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A Non-Dissociative Open-Flask Hydroboration with Ammonia Borane: Ready Synthesis of Ammonia-Trialkylboranes and Aminodialkylboranes

P. Veeraraghavan Ramachandran,* Michael P. Drolet and Ameya S. Kulkarni

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Under open-flask conditions, ammonia borane hydroborates olefins in refluxing tetrahydrofuran. Unlike conventional hydroboration, the Lewis base (ammonia) is not dissociated from the boron center. Terminal alkenes selectively provide ammoniatrialkylborane complexes. On the other hand, internal alkenes afford aminodialkylboranes via a metal-free hydroborationdehydrogenation sequence. Alkaline hydrogen peroxide oxidation of the products provides the corresponding alcohols in high yields.

The landmark discovery of ether-catalyzed addition of diborane to olefins by Brown and Rao,1 followed by the introduction of a variety of hydroborating agents, such as borane-tetrahydrofuran (BTHF), borane-dimethyl sulfide (BMS), catecholborane, 9-BBN, etc.² transformed organic synthesis. However, the necessity for strictly anhydrous conditions while handling these reagents, the low molarity and long-term instability of BTHF, and the stench of BMS are some of the drawbacks. N,N-Dialkylaniline-boranes,3 introduced to replace BTHF and BMS, have not been received with enthusiasm, probably owing to their cost, instability, and the presence of de-complexed, high-boiling anilines in the reaction mixture. The use of alkylamine-borane complexes has also been restricted due to the slow hydroboration, even at high temperatures.⁴ Accordingly, to improve their reactivity, Lewis acids,⁵ transition metal catalysts,⁶ or appending leaving groups on borane⁷ have been examined.

Our long-standing interest in borane chemistry^{2b} as well as their utility as energetic materials⁸ led to a recent report on the large-scale preparation of amine-boranes via a transamination of ammonia borane⁹ (AB, **1**) in refluxing tetrahydrofuran (THF).¹⁰ During this process, we observed complete suppression of the thermal dehydrogenation of AB.¹¹ The role of the added nucleophile in suppressing the dehydrogenation was further substantiated with a facile phosphine-ammonia exchange.^{10a} We envisioned a possible extension to poorly nucleophilic alkenes, which promised an AB-mediated hydroboration with significant advantages, such as: (i) an open-flask hydroboration protocol with (ii) an air- and moisture-stable, (iii) low molecular weight, high-borane content (45%), (iv) solid reagent which is (v) readily synthesized¹² or commercially available. Reported herein are the details of a convenient open-flask hydroboration of terminal alkenes to trialkylborane-ammonia complexes and internal alkenes to aminodialkylboranes,^{13,14} wherein, remarkably, the Lewis base is retained in the products (Scheme 1).



The project was begun by treating 1-octene (2a) with 0.33 equiv. of AB in 1 M THF at room temperature (rt) when no reaction was observed. Heating to reflux for 1 h revealed complete consumption of AB and a sharp singlet at δ -6 ppm, by ¹¹B NMR spectroscopy. *Notably, none of the AB dehydrogenation products were observed, similar to the nucleophilic displacement reaction*. The high field resonance of the initial product peak indicated a tetra-coordinated boron, probably an ammonia-trioctylborane complex (**3a**). Although stable under the reaction conditions, efforts to isolate the product by complete evaporation of the solvent *in vacuo* led to its degradation.¹⁵

In another reaction, after an hour of reflux, an equivalent of BF₃-Et₂O was added to the reaction mixture. The δ -6 ppm peak in the ¹¹B NMR spectrum shifted to δ 80 ppm (trioctylborane), with an additional peak at δ -1 ppm (BF₃-NH₃)

Herbert C. Brown Center of Borane Research, Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, Indiana 47907-2084.

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corroborating our presumption that ammonia remained complexed in the product.¹⁶ For further verification, a reaction was conducted in THF- d_8 wherein analysis by ¹H NMR spectroscopy revealed complete consumption of all three equiv. of 1-octene upon reflux for 1 h.¹⁷ Moreover, alkaline hydrogen peroxide oxidation of **3a** yielded 89% of octanol (**4a**) validating that all three equivalents of olefin have been hydroborated (Table 1, entry 1). Significantly, the ratio of the 1°- and 2°-isomers of the alcohol is 98:2, compared to 94:6 obtained with BTHF or BMS.¹⁸ Considering that this ratio is a combination of the regioselectivities achieved over three separate hydroboration steps, we believe that the first hydroboration step might have occurred with better regioselectivity compared to that with BTHF or BMS.¹⁹

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Table 1. Hydroboration-Oxidation of Terminal Alkenes ^a										
R ²	1 (0.33 equiv) 2 M THF reflux	$\left(\mathbb{R}^{2} \xrightarrow{\mathbb{R}^{1}}_{3} \xrightarrow{\mathbb{R}^{2}}_{3}\right)^{B}$	NaOH/ NH ₃	$\rightarrow \mathbb{R}^{2}$	_ОН					
Entry	Olefin (2)	Time (h)	Alcohol (4)	Yield ^b (%)	1º:2ºc					
1	C ₆ H ₁₃ 2a	1	4a	89	98:2					
2	C ₈ H ₁₇ 2b	1	4b	90	97:3					
3	C ₆ H ₁₃ 2c	4	4c	77	99:1					
4	2d	1	4d	71	93:7					
5	2e	1	4e	94	80:20					
6	2f	3	4f	59	>99:1					
7	Br	1	4g	78	>99:1					
8	TBSO 2h	1	4h	81	98:2					

^{*a*}All of the reactions were conducted using 5 mmol AB and 15 mmol of the alkene in 2.5 mL THF under open-flask conditions. ^{*b*}Yield of the isolated alcohol. ^{*c*}Ascertained by ¹H NMR spectroscopy.

Probing the reaction for concentration, temperature, and solvent, revealed refluxing THF at 2 M concentration with respect to AB as optimal.²⁰ Hydroboration-oxidation of a variety of terminal olefins was then undertaken (Table 1). 1-Decene (**2b**), after 1 h reflux, followed by oxidation yielded

90% of decanol (4b) in a 97:3 ratio of the 1°- and 2° Artisements

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(entry 2). A 2,2-disubstituted terminal elefite 42-34 ethyleet51E ene, 2c) and an exo-methylene cycloalkene (β -pinene, 2d) led the formation of the corresponding ammoniato trialkylboranes, 3c and 3d, respectively (entries 3-4). Unlike 3a, these complexes began to dissociate to the trialkylborane (¹¹B NMR: δ 80 ppm) before the complete consumption of AB. Justifiably, the stability of trialkylborane-ammonia complexes is governed by the steric environment around boron. Oxidation of 3c and 3d yielded 77% and 71% of the corresponding alcohol 4c and cis-myrtanol (4d), respectively. Styrene (2e) yielded 83% of phenethanol (4e), as a 4:1 mixture of internal and terminal alcohols (entry 5), similar to that obtained with BTHF.¹⁸ Olefins containing heteroatoms (2f, 2g, and 2h) also underwent hydroboration-oxidation to provide the alcohols in good to high yields and excellent regioselectivities (entries 6-8).

Surprisingly, an internal alkene, cis-2-butene (2i), after 4 h reflux with 0.33 equiv. of AB, revealed a major singlet significantly downfield at δ 48 ppm, along with the expected resonances for the ammonia-tri-sec-butylborane (δ -6 ppm) and unreacted AB (δ -22 ppm). To clarify this deviation from the hydroboration of terminal alkenes, a higher boiling substrate, cyclohexene (2j), was hydroborated with 0.5 equiv of AB.21 After 1 h reflux, all of the AB was consumed with a concurrent gas evolution. Similar to cis-2-butene hydroboration, analysis by ¹¹B NMR spectroscopy showed a major singlet at δ 48 ppm and a minor peak at δ -6 ppm (ammonia-tricyclohexylborane). Unlike the hydroboration of terminal alkenes, the product could be isolated in 95% yield (Table 2, entry 1), which was determined to be aminodicyclohexylborane (5j) by NMR^{16b,c} and HRMS techniques. Further purification was possible by distillation (77% yield). Though stable under the reaction conditions, 5j must be stored under an inert atmosphere to prevent hydrolysis. Thus, the first metal-free one-pot hydroborationdehydrogenation sequence with direct access to the difficult to prepare aminodialkylboranes (5) has been realized (Scheme 2).

Current approaches to aminodialkylboranes: a) From tetramethyldiborane¹³

$$B_{H}^{\prime\prime}B_{H}^{\prime}+2 \text{ NH}_{3} \longrightarrow 2 B_{H}^{\prime}B_{2}^{\prime}$$

b) From dialkylborane derivatives¹⁴

$$R_2B-X \xrightarrow{NH_3} R_2B-NH_2$$

This work: "Metal-free" tandem hydroboration-dehydrogenation



Scheme 2: Routes to aminodialkylboranes

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Current approaches to 5 are multi-step and involve the use of non-commercial, highly pyrophoric, and moisture-sensitive reactants. These include the treatment (i) of tetramethyldiborane with ammonia¹³ and (ii) preparation of dialkylborane derivatives, followed by amine exchange.¹⁴ Thus, our open-flask one-pot hydroboration-dehydrogenation sequence represents a significant improvement over the current routes to aminodialkylboranes. We believe that the sequence proceeds via the thermally unstable ammoniadialkylborane intermediate.²² Oxidation of 5j yielded cyclohexanol in 80% yield.

Table 2. Synthesis of Aminodialkylboranes (5) ^a									
R	\mathbf{R}^{1}	I (0.5 equiv) (R ^{2² 2 M THF reflux}	R ¹ B-NH ₂ R ³ 5	NaC + H₂ ∮ <u>H₂</u> C 0 °C	DH/ D_2 rt R^2 F R^2 F R^4	_OH ₹3			
-	Entry	Entry Olefin (2)	Time Ratio ^b		Yield (%)				
_	,		(h)	(5:3)	5	4 ^c			
	1	2j	1	90:10	95 (77) ^d	80			
	2	2k	1	>99:<1	99	81			
	3	C ₃ H ₇ _C ₂ H ₅ 2 I	2	>99:<1	97	87			
	4	C_3H_7 C_3H_7 2m	1	>99:<1	95	72			
	5	2n	3	>99:<1	92	87			
	6	20	1	>99:<1	97	87			
	7		1	95:5	92 ^e	98 ^f			
	8	2q	3	>99:<1	97	84			

^{*a*}All of the reactions were conducted using 5 mmol AB and 10 mmol of the alkene in 2.5 mL THF. ^{*b*}Ascertained by ¹¹B NMR spectroscopy. ^{*c*}Yield of the isolated alcohols (**4**) after alkaline hydrogen peroxide oxidation. ^{*a*}Yield in parenthesis after distillation. ^{*e*}After precipitation of ammonia-trialkylborane complex. ^{*f*}The enantiomeric excess of the olefin was retained in the product.

A series of internal olefins were then hydroborated to obtain the corresponding aminodialkylboranes (5) and, after oxidation, the alcohols (4) in high yields and purity (Table 2). Norbornene (2k) furnished 99% of aminodi*exo*-norbornylborane (5k) selectively (entry 2). (*Z*)-hept-3-ene (2I)

yielded the corresponding aminodialkylborane (51), tine 97% yield, albeit as a 1:1 mixture of 4- and 3DSUbStituted Stochiets (entry 3), and (Z)-oct-4-ene (2m) afforded aminodi(octan-4yl)borane (5m) in 95% yield (entry 4). Trisubstituted olefins, 2methylpent-2-ene (2n) and 1-methylcyclohexene (2o) also underwent hydroboration-dehydrogenation providing the corresponding aminodialkylboranes 5n and 5o, respectively in 92% and 97% yields (entries 5-6). In all of the above cases, the aminodialkylboranes were essentially pure and necessitated no purification. Cyclic trisubstituted olefins, $(+)-\alpha$ -pinene (2p), and (+)-3-carene (2g)) were refluxed with AB to yield 92% of aminodiisopinocampheylborane (5p) and 97% of aminodiiso-4caranylborane (5q), respectively (entries 7-8). While 5q was pure, 5p was obtained as a 95:5 mixture with the ammoniatrialkylborane complex, which could be purified.²⁰ Oxidation of all of the above aminodialkylboranes (5) provided the corresponding 2°-ols (4) in high yields (Table 2).

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Attempted preparation of the ammonia-trialkylborane complexes from two representative internal olefins (**2j** and **2p**), despite being used in excess (3-5 equiv), yielded the aminodialkylborane as the predominant product. Efforts to selectively prepare aminodialkylboranes from terminal olefins using two equiv. olefin also failed.²⁰ A representative tetrasubstituted olefin, 2,3-dimethylbut-2-ene (**2r**), after 4 h reflux, provided a mixture of ammonia-thexylborane and its dehydrogenation products, including *B*-alkylsubstituted borazine.

Although tremendous progress has been made with regard to the applications of conventional uncatalyzed hydroboration, conflicting opinions exist regarding its mechanism. On the basis of experimental observations, Brown and co-workers²³ proposed the dissociation of borane-Lewis base complex as an essential step prior to the four-centered, concerted synaddition. Conversely, Pasto,²⁴ Schleyer,²⁵ and their coworkers suggested a direct attack of the nucleophilic olefin on the tetra-coordinated boron-Lewis base complex to form an early or late transition state en route to the uncomplexed hydroborated product. Houk²⁶ and coworkers have described the transition-state structures for hydroboration using ab initio calculations and predicted that the Lewis base "is dissociated from the reacting borane in the transition state corresponding to the saddle point." All of these proposals invoke the decomplexation of the Lewis base from the boron center.

In contrast, NH₃ remains complexed to the product after hydroboration with AB, pointing to a mechanism wherein the Lewis base may not be fully dissociated. This could be envisioned via a nucleophilic attack of the olefin on AB leading to an S_N2 -like transition state with association of NH₃ to the boron center. Alternatively, for a dissociative hydroborationre-complexation to occur, the gaseous NH₃ should remain trapped in a solvent cage at elevated temperatures in refluxing THF, which is unlikely. Assuming loss of even traces of ammonia, the presence of BTHF or free trialkylborane should be observed. Neither was detected by ¹¹B NMR spectroscopy supporting a non-dissociative hydroboration.

Apart from those discussed above, other pathways also could be implicated in hydroboration with AB. Autrey and

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coworkers have reported the isomerization of AB to diammoniate of diborane (DADB) prior to dehydrogenation in glyme at 80 °C.¹¹ On this basis, hydroboration via the intermediacy of DADB is a possibility. However, no DADB was observed during the course of our experiments. Likewise, the precursor to DADB, ammonia diborane (AaDB) was also not observed in the ¹¹B NMR spectrum.²⁷

In summary, a novel, convenient, open-air hydroboration protocol²⁸ using AB in refluxing THF has been described. This is the first report of an uncatalyzed hydroboration wherein the Lewis base (ammonia) is retained in the product. This safe alternative to traditional hydroboration provides either trialkylborane-ammonia complexes from terminal alkenes or aminodialkylboranes from internal alkenes. Oxidation of these hydroboration products provides the corresponding alcohols in high yields. The high borane content (45%) and air-stability of AB are major advantages to this protocol. We believe that the ability to carry out hydroboration without the need for inert conditions will have tremendous implications in organic synthesis, industrial chemistry, and chemical education. Synthetic applications of aminodialkylboranes are being currently pursued in our laboratories.

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