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Organoboranes

A General, Practical Triethylborane-Catalyzed Reduction of Carbonyl Functions to Alcohols

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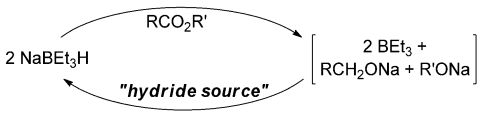
Abstract: A combination of the abundant and low-cost triethylborane and sodium alkoxide generates a highly efficient catalyst for reduction of esters, as well as ketones and aldehydes, to alcohols using an inexpensive hydrosilane under mild conditions. The catalyst system exhibits excellent chemoselectivity and a high level of functional group tolerance. Mechanistic studies revealed a resting state of sodium triethylalkoxylborate that is the product of the reaction of BEt_3 with sodium alkoxide. This borate species reacts with hydrosilane to form $NaBEt_3H$, which rapidly reduces esters.

The reduction of carbonyl compounds and carboxylic acid derivatives to alcohols is one of the most fundamental transformations in organic synthesis.[1] Stoichiometric reactions using organometallic hydrides, such as $LiAlH_4$, $NaBH_4$, and DIBAL–H (diisobutylaluminium hydride), are prevalent on a laboratory-scale.[2] However, these highly reactive pyrophoric agents are air-, and moisture-sensitive, are not compatible with many functional groups, and require exigent reaction conditions. Moreover, the use of stoichiometric amounts of such reducing agents creates a cost hurdle on bulk scale synthesis. Thus, attention has been given to the development of catalytic methods for reduction of carbonyl functions. Transition-metal-catalyzed hydrogenation of ketones and aldehydes has been well established,[3] but hydrogenation of the less reactive carboxylic esters is still a challenge.[4] Known examples require harsh reaction conditions (high pressures and temperatures) and functionalities such as olefin, alkyne, cyanide and nitro groups often compete favorably over esters for hydrogenation.[5]

Catalytic hydrosilylation is an attractive alternative to hydrogenation for a mild and selective ester reduction.[6] Various transition-metal catalyst systems with Ti,[7] Rh,[8] Ru,[9] Mo,[10] Zn,[11] Mn,[12] and Fe[13] metals have been reported for ester hydrosilylations.[14] Nevertheless, most of the protocols require either expensive reducing agents or high reaction temperatures. Remarkably, catalysts based on earth-abundant boron have also been developed. Seminal work by Piers showed that the strong Lewis acid $B(C_6F_5)_3$ catalyzes ester hydrosilylation to form aldehydes with Ph_3SiH as the reductant.[15] It is noted that selective ester hydrosilylation is difficult to control because silyl acetals are susceptible to over-reduction to silyl ethers and alkanes. While olefins, internal alkynes, and halogens can be tolerated, nitrile and alcohol functionalities are difficult. The mechanism involves novel activation of the Si–H bond of hydrosilane by $B(C_6F_5)_3$ through η^1 coordination,[15b,16] which has been termed as 'frustrated Lewis pair' bond activation.[17]

The development of low-cost and abundant non-transition-metal catalysts for ester reductions is of significant interest. Triethylborane (BEt_3) is manufactured on a tremendous scale in industry and far less expensive than $B(C_6F_5)_3$ (>100 times less). However, BEt_3 is a weak Lewis acid, and hence itself cannot catalyze ester hydrosilylations through silane activation as $B(C_6F_5)_3$ does. It is worth noting that BEt_3 is a precursor to $NaBEt_3H$,[18] a powerful and selective reducing agent. On the other hand, ester reductions with $NaBEt_3H$ would produce BEt_3 and sodium alkoxides. We became intrigued with the possibility of the conversion of BEt_3 to $NaBEt_3H$ using a suitable hydride source under the conditions applied to $NaBEt_3H$-mediated ester reductions (Scheme 1). Herein, we report a mild, general, user-friendly, and high-yielding BEt_3-catalyzed method for reduction of esters, as well as aldehydes and ketones. The procedure uses polymethylhydrosiloxane (PMHS), an inexpensive waste product of silicon industry, as the reducing agent.



Scheme 1. Conversion of BEt_3 to $NaBEt_3H$ under the conditions for $NaBEt_3H$-mediated ester reductions.

We commenced the study by investigating the reduction of methyl phenylacetate (**1a**) with PMHS as a model reaction (Table 1). As expected, in the presence of BEt_3 (5 mol%), no reaction took place between **1a** and PMHS (3 equiv of Si–H relative to **1a**) in Et_2O at room temperature (Table 1, entry 1). However, with the addition of NaOMe (5 mol%) the reaction occurred, and 2-phenylethanol (**2a**) was obtained in 99% yield (94% isolated yield) after hydrolysis with NaOH (aq) and MeOH (Table 1, entry 2). Control experiments (1) without NaOMe and BEt_3, and (2) with NaOMe, but without BEt_3 did not afford the

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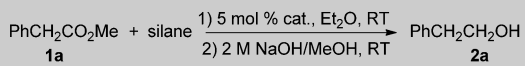
Table 1. BEt_3/base- or $NaBEt_3H$-catalyzed reduction of methyl phenylacetate (**1a**) with hydrosiloxane.[a]



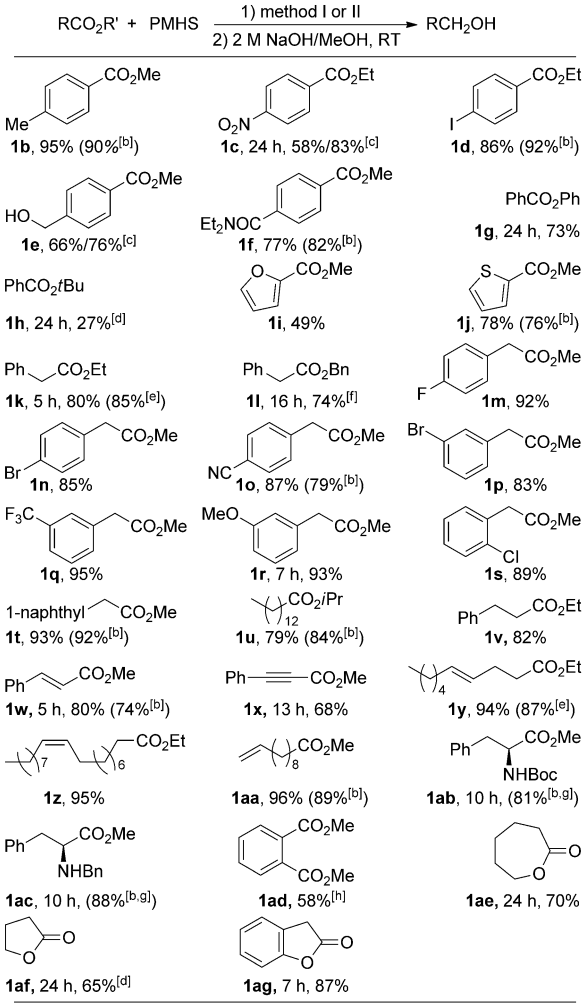
	Catalyst	Silane [equiv]	Time [h]	Yield [%][b]
1	BEt_3	PMHS (3)	8	0
2	BEt_3/NaOMe	PMHS (3)	8	99 (94)
3	–	PMHS (3)	8	0
4	NaOMe	PMHS (3)	8	0
5	BEt_3/NaOEt	PMHS (3)	8	96
6	BEt_3/NaO*t*Bu	PMHS (3)	8	95
7	BEt_3/LiO*t*Bu	PMHS (3)	8	0
8	BEt_3/KO*t*Bu	PMHS (3)	8	88
9	KO*t*Bu	PMHS (3)	10	0
10	$B(OMe)_3$/NaOMe	PMHS (3)	8	0
11	$NaBEt_3H$	PMHS (3)	8	94 (90)
12	$NaBEt_3H$	$(EtO)_3SiH$ (3)	10	79
13	$NaBEt_3H$	$(EtO)_2MeSiH$ (3)	10	88
14	$NaBEt_3H$	$PhSiH_3$ (2)	10	85
15	$NaBEt_3H$	Ph_2SiH_2 (2)	10	16
16	$NaBEt_3H$	Et_3SiH (3)	10	2
17	$NaBEt_3H$	Ph_3SiH (3)	10	2
18	$NaBH_4$	PMHS (3)	10	1
19	NaH	PMHS (3)	10	0
20	$LiAlH_4$	PMHS (3)	10	6

[a] Conditions: **1a** (1.0 mmol), silane (3.0–6.0 mmol Si–H), catalyst (50.0 μmol) and Et_2O (4.0 mL) at RT. [b] Yields are determined by ^1H NMR spectroscopy with mesitylene as the internal standard. Isolated yields are given in parentheses.

desired product (Table 1, entry 3 versus entry 4). The reactions with BEt_3/NaOEt and BEt_3/NaO*t*Bu gave **2a** in 96 and 95% yield, respectively (Table 1, entries 5 and 6). Whereas a combination of BEt_3 and LiO*t*Bu is inactive, the reaction employing BEt_3/KO*t*Bu produced **2a** in 88% yield (Table 1, entries 7 and 8). Earlier work showed that KO*t*Bu itself can induce the redistribution of PMHS to form $MeSiH_3$ or SiH_4, which is responsible for ester reductions.[14] However, under our condition (at ambient temperature), the reaction of **1a** with PMHS and KO*t*Bu (5 mol%) in the absence of BEt_3 gave no reduction product **2a** after 10 h (Table 1, entry 9). Notably, a combination of NaOMe and $B(OMe)_3$, a weaker Lewis acid compared to BEt_3, is inactive for ester reduction (Table 1, entry 10).

If BEt_3 was converted to $NaBEt_3H$ in the presence of sodium alkoxide and PMHS as we proposed (vide supra), $NaBEt_3H$ itself may serve as the catalyst for ester reduction. Indeed, with no additional base, the reaction of **1a** with PMHS and $NaBEt_3H$ (5 mol%) produced **2a** in 94% yield (90% isolated yield) after 8 h at room temperature (Table 1, entry 11). The $NaBEt_3H$-catalyzed reductions with other silanes, such as $(EtO)_3SiH$, $(EtO)_2MeSiH$, and $PhSiH_3$, occurred smoothly (Table 1, entries 12–14), but those with Ph_2SiH_2, Ph_3SiH, and Et_3SiH exhibited low or no activity (Table 1, entries 15–17). Finally, we studied the reactions with PMHS using $NaBH_4$, NaH, and $LiAlH_4$ (5 mol% each), but none of them are effective for ester reduction (Table 1, entries 18–20).

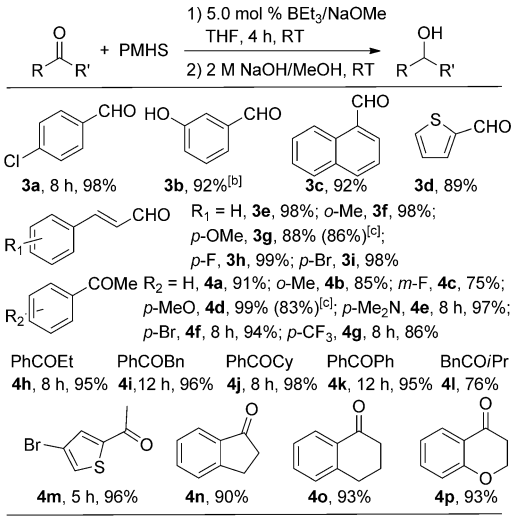
As summarized in Scheme 2, by using $NaBEt_3H$ (method I) or BEt_3/NaOMe (method II) as the catalyst, a large number of aromatic and aliphatic esters with various functional groups underwent reduction with PHMS in high yield at room temperature. Methyl, ethyl, and phenyl benzoate derivatives (**1a**–**1g**) were reduced smoothly to benzylic alcohols, but *tert*-butyl benzoate (**1h**) was less reactive (27%) presumably due to steric effect. Nevertheless, isopropyl tetradecanoate (**1u**) was reduced in high yield. Remarkably, reactive functional groups, such as free alcohol (**1e**), nitro (**1c**), iodo (**1d**), cyano (**1o**), and amide (**1f**) groups can be tolerated. The reaction of methyl 4-(hydroxymethyl)benzoate (**1e**) or 4-nitrobenzoate (**1c**) with $(EtO)_2MeSiH$ resulted in higher yield than that with PMHS. Heteroaromatic esters, furan-2-carboxylate (**1i**) and thiophene-2-



Scheme 2. $NaBEt_3H$- or BEt_3/NaOMe-catalyzed reductions of esters to alcohols; [a] Unless otherwise stated, method I was used for reductions. Method I: ester (1.0 mmol), PMHS (3.0 mmol of Si–H), $NaBEt_3H$ (50.0 μmol, 1 M in THF) and Et_2O (4.0 mL) at room temperature (RT), 8 h or stated otherwise. Yields shown are of isolated products. [b] Method II: ester (1.0 mmol), PMHS (3.0 mmol of Si–H), BEt_3 (50.0 μmol, 1 M in THF), NaOMe (50.0 μmol) and Et_2O (4.0 mL), 6 h at RT. Yields shown are of isolated products. [c] Used $(EtO)_2SiMeH$ instead of PMHS. [d] Yield was determined by ^1H NMR spectroscopy with mesitylene as the internal standard. [e] Reagents and solvent were used without drying, and manipulations were carried out under air. [f] Formed a 1:1 ratio of phenylethanol/benzyl alcohol as determined by ^1H NMR analysis. These two products were not separated. [g] PMHS (4.0 mmol of Si–H). [h] PMHS (6.0 mmol of Si–H).

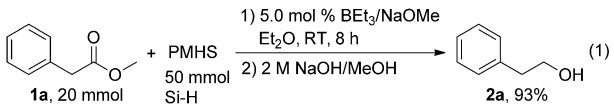
carboxylate (**1 j**) were reduced in useful yields. Substrates containing a triple bond (**1 x**), and double bonds regardless of their position (**1 w**, **1 y**, **1 z** and **1 aa**) underwent reduction chemoselectively, while retaining the original stereochemistry of the C–C double bonds. Chiral β-amino alcohols play an important role in pharmaceutical therapy and as chiral auxiliaries in organic synthesis. The reductions of chiral α-amino acid methyl esters (**1 ab** and **1 ac**) using this method gave optically pure β-amino alcohols in high isolated yields without racemization of the stereogenic centers. Lactones, such as ε-caprolactone (**1 ae**), butyrolactone (**1 af**), and phthalide (**1 ag**), were reduced to diols. This method is complimentary to Ti- or Fe-catalyzed hydrosilylation of lactones to form lactols.[7d,19]

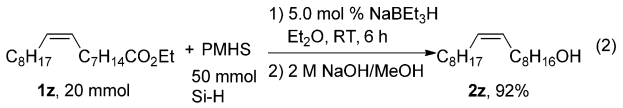
BEt_3/NaOMe is also effective for the reductions of aldehydes and ketones (Scheme 3). Aromatic, heteroaromatic and aliphatic aldehydes and ketones were all reduced with high yields. α,β-Unsaturated aldehydes (**3 e**–**3 i**) underwent chemoselective reduction to form allyl alcohols. Functionalities, including free alcohol (**3 b**), halides (**3 a**, **3 h**, **3 i**, **4 f**, and **4 m**), ether (**4 d**), and amino (**4 e**) groups were also tolerated.



Scheme 3. BEt_3/NaOMe-catalyzed reductions of aldehydes and ketones to alcohols; [a] Conditions: aldehyde or ketone (1.0 mmol), PMHS (2.0 mmol of Si–H), BEt_3 (50.0 μmol, 1 M in THF), NaOMe (50.0 μmol) and THF (4.0 mL) at RT, 4 h or stated otherwise. Yields shown are of isolated products. [b] PMHS (3.0 mmol of Si–H). [c] Reagents and solvent were used without drying, and manipulations were carried out under air.

Importantly, the reactions are scalable and can be carried out under ambient conditions without the need of a dry-box and extensive drying of the reagents. For example, the BEt_3/NaOMe-catalyzed reduction of methyl phenylacetate **1 a** [Eq. (1)] and $NaBEt_3H$-catalyzed reduction of methyl oleate **1 z** [Eq (2)], both performed on a 20 mmol scale in air using reagents without drying, afforded the desired products **2 a** and **2 z** in excellent isolated yields.





To gain insight into the mechanism, we conducted ^{11}B NMR studies of stoichiometric reactions (Figure 1). The resonance of BEt_3 ($\delta = 83.1$ ppm) remained almost unchanged upon the addition of PMHS (see Figure S2 in the Supporting Information for more details). However, upon mixing BEt_3 with one equiv of NaOMe, a new resonance at $\delta = 0.6$ ppm was observed (Figure 1 b), which is characteristic of an anionic four-coordinate boron atom.[20] We hypothesized that the reaction of BEt_3 with NaOMe formed $Na^+BEt_3(OMe)^-$ (**5**). Subsequent addition of PMHS (2 equiv of Si–H) to **5** generated $NaBEt_3H$, as evidenced by the formation of a sharp resonance at $\delta = -12.1$ ppm (Figure 1 c; for comparison, the resonance for commercially available $NaBEt_3H$ appears at $\delta = -11.9$ ppm). Addition of two equiv of ester **1 a** resulted in the appearance of a broad resonance at 1.2 ppm (Figure 1 d), which is close to that for **5**, suggesting that the reduction of **1 a** with $NaBEt_3H$ occurred to form a putative borate, $Na^+BEt_3(OCH_2Bn)^-$ (**6**). Compound **6** was independently prepared by the reaction of BEt_3 with $NaOCH_2Bn$ (see the Supporting Information, Figure S1). Finally, the reaction of this borate species with PMHS (5 equiv of Si–H) regenerates $NaBEt_3H$.

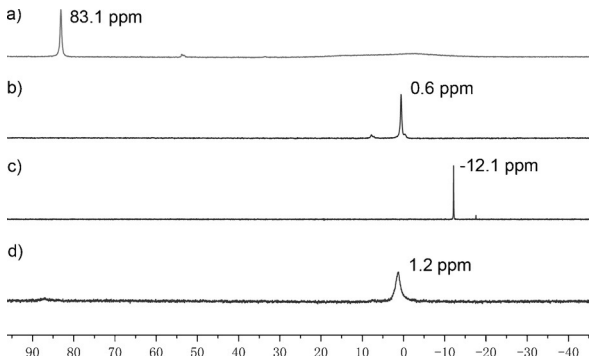
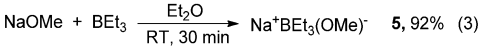
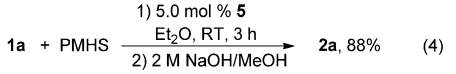


Figure 1. ^{11}B NMR spectra, a) BEt_3 in diethyl ether. b) $BEt_3 + 1$ NaOMe → $NaBEt_3(OMe)$. c) $(BEt_3 + 1$ NaOMe$) + 2$ PMHS → $NaBEt_3H$. d) [$(BEt_3 + 1$ NaOMe$) + 2$ PMHS$] + 2$ **2 a** → $NaBEt_3(OCH_2Bn)$.

To the best of our knowledge, examples of triorganylalkoxylborates are rare, although organyltrialkoxylborates and diorganyldialkoxylborates have been reported by Brown and others.[20] To access the potential intermediacy of triethylalkoxylborate to lie on the reaction pathway, we sought to synthesize and characterize the borate. Treatment of BEt_3 with NaOMe in Et_2O formed compound **5** [Eq. (3)] as a white solid,



which was isolated (92% yield) and fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy, and elemental analysis. The reaction of methyl phenylacetate **1a** with PMHS catalyzed by the isolated borate **5** (5 mol%) gave **2a** in 88% isolated yield after 3 h [Eq. (4)]. The data indicates that the borate species is competent to be an intermediate in the catalytic process.



1a + PMHS → **2a**, 88% (4)

Monitoring the boron species formed in the catalytic reaction at room temperature by ^{11}B NMR spectroscopy revealed that $Na^{+}BEt_3(OR)^{-}$ is the resting state of the catalyst. $NaBEt_3H$ reacts rapidly with esters, thus it cannot be detected during the catalytic process until the full consumption of esters. The borate species is finally converted to $NaBEt_3H$ in the presence of excess hydrosiloxane (see Figure S3 in the Supporting Information).

On the basis of the preliminary data, we propose the conversion of BEt_3 by sodium alkoxide to form a borate that subsequently reacts with PMHS to generate $NaBEt_3H$ and polymethylalkoxylsiloxane (**7**) by hydride transfer. Reduction of carbonyl functions with $NaBEt_3H$ then regenerates sodium borates. Subsequently, hydrolysis of **7** delivers the alcohol product (Figure 2).

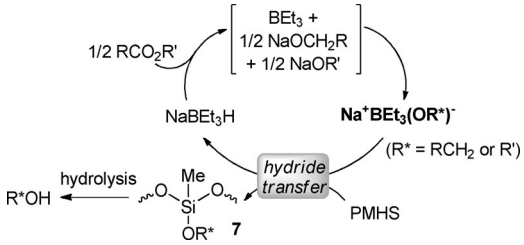


Figure 2. Proposed mechanism for BEt_3-catalyzed ester reduction with PMHS.

In summary, we have described a novel strategy for the first examples of BEt_3-catalyzed reductions of esters, ketones, and aldehydes to alcohols using an inexpensive hydrosiloxane. Featuring low-cost and abundant catalyst and reagents, mild reaction conditions, high efficiency, tolerance toward various functional groups, and operational simplicity, this sytem is a general and practical route for reduction of carbonyl functions. Preliminary mechanistic investigation revealed that the reaction does not occur through classical hydrosilylation, but involves hydride transfer from hydrosilane to a borate, resulting in the formation of $NaBEt_3H$ that probably acts as the 'true' reductant. Further studies with respect to the mechanim of hydride transfer and the design of chiral borates for enantioselective catalytic reduction of carbonyl groups are under way.

Experimental Section

General procedure for hydrosilylation of esters, aldehydes and ketones.

Method I: In a N_2-filled glovebox or under Ar atmosphere, a 20 mL oven-dried Schlenk tube was charged with ester (1.0 mmol), PMHS (3.0–6.0 mmol) and dry diethyl ether (4 mL). The reaction mixture was stirred at room temperature and $NaBEt_3H$ (50.0 μmol, 1 M in THF) was added by a syringe under Ar. After the allotted time, the reaction was quenched by adding MeOH (1 mL) and 2 M NaOH (1 mL) at 0 °C. The mixture was stirred for further 2 h at room temperature and was then extracted with diethyl ether (3×20 mL). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The product was purified by flash chromatography using an ethyl acetate/petroleum ether mixture.

Method II: In a N_2-filled glovebox or under Ar atmosphere, a 20 mL oven dried Schlenk tube was charged with dry diethyl ether (4 mL), BEt_3 (50.0 μmol, 1 M in THF) and NaOMe (50.0 μmol). The resulting mixture was stirred for 2 min and became colorless. Then ester (1.0 mmol) and PMHS (3.0–6.0 mmol) were added to the solution by a syringe. After the allotted time, the reaction was quenched by adding MeOH (1 mL) and 2 M NaOH (1 mL) at 0 °C. The mixture was stirred for further 2 h at room temperature and was then extracted with diethyl ether (3×20 mL). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The product was purified by flash chromatography using an ethyl acetate/petroleum ether mixture.

Acknowledgements

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Keywords: borates · esters · homogeneous catalysis · silanes · triethylboranes

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