Pure Appl. Chem., Vol. 78, No. 7, pp. 1377–1387, 2006.
doi:10.1351/pac200678071377

Aminoboranes as new iminium ion generators in amination reactions*

Michinori Suginome

Department of Synthetic Chemistry and Biological Chemistry, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

Abstract: The utilization of aminoborane derivatives in amination reactions such as Strecker-type aminative cyanation, Mannich-type reaction, and reductive amination is described. Bis(dialkylamino)cyanoboranes and bis(dialkylamino)boron enolates underwent the concurrent transfer of the amino group and either the cyano or the enoxy group from the boron to carbonyl carbon atom in their reaction with aldehydes, leading to the formation of α-amino nitriles and β-amino ketones, respectively. Bis(dialkylamino)borane derivatives that lack the additional nucleophilic groups on the boron atoms were found to serve as effective generators of iminium ions from aldehydes. In the presence of these aminoboranes, reactions of aldehydes with ketene silyl acetals or silyl enol ethers take place, giving Mannich-type products, i.e., β-amino esters and ketones, selectively. Using diisopropylamino-substituted boron compounds, which are designed as "universal" iminium ion generators, reactions of free *sec*-amines, aldehydes, and ketene silyl acetals proceed efficiently, giving β-amino esters in which the amino groups are derived exclusively from the free amines. The use of the universal iminium ion generator is also effective for reductive amination of aldehydes, in which $NaBH_4$ is used as a hydride donor.

Keywords: organic synthesis; boron; α-amino nitriles; β-amino esters; β-amino ketones.

INTRODUCTION

Organoboron compounds play a key role in synthetic organic chemistry, as essential agents in the efficient and selective execution of a variety of fascinating transformations [1]. In particular, remarkable progress has been made in the transition-metal-catalyzed synthesis and reactions of organoboron compounds. Further developments of boron-based reactions are highly important for the efficient synthesis of organic molecules.

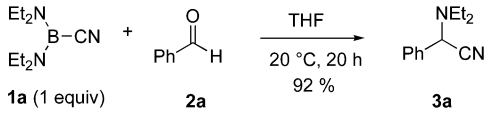
We have been involved in the development of new boron reagents for organic synthesis. Our focus has been on the interesting reactivities of silylboranes [2–7] and cyanoboranes [8–10], which are now recognized as versatile boron reagents in organic synthesis. In the course of our study on cyanoboranes, we became aware of the interesting function of amino groups bound to the boron atom. The function of the amino-substituted boron compounds could be attributed to "efficient iminium ion generation" from carbonyl derivatives, which is generally accepted as the key step in a wide variety of amination reactions such as Strecker-type aminative cyanation [11], Mannich reaction [12,13], and reductive amination [14,15].

*Paper based on a presentation at the 12th International Meeting on Boron Chemistry (IMEBORON-XII), Sendai, Japan, 11–15 September 2005. Other presentations are published in this issue, pp. 1299–1453.

Aminoboranes have been utilized as important synthetic intermediates in the synthesis of organoboron compounds [16]. The major role of the amino groups on the boron atoms is to protect the boron compounds from excessive substitution by strong nucleophiles, such as alkoxide and organometallic reagents. The additional and important feature of the amino groups is the easiness of deprotection, which is achieved just by treating them with alcohols. However, in spite of the frequent use of aminoboranes in the synthesis of organoboron compounds, they found no particular applications in synthetic organic chemistry. Herein, we describe a new synthetic function of aminoborane derivatives for efficient iminium ion generation from carbonyl compounds. We demonstrate Strecker-type aminative cyanation [8], Mannich reaction [17,18], and reductive amination reaction [19] with the use of aminoborane as new iminium ion generators.

AMINATIVE CYANATION (STRECKER-TYPE REACTION) WITH BIS(DIALKYLAMINO)CYANOBORANES

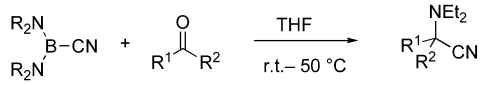
Our recent reports have shown that cyanoboranes bearing amino groups on the boron atom undergo transition-metal-catalyzed additions to carbon–carbon triple bonds [9,10]. In the course of the research project, we examined reactions of bis(dialkylamino)cyanoboranes with carbonyl compounds. Initial experiment was carried out for benzaldehyde in tetrahydrofuran (THF) with the use of an equimolar amount of bis(diethylamino)cyanoborane at room temperature, resulting in the formation of a cyanation product in high yield (eq. 1). The cyanation product was identified as α-amino nitrile **3a**, in which not only the cyano group, but also the diethylamino group was introduced nucleophilically to the carbonyl carbon atom. The finding on the highly efficient, concurrent transfer of the amino and the cyano groups prompted us to examine the generality of the reaction.



(1)

Under the same reaction conditions, a series of aldehydes including *p*-substituted aromatic, heteroaromatic, α,β-unsaturated, and aliphatic aldehydes were reacted with a molar equivalent of bis(diethylamino)cyanoborane, giving the corresponding α-diethylamino nitriles in high yields (Table 1, entries 1–9). Moreover, amino nitriles having other amino groups were obtained by using boron cyanides bearing the corresponding amino groups (entries 10–14).

Table 1 Reaction of bis(dialkylamino)cyanoboranes with carbonyl compounds[a].



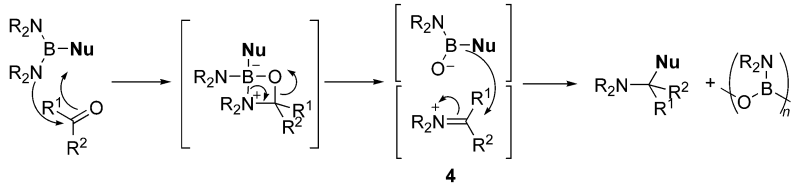
1 (1.0-1.1 equiv) **2** **3**

Entry	R^1, R^2 (aldehyde or ketone)	**1** (NR_2)	Temp/°C	Time/h	% Yield[b]
1	**2b** (R^1 = *p*-$MeOC_6H_4$, R^2 = H)	**1a** (NEt_2)	r.t.	8	93
2	**2c** (R^1 = *p*-$NO_2C_6H_4$, R^2 = H)	**1a**	r.t.	11	92
3	**2d** (R^1 = 2-furyl, R^2 = H)	**1a**	r.t.	20	94
4	**2e** (R^1 = 2-pyridyl, R^2 = H)	**1a**	r.t.	23	99
5	**2f** (R^1 = (*E*)-PhCH=CH, R^2 = H)	**1a**	r.t.	6	95
6	**2g** (R^1 = *n*-Hexyl, R^2 = H)	**1a**	r.t.	1	96
7	**2h** (R^1 = $PhCH_2CH_2$, R^2 = H)	**1a**	r.t.	1	94
8	**2i** (R^1 = *c*-Hexyl, R^2 = H)	**1a**	r.t.	7	98
9	**2j** (R^1 = *t*-Bu, R^2 = H)	**1a**	r.t.	14	97
10	**2i**	**1b** (NBn_2)	r.t.	4	92
11	**2i**	**1c** (pyrrolidino)	r.t.	1	99
12	**2i**	**1d** (morpholino)	r.t.	2	99
13[c]	**2i**	**1e** (NPr^i_2)	50 °C	30	92
14[c]	**2a** (R^1 = Ph, R^2 = H)	**1e**	50 °C	150	99
15	**2k** (R^1 = Me, R^2 = Me)	**1d**	r.t.	20	99
16	**2l** (R^1 = $PhCH_2CH_2$, R^2 = Me)	**1d**	50 °C	24	99
17	**2m** (R^1 = Ph, R^2 = Me)	**1d**	50 °C	24	92
18	**2n** (R^1, R^2 = $-(CH_2)_5-$)	**1d**	r.t.	5	96
19	**2o** (R^1, R^2 = $-(CH_2)_4-$)	**1d**	r.t.	5	92

[a]**1** (0.40 mmol) and aldehyde or ketone (0.40 mmol) were reacted in THF (0.7 mL) at room temperature unless otherwise noted.
[b]Isolated yield.
[c]1.1 equiv of **1e** was used.

The reaction could also be applied to ketones (entries 15–19). Cyclohexanone, cyclopentanone, and acetone underwent the aminative cyanation at room temperature in high yields. Higher temperature (50 °C) was needed to obtain the α-amino nitrile products in high yields in the reaction of acetophenone and 4-phenylbutan-2-one (entries 16 and 17).

We presume the reaction mechanism as follows (Scheme 1). Nucleophilic attack of the amino group on the boron atom to the carbonyl carbon atom is followed by four-membered ring formation. Cleavage of the B–N and C–O bonds in the four-membered ring intermediate generates an iminium ion **4** with a boron-containing counter anion. The boron-bound nucleophilic group attacks the iminium ion, leading to the formation of the α-amino nitrile.

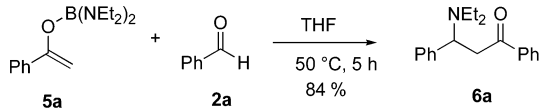


Scheme 1 Possible mechanism for the aminative nucleophilic reaction using bis(dialkylamino)boranes having a nucleophilic group on the boron atom.

MANNICH-TYPE REACTION USING BIS(DIALKYLAMINO)BORON ENOLATES

On the basis of the presumed reaction mechanism, we examined the reactivity of aminoborane derivatives that carry other nucleophilic group on the boron atom (**Nu** in Scheme 1). We were particularly interested in the reactivity of bis(dialkylamino)boron enolates, which carries nucleophilic enoxy group on the boron atom in place of the cyano group in the bis(dialkylamino)boron cyanides.

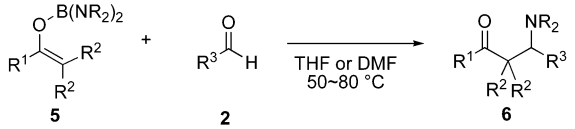
The bis(dialkylamino)boron enolates were prepared via the generation of the corresponding lithium enolate and subsequent reaction with bis(dialkylamino)boron chloride. For instance, bis(diethylamino)boron enolate **5a** of acetophenone was isolated by distillation in 89 % yield. The aminoboron enolate **5a** was then subjected to the reaction with benzaldehyde at 50 °C in THF. Within 5 h, β-amino ketone **6a**, a Mannich product, was formed in 84 % yield with no formation of the corresponding aldol product (eq. 2).



(2)

Mannich-type products were also obtained in the reactions of the aminoboron enolates **5a** with substituted benzaldehydes, paraformaldehyde, and polymeric glyoxylic acid ethyl ester (Table 2, entries 1–4 and 9). The generality of the new Mannich-type reaction was further examined by using several aminoboranes having different amino and enoxy groups (entries 5–10). A series of benzaldehyde-derived boron enolates having diallylamino and pyrrolidino groups afforded the corresponding β-amino ketones in high yields (entries 5 and 6). In these reactions, use of dimethylformamide (DMF) as a solvent resulted in acceleration of the reaction rate. The boron enolate having a disubstituted β-carbon atom gave the corresponding product, although a little higher temperature was needed (entry 7). In this reaction, it was found to be essential to use DMF as a solvent. The acetone-derived diaminoboron enolate successfully gave the corresponding Mannich-type product in high yield (entry 8).

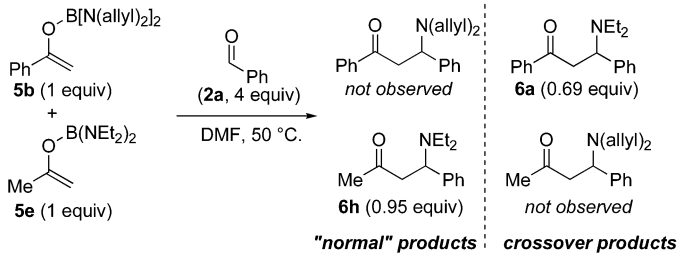
Table 2 Reaction of bis(dialkylamino)boron enolates with carbonyl compounds[a].



Entry	Enolate **5** (R^1, R^2, NR_2)	**2** (R^3)	Temp/°C	Solvent	Product (% yield)[b]
1	**5a** (Ph, H, NEt_2)	**2a** (Ph)	50	THF	**6a** (84)
2	**5a**	**2b** (*p*-$MeOC_6H_4$)	50	THF	**6b** (87)
3	**5a**	**2p** (*p*-NCC_6H_4)	50	THF	**6c** (97)
4	**5a**	**2q** (H)	50	DMF	**6d** (90)
5	**5b** (Ph, H, $N(allyl)_2$)	**2a**	50	THF	**6e** (88)
6	**5c** (Ph, H, pyrrolidino)	**2a**	50	THF	**6f** (66)
7	**5d** (Ph, Me, NEt_2)	**2a**	80	DMF	**6g** (63)
8	**5e** (Me, H, NEt_2)	**2a**	50	THF	**6h** (84)
9	**5a**	**2r** (CO_2Et)	50	DMF	**6i** (86)
10	**5d**	**2r**	50	DMF	**6j** (83)

[a]**5** (0.25 mmol) and aldehyde (0.50 mmol) were reacted in THF (0.5 mL) or DMF (0.5 mL) at the indicated temperatures.
[b]NMR yield.

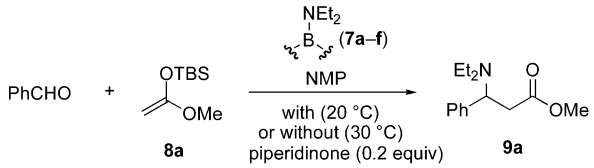
To get insight into the reaction mechanism, we carried out a crossover experiment using two different diaminoboron enolates, i.e., bis(diallylamino)boron enolate of acetophenone (**5b**) and bis(diethylamino)boron enolate of acetone (**5e**) (eq. 3). Before carrying out the crossover experiment, it had been confirmed that no exchange of the amino groups between the two boron enolates took place in the absence of aldehyde under otherwise identical reaction conditions. A 1:1 mixture of the two boron enolates was then reacted with excess benzaldehyde in DMF at 50 °C, affording two β-amino ketone products. The major product (95 % yield) was identified as the β-amino ketone **6h**, which was derived from a sole boron enolate **5e**. The other product **6a** (69 %) was identified as a crossover product, whose amino group and the carbonyl moiety were derived from the two boron enolates **5e** and **5b**, respectively. No amino ketones bearing diallylamino group were detectable. The selective transfer of Et_2N group over $(allyl)_2N$ group was also observed in the reaction of benzaldehyde with (diallylamino)(diethylamino)boron enolate of acetophenone, which afforded β-diethylamino ketone exclusively in good yield. The formation of the crossover product suggests that the iminium cation may exist as a loose ion pair with the boron-based counter anion that carries the nucleophilic group (Scheme 1). Furthermore, the results also indicate that the iminium ions have a certain lifetime before undergoing the nucleophilic addition.



(3)

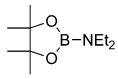
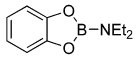
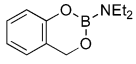
MANNICH-TYPE REACTION USING AMINOBORANES DEVOID OF ADDITIONAL NUCLEOPHILIC GROUPS

The successful Mannich-type reaction using diaminoboron enolate prompted us to modify the reaction system to expand the scope of the reaction. Our major concern was to use external nucleophiles instead of the internal nucleophilic group, which was located within the aminoboron reagent. Being encouraged by the result of the crossover experiment shown above, we examined iminium ion generation by use of aminoboranes that carried no additional nucleophilic groups on the boron atom. We carried out reactions of benzaldehyde and ketene silyl acetal **8a** in the presence of several aminoboranes (eq. 4, Table 3). We obtained Mannich-type product in all the reactions, although the yields varied with the structure of the aminoboranes. While tris(diethylamino)borane gave only poor yield for the formation of **9a** (entry 1), the use of isopropoxydiaminoborane and phenyldiaminoborane gave **9a** in acceptable yields (entries 2 and 3). Furthermore, the monoaminoborane derivatives, derived from catechol and salicyl alcohol, afforded **9a** in high yields (entries 5 and 6), whereas the corresponding pinacol derivative showed much lower reactivity (entry 4). It should be remarked here that the use of a catalytic amount of 2-piperidinone as an additive accelerates the reaction, allowing us to lower the reaction temperature to 20 °C. To confirm the effectiveness of the aminoboranes, some other amino sources, including free amine, silylamine, and stannylamine, were employed for the reaction of benzaldehyde with the ketene silyl acetal **8a** (entries 7–9). No reaction took place at all, indicating clearly that the attachment of the amine component to the boryl group was indispensable for the success in the Mannich-type reaction.



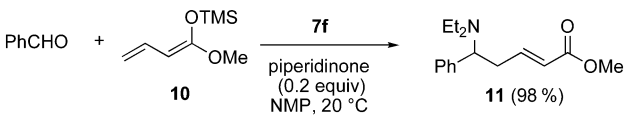
(4)

Table 3 Reactions of silyl ketene acetal **8a** with benzaldehyde in the presence of aminoboranes **7a–f** or other amino sources[a].

Entry	Iminium ion generator	% Yield of **9a**[b]
1	$B(NEt_2)_3$ (**7a**)	31
2	*i*-PrO$B(NEt_2)_2$ (**7b**)	88 (94[c])
3	Ph$B(NEt_2)_2$ (**7c**)	74 (66[c])
4	 (**7d**)	34
5	 (**7e**)	83 (70[c])
6	 (**7f**)	95 (99[c])
7	Me_3SnNEt_2	0
8	Me_3SiNEt_2	0
9	$HNEt_2$	0

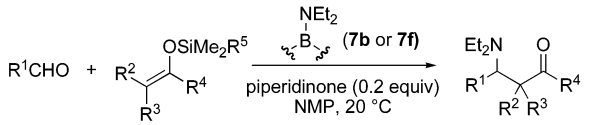
[a]**8a** (1.0 equiv), aldehyde (2.0 equiv), and aminoborane (1.0 equiv) in *N*-methylpyrrolidine (0.5 mL) were reacted at 30 °C for 3 h unless otherwise noted.
[b]NMR yield.
[c]Yields in parentheses were obtained with use of 2-piperidinone (0.2 equiv) at room temperature.

Reactions of some other aldehydes and ketene silyl acetals were carried out in the presence of aminoboranes **7b** and **7f** (Table 4). Aliphatic and aromatic aldehydes having functional groups successfully afforded the corresponding Mannich-type products in moderate to good yields (entries 1–4). β-Disubstituted silyl ketene acetal also afforded the β-amino ester in high yield (entry 5). β-Amino ketone was obtained in the reaction of a silyl enol ether (entry 6). It may be interesting to note that reaction of conjugated ketene silyl acetal **10** with benzaldehyde in the presence of aminoborane **7f** provided δ-amino-α,β-unsaturated ester **11** via vinylogous Mannich reaction (eq. 5).



(5)

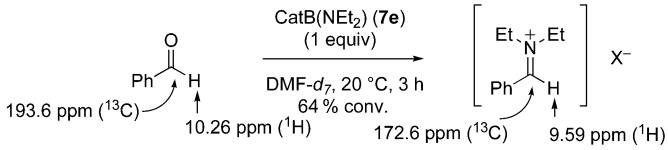
Table 4 Reactions of aldehydes with silyl ketene acetals in the presence of aminoboranes[a].



Entry	Nucleophile	Aldehyde	Aminoborane	% Yield[b]
1	**8a**	*n*-PrCHO	**7b**	96
2	**8a**	$THPO(CH_2)_5CHO$	**7f**	98
3	**8a**	$BocNHCH_2CH_2CHO$	**7f**	64
4	**8a**	*p*-$BocNHC_6H_4CHO$	**7f**	94
5		PhCHO	**7f**	88
6		PhCHO	**7b**	77

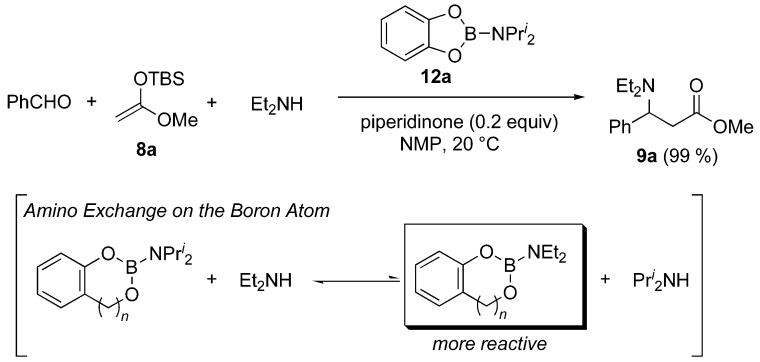
[a]Silyl ketene acetals or a silyl enol ether (1.0 equiv), aldehyde (2.0 equiv), and aminoborane (1.0 equiv) with 2-piperidinone (0.2 equiv) in *N*-methylpyrrolidine (0.5 mL) were reacted at 20 °C for 1–3 h.
[b]Isolated yield.

The intermediary formation of the iminium ion was confirmed by the NMR observation of a stoichiometric reaction of benzaldehyde with aminoborane **7e** in deuterated DMF at room temperature (eq. 6). We observed the appearance of a new signal at 9.59 and 172.6 ppm in ^1H and ^{13}C NMR measurements, respectively, which are comparable to those observed for the related iminium ion [20].



(6)

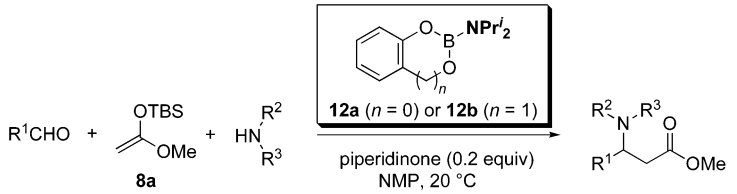
It has thus far been demonstrated that the aminoborane derivatives enable aminative C–C bond-forming reactions in which the amino group on the boron atom is incorporated into the products. However, it does not seem to be ideal that the aminoboranes that carry requisite amino groups have to be prepared for every synthesis. To make the reaction system ideal, we designed a "universal iminium ion generator", taking advantage of amino group exchange on the boron atom. The design of a universal iminium ion generator involves the use of bulky amino groups on the boron atom. The bulky amino group hardly forms an iminium ion but undergoes exchange with less sterically hindered free amines, leading to the generation of more reactive aminoboranes. To check the possibility, a reaction of diethylamine, benzaldehyde, and ketene silyl acetal **8a** in the presence of aminoborane **12a** bearing a diisopropylamino group on the boron atom was carried out. We observed highly selective incorporation of the diethylamino group with no formation of the corresponding diisopropylamino derivative (eq. 7).

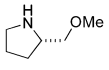


(7)

The "universal" iminium ion generators were found to be suitable for the reactions of various *sec*-amines with aromatic and aliphatic aldehyde, including those having functional groups (Table 5). It should be remarked here that the reaction of 2-methoxymethylpyrrolidine proceeded in a highly stereoselective manner to give the corresponding products in high diastereomeric ratio (entry 6).

Table 5 Aminoborane-mediated coupling of aldehyde, silyl ketene acetal, and *sec*-amine[a].



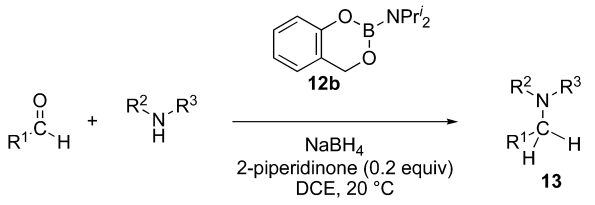
Entry	HNR^2R^3	R^1CHO	Aminoborane	% Yield[b]
1	Et_2NH	PhCHO	**12a**	99
2	(PMB)MeNH[c]	PhCHO	**12a**	71
3		PhCHO	**12a**	83
4		PhCHO	**12a**	96
5		*n*-PrCHO	**12b**	94
6[d]		PhCHO	**12b**	88 (91:9)
7	Et_2NH	$THPO(CH_2)_5CHO$	**12b**	73
8	Et_2NH	$BocNHC_6H_4CHO$	**12b**	98

[a]**8a** (1.0 equiv), aldehyde (1.5 equiv), *sec*-amine (1.0 equiv), and aminoborane (1.0 equiv) with 2-piperidinone (0.2 equiv) in *N*-methylpyrrolidine (0.5 mL) were reacted at 20 °C for 1–3 h.
[b]Isolated yield.
[c]PMB: *p*-methoxybenzyl.
[d]The reaction was carried out at –10 to 20 °C.

REDUCTIVE AMINATION

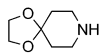
Reductive amination is one of the most convenient methods for the synthesis of amine derivatives from carbonyl compounds, proceeding via the formation of iminium ion intermediate. Typically, reductive amination of aldehydes has been achieved with weak hydride donors such as $NaBH_3CN$ or $NaBH(OAc)_3$ to suppress direct reduction of carbonyl compounds to alcohols. We found that amino-

borane derivatives are suitable for the reductive amination reaction. The bulky aminoborane **12b** again served as the highly efficient reagent for the iminium ion generation, leading to the reductive coupling of *sec*-amines with aldehydes in the presence of $NaBH_4$, which have rarely been utilized as a hydride donor in reductive amination (eq. 8). Examples are shown in Table 6, demonstrating that various aldehydes, including aromatic and aliphatic amines with a series of secondary amines including benzyl, allyl, cyclic, and aromatic amines, can take part in the reaction. The new reagent system allows reductive amination of 2,4,6-trimethoxybenzaldehyde, which showed poor reactivity in the conventional reductive amination systems (entry 6) [21].



(8)

Table 6 Reductive amination with *sec*-amines using aminoborane **12b** with $NaBH_4$[a].

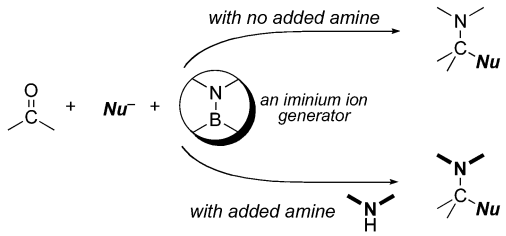
Entry	R^1CHO	R^2R^3NH (equiv)	% Yield[b]
1	PhCHO	Et_2NH (1.5)	99
2	*p*-$O_2NC_6H_4CHO$	Et_2NH (1.5)	96
3	*p*-BrC_6H_4CHO	Et_2NH (1.5)	95
4	*p*-$MeOC_6H_4CHO$	Et_2NH (1.5)	84
5	2,4-$(MeO)_2C_6H_3CHO$	Et_2NH (1.0)	84
6	2,4,6-$(MeO)_3C_6H_2CHO$	Et_2NH (1.0)	88
7	2-NapCHO	Et_2NH (1.0)	87
8	2-NapCHO	Me_2NH (2.0)	84
9	PhCHO	Bn_2NH (1.5)	97
10	2-NapCHO	 (1.5)	98
11	2-NapCHO	 (1.5)	99
12	2-NapCHO	$(allyl)_2NH$ (1.0)	84
13	2-NapCHO	 (1.0)	92
14	$PhCH_2CH_2CHO$	Et_2NH (1.0)	83
15	2-NapCHO	PhMeNH (2.0)	80

[a]Aldehydes (0.24 mmol) were reacted with amines in the presence of aminoborane **12b** (0.24 mol), sodium borohydride (0.26 mmol), and 2-piperidinone (0.048 mmol) in 1,2-dichloroethane at room temperature for 1–3 h.
[b]Isolated yield.

SUMMARY AND CONCLUSION

Using aminoboranes as iminium ion generators, a variety of amination reactions that proceed through iminium ion formation have been demonstrated under nonacidic, mild reaction conditions (eq. 9). Bis(dialkylamino)cyanoboranes and bis(dialkylamino)boron enolates underwent the concurrent transfer of the amino group and either cyano or enoxy group from the boron to carbonyl carbon atom in their reactions with aldehydes, leading to the formation of α-amino nitriles and β-amino ketones, respectively. Bis(dialkylamino)borane derivatives that lack the additional nucleophilic groups on the boron

atom were found to serve as effective generators of iminium ions from aldehyde. The dialkylamino group on the boron atom forms the iminium ion intermediate efficiently, which undergoes the nucleophilic attack of "external" nucleophiles such as ketene silyl acetal, silyl enol ethers, and sodium borohydride, resulting in the formation of β-amino esters, β-amino ketones, and reductive amination products, respectively, in high yields. Improvement of the reaction efficiency and reaction scope is now being undertaken in this laboratory.



(9)

ACKNOWLEDGMENTS

Financial support for this project was provided by the Japan Science and Technology Corporation (PRESTO, "Synthesis and Control" Area) and in part by a Grant-in-Aid for Scientific Research from Ministry of Education, Culture, Sports, Science, and Technology, Japan. The author is indebted to Prof. Masahiro Murakami for valuable discussion and suggestions on this project. The author also thanks Mr. Akihiko Yamamoto, Dr. Lars Uehlin, Mr. Tomoaki Hasui, and Mr. Yusuke Tanaka for their significant contributions to the project.

REFERENCES

1. A. Suzuki, H. C. Brown. *Organic Synthesis via Boranes*, Vol. 3, Aldrich, Milwaukee (2003).
2. M. Suginome, H. Nakamura, Y. Ito. *J. Chem. Soc., Chem. Commun.* 2777 (1996).
3. M. Suginome, H. Nakamura, Y. Ito. *Angew. Chem., Int. Ed.* **36**, 2516 (1997).
4. M. Suginome, H. Nakamura, T. Matsuda, Y. Ito. *J. Am. Chem. Soc.* **120**, 4248 (1998).
5. M. Suginome, T. Matsuda, Y. Ito. *J. Am. Chem. Soc.* **122**, 11015 (2000).
6. M. Suginome, Y. Ohmori, Y. Ito. *J. Am. Chem. Soc.* **123**, 4601 (2001).
7. M. Suginome, T. Ohmura, Y. Miyake, S. Mitani, Y. Ito, M. Murakami. *J. Am. Chem. Soc.* **125**, 11174 (2003).
8. M. Suginome, A. Yamamoto, Y. Ito. *Chem. Commun*. 1392 (2002).
9. M. Suginome, A. Yamamoto, M. Murakami. *J. Am. Chem. Soc.* **125**, 6358 (2003).
10. M. Suginome, A. Yamamoto, M. Murakami. *Angew. Chem., Int. Ed.* **44**, 2380 (2005).
11. M. North. *Comprehensive Organic Functional Group Transformation*, Vol. 3, A. R. Katritzky, O. Meth-Cohn, C. W. Rees (Eds.), p. 611, Elsevier, New York (1995).
12. E. D. Kleinman. *Comprehensive Organic Synthesis*, Vol. 2, B. M. Trost (Ed.), p. 893, Pergamon, Oxford (1991).
13. M. Arend, B. Westermann, N. Risch. *Angew. Chem., Int. Ed.* **37**, 1044 (1998).
14. R. O. Hutchins. *Comprehensive Organic Synthesis*, Vol. 8, B. M. Trost (Ed.), p. 25, Pergamon, Oxford (1991).
15. E. W. Baxter, A. B. Reitz. *Org. React*. **59**, 1 (2002).
16. J. D. Odom. *Comprehensive Organometallic Chemistry I*, Vol. 1, G. Wilkinson, F. G. A. Stone, E. W. Abel (Eds.), p. 254, Elsevier, Amsterdam (1982).
17. M. Suginome, L. Uehlin, A. Yamamoto, M. Murakami. *Org. Lett*. **6**, 1167 (2004).
18. M. Suginome, L. Uehlin, M. Murakami. *J. Am. Chem. Soc*. **126**, 13196 (2004).

19. M. Suginome, Y. Tanaka, T. Hasui. *Synlett* 1047 (2006).
20. Y. Yamamoto, T. Nakada, H. Nemoto. *J. Am. Chem. Soc.* **114**, 121 (1992).
21. C. D. Gutierrez, V. Bavetsias, E. McDonald. *Tetrahedron Lett.* **46**, 3595 (2005).