Titanyl Acetylacetonate as an Efficient Catalyst for a Mild and Convenient Reduction of Carbonyl Compounds with NaBH₄ under Aprotic Condition

Behzad Zeynizadeh

Department of Chemistry, Faculty of Sciences, Urmia University, Urmia 57159-165, Iran

Reprint requests to B. Zeynizadeh. E-mail: b.zeynizadeh@mail.urmia.ac.ir

Titanyl acetylacetonate, $TiO(acac)_2$, is used as an efficient catalyst for the reduction of carbonyl compounds with sodium borohydride under aprotic condition. Reduction reactions are performed in CH_3CN and THF. The corresponding alcohols are obtained in high to excellent yields and the chemoselective reduction of aldehydes over ketones is achieved successfully.

Key words: Titanyl Acetylacetonate, Carbonyl Compounds, Borohydride Reduction

Introduction

Sodium borohydride has been known as a mild reducing agent and is a useful reagent for the reduction of aldehydes and ketones in alcoholic solvents [1]. In contrast to the easy handling of $NaBH_4$, several limiting features also exist, *e. g.*: essential need to use polar and protic solvents, limited number of functional group that can be reduced, the sometimes low reaction rate, and a low selectivity between carbonyl compounds. The synthetic organic chemists, being faced with the need to prepare compounds of ever-increasing complexity, have developed numerous selective reducing agents [1]. Reagents that are capable to reduce a given functional group have been prepared by modifying the reducing power of complex metal hydrides, including reagents more reactive than sodium borohydride. Among these modifications are the following: replacement of one or more hydrides with other substituents [2], change of the sodium cation to another metal [3], quaternary ammonium [4] and phosphonium [5] cations, a concurrent cation and hydride exchange [6], ligand-transition metal borohydrides [7] and finally combination of the hydride transferring agents with Lewis acids, additives [8], solid supports [9] and mixed solvent systems [10]. The preparation and application of modified borohydrides in organic synthesis have been reviewed extensively [11].

In our literature review, as far as we know, the combination of Ti(IV) and $NaBH_4$ have been done rarely and in the form of the $TiCl_4/NaBH_4$ system has been used for the reduction of nitrosamines [12], carboxylic acids, amides, oximes, sulfoxides [13], and deoxygenation of heteroaromatic amine oxides [14]. All of the reduction reactions were performed in dimethoxyethane and via a low-valent titanium-borane complex as the active species. The use of the $NaBH_4/Ti(O\text{-}iPr)_4$ system has also been reported for synthesis of disubstituted ureas from aldehydes [15]. In spite of the successful transformations achieved with these systems, it must be stated that performing of the reduction reactions in DME as an expensive solvent, highly air-or moisture-sensitivity of $TiCl_4$ or $Ti(O\text{-}iPr)_4$ and finally consumption of Ti(IV) in equivalent amounts put some restrictions on the usage of these systems as a general procedures in organic synthesis.

Due to the lack of information, our continuous efforts towards the development of new modified borohydride agents [5a, 11a,b, 16] and new applications of Ti(IV) in organic synthesis [17], led us to investigate the reducing potential of a combination system of sodium borohydride in the presence of air- and moisture-stable Ti(IV) compound titanyl acetylacetonate, $TiO(acac)_2$, for the reduction of carbonyl compounds with the hope that this new combination system shows good or excellent efficiency and selectivity without having the mentioned limitations. Herein, we preliminarily report new insight in a mild, convenient and catalytic method for the reduction of carbonyl compounds such as aldehydes and ketones with sodium borohydride and titanyl acetylacetonate in CH_3CN and THF.

Table 1. Reduction of aldehydes to alcohols with NaBH$_4$-TiO(acac)$_2$.[a]

[a] All reactions were performed in CH$_3$CN at room temperature; [b] yields referred to isolated pure products.

Entry	Substrate	Product	Molar Ratio NaBH$_4$/Ti(IV)/Subs.	Time (min)	Yield (%)[b]	M. p. or B. p. (°C) found	reported
1	C$_6$H$_5$–CHO	C$_6$H$_5$–CH$_2$OH	1:0.05:1	15	93	204–205	205 [18a]
2	Cl–C$_6$H$_4$–CHO	Cl–C$_6$H$_4$–CH$_2$OH	1:0.05:1	5	97	70–71	70–72 [18a]
3	Me–C$_6$H$_4$–CHO	Me–C$_6$H$_4$–CH$_2$OH	1.2:0.07:1	75	94	60–61	59–61 [18a]
4	MeO–C$_6$H$_4$–CHO	MeO–C$_6$H$_4$–CH$_2$OH	1.2:0.08:1	90	98	23–25	23–25 [18a]
5	HO–C$_6$H$_4$–CHO	HO–C$_6$H$_4$–CH$_2$OH	1.3:0.1:1	80	95	119–121	118–122 [18a]
6	H$_2$N–C$_6$H$_4$–CHO	H$_2$N–C$_6$H$_4$–CH$_2$OH	1.2:0.07:1	17	91	63–65	60–65 [18a]
7	1-naphthaldehyde	1-naphthalenemethanol	1:0.05:1	60	98	62–63	61–63 [18a]
8	o-O$_2$N–C$_6$H$_4$–CHO	o-O$_2$N–C$_6$H$_4$–CH$_2$OH	1:0.05:1	3	94	30–31	30–32 [18a]
9	m-NO$_2$–C$_6$H$_4$–CHO	m-NO$_2$–C$_6$H$_4$–CH$_2$OH	1:0.05:1	10	95	70–71	70–72 [18a]
10	C$_6$H$_4$(CHO)$_2$	C$_6$H$_4$(CH$_2$OH)$_2$	1.2:0.07:1	2	96	64–65	63–65 [18a]
11	MeO–C$_6$H$_4$–CHO	MeO–C$_6$H$_4$–CH$_2$OH	1:0.05:1	20	96	250/723	250/723 [18a]
12	Cl–C$_6$H$_4$–CHO	Cl–C$_6$H$_4$–CH$_2$OH	1:0.05:1	2	94	236	237 [18a]
13	Br–C$_6$H$_3$(OH)–CHO	Br–C$_6$H$_3$(OH)–CH$_2$OH	1:0.05:1	3	96	109–111	110–112 [18a]
14	Br–C$_6$H$_2$(OH)(CHO)$_2$	Br–C$_6$H$_2$(OH)(CH$_2$OH)$_2$	1.2:0.05:1	3	92	—	—
15	MeO(NO$_2$)(HO)–C$_6$H$_2$–CHO	MeO(NO$_2$)(HO)–C$_6$H$_2$–CH$_2$OH	1:0.05:1	5	95	—	—
16	(HO)$_2$–C$_6$H$_3$–CHO	(HO)$_2$–C$_6$H$_3$–CH$_2$OH	1:0.05:1	10	94	115–116	114–115 [18b]
17	citral (CHO)	citral alcohol (CH$_2$OH)	1:0.05:1	30	91	113/12	113/12 [18a]
18	CH$_3$(CH$_2$)$_n$CHO	CH$_3$(CH$_2$)$_n$CH$_2$OH	1:0.05:1	3	90	135–137	136–138 [18a]

Results and Discussion

Reduction of aldehydes and ketones to the corresponding alcohols is a well known reaction and widely used procedure in organic synthesis. This goal is usually achieved with NaBH$_4$ in protic solvents such as ethanol or isopropyl alcohol [1]. Titanyl acetylacetonate, TiO(acac)$_2$, a yellowish powder, is not an air-sensitive or hygroscopic compound and has a good solubility in aprotic solvents *e.g.*, THF or CH$_3$CN. We performed the reduction of a variety of aldehydes and ketones to their corresponding alcohols with NaBH$_4$ and catalytic amounts of TiO(acac)$_2$ under aprotic conditions. In order to find the appropriate solvent and to optimize the reaction conditions, benzaldehyde and acetophenone were selected as model compounds and applied in Et$_2$O, CH$_2$Cl$_2$, CHCl$_3$, CH$_3$CN and THF at room temperature or under reflux condition with differ-

Table 2. Reduction of ketones to alcohols with $NaBH_4/TiO(acac)_2$.[a]

Entry	Substrate	Product	Solvent	Molar Ratio $NaBH_4$/Ti(IV)/Subs.	Time (h)	Yield (%)[b]	M.p. or B.p. (°C) found	reported
1	Ph₂C=O	Ph₂CH–OH	CH_3CN	2:0.2:1	3	98	66–67	65–67 [18a]
2	HO–C₆H₄–COPh	HO–C₆H₄–CH(OH)Ph	CH_3CN	2:0.2:1	8	50	—	—
3	Ph–C₆H₄–COCH₃	Ph–C₆H₄–CH(OH)CH₃	THF	2:0.2:1	0.28	96	—	—
4	fluorenone	fluorenol	THF	2:0.2:1	0.15	97	154–155	153–154 [18a]
5	Cl,O,OH benzophenone deriv.	Cl,OH,OH deriv.	THF	2:0.2:1	0.13	92	—	—
6	bicyclohexyl ketone =O	bicyclohexyl –OH	THF	2:0.2:1	1.75	94	116–118	118–119 [18b, c]
7	cyclohexanone =O	cyclohexanol –OH	THF	1:0.1:1	0.08	90	161	160–161 [18a]
8	O= cyclohexane =O	HO– cyclohexane –OH	THF	1:0.2:1	0.17	93	98–99	98–100 [18a]
9	C₆H₅–COCH₃	C₆H₅–CH(OH)CH₃	THF	2:0.2:1	3.5	97	203/745	204/745 [18a]
10	C₆H₅–COCH₃	C₆H₅–CH(OH)CH₃	CH_3CN	2:0.2:1	4.5	94	203/745	204/745 [18a]
11	Cl–C₆H₄–COCH₃	Cl–C₆H₄–CH(OH)CH₃	THF	2:0.2:1	0.67	95	119/10	119/10 [18a]
12	1-indanone	1-indanol	THF	2:0.2:1	0.75	96	51–53	50–54 [18a]
13	1-indanone	1-indanol	CH_3CN	2:0.2:1	2.5	80	51–53	50–54 [18a]
14	Ph–CH₂CH₂–CO–CH₃	Ph–CH₂CH₂–CH(OH)–CH₃	THF	2:0.2:1	0.67	93	129/16	128–130/16 [18d]
15	Ph–CO–CH₂CH₂–CH₃	Ph–CH(OH)–CH₂CH₂–CH₃	THF	2:0.2:1	1.17	94	45–46	45–47 [18a, e]
16	ferrocenyl–COCH₃	ferrocenyl–CH(OH)CH₃	THF	2:0.2:1	4.25	95	78–79	77–79 [18e]
17	benzosuberone =O	benzosuberol HO–	THF	2:0.2:1	1.2	97	—	—
18	Br,O,O,Br deriv.	Br,OH,OH,Br deriv.	THF	2:0.2:1	0.17	92	—	—
19	camphor	borneol	THF	4:0.3:1	10	80	205–207	206–208 [18a, e]
20	steroid ketone	steroid alcohol	THF	4:0.3:1	2.5	94	183–184	184 [18f]

[a] All reactions were performed under reflux conditions; [b] yields referred to isolated pure products.

ent molar ratios of $TiO(acac)_2$ and $NaBH_4$. We found that for the complete conversions to alcohols, performing of the reduction reaction of aldehydes at room temperature in CH_3CN and ketones in refluxing CH_3CN or THF with catalytic amounts of titanyl acetylacetonate (5–30 mol%) is optimal. The usefulness of this reduc-

Entry	Substrate 1	Substrate 2	Condition	Solvent	Molar Ratio[a]	Time (min)	Conv. 1/Conv. 2 (%)[b]
1	⬡–CHO	⬡–COCH$_3$	r. t.	CH$_3$CN	1:0.05:1	15	100:0
2	⬡–CHO	Ph–CO–Ph	r. t.	CH$_3$CN	1:0.05:1	15	100:0
3	⬡–CHO	⬡=O	r. t.	CH$_3$CN	1:0.05:1	20	80:20
4	⬡–CHO	⬡=O	r. t.	CH$_3$CN	1:0.05:1	15	100:0
5	⬡–CHO	indanone	r. t.	CH$_3$CN	1:0.05:1	15	100:0
6	indanone	camphorquinone	reflux	THF	2:0.2:1	45	100:0
7	fluorenone	indanone	reflux	THF	2:0.2:1	9	100:0

Table 3. Competitive reduction of aldehydes and ketones to alcohols with NaBH$_4$/TiO(acac)$_2$.

[a] Molar ratio as: NaBH$_4$/Ti(IV)/subs. 1/subs. 2; [b] conversions refer to TLC monitoring and isolated products.

ing system was demonstrated by subjecting a variety of structurally different aromatic and aliphatic aldehydes and ketones towards the NaBH$_4$/TiO(acac)$_2$ reducing system (Tables 1 and 2).

Reduction of aldehydes was carried out in CH$_3$CN at room temperature. The progress of the reactions was followed by TLC, and the reaction conditions, and isolated yields of the products are summarized in Table 1. As it is shown, the molar ratio of titanyl acetylacetonate and NaBH$_4$ is varied according to the nature of the substrates and 1–1.3 molar equivalents of NaBH$_4$, accompanied by 0.05–0.1 molar equivalents of titanyl acetylacetonate per one equivalent of the substrate is sufficient for complete conversion of aldehydes to the corresponding alcohols. The efficiency of the reactions was excellent and the product alcohols were obtained in 90–98% yields. Reductions of ketones could also be achieved easily with this reducing system, due to their lower reactivity relative to aldehydes, their reduction requires higher temperature and molar amounts of catalyst and NaBH$_4$. The reactions were performed in refluxing CH$_3$CN or THF and with 0.1–0.3 molar amounts of titanyl acetylacetonate and 2–4 molar amounts of NaBH$_4$ (Table 2). The obtained results given in Tables 1 and 2 show that the substitution pattern on the aromatic ring has an influence on the reaction rate. Generally, the substrates with electron-withdrawing groups are reduced faster than that of electron-releasing ones.

Since aldehydes are reduced faster than ketones and occur at lower temperature, we thought that this reducing system can act as a good chemoselective system
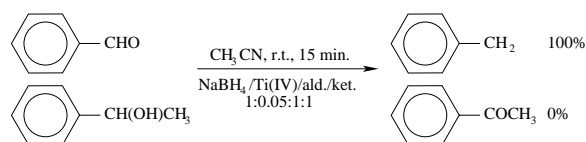
Scheme 1.

for discrimination of aldehydes over ketones or less hindered ketones over hindered ones. In order to show the chemoselectivity towards various carbonyl compounds, we performed the competitive reduction of benzaldehyde in the presence of an equimolar amount of acetophenone with 0.05 equivalent of titanyl acetylacetonate and one equivalent of NaBH$_4$ at room temperature. We observed that the aldehyde was reduced with excellent selectivity (Scheme 1). In Table 3, we see the general trend of chemoselective reduction of various carbonyl compounds and in most cases the selectivity ratios are excellent.

In order to show both advantages and limitations of the NaBH$_4$/TiO(acac)$_2$ system, we compared our results with those of reported for NaBH$_4$/Dowex1-x8 [16d], Zn(BH$_4$)$_2$(bpy) [11a], Zn(BH$_4$)$_2$(py) [16a], Zn(BH$_4$)$_2$(Ph$_3$P)$_2$ [7b], Ph$_3$PMeBH$_4$ [5b,c], and 4-aza-N-benzylbicyclo[2.2.2]octylammonium boronate [4a,b] (Table 4). The comparison reveals that reduction reactions of this system are either more efficient or comparable with the others.

Conclusion

In this study, we have investigated the potential of NaBH$_4$/TiO(acac)$_2$ for the reduction of a variety of

Entry	Substrate	Molar Ratio (Reag./Subs.), Time (h) and Yield (%)						
		I	II [16d]	III [11a]	IV [17a]	V [7b]	VI [5b, c]	VII [4a, b]
1	Ph-CHO	1^a/0.25/93	1^b/0.05/96	0.25/0.02/95	1/0.5/91	—	1/d/90	1/0.25/90
2	Cl-Ph-CHO	1^a/0.08/97	1^b/0.15/99	0.25/0.08/98	1/0.2/99	1/d/88	1/d/86	1/0.23/90
3	MeO-Ph-CHO	1.2^a/1.5/98	1.5^b/3/99	0.35/0.17/99	1/1.3/96	1/0.17/89	1/d/83	2/0.8/85
4	naphthaldehyde	1^a/1/98	—	0.25/0.13/99	1/0.8/95	1.5/d/100	1/d/100	1/0.25/90
5	Ph-CO-Ph	2^a/3/98	3^c/3.2/98	1/0.75/99	2/4.3/97	—	—	2/21.5/90
6	fluorenone	3^a/0.15/97	2^c/1.8/94	1/1.5/94	2/5.3/98	2/0.33/85	1.6/18/80	—
7	cyclohexanone	1^a/0.08/90	1.5^c/1.25/90	0.5/0.15/88	2/2/89	1/1/95	1/10/95	—

Table 4. Comparison of reduction of aldehydes and ketones to alcohols with NaBH$_4$/TiO(acac)$_2$ and other reported reagents.
I: NaBH$_4$/TiO(acac)$_2$;
II: NaBH$_4$/Dowex1-x8;
III: Zn(BH$_4$)$_2$(bpy);
IV: Zn(BH$_4$)$_2$(py);
V: Zn(BH$_4$)$_2$(Ph$_3$P)$_2$;
VI: Ph$_3$PMe(BH$_4$);
VII: [PhCH$_2$(dabco)]BH$_4$;
^{a} in the presence of 5 – 20 mol-% TiO(acac)$_2$; ^{b,c} referred to using of 10 and 20 mg of Dowex1-x8 per one mmol of substrate, respectively; ^{d} immediately.

structurally different carbonyl compounds under aprotic condition in CH$_3$CN and THF. Titanyl acetylacetonate as an air-or moisture-stable Ti(IV) species was used as an efficient catalyst in the reduction reactions. Reduction of aldehydes was carried out at room temperature and of ketones under reflux conditions. The corresponding alcohols were obtained in high to excellent yields. The chemoselective reduction of aldehydes over ketones was also achieved successfully by this system. Comparison of the obtained results with NaBH$_4$/TiO(acac)$_2$ and other reported reagents shows an excellent efficiency of this system towards reduction of carbonyl compounds. Easy work-up procedure as well as the previous advantages could make this new modified boronate an attractive and practical bench-top reducing system and a synthetically useful addition to the present methodologies.

Experimental Section

All products were characterized by a comparison with those of authentic samples (melting or boiling points) or their IR and ^{1}H NMR spectra. All yields refer to isolated pure products. TLC (silica gel PolyGram SILG/UV 254 plates) accomplished the purity determination of the substrates, products and reactions monitoring.

A typical procedure for reduction of aldehydes to the corresponding alcohols with the NaBH$_4$/TiO(acac)$_2$ system

In a round-bottomed flask (15 ml) equipped with a magnetic stirrer, a solution of 4-chlorobenzaldehyde (0.14 g, 1 mmol) and TiO(acac)$_2$ (0.013 g, 0.05 mmol) in CH$_3$CN (5 ml) was prepared. Sodium borohydride (0.037 g, 1 mmol) was then added and the mixture was stirred magnetically at room temperature for 5 min. TLC monitored the progress of the reaction (eluent: CCl$_4$/Et$_2$O (5/2)). After completion of the reaction, distilled water (7 ml) was added and the reaction mixture was magnetically stirred for 10 min. Then, the mixture was extracted with CH$_2$Cl$_2$ (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 (eluent: CCl$_4$/Et$_2$O (5/2)) afforded pure crystals of 4-chlorobenzyl alcohol (0.138 g, 97% yield, Table 1).

A typical procedure for reduction of ketones to the corresponding alcohols with the NaBH$_4$/TiO(acac)$_2$ system

In a round-bottomed flask (15 ml) equipped with a magnetic stirrer and condenser, a solution of benzophenone (0.182 g, 1 mmol) and TiO(acac)$_2$ (0.052 g, 0.2 mmol) in CH$_3$CN (5 ml) was prepared. Sodium borohydride (0.076 g, 2 mmol) was then added and the reaction mixture was magnetically stirred under reflux condition for 3 h. TLC monitored the progress of the reaction (eluent: CCl$_4$/Et$_2$O (5/2)). After completion of the reaction, distilled water (7 ml) was added and the reaction mixture was magnetically stirred for 10 min. Then, the mixture was extracted with CH$_2$Cl$_2$ (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 (eluent: CCl$_4$/Et$_2$O (5/2)) afforded pure crystals of diphenylmethanol (0.18 g, 98% yield, Table 2).

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