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Metal-Free Ammonia Borane-Catalyzed Hydroboration of Lactones and Esters to Alcohols

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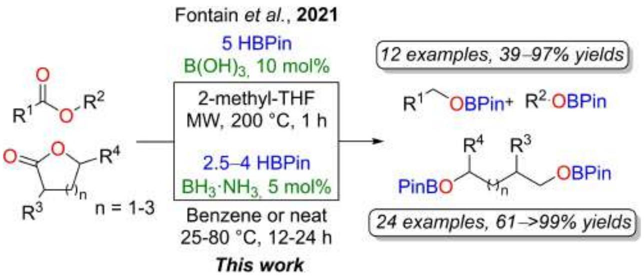
Herein we describe an efficient methodology for metal-free hydroborative cleavage of lactones and esters with HBPin (Pin = pinacol) to the corresponding alcohol derivatives using ammonia borane as a pre-catalyst. The reactions proceed under mild conditions, can be performed in a solvent-free manner, and do not require an inert atmosphere. Combined experimental and computational mechanistic studies suggest a novel mechanism that involves μ-aminodiboranes as catalytically active species.

Introduction

Esters and lactones are prevalent in biomass and plant-based oils and are considered valuable renewable sources of chemical feedstock.[1] The reductive cleavage of esters to alcohols spans the interest of both academic and industrial chemists.[1,2] However, compared to aldehydes and ketones, the reduction of esters is more challenging due to their significantly lower electrophilicity.[2] Conventional reduction protocols require the use of rather aggressive reductants, such as $LiAlH_4$ and $LiBH_4$, which suffer from low functional group tolerance and may pose significant safety concerns.[3] As an alternative, more selective, and atom-economic method, catalytic hydrogenation of esters has been extensively developed, but the reactions typically require rather harsh conditions (high H_2 pressures and temperatures) and the use of expensive high-pressure equipment.[4] In contrast, the reduction of esters using hydroelementation approach offers milder reaction conditions and allows the operational simplicity of transformations.[5,6] The majority of such protocols involve hydrosilylation reactions,[5] whereas the hydroboration approach is comparatively underdeveloped.[6] Although the stoichiometric reduction of esters and lactones with $BH_3 \cdot SMe_2$ and $BH_3 \cdot THF$ is well established, these reagents have associated handling risks due to their highly reactive and pyrophoric nature, which causes serious safety concerns upon scaling up these transformations.[6g,7] In contrast, the use of deactivated and hence less reactive hydroboranes such as HBPin and HBCat, mainly requires transition metal or main group metal catalysts.[6] These catalytic systems typically suffer from air and moisture sensitivity, whereas the application of transition metals may also cause environmental concerns. Unlike for aldehydes, ketones, and even carboxylic acids, catalytic hydroboration of which under metal-free conditions is well-illustrated,[8] the reports on metal-free hydroboration of esters and lactones with HBPin are scarce.[6i,8e,9] A noteworthy example has been recently reported by Fontaine et al., who demonstrated the use of $B(OH)_3$ as a pre-catalyst in the hydroboration of lactones, esters, and carbonates with HBPin excess at 200 °C under microwave irradiation (Scheme 1).[6i] The reactions were suggested to proceed via the in situ generation of BH_3, which acted as the reducing agent and was then recovered through O–B/B–H transborylation with HBPin. Similar BH_3-catalyzed processes have been previously discussed by Thomas et al. as "hidden" routes in metal-catalyzed hydroboration reactions.[10]

In our search for more convenient and easy-to-handle BH_3 precursors, we turned to ammonia borane (AB), a more robust alternative to $BH_3 \cdot SMe_2$ and $BH_3 \cdot THF$ with increased hydridic BH character. AB is applied as a mild reducing agent for carbonyl compounds;[11] however, the reduction of esters with AB requires the use of a catalyst.[12] Considering all this, we envisioned that AB might serve as a suitable and robust pre-catalyst for the hydroboration of lactones and esters with HBPin (Scheme 1). Herein we report our findings, representing a rare example of an effective and easy-to-handle metal-free catalytic



Scheme 1. Metal-free hydroboration of esters and lactones with HBPin.

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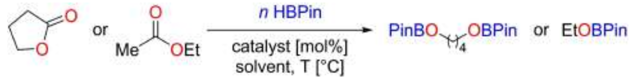
Supporting information for this article is available on the WWW under https://doi.org/10.1002/cctc.202400876 system for efficient hydroboration of lactones and esters to alcohols. The reactions proceed under mild conditions, do not require additional external stimuli, and do not necessitate inert atmosphere conditions. A comparison of the activity of AB with other borane (pre)catalysts and mechanistic aspects of AB-catalyzed hydroboration reactions are also discussed.

Results and Discussion

We started our studies with the hydroboration of γ-butyrolactone and EtOAc as model substrates (Table 1). First, no or very little conversions of both substrates were observed upon their treatment with HBPin under catalyst-free conditions.[13] In contrast, the reaction of γ-butyrolactone in benzene (0.65 M) with 2.5 equiv. of HBPin in the presence of 5 mol% of AB showed complete conversion of the substrate to the corresponding diborate within 24 h at 50 °C (Table 1, entry 1). Noteworthy, >99% conversion of γ-butyrolactone was also detected when the reaction was repeated in air. Lowering the reaction temperature to 25 °C, reducing the reaction time to 12 h, and/or lowering the AB loading to 2.5 mol%, all resulted in reduced yields of the product (42–87%; Table 1, entries 2–4). Nonetheless, the quantitative hydroboration of γ-butyrolactone at 25 °C could be achieved within 12 h by increasing the concentration of the reaction mixture to 1.82 M (Table 1, entry 5) or conducting the reaction in neat HBPin (Table 1, entry 6).

Table 1. Evaluation of the reaction conditions for catalytic hydroboration of γ-butyrolactone and ethyl acetate with HBPin.[a]



Entry	Cat. [mol%]	n	Solvent [M]	T [°C]/t [h]	Conv. [%][b]
γ-Butyrolactone					
1	$NH_3 \cdot BH_3$ (5)	2.5	C_6H_6 (0.65)	50/24	>99[c]
2	$NH_3 \cdot BH_3$ (5)	2.5	C_6H_6 (0.65)	25/24	42
3	$NH_3 \cdot BH_3$ (5)	2.5	C_6H_6 (0.65)	50/12	73
4	$NH_3 \cdot BH_3$ (2.5)	2.5	C_6H_6 (0.65)	50/24	87
5	$NH_3 \cdot BH_3$ (5)	2.5	C_6H_6 (1.82)	25/12	>99[c,d]
6	$NH_3 \cdot BH_3$ (5)	4	–	25/12	>99[e]
7	$BH_3 \cdot SMe_2$ (5)	2.5	C_6H_6 (0.65)	50/24	44[f]
8	$BH_3 \cdot SMe_2$ (5)	2.5	C_6H_6 (1.82)	25/12 (24)	35 (43)
9	$BH_3 \cdot SMe_2$ (5)	4	–	25/12	64
Ethyl acetate					
10	$NH_3 \cdot BH_3$ (5)	2.5	C_6H_6 (0.65)	50/24	68
11	$NH_3 \cdot BH_3$ (5)	2.5	C_6H_6 (0.65)	80/24	86[c]
12	$NH_3 \cdot BH_3$ (2.5)	2.5	C_6H_6 (0.65)	80/24	85
13	$NH_3 \cdot BH_3$ (5)	2.5	C_6H_6 (1.82)	50/24	89[g]
14	$NH_3 \cdot BH_3$ (5)	2.5	C_6H_6 (1.82)	80/24	>99
15	$NH_3 \cdot BH_3$ (5)	4	–	50/24	85
16	$NH_3 \cdot BH_3$ (5)	4	–	80/24	>99
17	$BH_3 \cdot SMe_2$ (5)	2.5	C_6H_6 (1.82)	80/24	61

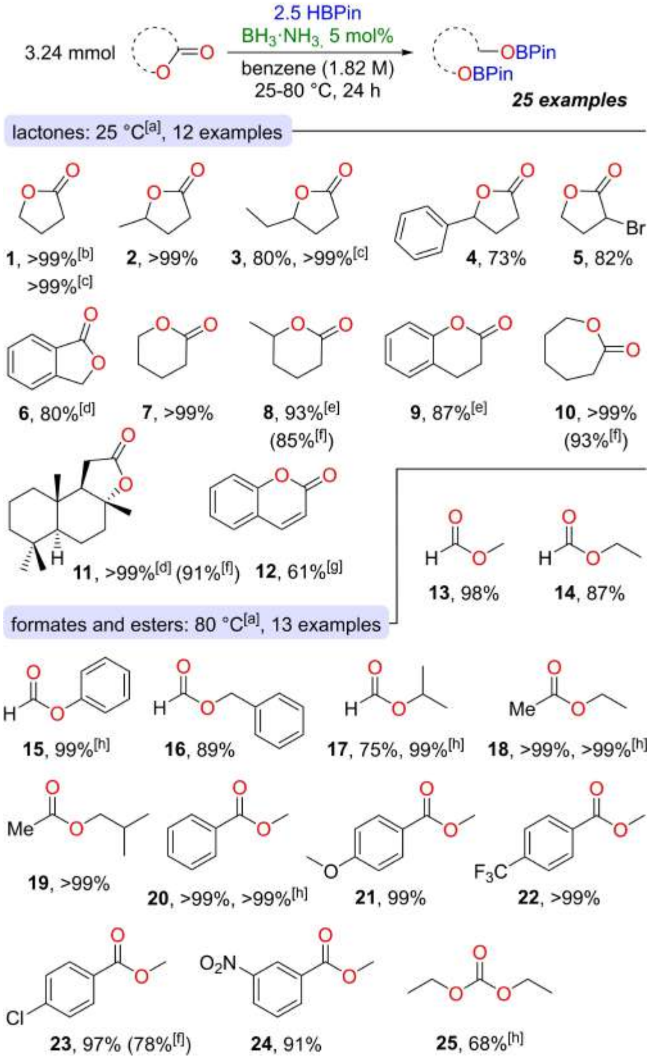
[a] 3.24 mmol of the substrate. [b] Determined by ^{1}H-NMR using mesitylene or 1,3,5-trimethoxybenzene as internal standard. [c] Analogous conv. were detected when reactions were performed in air. [d] 86% conv. in 6 h. [e] 95% conv. in 6 h. [f] 57% conv. with 5 mol% of $BH_3 \cdot THF$. [g] 87% conv. in THF-d_8 (1.82 M).

Compared to γ-butyrolactone, AB-catalyzed hydroboration of EtOAc required more forcing conditions, and the quantitative formation of EtOBPin in both benzene (1.82 M) and neat HBPin was achieved within 24 h at 80 °C (Table 1, entries 14 and 16). Reducing the temperature to 50 °C and/or diluting the reaction to 0.65 M showed decreased yields of EtOBPin (40–89%; Table 1, entries 10–13 and 15). Noteworthy, identical EtOAc conversions to EtOBPin were also detected when reactions were performed in air (Table 1, entry 11) and when benzene was replaced with THF-d_8 (Table 1, entry 13).

To compare the catalytic activity of AB and other BH_3 adducts, hydroboration of γ-butyrolactone and EtOAc was attempted using 5 mol% of $BH_3 \cdot SMe_2$ and $BH_3 \cdot THF$. To our surprise, both adducts showed significantly reduced catalytic activities compared to AB (35–64%; Table 1, entries 7–9 and 17). Notably, rather low conversions of γ-butyrolactone (up to 62%) were also observed in the hydroboration reactions catalyzed by $B(OH)_3$, BPh_3, $NaBPh_4$, and $KB(C_6F_5)_4$.[13]

Having identified the optimal reaction conditions, we then investigated the scope of AB-catalyzed hydroboration of lactones and esters (Scheme 2). A series of substituted γ-butyrolactones **1**–**5**, δ-valerolactone **7**, and caprolactone **10** showed up to >99% conversions to the corresponding diborate products within 12–24 h at 25 °C in C_6D_6 (1.82 M). The hydroboration of phthalide **6**, δ-hexalactone **8**, and dihydrocoumarin **9** required heating at 50–80 °C for 24 h, although high yields (87% to >99%) of diborate products were also detected. The efficacy of the AB-catalyzed hydroboration was also demonstrated in the hydroborative cleavage of naturally occurring (+)-Sclareolide **11** to borylated Ambradiol (>99% at 80 °C in 24 h; Scheme 2), which is considered a convenient precursor to Ambrox, an important product in the perfume industry.[14] In contrast, the hydroboration of coumarin **12** proved more sluggish, and only 61% conversion to the corresponding diborate was observed when the reaction was conducted at 50 °C for 24 h in C_6D_6, but only traces of C=C hydroboration products were detected.

Analogously, AB proved effective in the hydroboration of formates and esters. The reactions were performed in benzene (1.82 M) and/or in neat HBPin at 80 °C for 24 h and showed good to excellent conversions of substrates to the corresponding alcohol derivatives (Scheme 2). Lowering the reaction temperature below 80 °C resulted in the partial formation of borylated acetal intermediates RC(H)(OR')(OBPin), which seem to be more stable compared to those derived from lactones. Interestingly, such reactivity difference of lactones vs. esters allowed for chemoselective reduction of lactones in the presence of ester functionalities. Thus, AB-catalyzed hydroboration of γ-butyrolactone was selectively achieved (86%

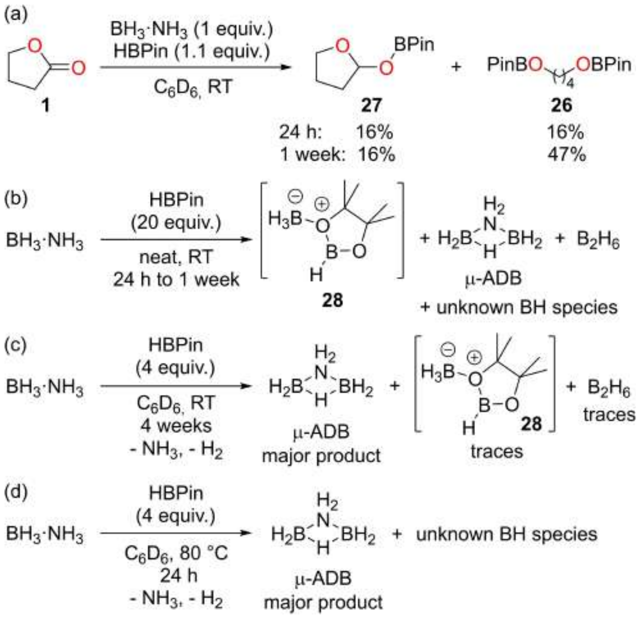


Scheme 2. Scope of AB-catalyzed hydroboration reactions. Conversions were determined by ^{1}H-NMR using either mesitylene or 1,3,5-trimethoxybenzene as internal standards. [a] Unless noted otherwise. [b] In 12 h. [c] In neat HBPin (4 equiv.); 12 h, 25 °C. [d] At 80 °C. [e] At 50 °C. [f] Isolated yield of the corresponding alcohol product. [g] In 0.65 M solution of C_6H_6; 24 h at 80 °C. [h] In neat HBPin (4 equiv.); 24 h, 80 °C.

conv. in 12 h at 25 °C) in the presence of equimolar amounts of methyl benzoate (see Figure S1 in the SI). Lastly, AB was also found active in the hydroboration of diethyl carbonate, showing 68 % conversion to EtOBPin and MeOBPin (Scheme 2).

To shed some light on the mechanism of AB-catalyzed hydroboration reactions and the observed difference in catalytic activities of AB and $BH_3 \cdot SMe_2$, we performed a series of control experiments. First, the stoichiometric treatment of γ-butyrolactone with AB in C_6D_6 at 25 °C did not show any productive reaction within 24 h. Heating this mixture at 80 °C for 24 h resulted in the partial conversion of AB to cyclotriborazane (CBT; $B_3N_3H_{12}$) ($\delta_B = -12.1$ ppm; *t*, $^1J_{B\text{-}H} = 102.9$ Hz);[15] however, only trace amounts of the lactone reduction product were detected. On the other hand, the treatment of a 1:1 mixture of AB and γ-butyrolactone with 1.1 equiv. of HBPin in C_6D_6 at 25 °C resulted in a mixture of the diborate product **26** and a borylated lactol **27** (Scheme 3a). In contrast, almost selective formation of $PinBOCH_2OEt$ (90 %) was observed upon AB-catalyzed hydroboration of ethyl formate in neat HBPin (4 equiv.) at 25 °C for 12 h.[13] These observations suggest that the reduced reactivity of esters vs. lactones in AB-catalyzed hydroboration reactions is likely a result of more arduous C–O bond cleavage of the acetal intermediates derived from esters.

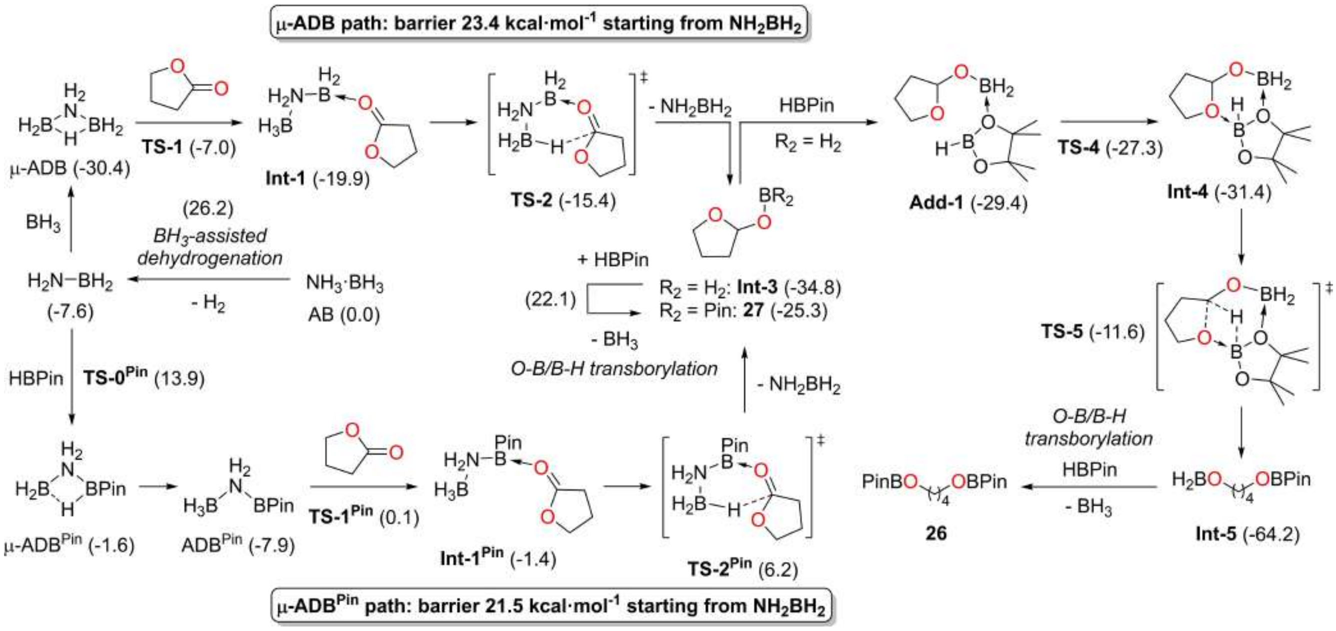
The room temperature solvent-free treatment of AB with 20 equiv. of HBPin for 24 h (Scheme 3b) revealed the formation of trace amounts of a $BH_3 \cdot HBPin$ adduct **28** ($\delta_B = -13.6$ ppm; *q*, $^1J_{B\text{-}H} = 98.3$ Hz)[6i] and an unknown four-coordinate boron species having one terminal B–H ($\delta_B = -14.5$ ppm; *br d*, $^1J_{B\text{-}H} = 160.3$ Hz).[13] Traces of μ-aminodiborane (μ-ADB)[12b,16] ($\delta_B = -27.8$ ppm[17]) and B_2H_6 ($\delta_B = 16.6$ ppm[18]) could be also detected by $^{11}B\{^1H\}$-NMR. Leaving this reaction at 25 °C for a week resulted in an accumulation of μ-ADB and the formation of a mixture of products mainly consisting of **28** (minor product) and μ-ADB (major product) (see Figure S22 in the SI). When AB was treated with 4 equiv. of HBPin in C_6D_6, no productive reaction was observed within 24 h at 25 °C. However, leaving this reaction for 4 weeks resulted in the partial dehydrogenation of AB and the generation of μ-ADB, along with trace amounts of B_2H_6 and **28** (Scheme 3c and Figure S24 in the SI). Repeating the reaction in C_6D_6 at 80 °C for 24 h (Scheme 3d) revealed almost complete consumption of AB accompanied by the release of H_2 and formation of a mixture of B_2H_6, μ-ADB, and the previously observed unknown four-coordinate boron species ($\delta_B = -14.5$ ppm[13]). Only traces of the $BH_3 \cdot HBPin$ adduct **28** were detected by $^{11}B\{^1H\}$-NMR (see Figures S25–S27 in the SI). Noteworthy, partial dehydrogenation of AB to μ-ADB, cyclotriborazane (CBT; $B_3N_3H_{12}$),[15] and borazine ($B_3N_3H_6$; $\delta_B = 29.5$ ppm)[15] was also observed upon thermolysis of AB in C_6D_6 at 80 °C for 24 h in the absence of HBPin.[13] Finally, both **28** (minor) and μ-ADB (major) were detected in the $^{11}B\{^1H\}$-



Scheme 3. Mechanistic control experiments.

NMR spectra taken directly from reaction mixtures after AB-catalyzed hydroboration of ethyl formate in neat HBPin (see Figure S12 in the SI) and hydroboration of γ-valerolactone with HBPin in C_6D_6 (see Figure S30 in the SI). Altogether, these observations suggest that apart from the BH_3-mediated route, reported previously by Fontaine et al. for $B(OH)_3$-catalyzed reactions,[6i] the AB-catalyzed hydroboration of lactones and esters could also include a concurrent μ-aminodiborane-mediated pathway (Scheme 4), although, the possible participation of polyaminoborane species cannot be completely ruled out. Such involvement of μ-aminodiboranes could render the observed greater catalytic activity of AB vs. $BH_3\cdot SMe_2$ and agrees well with the recently reported reactivity of μ-ADB with esters[12b] and carboxamides.[19]

To gain a better understanding of the role of μ-aminodiborane species, we performed density functional theory (DFT)[20] studies of the μ-ADB-mediated hydroboration of γ-butyrolactone.[13] Geometries were optimized using the meta-GGA functional M06-L[21] and the def2-SVP[22] basis set. Single-point calculations were conducted on the optimized geometries with the range-separated meta-GGA hybrid functional ωB97M-V[23] and the def2-TZVPP[22] basis set. This method demonstrated a high accuracy in comparison to high-level ab initio method results in our previous work.[24] The DFT-derived mechanism with ωB97M-V/def2-TZVPP is shown in Scheme 4 (calculations with M06-L/def2-SVP are shown in the SI and revealed very similar results). Note that the BH_3-catalyzed route has been previously investigated by Fontaine et al.[6i] The generation of μ-ADB could occur via the dehydrogenation of AB with BH_3 (for low-temperature reactions; see Scheme S2 in the SI) and/or via thermal dehydrogenation of AB to NH_2BH_2 (for instance, during high-temperature transformations with esters), followed by the abstraction of BH_3 from AB.[13] Both routes were previously reported by Nguyen and Dixon et al.[16,25] In addition, thermal dehydrogenation of AB to μ-ADB at 80 °C was observed experimentally (vide supra), and such thermolysis of AB to μ-ADB was previously suggested as a key step in the catalyst-free reduction of nitriles with AB.[15] The reaction of μ-ADB with γ-butyrolactone generates the borylated lactol intermediate **Int-3** and NH_2BH_2 (Scheme 4). This process is exergonic by 4.4 $kcal\cdot mol^{-1}$ and has an associated barrier of 23.4 $kcal\cdot mol^{-1}$ for the formation of the μ-ADB-lactone adduct (**Int-1**). Subsequently, **Int-3** may be involved in the O–B/B–H transborylation[6i] with HBPin ($\Delta G^{\neq}=22.1\ kcal\cdot mol^{-1}$; Scheme 4) to liberate **27** (observed experimentally; Scheme 3a) and BH_3, or undergo either an intramolecular C–O bond cleavage ($\Delta G^{\neq}=24.4\ kcal\cdot mol^{-1}$; see Scheme S1 in the SI)[12b] or addition of HBPin via **TS-5** with an associated barrier of 23.2 $kcal\cdot mol^{-1}$ (Scheme 4). The latter pathway was found to be somewhat more energetically favorable[13] and provides the borylated diol intermediate **Int-5**, which after O–B/B–H transborylation with HBPin affords **26** and BH_3.[6i] μ-ADB can be then recovered by the reaction of NH_2BH_2 with the released BH_3.[16,25] However, considering relatively low concentrations of BH_3 in the reaction mixture under catalytic conditions, an alternative and more likely scenario involves the reaction of NH_2BH_2 with HBPin ($\Delta G^{\neq}=21.5\ kcal\cdot mol^{-1}$; Scheme 4 and Scheme S2 in the SI), present in the system in large excess (2.5–4.0 equiv. to the substrate). This affords $H_2B(\mu\text{-}NH_2)(\mu\text{-}H)BPin$ (μ-ADB^{Pin}), which analogously to μ-ADB could mediate the hydroboration of lactones to borylated lactols with an even lower energy barrier of 14.1 $kcal\cdot mol^{-1}$ (Scheme 4).[13] Such a predominant μ-ADB^{Pin} route is also supported by experimental observations, showing no reduction of γ-butyrolactone with AB in the absence of HBPin (vide supra).



Scheme 4. A plausible mechanism of the μ-aminodiborane-mediated (μ-ADB and μ-ADB^{Pin}) hydroboration of γ-butyrolactone with HBPin. Relative (to AB) Gibbs free energies were obtained using ωB97M-V/def2-TZVPP//M06-L/def2-SVP in benzene and are given in $kcal\cdot mol^{-1}$.

Conclusions

In summary, we have demonstrated a rare example of a metal-free methodology for efficient hydroborative cleavage of lactones and esters to alcohols using easy-to-handle AB as a pre-catalyst. The developed method shows a broad substrate scope, and reactions could be performed under solvent-free conditions. Moreover, chemoselective reduction of lactones in the presence of esters was accomplished. Combined experimental and DFT mechanistic studies revealed a novel μ-aminodiborane-mediated route, resulting in the greater catalytic activity of AB compared to $BH_3 \cdot SMe_2$ and $BH_3 \cdot THF$. Such reactivity of amine-boranes can now be transferred to other metal-free hydroboration reactions, and their further applications as hydroboration (pre)catalysts are currently under investigation in our laboratories.

Experimental

General Details

All manipulations were carried out using conventional inert atmosphere glovebox (LC Technology Solutions Inc.) and Schlenk techniques. Benzene, benzene-d_6, and THF-d_8 were purchased from Sigma-Aldrich (Merk) and additionally dried by distillation from sodium. All reagents, including ammonia borane (AB), HBPin, diethyl carbonate, lactones, formates, and esters (except methyl 4-methoxybenzoate, methyl 4-chlorobenzoate, methyl 3-nitro benzoate and methyl 3-(trifluoromethyl)benzoate, which were prepared from MeOH and the corresponding carboxylic acids[26]) were purchased from VWR and Sigma-Aldrich (Merk) and used without further purification. NMR spectra were obtained with JEOL ECA-500 MHz spectrometer (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{11}B: 160 MHz, and ^{19}F: 471 MHz). All catalytic reactions were performed using 10 mL and/or 20 mL pressure vials (Supelco headspace vials) equipped with magnetic screw caps having PTFE-faced butyl septa. Mechanistic studies were performed using NMR tubes equipped with Teflon valves. For details of computation studies, see the Supporting Information.

General Procedure for Hydroboration Reactions

Conditions A: Reactions in Benzene. HBPin (1175.3 μL, 8.1 mmol; 2.5 equivalents to the substrate) was mixed with a lactone or an ester (3.24 mmol) in C_6D_6 (or C_6H_6) to reach 0.65 M or 1.82 M mixture. The resulting mixture was added to a solid $NH_3 \cdot BH_3$ (5.0 mg, 0.162 mmol; 5.0 mol% to the substrate) in a Supelco headspace vial, which was sealed with a magnetic screw cap having PTFE-faced butyl septum. Depending on the substrate, the resulting mixture was left with stirring for 12–24 h either at room temperature or at 50 or 80 °C (oil bath). After the completion of the reaction, either mesitylene or 1,3,5-trimethoxybenzene (0.1–0.2 equiv. to the substrate) as internal standards were added, and the mixture was transferred to an NMR tube and submitted for NMR analysis. Conversions of the substrates and yields of the hydroboration products were calculated by the integration of product resonances against those for internal standards. Control experiments without the catalyst (Table S1 in the SI, entries 1, 2, 20, and 21) and hydroboration experiments with 5 mol% of $BH_3 \cdot SMe_2$, $BH_3 \cdot THF$, $B(OH)_3$, BPh_3, $NaBPh_4$, and $KB(C_6F_5)_4$ (Table S1 in the SI, entries 12–19 and 32) were performed analogously.

The products of AB-catalyzed hydroboration of δ-hexalactone, caprolactone, (+)-Sclareolide, and methyl 4-chlorobenzoate (compounds **8**, **10**, **11**, and **23** in Scheme 2, respectively; reactions were performed as described above at 1.82 M concentrations) were isolated as the corresponding alcohols. For the reduction of δ-hexalactone (**8**) and caprolactone (**10**), after the reaction completion, the solvent was evaporated, and the residue was stirred with MeOH (15 mL) for 4.5 h at room temperature. The resulting mixture was filtered, MeOH was pumped off, and the product was purified by silica gel column chromatography using an ethyl acetate/petroleum ether mixture (2 : 1) as eluent to give 326 mg of hexane-1,5-diol as a yellow oil (85% yield) and 356 mg of 1,6-hexanediol as a white powder (93% yield).

For hydroboration of (+)-Sclareolide (**11**) and methyl 4-chlorobenzoate (**23**), after the reaction completion, the resulting mixture was diluted with 10 mL of benzene and filtered through Celite. The filtrate was concentrated to approximately 5 mL, 1 M aqueous NaOH (30 mL) was added, and the mixture was stirred for 1 h at room temperature. The crude mixture was then extracted with diethyl ether (3×20 mL) and the collected organic extract was dried with anhydrous magnesium sulfate. The solution was filtered and evaporated, and the products were purified by silica gel column chromatography using ethyl acetate/petroleum ether mixtures as eluents (1 : 2 and 1 : 5 for Ambradiol and 4-chlorobenzyl alcohol, respectively). Isolated yields of Ambradiol (753 mg, white solid) and 4-chlorobenzyl alcohol (360 mg, white solid) were found to be 91% and 78%, respectively. NMR data for all isolated alcohols can be found in the Supporting Information.

Conditions B: Solvent-Free Reactions. HBPin (1880.5 μL, 12.96 mmol; 4 equivalents to the substrate), a lactone or an ester (3.24 mmol), and $NH_3 \cdot BH_3$ (5.0 mg, 0.162 mmol; 5.0 mol% to the substrate) were mixed in a Supelco headspace vial, which was sealed with a magnetic screw cap having PTFE-faced butyl septum. Depending on the substrate, the resulting mixture was left with stirring for 12–24 h either at room temperature or at 50 or 80 °C (oil bath). After the completion of the reaction, 0.1–0.2 equiv. of mesitylene or 1,3,5-trimethoxybenzene (internal standards) and 0.6 mL of C_6D_6 were added, and the resulting mixture was transferred to an NMR tube and submitted for NMR analysis. Yields of the hydroboration products were calculated by the integration of product resonances against those for internal standards. Control solvent-free experiments without the catalyst (Table S1 in the SI, entries 3 and 22) and solvent-free hydroboration reactions with 5 mol% of $BH_3 \cdot SMe_2$ in place of $NH_3 \cdot BH_3$ were performed analogously.

Supporting Information

Complete experimental details, control experiments, spectral and computational data, as well as relevant figures, can be found in the Supporting Information at https://doi.org/10.1002/cctc.202400876.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: ammonia borane · hydroboration · lactones · esters · aminodiborane

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