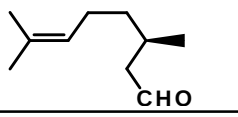
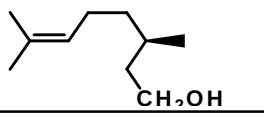
14			1:0.5:0.02	4	96
15			1:0.5:0.02	2	94
16			1:0.5:0.02	3	96

[a] All reactions were carried out in H_2O (2 ml) at room temperature; [b] Molar ratio as Subs./$NaBH_4/Cu(dmg)_2$; [c] Isolated yields.

TABLE 2 : Reduction of aldehydes with $NaBH_4/Cu(dmg)_2/CH_3CN$ system[a]

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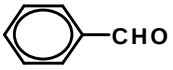
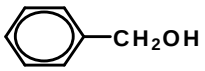
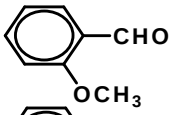
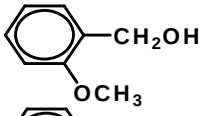
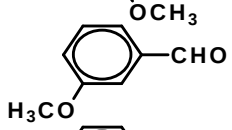
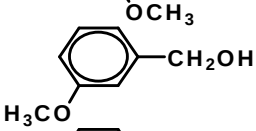
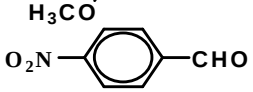
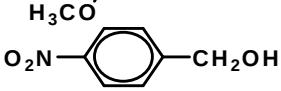
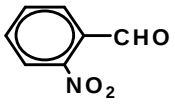
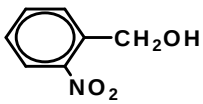
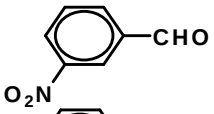
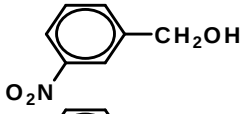
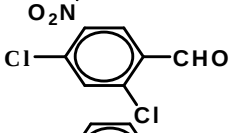
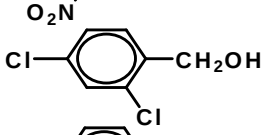
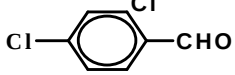
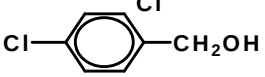
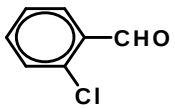
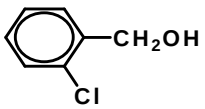
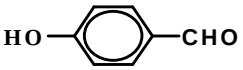
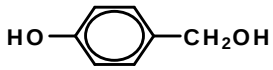
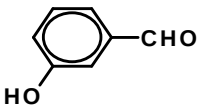
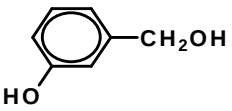
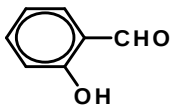
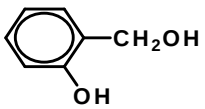
1			1:1:0.02	5	95
2			1:1:0.02	4	93
3			1:1:0.02	14	96
4			1:1:0.02	8	96
5			1:1:0.02	8	98
6			1:1:0.02	3	99
7			1:1:0.02	2	99
8			1:1:0.02	6	95
9			1:1:0.02	2	96
10			1:1:0.02	18	94
11			1:1:0.02	5	99
12			1:1:0.02	3	95
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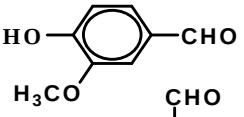
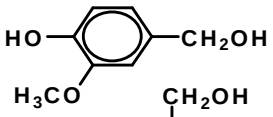
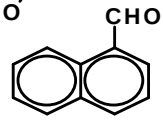
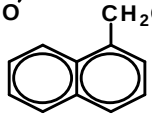
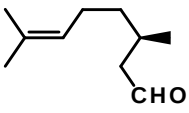
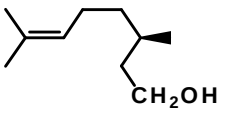
14			1:1:0.02	5	95
15			1:1:0.02	10	92
16			1:1:0.02	30	96

[a] All reactions were carried out in CH_3CN (2 ml) at room temperature; [b] Molar ratio as Subs./$NaBH_4$/$Cu(dmg)_2$; [c] Isolated yields.

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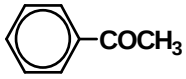
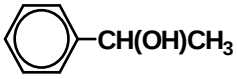
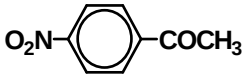
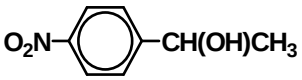
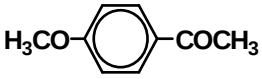
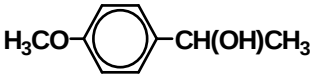
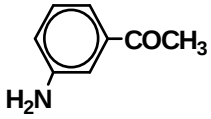
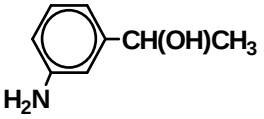
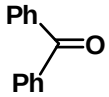
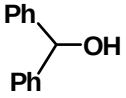
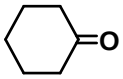
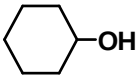
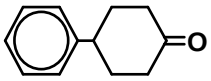
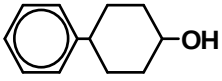
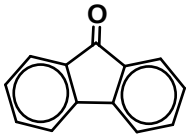
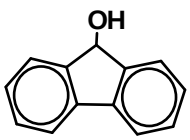
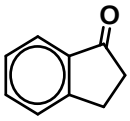
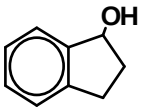
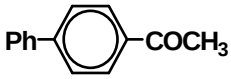
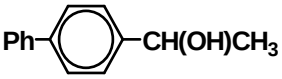
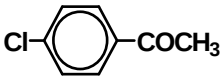
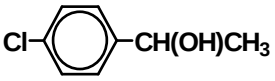
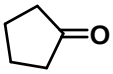
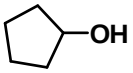
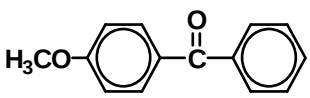
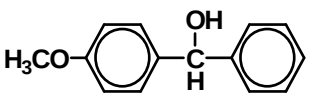
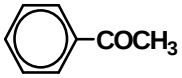
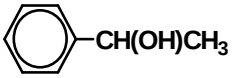
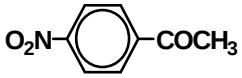
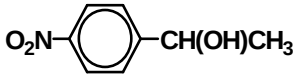
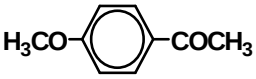
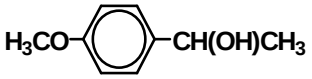
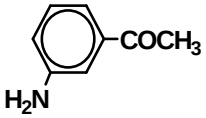
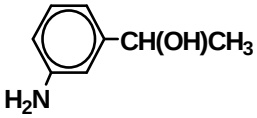
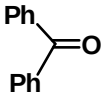
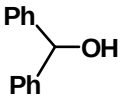
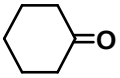
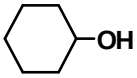
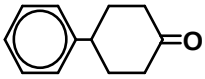
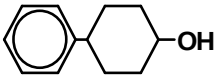
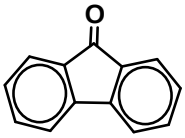
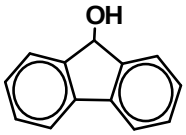
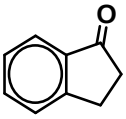
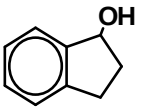
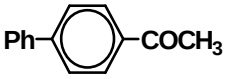
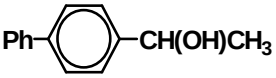
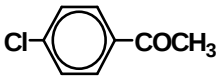
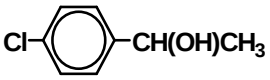
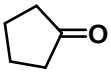
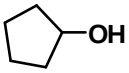
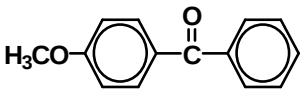
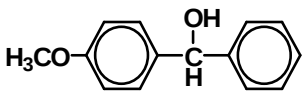
TABLE 3 : Reduction of ketones with $NaBH_4/Cu(dmg)_2/H_2O$ system[a]

Entry	Substrate	Product	Molar ratio[b]	Time (min)	Condition	Yield (%)[c]
1			1:2:0.01	Immediate	r.t.	94
2			1:2:0.01	Immediate	r.t.	97
3			1:2:0.01	Immediate	r.t.	96
4			1:2:0.01	Immediate	r.t.	91
5			1:2:0.01	15	reflux	93
6			1:2:0.01	Immediate	r.t.	95
7			1:2:0.01	Immediate	r.t.	96
8			1:2:0.01	Immediate	r.t.	91
9			1:2:0.01	Immediate	r.t.	92
10			1:2:0.01	Immediate	r.t.	95
11			1:2:0.01	Immediate	r.t.	93
12			1:2:0.01	Immediate	r.t.	91
13			1:2:0.01	18	r.t.	96

[a] All reactions were carried out in H_2O (2 ml); [b] Molar ratio as Subs./$NaBH_4$/$Cu(dmg)_2$; [c] Isolated yields.

TABLE 4 : Reduction of ketones with $NaBH_4/Cu(dmg)_2/CH_3CN$ system[a]

Entry	Substrate	Product	Molar ratio[b]	Time (min)	Condition	Yield (%)[c]
1			1:2:0.01	35	reflux	97
2			1:2:0.01	10	r.t.	98
3			1:2:0.01	25	reflux	98
4			1:2:0.01	10	reflux	96
5			1:2:0.01	25	reflux	97
6			1:2:0.01	15	r.t.	95
7			1:2:0.01	15	reflux	97
8			1:2:0.01	25	reflux	97
9			1:2:0.01	25	reflux	96
10			1:2:0.01	15	reflux	96
11			1:2:0.01	15	reflux	97
12			1:2:0.01	10	r.t.	98
13			1:2:0.01	70	reflux	95

[a] All reactions were carried out in CH_3CN (2 ml); [b] Molar ratio as Subs./$NaBH_4/Cu(dmg)_2$; [c] Isolated yields.

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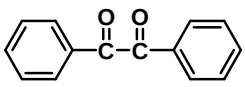
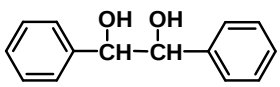
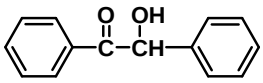
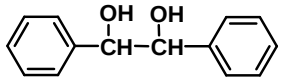
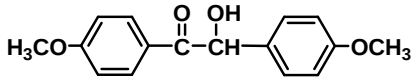
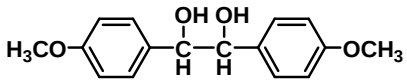
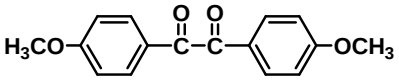
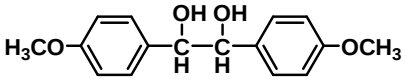
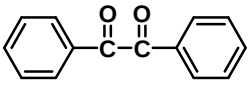
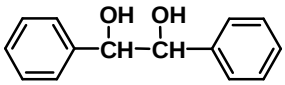
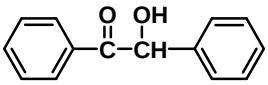
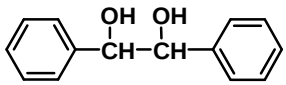
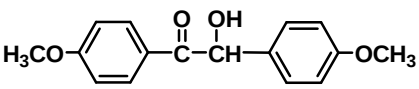
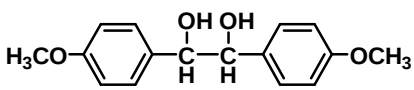
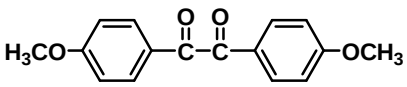
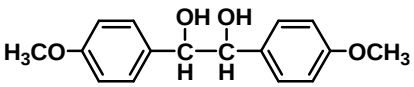
TABLE 5 : Reduction of α-diketones and acyloins with $NaBH_4/Cu(dmg)_2/H_2O$ system[a]

Entry	Substrate	Product	Molar ratio[b]	Time (min)	Yield (%)[c]
1			1:2:0.01	5	96
2			1:2:0.01	10	93
3			1:2:0.01	20	91
4			1:2:0.01	35	95

[a] All reactions were carried out in H_2O (2 ml) at room temperature; [b] Molar ratio as Subs./$NaBH_4$ /$Cu(dmg)_2$; [c] Isolated yields.

TABLE 6 : Reduction of α-diketones and acyloins with $NaBH_4/Cu(dmg)_2/CH_3CN$ system[a]

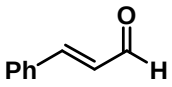
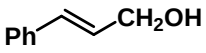
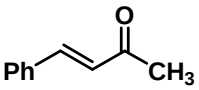
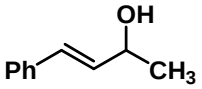
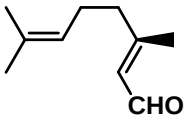
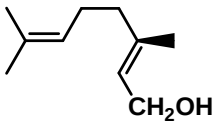
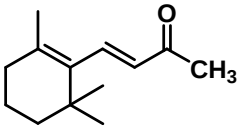
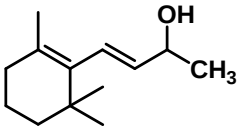
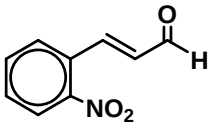
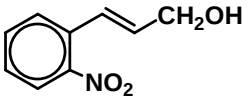
Entry	Substrate	Product	Molar ratio[b]	Time (min)	Yield (%)
1			1:2:0.01	8	91
2			1:2:0.01	15	95
3			1:2:0.01	25	93
4			1:2:0.01	35	94

[a] All reactions were carried out in CH_3CN (2 ml) under reflux conditions; [b] Molar ratio as Subs./$NaBH_4$ /$Cu(dmg)_2$; [c] Isolated yields.

diketones to their vicinal diols in CH_3CN in reflux condition (TABLE 1).

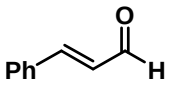
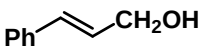
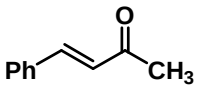
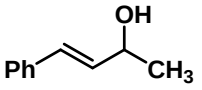
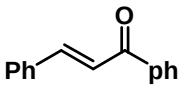
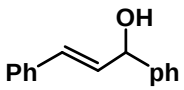
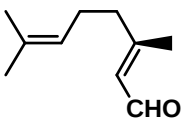
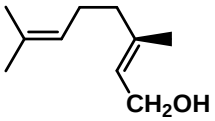
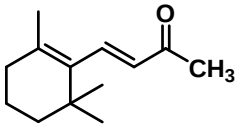
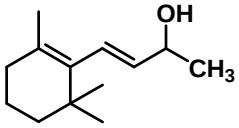
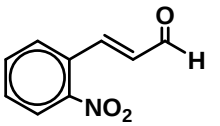
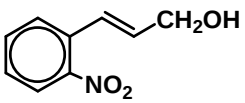
Our attempts to reduction of α-diketones to acyloins wereunsatisfactory and only vicinal diols were identified as the sole products. In addition, the reduction ofacyloins to vicinal diols is also the subject of interests. The using of non-hydridicreductantsand modified borohydrideagents has been reported for this achievement. We also applied our system to this goal. We observed that benzoin was efficiently reduced to hydrobenzoinin reflux condition. A variety of acyloins were readily reduced to their corresponding vicinal diols in excellent yields (91-95%) (TABLE 6). The results in Table 6 show that the rate of reductions for acyloin compounds is generally slower than α-diketonesunder the same conditions. The hydrogen evolution from the reaction of hydroxy group of acyloin and sodium borohydride, and hence the formation of

TABLE 7 : Reduction of conjugated carbonyl compounds with $NaBH_4/Cu(dmg)_2$ system in H_2O[a]

Entry	Substrate	Products	Molar ratio[b]	Ratio of 1,2 /1,4	Time (min)	Yield (%)[c]
1			1:0.5:0.02	100:0	3	91
2			1:2:0.01	100:0	13	92
3			1:2:0.01	100:0	3	96
4			1:2:0.01	100:0	10	93
5			1:2:0.01	100:0	23	96

[a] All reactions were carried out in H_2O (2 ml) at room temperature; [b] Molar ratio as Subs./$NaBH_4/Cu(dmg)_2$; [c] Isolated yields.

TABLE 8 : Reduction of conjugated carbonyl compounds with $NaBH_4/Cu(dmg)_2$ system in CH_3CN[a]

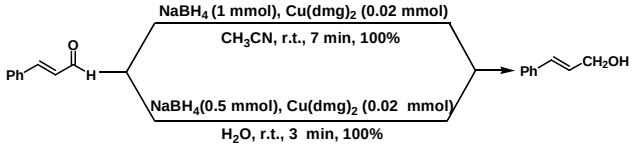
Entry	Substrate	Products	Molar ratio[b]	Ratio of 1,2 /1,4	Time (min)	Yield (%)[c]
1			1:1:0.02	100:0	7	97
2			1:2:0.01	100:0	25	97
3			1:2:0.01	100:0	33	92
4			1:2:0.01	100:0	14	94
5			1:2:0.01	100:0	16	95
6			1:2:0.01	100:0	35	91

[a] All reactions were carried out in CH_3CN (2 ml) at room temperature; [b] Molar ratio as Subs./$NaBH_4/Cu(dmg)_2$; [c] Isolated yields.

alkoxy moiety bound to boron atom may play a role in part to the rate being diminished.

Regioselective 1,2-reduction of conjugated enones

Aregioselective reduction of α,β-unsaturated aldehydes and ketones is an easy way to obtain allylic alcohols which are important synthetic materials in organic synthesis. Such achievement with $NaBH_4$ is highly solvent-dependent andgenerally the results does not show a useful regioselectivity. Regioselective 1,2-reduction of conjugated enones is usually achieved using modified borohydride agents, which are formed a) by the replacement of hydride with sterically bulky substituents or electron-withdrawing/releasing groups in order to discriminate between the structural and electronic environments of the carbonyl groups, b) by changing the metal cation, c) by combination with metal salts and mixed solvents, and d) finally immobilization on polymeric supports. Recently, non-free hydride reducing systems achieved a perfect conversion. For this purpose, $NaBH_4$ in combination with catalytic amount of $Cu(dmg)_2$ is also efficient to provide the corresponding allylic alcohols at room temperature in high to excellent yields (91-97%) (TABLE 8)(Scheme 4).



Scheme 4

CONCLUSION

In conclusion, we have shown that $NaBH_4$/$Cu(dmg)_2$ system reduces aldehydes and ketones to their corresponding alcohols, and α,β-unsaturated carbonyl compounds to their corresponding allylic alcohols. This reducing system is also efficient for the reduction of α-diketones and acyloins to their corresponding vicinal diols. Excellent regioselectivity, convenient procedure, mild reaction conditions, high yields of the products as well as a simple work-up procedure affords this system to be an attractive method for a synthetically useful methodology.

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