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# Ammonia borane as a metal free reductant for ketones and aldehydes: a mechanistic study

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ABSTRACT

Without a catalyst ketones and aldehydes were reacted in THF with ammonia borane (**AB**) to proceed hydroboration forming alkyl borates. Mechanistic studies revealed that dissociation of ammonia from **AB** occurred before the hydroboration step. When methanol was used as the solvent, metal free methanolysis of **AB** would take place with the ketone/aldehyde being directly hydrogenated by the $MeOH \cdot BH_3$ complex.



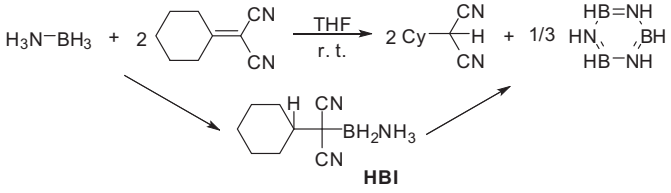
## 1. Introduction

Ammonia borane ($NH_3BH_3$, **AB**) has attracted great attention as a potential hydrogen storage material with very high volumetric and gravimetric storage densities.[1] Chemical $H_2$ storage requires reactions for fueling and re-fueling of the storage compounds. In this context intensive studies were carried out on the dehydrogenations of **AB**,[2] either thermally,[3] catalytically[4] or by other methods.[5] Besides these dehydrogenation reactions, we became interested in its use as an in situ hydrogen source for direct reduction of polar unsaturated compounds, which constitutes an important fundamental reaction mode of organic synthesis.

We have previously reported that polarized olefins, such as 2-cyclohexylidenemalononitrile can be hydrogenated by **AB** as a hydrogen donor without use of a catalyst.[6] A hydroboration intermediate **HBI** was detected in low temperature NMR studies indicating a two-step mechanism with hydride before proton transfer (Scheme 1).[7]

Hydrogenation of aromatic imines bearing polar C=N double bonds could also be achieved applying **AB**.[8] Detailed mechanistic studies revealed a 'polarity matched' concerted pathway with a double-hydrogen transfer process.

Ketones and aldehydes, possessing a polarized C=O bond related to imines, were now subjected to reactions with **AB**. We presumed mechanistic analogies for all these H transfer processes.




**Scheme 1.** Transfer hydrogenation of polarized olefin by **AB** via the hydroboration intermediate **HBI**.

## 2. Results and discussions

### 2.1. Reactions of ketones and aldehydes with AB in THF

Benzophenone (**1a**) indeed reacts with **AB** in THF at room temperature, but at a rather low rate, which could naturally be accelerated by heating (Table 1, entry 1). However, diphenylmethanol (**2a**) originating from transfers of the $H_B$ and $H_N$ atoms of **AB** could not be detected by in situ NMR investigations (Scheme 2). The $^{11}B$ NMR spectrum revealed that an alkyl borate was formed (signal at 19 ppm in $^{11}B$ NMR). $^1H$ and $^{13}C$ NMR studies confirmed that hydroboration of **1a** had taken place establishing the tribenzhydryl borate **3a** (Scheme 2). Related hydroboration reactions were also reported from the reactions of ketones with other B–H containing compounds.[9] Only $H_B$ and not $H_N$ of **AB** seemingly got involved in the reaction, since a broad signal appeared in the $^1H$ NMR spectra at 0.4 ppm belonging to free ammonia ($NH_3$).

Reactions of **AB** with various ketones were carried out to yield the corresponding hydroboration products (Table 1). In most of

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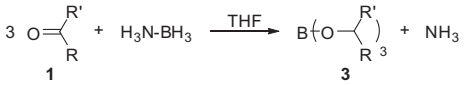
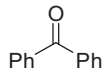
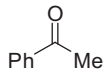
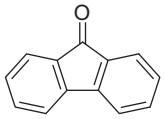
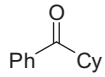
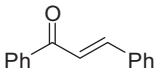
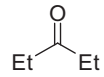
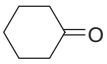
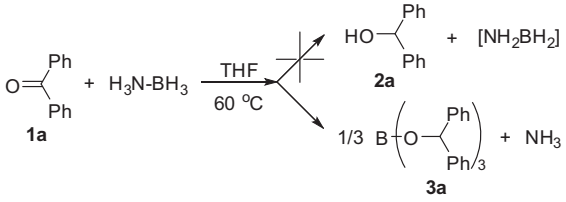
**Table 1**
Hydroboration of ketones with **AB**



| Entry | Substrate | | Temperature | Time[a] |
|---|---|---|---|---|
| 1 |  | **1a** | rt<br>60 °C | 1 day<br>2 h |
| 2 |  | **1b** | 60 °C | 1.5 h |
| 3 |  | **1c** | 60 °C | 1.5 h |
| 4 |  | **1d** | 60 °C | 4 h |
| 5[b] |  | **1e** | 60 °C | 10 h |
| 6 |  | **1f** | 60 °C | 1 h |
| 7 |  | **1g** | rt | 0.5 h |

[a] Required reaction time for completely hydroboration of the ketones by **AB** with 2/1 molar ratio (**AB** in slightly excess).
[b] The hydroboration reaction occurred mainly at the C=O bond.

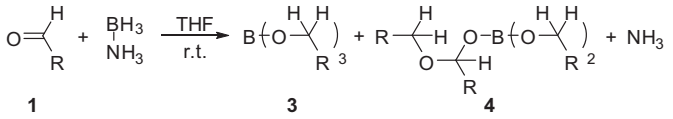


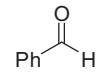
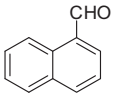
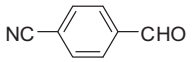
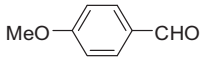
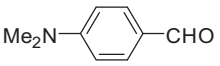
**Scheme 2.** Reaction of benzophenone (**1a**) with **AB** in THF at 60 °C producing **3a** via hydroboration.

the ketone reactions temperatures of 60 °C were required and the reactions were completed within several hours (entries 1–6). Cyclohexanone **1g** was the only exception among the tested ketones, which was converted by **AB** under milder conditions requiring only half an hour at room temperature (entry 7).

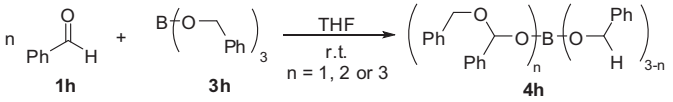
The hydroboration reactions were found to be much faster with aldehydes than with ketones. Benzaldehyde (**1h**) was completely hydroborated at room temperature in less than half an hour (Table 2, entry 1). Beside the tribenzyl borate **3h**, acetal derived borate esters were additionally obtained even in presence of excess **AB**. The more reactive aldehyde **1h** seemed to undergo a follow-up process. NMR studies revealed the existence of new borate esters bearing $PhCH_2$–O–CH–O units like in **4h**, formed via a subsequent step or steps of **3h** with **1h** (Scheme 3).[10] The exact composition of **4h**, in particular whether $n$=1 or 2 could not be determined due to the instability of the borate compound to GC, MS, column chromatography and severe signal overlaps in the $^{11}$B NMR and $^{1}$H NMR spectra.

**Table 2**
Hydroboration of aldehydes with **AB**



| Entry | Substrate | | Time[a] | **3**/**4**[b] |
|---|---|---|---|---|
| 1 |  | **1h** | 0.5 h | 0.6/0.4 |
| 2 |  | **1i** | <0.5 h | 0.8/0.2 |
| 3 |  | **1j** | <5 min | 0.7/0.3 |
| 4 |  | **1k** | 1.5 h | 0.7/0.3 |
| 5 |  | **1l** | >2 days | 0.8/0.2 |

[a] Required reaction time for completely hydroboration of the aldehydes by **AB** with 2/1 molar ratio of aldehydes to **AB**.
[b] The molar ratio of the borate esters **3** to **4** were determined by integrations of the –O–*CH*–O– in compassion to that of the –*CH*$_2$–O– portion of the in situ $^{1}$H NMR spectra.



**Scheme 3.** Insertion reactions of benzaldehyde (**1h**) into tribenzyl borate (**3h**) forming the borate esters **4h**.

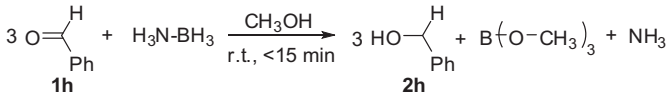
Similar reactions were observed in the hydroborations of other aldehydes with **AB** varying however in the product ratios of type **3** and **4** compounds (Table 2, '*n*' assumed to be 1).

It is worth mentioning that we tested the reaction of **AB** with phenylmethanol **2h**, which was found to be very slow, only trace amounts of **3h** were observed in the $^{11}$B NMR spectrum after several hours even at 60 °C. Since no alcohol **2h** was detected in the reaction mixture of **1h** with **AB** in THF, the formation of **3h** via the subsequent reaction of **2h** with **AB** was excluded to proceed.

## 2.2. Reactions of ketones and aldehydes with AB in methanol

Alcohol metathesis of the trialkyl borates in methanol was a convenient way to set the alcohols from the trialkyl borates.[9b] In this context it should be mentioned that the direct alcoholysis of **AB** always needs a transition metal catalyst.[11] In addition the methanolysis of the borate ester could accelerate the hydroboration process under certain kinetic circumstances. Therefore, **AB** was put in methanol together with **1h**. Compound **2h** and trimethyl borate were formed spontaneously at room temperature, while the acetal derivatives (alcoholysis products of **4h**) were nearly undetectable (Scheme 4). On total the formation of **2h** constitutes by hydrogenation of **1h** via consecutive transfer of hydride and proton.

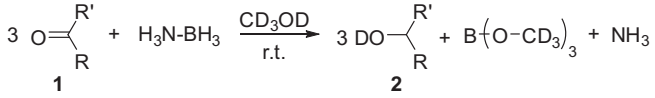
This metal free methanolysis of **AB** was tested by NMR scale reactions with a broad range of ketones and aldehydes using deuterated methanol. In all cases the corresponding alcohol and




**Scheme 4.** Metal free methanolysis of **AB** and hydrogenation of benzaldehyde **1h**.

trimethyl borate were obtained nearly quantitatively (Table 3), and the reactions became faster than the hydroborations in THF, only several minutes to several hours were required at room temperature.

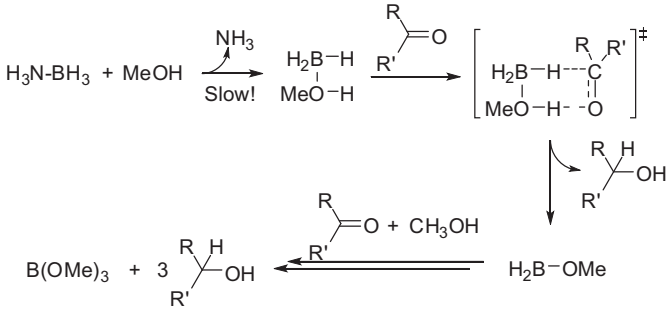
**Table 3**
Hydrogenation of ketones and aldehydes with **AB** in methanol-$d_4$




| Entry | Substrate | Product | Time[a] |
|---|---|---|---|
| 1 | **1a** | **2a** | 3 h |
| 2 | **1b** | **2b** | 6 h |
| 3 | **1c** | **2c** | 1 h |
| 4 | **1d** | **2d** | 4 h |
| 5 | **1e** | **2e** | 6 h |
| 6 | **1f** | **2f** | 2 h |
| 7 | **1g** | **2g** | 15 min |
| 8[b] | **1h** | **2h** | 10 min |
| 9 | **1i** | **2i** | 10 min |
| 10 | **1j** | **2j** | <5 min |
| 11 | **1k** | **2k** | 1 h |
| 12 | **1l** | **2l** | 1 days |

[a] Required reaction time for completely hydrogenation of the unsaturated substrates **1** by **AB** with 2/1 molar ratio of **1** to **AB**.
[b] The formation of the acetal derived alcohol was not obtained to the limit of NMR, neither for other aldehydes.

The acceleration might come about via hydrogen bonding of methanol in crucial transition states of the hydroboration step, or via formation of a MeOH·$BH_3$ complex from **AB**, which undergoes double H transfer to the substrate with a complete switch in the mechanism.[12] Unfortunately these two mechanisms cannot easily be distinguished by the tool of isotopic substitution as applied to unravel the mechanisms for the hydroboration reactions in THF. The enormous acceleration is explained on the basis of the appearance of a new double H transfer transition state, apparently low-lying in energy (Scheme 5).




**Scheme 5.** Possible reaction route for transfer hydrogenation of carbonyl compounds by **AB** in methanol.

## 3. Mechanistic studies of the hydroboration process

### 3.1. Deuterium labeling and kinetic isotope effects

Further studies were envisaged to clarify the way of the $H_B$ atoms transfer and potentially also the transfer of the $H_N$ atoms of **AB** in THF. Benzophenone **1a** was exemplarily employed to react with deuterated **AB** derivatives $BD_3NH_3$ (**AB**(**D**)), $BH_3ND_3$ (**A**(**D**)**B**), and $BD_3ND_3$ (**A**(**D**)**B**(**D**)) in THF at 60 °C, respectively. The reactions were pursued by various NMR spectroscopies.

In the reaction of **1a** with **AB**(**D**), a $D_C$ signal was observed at 6.4 ppm in the $^2$H NMR spectrum and a $C_D$ triplet in the $^{13}$C NMR spectrum, which corresponded to the –CD–O– fragment of the borate ester **3a**. From the reaction with **A**(**D**)**B**, only a $D_N$ signal was observed at 0.4 ppm in the $^2$H NMR spectrum, which was expected to belong to the $ND_3$ unit. In the sample reacted with **A**(**D**)**B**(**D**), no signals other than the mentioned $D_C$ and $D_N$ resonances were observed. Such findings exclude the formation of diphenylmethanol **2a**, which would be expected as the product of a transfer hydrogenation process.

The deuterium kinetic isotope effects (DKIE) were then investigated using excess amounts of **1a** to react with deuterated **AB** derivatives in THF at 60 °C (Fig. 1). Small primary DKIE values ($k_{AB}/k_{AB(D)}$=1.28 and $k_{A(D)B}/k_{A(D)B(D)}$=1.10) were determined with the ratios of the $H_B/D_B$ transfer rates indicating that the cleavages of the B–H bonds were only to some minor extent involved in the rate determining step (RDS).[13] Since there are three B–H bonds broken during the reaction course, the small DKIE may in addition suggest that only one of the B–H bonds breakage had kinetic influence.

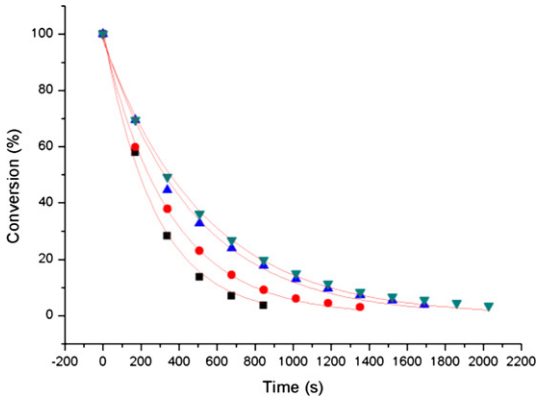



**Fig. 1.** Conversion chart of the reactions of 0.5 mmol **1a** with 0.1 mmol **AB**, **AB**(**D**), **A**(**D**)**B** or **A**(**D**)**B**(**D**) pursued by in situ $^{11}$B NMR in THF at 60 °C determined by the intensities of the boron signals in the $^{11}$B NMR spectra with 3 min intervals. The black squares stand for reactions with **AB**, red circles for **AB**(**D**), blue triangles for **A**(**D**)**B** and green triangles for **A**(**D**)**B**(**D**). Simulated DKIE values are: $k_{AB}/k_{AB(D)}$=1.28, $k_{AB}/k_{A(D)B}$=1.74, $k_{A(D)B}/k_{A(D)B(D)}$=1.10, and $k_{AB(D)}/k_{A(D)B(D)}$=1.49.

Normal DKIE values ($k_{AB}/k_{A(D)B}$=1.74 and $k_{AB(D)}/k_{A(D)B(D)}$=1.49) were observed in the reactions with the $H_N/D_N$ derivative (Fig. 1). Since $D_N$ incorporation was not detected in the product, it is supposed that the dissociation of $NH_3$ from **AB** became involved in the RDS exerting a secondary kinetic isotope effect. This would cope with related reports by H. C. Brown and Chandrasekharan.[14] For a secondary DKIE the given values were however large,[15] presumably due to relatively strong dihydrogen bonding in the respective transition state.[16]

### 3.2. Transfer hydrogenation followed by alcoholysis?

In order to exclude the possibility of a primary transfer hydrogenation of the C=O bond followed by alcoholysis of **AB**, an NMR sample with a 4/1 molar ratio of **1a** with **AB** was prepared in THF-$d_8$ and pursued by $^{11}$B NMR at low temperatures to acquire details of this reaction course. However, the expected dehydrocoupling products of **AB**, such as cyclotriborazane (**CTB**), B-(cyclodiborazanyl)aminoborohydride (**BCDB**) or borazine (**BZ**) were not found in the mixture, even at temperatures as low as –80 °C. This clearly excluded transfer hydrogenation with **AB** to take place before hydroboration.

Nevertheless, lowering of the temperature caused the signal for **3a** at around 19 ppm to decrease, while a broad signal gradually increased at around 2 ppm (Fig. 2). These two signals seemed to be in equilibrium and changed in intensity on each other's expense with increasing or decreasing temperature. The signal at 19 ppm turned reversibly into the signal at 2 ppm with lowering of the temperature.

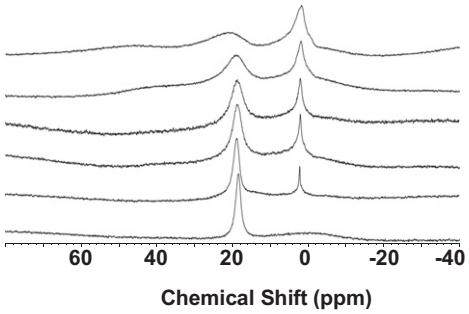
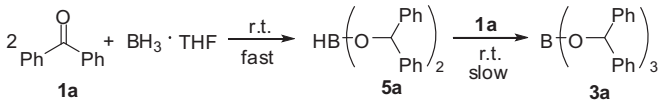



**Fig. 2.** In situ $^{11}$B NMR spectra at various temperatures for the completed reaction of **1a** and **AB** with 4/1 molar ratio in THF. Temperatures (in °C) from top to bottom: −80, −60, −40, −20, 0, 20. Besides a notable signal broadening with decreasing temperature, reversible exchanges between the two resonances at 19 ppm and 2 ppm occurred.

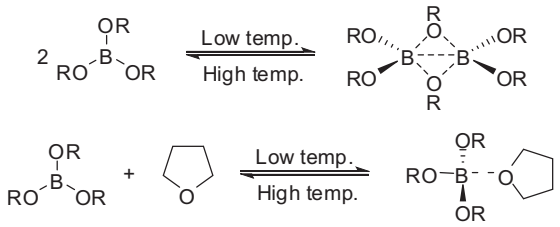
On the other hand, no significant difference was observed in the $^{1}$H and $^{13}$C NMR spectra at different temperatures except for a small shift of the broad signal for the $NH_3$ unit at 0.4 ppm in the $^{1}$H NMR spectrum. This could be explained in terms of fast and reversible coordination of $NH_3$ to a tricoordinate boron center. At room temperature, the ammonia dissociation became more prominent, recognizable in the $^{11}$B NMR via a low field shift (19 ppm). At lower temperatures the ammonia equilibrium shifts to the associated side showing then preference for the four-coordinated boron compound indicated by the signal at relatively high field at around 2 ppm. However, this assumption seems not fully valid. The ammonia attachment to boron could occur, but was not expected to be the dominating factor, since evacuation of the NMR tube and removal of all volatiles including the solvent furnished the same temperature dependent NMR behavior as described before.

Apparently the ammonia part of **AB** did not get involved in the hydroboration process. Therefore it seemed possible that other borane complexes, like $BH_3$·THF, would furnish the same or similar hydroboration results. Thus, $BH_3$·THF was reacted with **1a** at room temperature in THF. Formation of the dialkoxy borine derivative **5a** was observed at room temperature immediately after the sample was prepared, the same product as the reaction of diborane with ketones and aldehydes.[17] Compound **5a** slowly reacted with another equivalent of the substrate at room temperature, forming the boron ester compound **3a** (Scheme 6). In absence of $NH_3$, the boron ester exhibited the same temperature dependent equilibrium as shown in the NMR of Fig. 2.




**Scheme 6.** Hydroboration of benzophenone with $BH_3$·THF.

Up to now, there are still two possible equilibria hidden by the signals of the temperature dependent NMR equilibrium of Fig. 2: (a) a monomer–dimer equilibrium, which would lead to a four-coordinate borate dimer via two bridging oxygens prevailing at lower temperatures (Scheme 7, top); or (b) a complexation equilibrium of the borate ester with THF (Scheme 7, bottom).

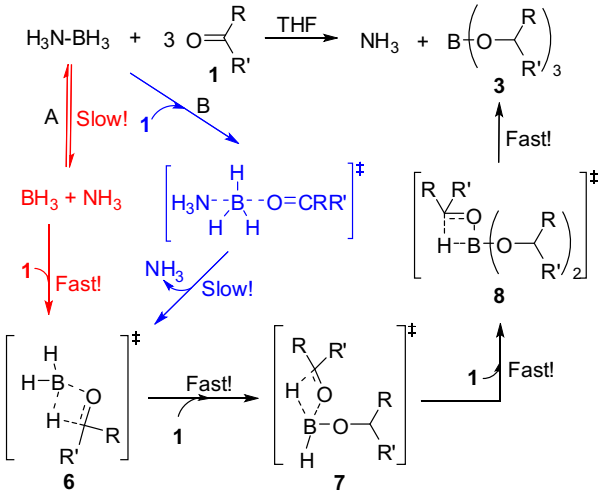



**Scheme 7.** Potential temperature dependent equilibria for borate esters in THF.

These two possibilities could be distinguished by substitution of the more donating solvent THF with less donating solvents, such as toluene. Thus, **3a** was dissolved in toluene and $^{11}$B NMR spectra were measured at low temperatures. The complete disappearance of the signal at 2 ppm clearly excluded dimer formation and stressed the importance of THF adducts.

### 3.3. Reaction course of the hydroboration in THF

Earlier reports on the mechanism of the hydroboration of carbonyl containing compounds involved a four-centered transition state, similar to that of **6**.[18,19] Our studies on ketone and aldehyde hydroborations support this hypothesis in the formation of alkyl borates (Scheme 8):




**Scheme 8.** Mechanism for the hydroboration of ketones and aldehydes with **AB**.

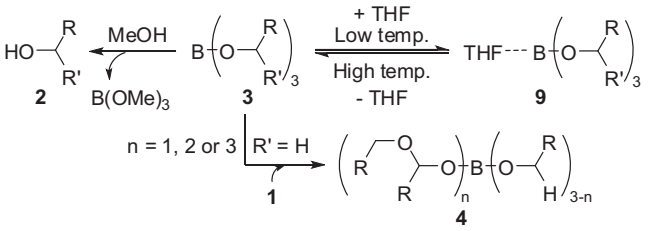
The first step and also the RDS could be the dissociation of $NH_3$ from **AB**. There are two possible pathways as shown in Scheme 8 (pathway A in red and B in blue). Along pathway A, dissociation of $NH_3$ from **AB** occurred first, then free $BH_3$ would coordinate the aldehyde or the ketone **1**, which insert into a B–H bond presumably via the four-membered ring structure **6** ($SN_1$ type). Along pathway B, release of $NH_3$ occurs by a $SN_2$ type replacement with **1** at **AB**, where steric pressure at the boron center would enforce $NH_3$ to leave and then to form **6**. Since no intermediate nor significant signal shifts were detected in the low temperature NMR studies, path A seems to be more reasonable. After this primary hydroboration step, another two substrate molecules would get to react with **6** via two related four-membered transition states **7** and **8** finally leading to the type **3** products.

With each consecutive hydroboration step it becomes more difficult for the substrate to access to the boron center. In Table 1 mono- and diaryl ketones of various steric demands are shown to

be subjected to the hydroboration reaction. Compared to **1a**, acetophenone (**1b**) and 9*H*-fluoren-9-one (**1c**) are less bulky, while cyclohexyl(phenyl)-methanone (**1d**) and (*E*)-chalcone (**1e**) are quite sterically hindered. The elapsed reaction times mirror this steric order: **1b** and **1c** require shorter reaction time, while **1d** and **1e** longer ones. The least sterically hindered ketone **1g** can react fastest with **AB** at room temperature stressing further the importance of the steric influence on the reaction rates.

A concerted transition state as in **6** accumulates electron density at the $C_C{=}O$ atoms.[20] Thus, substituents that help to decrease the electron density at this center would support the hydroboration process. Compounds **1j**, **k**, and **l** are *para*-substituted benzaldehyde derivatives. The electron withdrawing (EWD) group −CN substituted aldehyde **1j** reacted with **AB** much faster than **1h**, while the electron donating groups −OMe and $-NMe_2$ substituted substrates **1k** and **1l** displayed slower reactions (Table 2, entries 1 and 3–5). As mentioned before, such observations are supportive of a concerted transition state.[19,20]

Three types of reactions might occur with **3** as shown in Scheme 9: (1) if the reaction take place in THF, reversible complexation of **3** with THF forming the 4-coordinate borate **9**, in particular when the temperature is decreased; (2) compounds of type **3** could be reacted with methanol (or other lower alcohols) via alcohol metathesis giving trimethyl borate and the corresponding alcohol **2**; (3) For aldehydes, compounds of type **3** could be reacted further with **1** to end up in a mixture of **3** and **4**.




**Scheme 9.** Possible reactions concerning borate ester **3**.

## 4. Conclusion

In conclusion, as a class of unsaturated compounds containing polar C=O bonds, ketones and aldehydes can react with ammonia borane under mild conditions. In the reactions with THF as the solvent, borate esters as the only organic products are formed by hydroboration with H atoms transfer from the $BH_3$ part, much different from the reactions of ammonia borane with other polar unsaturated compounds, such as imines and polar olefins, which are hydrogenated with the transfers of both $H_B$ and $H_N$ atoms from ammonia borane. The hydroboration of ketones is relatively slow but uniform, while for aldehydes, rapid hydroboration occurs followed by insertion of the starting aldehyde into at least one of the B–O bonds of the trialkyl borates. Mechanistic studies revealed that dissociation of ammonia from ammonia borane is rate determining. When methanol is used as the solvent, direct hydrogenation of the carbonyl compounds would occur from a initially formed $MeOH{\cdot}BH_3$, presumably via a single step double H transfer.

## 5. Experimental section

### 5.1. General

All the manipulations were carried out under a nitrogen atmosphere using Schlenk techniques or in a drybox (Model MB-150B-G). Reagent grade benzene, toluene, hexane, diethyl ether, and THF were dried and distilled from sodium benzophenone ketyl prior to use. All the ketones and aldehydes were purchased from Aldrich or Fluka and used after being degassed. Commercial methanol and $CD_3OD$ were applied for reactions in methanol. NMR spectra were measured on a Varian Mercury spectrometer at 200 MHz for $^1H$, Varian Gemini-2000 spectrometer at 300.1 MHz for $^1H$, 96.3 MHz for $^{11}B\{^1H\}$, and 75.5 MHz for $^{13}C\{^1H\}$ and on a Bruker-DRX-500 spectrometer at 500.2 MHz for $^1H$ and 125.8 MHz for $^{13}C\{^1H\}$. Chemical shifts for $^1H$ and $^{13}C$ are given in parts per million relative to TMS and those for $^{11}B$ relative to $Et_2O{\cdot}BF_3$.

All of these mentioned reactions were carried out at least twice to check for reproducibility.

### 5.2. Reactions of AB with ketones in THF

A 0.5 mm Young NMR tube was charged in the glove box with ketone (0.2 mmol, for kinetics 0.5 mmol), **AB** (0.1 mmol), and with dry THF-$d_8$ (0.6 ml) as the reaction media. The tube was sealed with a screw cap and then heated in an oil bath to 60 °C right after shaking. For dynamic NMR experiments, the samples were heated in the NMR machine. The reactions were monitored by $^1H$ and $^{11}B$ NMR every several minutes (depending on the reaction rates). The typical resonances of the starting materials gradually decreased (−22.4 ppm in $^{11}B$ NMR for **AB**) while new signals of the saturated products appeared (the −CH–O– in $^1H$ NMR and 19 ppm in $^{11}B$ NMR). The disappearance of the starting material indicated completion of the hydroboration, $^{13}C$ NMR spectra were then recorded. Only borate resonances were observed in the $^{11}B$ NMR (around 19 ppm) and the signals in the $^1H$ NMR spectra were slightly broadened due to the quadrupole effect of $^{11}B$. Finally the solvent and the released $NH_3$ were removed under reduced pressure, the residue in the NMR tube was pure borate ester to the limit of NMR with nearly 100% yield. The methanolysis of borate esters were carried out by addition of excess methanol, forming the corresponding alcohols and trimethyl borate, while trimethyl borate and the excess methanol can be removed by high vaccum.[9b]

*5.2.1. Tribenzhydryl borate (**3a**)[21].* White solid: $\delta_H$ (ppm; 300 MHz; THF-$d_8$) 6.18 (s, 0.5H, −C*H*–O), 6.41 (s, 3H, −C*H*–O), 7.21–7.24 (m, 35H, $-C_6H_5$); $\delta_C$ (ppm; 75.5 MHz; THF-$d_8$) 77.41 (−CH–O), 78.22 (−CH–O), 127.20, 127.26, 127.59, 127.73, 128.86, 128.96, 144.95, 145.57; $\delta_B$ (ppm; 96.3 MHz; THF-$d_8$) 18.79. Diphenylmethanol (**2a**) was obtained exclusively after methanolysis of **3a**.

*5.2.2. Tris(1-phenylethyl) borate (**3b**)[22].* Colorless gel: $\delta_H$ (ppm; 300 MHz; THF-$d_8$) 1.33 (d, $J$=6 Hz, 3H, $-CH_3$), 1.43 (d, $J$=6 Hz, 3H, $-CH_3$), 1.47 (d, $J$=6 Hz, 3H, $-CH_3$), 5.35–5.45 (m, 3H), 7.04–7.42 (m, 15H); $\delta_C$ (ppm; 75.5 MHz; THF-$d_8$) 25.77, 25.88, 25.95, 71.97 (−CH–O), 125.98, 126.10, 126.19, 127.35, 127.54, 127.66, 128.80, 128.87, 128.92, 146.51; $\delta_B$ (ppm; 96.3 MHz; THF-$d_8$) 18.00. 1-Phenylethanol (**2b**) was obtained exclusively after methanolysis of **3b**.

*5.2.3. Tri(9H-fluoren-9-yl) borate (**3c**).* White solid: [Found: C, 84.31; H, 5.19%. $C_{39}H_{27}BO_3$ requires C, 84.48; H, 4.91%]; $\delta_H$ (ppm; 300 MHz; THF-$d_8$) 6.30 (s, 3H), 7.25–7.38 (m, 8H), 7.66–7.72 (m, 8H); $\delta_C$ (ppm; 75.5 MHz; THF-$d_8$) 76.59 (−CH–O), 120.72, 126.18, 128.37, 129.71, 141.49, 145.83; $\delta_B$ (ppm; 96.3 MHz; THF-$d_8$) 19.89. 9*H*-Fluoren-9-ol (**2c**) was obtained exclusively after methanolysis of **3c**.

*5.2.4. Tris(cyclohexyl(phenyl)methyl) borate (**3d**).* Colorless gel: $\delta_H$ (ppm; 300 MHz; THF-$d_8$) 0.65–1.83 (m, 33H), 4.90 (d, $J$=6 Hz, 1H,

−C*H*−O), 4.95 (d, *J*=6 Hz, 2H, −C*H*−O), 6.71–7.32 (m, 15H); $\delta_C$ (ppm; 75.5 MHz; THF-$d_8$) 27.09, 27.16, 27.23, 27.28, 27.48, 27.60, 28.63, 29.03, 29.19, 30.20, 30.40, 30.49, 46.01, 46.11, 80.39 (−*C*H−O), 80.44 (−*C*H−O), 127.13, 127.28, 127.37, 127.40, 127.55, 128.38, 128.48, 128.57, 144.16, 144.29, 144.40; $\delta_B$ (ppm; 96.3 MHz; THF-$d_8$) 18.36. Cyclohexyl(phenyl)-methanol (**2d**) was obtained exclusively after methanolysis of **3d**.

*5.2.5. Tris((E)-1,3-diphenylallyl) borate (**3e**).* Colorless gel: $\delta_H$ (ppm; 300 MHz; THF-$d_8$) 6.06 (d, *J*=6 Hz, 3H, −C*H*−O−B), 6.31–6.57 (m, 3H, −C*H*=C), 6.65–6.83 (m, 3H), 7.19–7.53 (m, 30H); $\delta_C$ (ppm; 75.5 MHz; THF-$d_8$) 76.93 (−*C*H−O), 127.13, 127.23, 127.32, 127.48, 128.01, 128.09, 128.24, 129.19, 130.49, 130.65, 130.73, 132.21, 137.90, 143.70; $\delta_B$ (ppm; 96.3 MHz; THF-$d_8$) 19.53. (*E*)-1,3-Diphenylprop-2-en-1-ol (**2e**) was obtained exclusively after methanolysis of **3e**.

*5.2.6. Tripentan-3-yl borate (**3f**)*[23]. Colorless gel: $\delta_H$ (ppm; 300 MHz; THF-$d_8$) 0.91 (t, *J*=7.4 Hz, 18H, −$CH_3$), 1.36–1.55 (m, 12H), 4.00–4.08 (m, 3H, −C*H*−O); $\delta_C$ (ppm; 75.5 MHz; THF-$d_8$) 10.45, 29.90, 75.34 (−*C*H−O); $\delta_B$ (ppm; 96.3 MHz; THF-$d_8$) 18.07. Pentan-3-ol (**2f**) was obtained exclusively after methanolysis of **3f**.

*5.2.7. Tricyclohexyl borate (**3g**)*[23,24]. Colorless gel: $\delta_H$ (ppm; 300 MHz; THF-$d_8$) 1.24–1.93 (m, 30H), 3.99–4.15 (m, 3H, −C*H*−O); $\delta_C$ (ppm; 75.5 MHz; THF-$d_8$) 24.68, 26.78, 35.17, 70.92 (−*C*H−O); $\delta_B$ (ppm; 96.3 MHz; THF-$d_8$) 17.70. Cyclohexanol (**2g**) was obtained exclusively after methanolysis of **3g**.

### 5.3. Reactions of AB with aldehydes in THF

In the glove box, a 0.5 mm Young NMR tube was charged with the aldehyde (0.2 mmol), **AB** (0.1 mmol), and dry THF-$d_8$ (0.6 ml). The tube was sealed with a screw cap and shaken to mix well. The reaction started immediately in the tube and was monitored by $^1$H and $^{11}$B NMR every several minutes (depending on the reaction rate). The typical resonance of the aldehyde rapidly decreased (the −HC=O on around 10 ppm in the $^1$H NMR, −22.4 ppm in the $^{11}$B NMR for **AB**) and new signals of the saturated products appeared. The total disappearance of the starting material indicated that the transformation completed, $^{13}$C NMR spectra were then recorded. Since the product is a mixture of compounds, 2D NMR[10] was applied to unravel the spectra of the product species for the reaction of 0.3 mmol of benzaldehyde (**1h**) with 0.1 mmol of **AB**. Reactions of the aldehydes with $BH_3$·THF were carried out to separate the resonances of the trialkyl borates from the spectra for the mixture products.

*5.3.1. Tribenzyl borate (**3h**)*[25]. Colorless gel: $\delta_H$ (ppm; 300 MHz; THF-$d_8$) 4.99 (s, 6H, −$CH_2$−O), 7.23–7.38 (m, 15H, −$C_6H_5$); $\delta_C$ (ppm; 75.5 MHz; THF-$d_8$) 66.26 (−$CH_2$−O), 127.46, 127.88, 128.98, 141.07; $\delta_B$ (ppm; 96.3 MHz; THF-$d_8$) 18.64.

*5.3.2. Tris(naphthalen-1-ylmethyl) borate (**3i**).* Light yellow gel: $\delta_H$ (ppm; 300 MHz; THF-$d_8$) 5.48–5.52 (m, 6H, −$CH_2$−O), 7.35–7.55 (m, 12H), 7.78–7.89 (m, 6H,), 8.09–8.14 (m, 3H); $\delta_C$ (ppm; 75.5 MHz; THF-$d_8$) 64.88 (−*C*H−O), 66.53, 124.45, 124.65, 125.90, 126.09, 126.18, 126.39, 126.49, 126.81, 126.89, 128.94, 129.08, 129.33, 129.38, 132.44, 134.88, 136.28; $\delta_B$ (ppm; 96.3 MHz; THF-$d_8$) 18.64.

*5.3.3. Tris(4-cyanobenzyl) borate (**3j**).* White powder: $\delta_H$ (ppm; 300 MHz; THF-$d_8$) 5.11 (s, 6H, −$CH_2$−O−), 7.51–7.53 (m, 6H), 7.70–7.72 (m, 6H,); $\delta_C$ (ppm; 75.5 MHz; THF-$d_8$) 65.73 (−$CH_2$−O−), 112.41, 119.24 (−*C*N), 127.86, 133.01, 146.02; $\delta_B$ (ppm; 96.3 MHz; THF-$d_8$) 18.48.

*5.3.4. Tris(4-methoxybenzyl) borate (**3k**)*[26]. Colorless gel: $\delta_H$ (ppm; 300 MHz; THF-$d_8$) 3.76 (s, 9H, O−Me), 4.86 (s, 6H, −$CH_2$−O), 6.84–6.88 (m, 6H), 7.23–7.32 (m, 6H); $\delta_C$ (ppm; 75.5 MHz; THF-$d_8$) 55.41 (O−$CH_3$), 65.96 (−$CH_2$−O), 114.35, 129.16, 133.11, 160.17; $\delta_B$ (ppm; 96.3 MHz; THF-$d_8$) 18.49.

*5.3.5. Tris(4-(dimethylamino)benzyl) borate (**3l**).* Yellow gel: $\delta_H$ (ppm; 300 MHz; THF-$d_8$) 2.90 (s, 18H, −N($CH_3$)$_2$), 4.80 (s, 6H, −$CH_2$−O−), 6.66–6.69 (m, 6H), 7.15–7.19 (m, 6H); $\delta_C$ (ppm; 75.5 MHz; THF-$d_8$) 40.96 (−N($CH_3$)$_2$), 66.18 (−$CH_2$−O−), 113.16, 129.62, 130.29, 150.77; $\delta_B$ (ppm; 96.3 MHz; THF-$d_8$) 18.71.

### 5.4. Reactions of ketones and aldehydes with AB in methanol

A 0.5 mm NMR tube was charged with ketone or aldehyde (0.2 mmol), **AB** (0.1 mmol), and deuterated methanol. The tube was covered with a plastic cap and inserted into the NMR machine after shaking. The reaction courses were monitored by $^1$H and $^{11}$B NMR every several minutes (depending on the reaction rates). The typical resonances of the starting materials gradually decreased while new signals of the saturated products appeared. After the ketone or aldehyde disappeared completely in the $^1$H NMR spectrum, $^{13}$C NMR spectrum was recorded. For a large scale reaction in normal methanol, the solvent and all volatile compounds (trimethyl borate and ammonia) were removed by high vacuum after the reaction, and the remaining alcohol was pure to the limit of the NMR with nearly 100% yield.

*5.4.1. Diphenylmethanol (**2a**)*[27,28]. White solid, $\delta_H$ (ppm; 300 MHz; $CD_3OD$) 5.51 (s, 1H, −C*H*−OD), 7.26–7.38 (m, 4H), 7.58–7.68 (m, 4H); $\delta_C$ (ppm; 75.5 MHz; $CD_3OD$) 75.44, 120.78, 126.05, 128.59, 129.77, 141.34, 147.35.

*5.4.2. 1-Phenylethanol (**2b**)*[27,29]. Colorless liquid, $\delta_H$ (ppm; 300 MHz; $CD_3OD$) 1.43 (d, *J*=6.5 Hz, 3H, −C*H*$_3$), 4.82 (q, *J*=6.5 Hz, 1H, −C*H*−OD), 7.18–7.40 (m, 5H); $\delta_C$ (ppm; 75.5 MHz; $CD_3OD$) 25.75 (−*C*$H_3$), 70.85 (−*C*H−OD), 126.47, 128.08, 129.27, 147.55.

*5.4.3. 9H-Fluoren-9-ol (**2c**)*[29,30]. White solid, $\delta_H$ (ppm; 300 MHz; $CD_3OD$) 5.51 (s, 1H, −C*H*−OD), 7.26–7.38 (m, 4H), 7.58–7.68 (m, 4H); $\delta_C$ (ppm; 75.5 MHz; $CD_3OD$) 75.44, 120.78, 126.05, 128.59, 129.77, 141.34, 147.35.

*5.4.4. Cyclohexyl-(phenyl)methanol (**2d**)*[28,31]. Colorless liquid, $\delta_H$ (ppm; 300 MHz; $CD_3OD$) 0.93–1.41 (m, 5H),1.54–1.80 (m, 5H), 1.92–1.99 (m, 1H), 4.33 (d, *J*=7 Hz, 1H, −C*H*−OD), 7.26–7.42 (m, 5H, −$C_6H_5$); $\delta_C$ (ppm; 75.5 MHz; $CD_3OD$) 26.87, 26.94, 27.32, 29.44, 30.27, 46.06, 78.91 (−*C*H−OH), 127.55, 127.76, 128.78, 145.53.

*5.4.5. (E)-1,3-Diphenylprop-2-en-1-ol (**2e**)*[27,32,33]. White solid, $\delta_H$ (ppm; 300 MHz; $CD_3OD$) 5.37 (d, *J*=6 Hz, 1H, −C*H*−OH), 6.45 (dd, *J*=6, 16 Hz, 1H, −CH(OH)−C*H*=CH−), 6.74 (d, *J*=16 Hz, 1H, −CH(OH)−CH=C*H*−); $\delta_C$ (ppm; 75.5 MHz; $CD_3OD$) 74.98 (−*C*H−OH), 118.30 (−*C*H=CH−Ph), 127.23, 127.36, 128.22, 128.53, 129.35, 129.59, 130.15, 133.67 (−CH=*C*H−Ph), 137.88, 144.84.

*5.4.6. Pentan-3-ol (**2f**)*[34]. Colorless liquid, $\delta_H$ (ppm; 300 MHz; $CD_3OD$) 0.92 (td, *J*=7.5 Hz, 6H, −C*H*$_3$), 1.31–1.56 (m, 4H, −$CH_2$),

3.27–3.40 (m, 2H, –C*H*–OD); $\delta_C$ (ppm; 75.5 MHz; $CD_3OD$) 10.39 (–$CH_3$), 30.510 (–$CH_2$), 75.32(–CH–OD).

*5.4.7. Cyclohexanol (**2g**)*[27,34]. Colorless liquid, $\delta_H$ (ppm; 300 MHz; $CD_3OD$) 0.92 (td, $J$=7.5 Hz, 6H, –$CH_3$), 1.31–1.56 (m, 4H, –$CH_2$), 3.27–3.40 (m, 2H, –C*H*–OD); $\delta_C$ (ppm; 75.5 MHz; $CD_3OD$) 10.39 (–$CH_3$), 30.510 (–$CH_2$), 75.32(–CH–OD).

*5.4.8. Phenylmethanol (**2h**)*[27,35,36]. Colorless liquid, $\delta_H$ (ppm; 300 MHz; $CD_3OD$) 4.59 (s, 2H, –$CH_2$), 7.15–7.50 (m, 4H); $\delta_C$ (ppm; 75.5 MHz; $CD_3OD$) 65.23 (–$CH_2$), 127.97, 128.23, 129.32, 142.67.

*5.4.9. Naphthalen-1-ylmethanol (**2i**)*[27,32,36]. Colorless liquid, $\delta_H$ (ppm; 300 MHz; $CD_3CN$) 3.28 (br, 1H, –$CH_2$–O*H*), 5.10 (s, 2H, $CH_2$–OH), 7.48–7.60 (m, 4H), 7.85–7.96 (m, 2H), 8.13–8.18 (m, 1H); $\delta_C$ (ppm; 75.5 MHz; $CD_3CN$) 62.98, 124.71, 125.62, 126.45, 126.66, 126.90, 128.63, 129.34, 132.06, 134.60, 137.16.

*5.4.10. 4-(Hydroxymethyl)benzonitrile (**2j**)*[27]. White solid, $\delta_H$ (ppm; 300 MHz; $CD_3CN$) 4.93 (s, 2H, –$CH_2$–O–), 7.50–7.53 (m, 2H), 7.66–7.69 (m, 2H); $\delta_C$ (ppm; 75.5 MHz; $CD_3CN$) 63.85 (–$CH_2$–O–), 111.18, 119.84 (–CN), 127.87, 130.08, 148.74.

*5.4.11. (4-Methoxyphenyl)methanol (**2k**)*[32]. $\delta_H$ (ppm; 300 MHz; $CD_3OD$) 3.75 (s, 3H, –$CH_3$), 4.51 (s, 2H, –$CH_2$), 6.87 (d, $J$=9 Hz, 2H), 7.26 (d, $J$=9 Hz, 2H); $\delta_C$ (ppm; 75.5 MHz; $CD_3OD$) 55.68 (–$CH_3$), 64.93 (–$CH_2$–OD), 114.72, 129.61, 134.69, 160.47.

*5.4.12. (4-(Dimethylamino)phenyl)methanol (**2l**)*[36]. White solid, $\delta_H$ (ppm; 300 MHz; $CD_3CN$) 2.94 (s, 6H, –N($CH_3$)$_2$), 3.65 (s, 1H, –$CH_2$–O*H*), 4.48 (s, 2H, –$CH_2$–OH), 6.74–6.78 (m, 2H), 7.18–7.23 (m, 2H); $\delta_C$ (ppm; 75.5 MHz; $CD_3CN$) 40.95 (–N($CH_3$)$_2$), 64.75 (–$CH_2$–O–), 113.38, 129.15, 129.95, 150.92.

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.06.104.

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