

Mild and Convenient Method for Reduction of Carbonyl Compounds with the NaBH₄/Charcoal System in Wet THF

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The NaBH₄/C (charcoal) system reduces a variety of carbonyl compounds such as aldehydes, ketones, acyloins and α -diketones to their corresponding alcohols in high to excellent yields. Reduction reactions were carried out in wet THF at r. t. In addition, regioselective 1,2-reduction of α,β -unsaturated aldehydes and ketones was achieved perfectly with this reducing system. By decreasing the amount of aprotic solvent, all reductions took place fast and efficiently under solid-gel condition.

Key words: Reduction, NaBH₄, Charcoal, Carbonyl Compounds

Introduction

Reduction is one of the most fundamental and useful reactions in organic synthesis. The discovery of NaBH₄ in the 1940s has provided an efficient route for the reduction of functionalized molecules and it is commonly used in organic laboratory nowadays [1]. However, in spite of its great convenience, this reagent suffers from some limitations: NaBH₄ is a remarkably mild reducing agent and reduces only aldehydes and ketones in protic solvents. In addition, the rate of reduction is sometimes slow and the chemo- and regioselectivity of the reduction of carbonyl compounds is decreased in alcoholic solvents. This situation made it desirable to develop means for controlling the reducing power of boronate reagents. In fact, advances have been realized by: (i) substitution of the hydride(s) with electron releasing or withdrawing groups, (ii) change of the sodium cation to another metal, quaternary ammonium and phosphonium cations, (iii) concurrent cation and hydride exchange, (iv) use of amino and phosphanyl ligands to alter the behavior of the metal hydride, (v) combination of borohydrides with metals, metal salts, Lewis acids, mixed solvent systems and some other additives, and (vi) finally use of polymers and solid supports for supporting the borohydride species. In this context, the applications of modified borohydride agents in organic synthesis have been reviewed extensively [2].

The literature review shows that the combination systems of H₂ or HCOONH₄ with Pd, Pt, Ru and Rh supported on carbon (catalytic hydrogenation or trans-

fer hydrogenation) have been widely used for the reduction of functional groups in organic synthesis [1, 3]. In addition, we found that the application of NaBH₄ in the presence of Pd/C has been only reported for the reduction of nitro compounds to their corresponding amines [4]. Although in the reported methods a mixture of transition metals and carbon showed an activity towards reduction, the literature did not show any application for the use of carbon alone as a promoter in combination with NaBH₄. This subject and our continuous efforts to explore the synthetic utilities of modified borohydride agents [5] encouraged us to investigate reduction of functional groups by the combination system of NaBH₄/C (charcoal) under wet condition. Herein, in a preliminary report, we wish to introduce a mild and convenient method for reduction of a variety of carbonyl compounds such as aldehydes, ketones, α,β -unsaturated carbonyl compounds, acyloins and α -diketones with the NaBH₄/charcoal system in wet THF at r. t.

Results and Discussion

Supporting of the transition metals on carbon (charcoal) and their use as catalysts in conjunction with molecular hydrogen or ammonium formate in the reduction of functional groups motivated us to investigate whether charcoal alone is a good promoter in the reduction of carbonyl compounds with NaBH₄. To investigate the influence of charcoal on the rate of reductions, we performed a set of experiments on the reduction of benzaldehyde as a model compound by NaBH₄

Entry	Reaction components Molar ratio	Solvent	Time [min]	Conversion [%]
1	PhCHO/NaBH ₄ (1 : 1)	THF (2 ml)	90	100
2	PhCHO/NaBH ₄ (1 : 1)	CH ₃ CN (2 ml)	100	100
3	PhCHO/NaBH ₄ (1 : 1)	CH ₂ Cl ₂ (2 ml)	5 h	40
4	PhCHO/NaBH ₄ (1 : 0.5)	THF-H ₂ O (2 : 0.1 ml)	20	100
5	PhCHO/NaBH ₄ /C (1 : 1 : 1)	THF (2 ml)	70	100
6	PhCHO/NaBH ₄ /C (1 : 0.5 : 1)	THF-H ₂ O (2 : 0.1 ml)	2	100
7	PhCHO/NaBH ₄ (1 : 0.5) + Charcoal (0.4g)	THF-H ₂ O (1 : 0.5 ml)	< 1	100
8	PhCOPh/NaBH ₄ (1 : 2)	THF (2 ml)	6 h	30
9	PhCOPh/NaBH ₄ (1 : 2)	THF-H ₂ O (2 : 0.1 ml)	6 h	50
10	PhCOPh/NaBH ₄ /C (1 : 2 : 2)	THF (2 ml)	6 h	40
11	PhCOPh/NaBH ₄ /C (1 : 2 : 2)	THF-H ₂ O (2 : 0.1 ml)	75	100
12	PhCOPh/NaBH ₄ (1 : 2) + Charcoal (0.4g)	THF-H ₂ O (1 : 0.5 ml)	15	100

Table 1. Reduction of benzaldehyde and benzophenone with the NaBH₄/C system under different conditions^a.

^a All reactions were carried out at r. t.

(Table 1). Our experiments showed that the reduction of PhCHO with one molar equivalent of NaBH₄ in the absence or presence of one molar equivalent of charcoal in THF (the more efficient aprotic solvent) took place within 70–90 min at r. t. However, we found that by adding a few drops of water to the reaction mixture, the rate of reaction was extremely accelerated with the evolution of hydrogen gas and it was completed in 2 min. The reaction conditions were optimized and they resulted in using the molar ratio of PhCHO/NaBH₄/charcoal (1 : 0.5 : 1) in a mixture of THF-H₂O (2 : 0.1 ml) at r. t. as optimal for the complete conversion (entry 6).

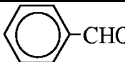
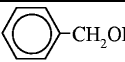

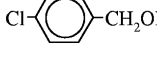
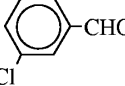
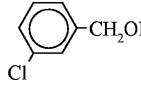
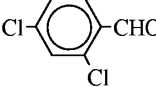
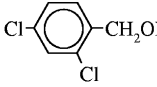
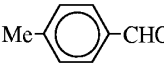
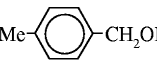

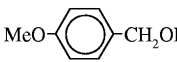
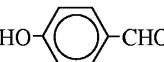
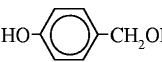
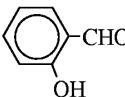
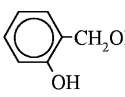
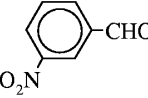
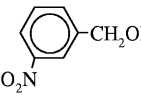

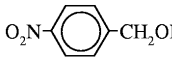
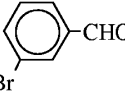
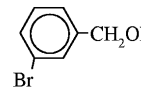
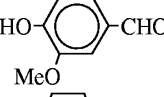
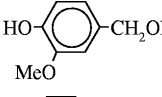
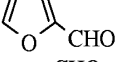
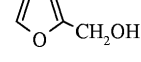
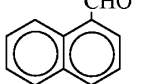
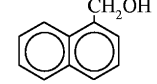
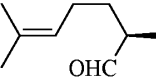
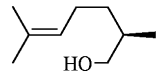
We applied the optimal conditions for the reduction of a variety of aromatic and aliphatic aldehydes to their corresponding primary alcohols. As shown in Table 2, the product alcohols were obtained in high to excellent yields within 2–6 min (method A). In another attempt, in order to minimize the amount of aprotic solvent, we performed the reduction of benzaldehyde (Table 1, entry 7) and other aldehydes (Table 2) in a solid-gel media with 0.5 molar equivalents of sodium borohydride in the presence of 0.4 g of charcoal in THF-H₂O (1 : 0.5 ml) (method B). The results show that the reactions were completed faster than by method A within 1–2 min. In the latter case, the corresponding alcohols were also obtained in high to excellent yields (88–98%).

At the next attempt, we turned our attention towards reduction of ketones by the NaBH₄/charcoal system with benzophenone as a model compound. Inherent low reactivity of ketones relative to aldehydes led us to perform the reduction with two molar equivalents of NaBH₄ and charcoal in a mixture of THF-H₂O (2 : 0.1 ml) at r. t. (Table 1, entry 11). The reaction was completed within 75 min and benzhydrol was obtained in 96% yield. In this case wet THF was also a more

efficient solvent for the reduction. To clarify the influence of charcoal under wet conditions, we performed reduction of benzophenone with two molar equivalents of NaBH₄ and charcoal in THF (2 ml) at r. t. for 6 h (Table 1, entry 10). The reaction had 40% conversion and the optimization experiments showed that the presence of charcoal or water alone had little influence on the rate of reduction. However, the presence of a small amount of water showed a great synergistic effect and completed the reduction in a shorter reaction time (75 min). The synthetic utility of the NaBH₄/C system in wet THF was further examined with the reduction of a variety of aliphatic and aromatic ketones. All ketones were reduced effectively to their corresponding secondary alcohols within 5–200 min at r. t. (Table 3) (method A). In order to perform reductions using less organic solvent, we also accomplished the reactions in a solid-gel media with two molar equivalents of NaBH₄ in the presence of charcoal (0.4 g) in THF-H₂O (1 : 0.5 ml) at r. t. and the product alcohols were obtained within 2–20 min in 83–98% (Table 3, method B).




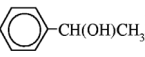
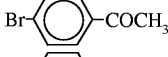
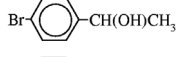
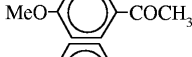
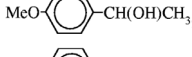
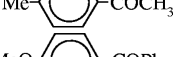
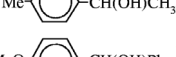
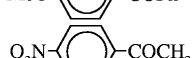
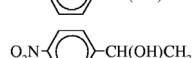
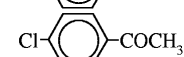
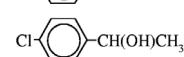
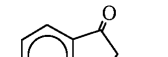
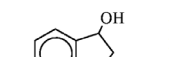
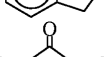
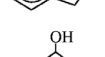
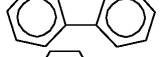
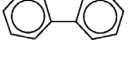




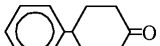
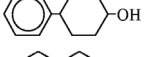
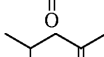



Transformation of acyloins and α -diketones to vicinal diols is a subject of interest in organic synthesis. This achievement was examined with the NaBH₄/charcoal system in wet THF. 1.5–2 molar equivalents of NaBH₄ in the presence of charcoal (two molar equivalents) reduce acyloins and α -diketones efficiently to their corresponding vicinal diols in THF-H₂O (2 : 0.1 ml) at r. t. (Table 4, method A). Under solid-gel condition these reactions were also carried out, using charcoal (0.4 g) and 1–1.5 molar equivalents of NaBH₄ in THF-H₂O (1 : 0.5 ml) at r. t. (Table 4, method B). In both methods, the vicinal diols were obtained in high to excellent yields. All attempts to carry out the reduction of α -diketones into acyloins were unsatisfactory and

Table 2. Reduction of aldehydes with the NaBH₄/charcoal system in wet THF^a.

Entry	Substrate	Product	Method	Molar ratio	Time [min]	Yield [%] ^b	M. p. or B. p. [°C]	
				NaBH ₄ /Subs.			found	reported
1			(A)	0.5 : 1	2	94	204 – 205	205 ⁷
			(B)	0.5 : 1	< 1	92		
2			(A)	0.5 : 1	3	92	70 – 71	70 – 72 ⁷
			(B)	0.5 : 1	< 1	94		
3			(A)	0.5 : 1	3	95	236	237 ⁷
			(B)	0.5 : 1	< 1	96		
4			(A)	0.5 : 1	3	94	56 – 58	55 – 58 ⁷
			(B)	0.5 : 1	< 1	96		
5			(A)	0.5 : 1	6	93	60 – 61	59 – 61 ⁷
			(B)	0.5 : 1	2	94		
6			(A)	0.5 : 1	6	92	259	259 ⁷
			(B)	0.5 : 1	2	92		
7			(A)	0.5 : 1	3	94	119 – 122	118 – 122 ⁷
			(B)	0.5 : 1	< 1	95		
8			(A)	0.5 : 1	6	92	84 – 85	83 – 85 ⁷
			(B)	0.5 : 1	2	90		
9			(A)	0.5 : 1	2	90	31 – 32	30 – 32 ⁷
			(B)	0.5 : 1	< 1	93		
10			(A)	0.5 : 1	2	97	93 – 94	92 – 94 ⁷
			(B)	0.5 : 1	< 1	94		
11			(A)	0.5 : 1	2	98	165/16 mmHg	165/16 mmHg ⁷
			(B)	0.5 : 1	< 1	96		
12			(A)	0.5 : 1	6	95	113 – 115	113 – 115 ⁷
			(B)	0.5 : 1	2	94		
13			(A)	0.5 : 1	2	89	169 – 170	170 ⁷
			(B)	0.5 : 1	< 1	88		
14			(A)	0.5 : 1	2	95	62 – 63	61 – 63 ⁷
			(B)	0.5 : 1	< 1	98		
15			(A)	0.5 : 1	2	90	225 – 226	225 – 226 ⁷
			(B)	0.5 : 1	< 1	90		
16	CH ₃ (CH ₂) ₅ CHO	CH ₃ (CH ₂) ₅ CH ₂ OH	(A)	0.5 : 1	2	83	176	176 ⁷
			(B)	0.5 : 1	< 1	88		

^a Method A: the reactions were carried out in the presence of one molar equivalent of charcoal in THF-H₂O (2 : 0.1 ml) at r. t.; Method B: the reactions were carried out in the presence of 0.4 g of charcoal in THF-H₂O (1 : 0.5 ml) at r. t. under solid-gel conditions; ^b yields refer to isolated pure products.

Table 3. Reduction of ketones with the NaBH₄/charcoal system in wet THF^a.

Entry	Substrate	Product	Method	Molar ratio	Time [min]	Yield [%] ^b	found	M. p. or B. p. [°C] reported
				NaBH ₄ /Subs.				
1			(A)	2 : 1	75	96	66–67	65–67 ⁷
			(B)	2 : 1	15	92		
2			(A)	2 : 1	100	95	204/745 mmHg	204/745 mmHg ⁷
			(B)	2 : 1	10	93		
3			(A)	2 : 1	30	95	36–38	38–38 ⁸
			(B)	2 : 1	10	96		
4			(A)	2 : 1	200	98	95–96/1 mmHg	94–96/1 mmHg ⁹
			(B)	2 : 1	18	94		
5			(A)	2 : 1	160	93	219–220	218–220 ⁸
			(B)	2 : 1	15	95		
6			(A)	2 : 1	200	94	68–69	67–69 ⁹
			(B)	2 : 1	20	94		
7			(A)	2 : 1	25	92	–	–
			(B)	1.5 : 1	5	92		
8			(A)	2 : 1	100	95	80–82/1 mmHg	80–82/1 mmHg ⁸
			(B)	2 : 1	10	98		
9			(A)	2 : 1	180	95	52–54	50–54 ⁷
			(B)	2 : 1	20	95		
10			(A)	2 : 1	20	96	153–154	153–154 ⁷
			(B)	2 : 1	10	97		
11			(A)	2 : 1	15	88	163–166	163–166 ⁷
			(B)	1 : 1	2	91		
12			(A)	2 : 1	10	85	160–161	160–161 ⁷
			(B)	1 : 1	2	83		
13			(A)	2 : 1	15	94	57–58	58 ¹⁰
			(B)	1 : 1	2	93		
14			(A)	2 : 1	5	90	115/749 mmHg	115/749 mmHg ⁷
			(B)	1 : 1	< 1	91		
15			(A)	2 : 1	5	84	132	132 ⁷
			(B)	1 : 1	< 1	87		

^a Method A: the reactions were carried out in the presence of two molar equivalent of charcoal in THF-H₂O (2 : 0.1 ml) at r. t.; Method B: the reactions were carried out in the presence of 0.4 g of charcoal in THF-H₂O (1 : 0.5 ml) at r. t. under solid-gel condition; ^b yields refer to isolated pure products.

only vicinal diols were recovered from the reaction mixture.

Regioselective 1,2-reduction of α,β -unsaturated aldehydes and ketones to give allylic alcohols is a widely used transformation in organic synthesis which is achieved with various hydride transferring agents [1]. Reduction of conjugated carbonyl compounds with sodium borohydride is highly solvent dependent and generally does not result in a useful regioselectivity [6]. The regioselectivity of the NaBH₄/charcoal system was examined with the reduction of cinnamaldehyde as a model compound in wet

THF. The reduction was carried out with the molar ratio of NaBH₄/C of 0.5 : 1 in THF-H₂O (2 : 0.1 ml) at r. t. (Table 5, entry 1, method A). The result shows that the product, cinnamyl alcohol, was obtained perfectly by this reducing system. This protocol was also successful in the reduction of citral and methacrolein within 2–10 min at r. t. (Table 5, entries 4, 6). The corresponding allyl alcohols were obtained regioselectively in 85–92% yields. Reduction of conjugated enones took place with two molar equivalents of NaBH₄ and charcoal in a mixture of THF-H₂O (2 : 0.1 ml) at r. t. Benzalacetone, benzalacetophenone,

Table 4. Reduction of acyloins and α -diketones with the NaBH₄/charcoal system in wet THF^a.

Entry	Substrate	Product	Method	Molar ratio NaBH ₄ /Subs.	Time [min]	Yield [%] ^b	M. p. or B. p. [°C] found reported
1			(A)	2 : 1	10	95	135 – 137 134 – 137 ⁷
			(B)	1.5 : 1	5	95	
2			(A)	1.5 : 1	7	93	135 – 137 134 – 137 ⁷
			(B)	1 : 1	3	92	
3			(A)	2 : 1	12	92	– –
			(B)	1.5 : 1	6	93	
4			(A)	1.5 : 1	5	94	– –
			(B)	1 : 1	3	94	
5			(A)	2 : 1	20	95	63 – 64 63 – 64 ¹¹
			(B)	1.5 : 1	5	98	

^a Method A: the reactions were carried out in the presence of two molar equivalents of charcoal in THF-H₂O (2 : 0.1 ml) at r. t.; Method B: the reactions were carried out in the presence of 0.4 g of charcoal in THF-H₂O (1 : 0.5 ml) at r. t. under solid-gel conditions; ^b yields refer to isolated pure products.

Table 5. Reduction of conjugated carbonyl compounds with the NaBH₄/charcoal system in wet THF^a.

Entry	Substrate	Product	Method	Molar ratio NaBH ₄ /Subs.	Time [min]	Yield [%] ^b	M. p. or B. p. [°C] found reported
1			(A)	0.5 : 1	2	92	249 – 250 250 ¹²
			(B)	0.5 : 1	< 1	93	
2			(A)	2 : 1	40	96	39 – 41 39 – 41 ¹¹
			(B)	2 : 1	10	96	
3			(A)	2 : 1	25	98	56 – 57 55 – 57 ¹²
			(B)	2 : 1	10	95	
4			(A)	0.5 : 1	10	92	231 – 232 231 – 232 ¹²
			(B)	0.5 : 1	2	92	
5			(A)	2 : 1	30	91	107/3 mmHg 107/3 mmHg ¹²
			(B)	1.5 : 1	10	94	
6			(A)	0.5 : 1	2	85	113 – 115 113 – 115 ⁷
			(B)	0.5 : 1	< 1	85	
7			(A)	2 : 1	2	85	96 – 97 96 – 97 ⁷
			(B)	1.5 : 1	< 1	87	

^a Method A: the reactions were carried out with 1 and 2 molar equivalents of charcoal in THF-H₂O (2 : 0.1 ml) at r. t.; Method B: the reactions were carried out in the presence of 0.4 g of charcoal in THF-H₂O (1 : 0.5 ml) at r. t. under solid-gel conditions; ^b yields refer to isolated pure products.

β -ionone and methyl vinyl ketone were the examples which were reduced by the NaBH₄/C system with perfect regioselectivity and efficiency in wet THF. Under solid-gel conditions, the reductions also took place fast and regioselectively with high yields of products (Table 5, method B).

The exact mechanism of this protocol is not clear, however, we think that the two following factors may play a role in the reductions: (i) Charcoal is a very finely porous material and the use of sodium borohydride in the presence of water makes it to finely disperse on the surface of charcoal and subsequently more

interaction with the substrate shows higher efficiency in the reductions. (ii) The hydrolysis of the alkoxyborate intermediate produced in the reaction mixture in the presence of water could promote the reductions.

Conclusions

In this investigation, we have shown that the combination system of NaBH₄/charcoal in wet THF reduces a variety of carbonyl compounds to their corresponding alcohols in high to excellent yields. Reduction reactions were carried out with 0.5–2 molar equivalents of NaBH₄ in the presence of 1–2 molar equivalents of charcoal in THF-H₂O (2:0.1 ml) (method A). By lowering the amount of aprotic solvent and increasing that for charcoal (0.4 g) (method B) and performing the reactions in a solid-gel media, we observed faster reduction rates. The combination system of NaBH₄/C in the case of conjugated aldehydes and ketones showed a perfect regioselectivity and efficiency. Reduction of acyloins and α -diketones by the NaBH₄/C system also produced efficiently the corresponding vicinal diols in wet THF. All reductions were accomplished at r.t. and therefore, under the aspects of the availability and cheapness of the reagents, high efficiency and regioselectivity of the reductions, shorter reaction times, easy work-up procedure, this new protocol for NaBH₄ reduction of carbonyl compounds could be a useful addition to the present methodologies.

Experimental Section

General

All substrates and reagents were purchased from commercially sources with the best quality and used without further purification. Charcoal was used in activated form (Merck). IR and ¹H NMR spectra were recorded on Thermo Nicolet Nexus 670 FT-IR and Bruker 300 MHz spectrometers, respectively. The products were characterized by their ¹H NMR or IR spectra and comparison with authentic sam-

ples (melting or boiling points). Organic layers were dried over anhydrous sodium sulfate. All yields refer to isolated pure products. TLC (silica gel 60 F₂₅₄ aluminum sheet) was applied for the purity determination of substrates, products and reaction monitoring.

Reduction of carbonyl compounds with the NaBH₄/charcoal system in wet THF; typical procedure

Method A: In a round-bottomed flask (10 ml) equipped with a magnetic stirrer, a solution of benzaldehyde (0.106 g, 1 mmol) in THF (2 ml) was prepared. To this solution, NaBH₄ (0.019 g, 0.5 mmol) and then charcoal (0.012 g, 1 mmol) was added and the mixture was stirred at r.t. for 30 sec. Afterwards, H₂O (0.1 ml) was added and the mixture was stirred at r.t. for 2 min. Completion of the reaction was monitored by TLC (eluent; CCl₄/Et₂O: 5/2). Water (5 ml) was then added to the reaction mixture and it was stirred for another 5 min. The mixture was extracted with CH₂Cl₂ (3 × 6 ml) and dried over anhydrous Na₂SO₄. Evaporation of the solvent and a short column chromatography of the resulting crude material over silica gel (eluent; CCl₄/Et₂O: 5/3) afforded the pure liquid benzyl alcohol (0.102 g, 94%, Table 2).

Method B: In a round-bottomed flask (10 ml) equipped with a magnetic stirrer, a solution of benzophenone (0.182 g, 1 mmol) in THF (1 ml) was prepared. To this solution, H₂O (0.5 ml) and charcoal (0.4 g) was added and the prepared solid-gel mixture was stirred at r.t. for 1 min. Afterwards, NaBH₄ (0.076 g, 2 mmol) was added and the mixture was stirred for another 15 min. The progress of the reaction was monitored by TLC (eluent; CCl₄/Et₂O: 5/2). At the end of the reaction, the mixture was filtered and washed with CH₂Cl₂ (3 × 6 ml). The filtrate was dried over anhydrous Na₂SO₄; evaporation of the solvent and a short column chromatography of the resulting crude material over silica gel (eluent; CCl₄/Et₂O: 5/3) gave white crystalline benzhydrol (0.169 g, 92%, Table 3).

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